February 25, 2003

Ms. Cindy Tibbott
U.S. Fish & Wildlife Service
317 South Allen Street
State College, Pennsylvania 16801

Dear Ms. Tibbott:

Subject: Proposed Bailey Mine Refuse Areas
Consol Pennsylvania Coal Company
Greene County, Pennsylvania
CEC Project 221379

Please find attached a map and description of the sample locations (Table 1) for the sediment samples collected by Moody & Associates Inc (Moody), a summary of the thirteen common polycyclic aromatic hydrocarbons (PAHs) analyzed for these sediment samples (Table 2), and the analytical laboratory sheets (Appendix A).

At our meeting on January 10, 2003, Mark Roberts stated that a reasonable freshwater sediment screening criteria for total PAHs (TPAH) was the probable effect concentration (PEC) of 22.8 ppm suggested by Consol in our December 5, 2002 presentation and based on the work of Ingersoll et al. (2000). All Moody sample results except CRDA 8 are below the PEC, without adjusting for organic carbon (Table 2). Sampling location CRDA 8 is located at the end of a flume that drains the coal load-out area. The drainage from the flume at CRDA 8 enters sediment Pond 6, where it is treated for sediment removal before being discharged from the facility.

You will note that the percent total organic carbon (TOC) for CRDA 8 is elevated. Agency representatives at the January 10th meeting stated that PAH values for samples with elevated TOC measurements should not be adjusted for organic carbon. Subsequent discussions with Dr. Ingersoll indicated that that the total PAH PEC value was established using sediment toxicity testing and sediment samples that ranged in TOC content from 1 to 3%. Dr. Ingersoll stated that it would be appropriate to adjust or normalize the sample results to 1-2% TOC and then direct comparisons to the PEC would be appropriate. Consequently, the Moody sample result with the elevated TOC was normalized to 2% TOC using the approach described by FWS in their letter to the

Civil & Environmental Consultants, Inc.

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Rec'd 2/28/2003

Since all PAH values are below the PEC, it does not appear that potential PAH toxicity at the facility is an issue. Furthermore, these data indicate that the current Bailey Mine discharge control facility is working to control PAH concentrations in Enlow Fork sediments below recommended levels.

We welcome the opportunity to meet with you to discuss these issues further. Please contact us with any questions or comments.

Very truly yours,

CIVIL & ENVIRONMENTAL CONSULTANTS, INC.

Mark Haibach

Mark R. Haibach, M.S.
Project Manager/Environmental Scientist

James E. Mudge, Ph.D.
Principal Environmental Scientist

Enclosures

cc: Jonathan Pachter, Consol
Albert Rogalla, U.S. Army Corps of Engineers, Pittsburgh District

E-221379.F25/W

TABLE 1
Sediment Sampling Locations at Bailey Mine Complex
Consol Pennsylvania Coal Company
Greene County, Pennsylvania
November 19, 2002

Sampling Station	Sampling Station Location
CRDA 1	Intersection of east groin drain, bench drain, and bench gravel drain at mid-level bench face of slurry impoundment (surface runoff from face of slurry dam)
CRDA 2	West groin drain at toe of slurry impoundment face
CRDA 3	Seepage zone at toe of coarse refuse face
CRDA 4	Pond 2 outlet (coarse refuse area sediment control pond)
CRDA 5	Pond 10 outlet (combined coarse refuse area and face/underdrain/seeps of slurry impoundment)
CRDA 6	Discharge from Pond 7 - Pond 7 is at downstream end of and in series with Pond 8 and blackwater pond (thickener dump and prep plant sediment controls)
CRDA 7	Discharge channel, downstream of CRDA 5 and upstream of CRDA 6
CRDA 8	Bottom of flume from coal loadout collection ditches, adjacent to raw coal silos, prior to draining into Pond 6
CRDA 9	Discharge channel (Talley Run) at discharge from Pond 5 (normally sediment control for loadout area and shop), with occasional contribution from Pond 6; just upstream of confluence with Enlow Fork
CRDA 10	Discharge channel (Talley Run) upstream of CRDA 9; essentially all drainage from facilities excepting clean coal silos and loadout
CRDA 11	Enlow Fork, about 1200 feet downstream of Talley Run confluence, just below discharges from sanitary plant and storage yards
CRDA 12	Enlow Fork about 1400 feet above Talley Run confluence
CRDA 13	Enlow Fork about 4000 feet above Talley Run confluence
CRDA 14	Enlow Fork about 6500 feet below Talley Run confluence

Notes:
1. Samples collected by Moody and Associates, Inc.

TABLE 2
PAH Analysis of Sediment Samples Collected at Bailey Mine Complex
Consol Pennsylvania Coal Company
Greene County, Pennsylvania
November 19, 2002

SAMPLE LOCATION / ANALYTE	2-Methylnaphthalene	Acenaphthene	Acenaphthalene	Anthracene	Benzo(a)anthracene	Benzo(a)pyrene	Chrysene	Dibenz(a,h)anthracene	Fluoranthene	Fluorene	Naphthalene	Phenanthrene	Pyrene	Percent Total Organic Carbon	Total PAHs (13 common)[1]	Total PAH Adjusted[2]
CRDA 1	2.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.3	1.9	0.6	<0.2	1.48	5.9	
CRDA 2	1.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	1	0.3	<0.2	2.02	3.5	
CRDA 3	0.6	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.8	0.2	<0.2	2.11	2.6	
CRDA 4	1.3	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	1	0.4	<0.2	0.96	3.7	
CRDA 5	0.6	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.4	0.2	<0.2	3.3	2.2	
CRDA 6	1	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.8	0.3	<0.2	1.24	3.1	
CRDA 7	1.7	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	1.4	0.5	<0.2	2.52	4.6	
CRDA 8	20	0.3	<0.2	0.4	0.5	0.2	0.5	<0.2	0.7	0.7	14	3.8	0.8	18.3	41.4	4.5
CRDA 9	0.5	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.5	<0.2	<0.2	5.82	2.0	
CRDA 10	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	1.22	1.3	
CRDA 11	0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.2	<0.2	<0.2	1.28	1.4	
CRDA 12	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.7	1.3	
CRDA 13	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.55	1.3	
CRDA 14	<0.2	<0.2	<0.2	<0.2	0.6	0.5	0.5	<0.2	1.4	<0.2	<0.2	<0.2	1	0.46	4.4	
PEC															22.8	22.8

All values are in units of mg/kg.

The consensus-based Probable Effect Concentration (PEC) for Total PAHs identified by Ingersoll et al. (2000).

[1] Non-detected values added to Total PAH value at 1/2 the detection value.

[2] Total PAH adjusted to 2% TOC, the average TOC value used by Ingersoll et al. to derive the PEC.

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PAH and Selenium by ICP

Certificate Of Analysis

Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

11548 Cotton Road
Meadville, PA 16335

Date Received 11/20/02
Time Received:
Delivered By: Customer

P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-1 **Client's Sample ID:** Bailey #1 Grab
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			11/20/02	14:15	Gaza	SW-846 3050B
Prep: Semi-Volatile Soxhlet Extraction			11/20/02	16:30	Hindle	SW-846 3540C
SPLP Leachate	Completed		11/20/02	20:00	Gaza	SW-846 1312
TCLP Extraction						
Sample Mass Extracted	50.0	grams	11/20/02	20:00	Gaza	SW-846 1311
Initial Volume of Extr. Fluid	1000	ml	11/20/02	20:00	Gaza	SW-846 1311
Initial pH	8.80		11/20/02	20:00	Gaza	SW-846 1311
Final pH	5.40		11/20/02	20:00	Gaza	SW-846 1311
Organics						
1-Methyl naphthalene	1.6	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
2-Methyl naphthalene	2.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Polynuclear Aromatic Hydrocarbons (PAH's)						
Acenaphthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Acenaphthylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(b)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(ghi)perylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(k)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Chrysene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Dibenz(a,h)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluorene	0.3	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Indeno(1,2,3-cd)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Naphthalene	1.9	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Phenanthrene	0.6	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C

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Company Name: Moody & Associates

Date Received 11/20/02
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P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-1 **Client's Sample ID:** Bailey #1 Grab
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Metals						
Selenium (Se)	<4	mg/kg	11/23/02	11:50	Kozakovsky	SW-846 6010B
General Chemistry						
Prep: TPH, Soxhlet Extraction			11/21/02	08:00	Buttray	SW-846 9071A
Solids, %	70.0	%	11/20/02	13:00	Gaza	SM 2540 G
Petroleum Hydrocarbons, Total	70	mg/kg	11/25/02	08:00	Buttray	EPA 418.1

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0013856-2 **Client's Sample ID:** Bailey #2 Grab
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			11/20/02	14:15	Gaza	SW-846 3050B
Prep: Semi-Volatile Soxhlet Extraction			11/20/02	16:30	Hindle	SW-846 3540C
SPLP Leachate	Completed		11/20/02	20:00	Gaza	SW-846 1312
TCLP Extraction						
Sample Mass Extracted	50.0	grams	11/20/02	20:00	Gaza	SW-846 1311
Initial Volume of Extr. Fluid	1000	ml	11/20/02	20:00	Gaza	SW-846 1311
Initial pH	8.20		11/20/02	20:00	Gaza	SW-846 1311
Final pH	5.40		11/20/02	20:00	Gaza	SW-846 1311
Organics						
1-Methyl naphthalene	0.7	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
2-Methyl naphthalene	1.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Polynuclear Aromatic Hydrocarbons (PAH's)						

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Company Name: Moody & Associates

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Date Received 11/20/02
Time Received:
Delivered By: Customer

P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-2 **Client's Sample ID:** Bailey #2 Grab

Date Sampled: 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Organics (Continued)						
Polynuclear Aromatic Hydrocarbons (PAH's) (Continued)						
Acenaphthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Acenaphthylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(b)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(ghi)perylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(k)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Chrysene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Dibenz(a,h)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluorene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Indeno(1,2,3-cd)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Naphthalene	1.0	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Phenanthrene	0.3	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Metals						
Selenium (Se)	<3	mg/kg	11/23/02	11:50	Kozakovsky	SW-846 6010B
General Chemistry						
Prep: TPH, Soxhlet Extraction			11/21/02	08:00	Buttray	SW-846 9071A
Solids, %	89.6	%	11/20/02	13:00	Gaza	SM 2540 G
Petroleum Hydrocarbons, Total	50	mg/kg	11/25/02	08:00	Buttray	EPA 418.1

Results expressed as mg/kg are calculated on a dry weight basis.

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Certificate Of Analysis

Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

11548 Cotton Road
Meadville, PA 16335

Date Received 11/20/02
Time Received:
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P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-3 **Client's Sample ID:** Bailey #3 Grab
Date Sampled: 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			11/20/02	14:15	Gaza	SW-846 3050B
Prep: Semi-Volatile Soxhlet Extraction			11/20/02	16:30	Hindle	SW-846 3540C
SPLP Leachate	Completed		11/20/02	20:00	Gaza	SW-846 1312
TCLP Extraction						
Sample Mass Extracted	50.0	grams	11/20/02	20:00	Gaza	SW-846 1311
Initial Volume of Extr. Fluid	1000	ml	11/20/02	20:00	Gaza	SW-846 1311
Initial pH	9.00		11/20/02	20:00	Gaza	SW-846 1311
Final pH	6.00		11/20/02	20:00	Gaza	SW-846 1311
Organics						
1-Methyl naphthalene	0.9	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
2-Methyl naphthalene	0.6	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Polynuclear Aromatic Hydrocarbons (PAH's)						
Acenaphthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Acenaphthylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(b)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(ghi)perylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(k)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Chrysene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Dibenz(a,h)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluorene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Indeno(1,2,3-cd)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Naphthalene	0.8	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Phenanthrene	0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C

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Certificate Of Analysis

Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

Date Received 11/20/02
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Meadville, PA 16335

P.O. Bailey

Project Name: Bailey Minc Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-3 **Client's Sample ID:** Bailey #3 Grab
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Metals						
Selenium (Se)	<4	mg/kg	11/23/02	11:50	Kozakovsky	SW-846 6010B
General Chemistry						
Prep: TPH, Soxhlet Extraction			11/21/02	08:00	Buttray	SW-846 9071A
Solids, %	82.0	%	11/20/02	13:00	Gaza	SM 2540 G
Petroleum Hydrocarbons, Total	50	mg/kg	11/25/02	08:00	Buttray	EPA 418.1

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0013856-4 **Client's Sample ID:** Bailey #4 Grab
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			11/20/02	14:15	Gaza	SW-846 3050B
Prep: Semi-Volatile Soxhlet Extraction			11/20/02	16:30	Hindle	SW-846 3540C
SPLP Leachate	Completed		11/20/02	20:00	Gaza	SW-846 1312
TCLP Extraction						
Sample Mass Extracted	50.0	grams	11/20/02	20:00	Gaza	SW-846 1311
Initial Volume of Extr. Fluid	1000	ml	11/20/02	20:00	Gaza	SW-846 1311
Initial pH	8.90		11/20/02	20:00	Gaza	SW-846 1311
Final pH	6.10		11/20/02	20:00	Gaza	SW-846 1311
Organics						
1-Methyl naphthalene	1.0	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
2-Methyl naphthalene	1.3	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Polynuclear Aromatic Hydrocarbons (PAH's)						

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Certificate Of Analysis

Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

11548 Cotton Road
Meadville, PA 16335

Date Received 11/20/02
Time Received:
Delivered By: Customer

P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-4 **Client's Sample ID:** Bailey #4 Grab

Date Sampled: 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Organics (Continued)						
Polynuclear Aromatic Hydrocarbons (PAH's) (Continued)						
Acenaphthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Acenaphthylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(b)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(ghi)perylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(k)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Chrysene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Dibenz(a,h)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluorene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Indeno(1,2,3-cd)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Naphthalene	1.0	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Phenanthrene	0.4	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Metals						
Selenium (Se)	<5	mg/kg	11/23/02	11:50	Kozakovsky	SW-846 6010B
General Chemistry						
Prep: TPH, Soxhlet Extraction			11/21/02	08:00	Buttray	SW-846 9071A
Solids, %	54.9	%	11/20/02	13:00	Gaza	SM 2540 G
Petroleum Hydrocarbons, Total	310	mg/kg	11/25/02	08:00	Buttray	EPA 418.1

Results expressed as mg/kg are calculated on a dry weight basis.

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Certificate Of Analysis

Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

Date Received 11/20/02
Time Received:
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11548 Cotton Road
Meadville, PA 16335

P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-5 **Client's Sample ID:** Bailey #5 Grab

Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			11/20/02	14:15	Gaza	SW-846 3050B
Prep: Semi-Volatile Soxhlet Extraction			11/20/02	16:30	Hindle	SW-846 3540C
SPLP Leachate	Completed		11/20/02	20:00	Gaza	SW-846 1312
TCLP Extraction						
Sample Mass Extracted	50.0	grams	11/20/02	20:00	Gaza	SW-846 1311
Initial Volume of Extr. Fluid	1000	ml	11/20/02	20:00	Gaza	SW-846 1311
Initial pH	9.20		11/20/02	20:00	Gaza	SW-846 1311
Final pH	6.40		11/20/02	20:00	Gaza	SW-846 1311
Organics						
1-Methyl naphthalene	0.4	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
2-Methyl naphthalene	0.6	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Polynuclear Aromatic Hydrocarbons (PAH's)						
Acenaphthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Acenaphthylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(b)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(ghi)perylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(k)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Chrysene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Dibenz(a,h)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluorene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Indeno(1,2,3-cd)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Naphthalene	0.4	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Phenanthrene	0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C

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Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

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Date Received 11/20/02
Time Received:
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P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-5 **Client's Sample ID:** Bailey #5 Grab
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Metals						
Selenium (Se)	<4	mg/kg	11/23/02	11:50	Kozakovsky	SW-846 6010B
General Chemistry						
Prep: TPH, Soxhlet Extraction			11/21/02	08:00	Buttray	SW-846 9071A
Solids, %	75.6	%	11/20/02	13:00	Gaza	SM 2540 G
Petroleum Hydrocarbons, Total	150	mg/kg	11/25/02	08:00	Buttray	EPA 418.1

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0013856-6 **Client's Sample ID:** Bailey #6 Grab
Date Sampled. 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			11/20/02	14:15	Gaza	SW-846 3050B
Prep: Semi-Volatile Soxhlet Extraction			11/20/02	16:30	Hindle	SW-846 3540C
SPLP Leachate	Completed		11/20/02	20:00	Gaza	SW-846 1312
TCLP Extraction						
Sample Mass Extracted	50.0	grams	11/20/02	20:00	Gaza	SW-846 1311
Initial Volume of Extr. Fluid	1000	ml	11/20/02	20:00	Gaza	SW-846 1311
Initial pH	9.20		11/20/02	20:00	Gaza	SW-846 1311
Final pH	5.30		11/20/02	20:00	Gaza	SW-846 1311
Organics						
1-Methyl naphthalene	0.7	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
2-Methyl naphthalene	1.0	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Polynuclear Aromatic Hydrocarbons (PAH's)						

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Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

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Date Received 11/20/02
Time Received:
Delivered By: Customer

P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-6 **Client's Sample ID:** Bailey #6 Grab
Date Sampled: 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Organics (Continued)						
Polynuclear Aromatic Hydrocarbons (PAH's) (Continued)						
Acenaphthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Acenaphthylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(b)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(ghi)perylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(k)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Chrysene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Dibenz(a,h)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluorene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Indeno(1,2,3-cd)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Naphthalene	0.8	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Phenanthrene	0.3	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Metals						
Selenium (Se)	<4	mg/kg	11/23/02	11:50	Kozakovsky	SW-846 6010B
General Chemistry						
Prep: TPH, Soxhlet Extraction			11/21/02	08:00	Buttray	SW-846 9071A
Solids, %	78.2	%	11/20/02	13:00	Gazn	SM 2540 G
Petroleum Hydrocarbons, Total	100	mg/kg	11/25/02	08:00	Buttray	EPA 418.1

Results expressed as mg/kg are calculated on a dry weight basis.

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Certificate Of Analysis

Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

Date Received 11/20/02
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P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-7 **Client's Sample ID:** Bailey #7 Grab
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			11/20/02	14:15	Gaza	SW-846 3050B
Prep: Semi-Volatile Soxhlet Extraction			11/20/02	16:30	Hindle	SW-846 3540C
SPLP Leachate	Completed		11/20/02	20:00	Gaza	SW-846 1312
TCLP Extraction						
Sample Mass Extracted	50.0	grams	11/20/02	20:00	Gaza	SW-846 1311
Initial Volume of Extr. Fluid	1000	ml	11/20/02	20:00	Gaza	SW-846 1311
Initial pH	9.10		11/20/02	20:00	Gaza	SW-846 1311
Final pH	6.00		11/20/02	20:00	Gaza	SW-846 1311
Organics						
1-Methyl naphthalene	1.1	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
2-Methyl naphthalene	1.7	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Polynuclear Aromatic Hydrocarbons (PAH's)						
Acenaphthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Acenaphthylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(b)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(ghi)perylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(k)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Chrysene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Dibenz(a,h)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluorene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Indeno(1,2,3-cd)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Naphthalene	1.4	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Phenanthrene	0.5	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C

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Certificate Of Analysis

Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

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Date Received 11/20/02
Time Received:
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P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-7 **Client's Sample ID:** Bailey #7 Grab
Date Sampled: 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Metals						
Selenium (Se)	<5	mg/kg	11/23/02	11:50	Kozakovsky	SW-846 6010B
General Chemistry						
Prep: TPH, Soxhlet Extraction			11/21/02	08:00	Buttray	SW-846 9071A
Solids, %	50.7	%	11/20/02	13:00	Gaza	SM 2540 G
Petroleum Hydrocarbons, Total	360	mg/kg	11/25/02	08:00	Buttray	EPA 418.1

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0013856-8 **Client's Sample ID:** Bailey #8 Grab
Date Sampled: 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			11/20/02	14:15	Gaza	SW-846 3050B
Prep: Semi-Volatile Soxhlet Extraction			11/20/02	16:30	Hindle	SW-846 3540C
SPLP Leachate	Completed		11/20/02	20:00	Gaza	SW-846 1312
TCLP Extraction						
Sample Mass Extracted	50.0	grams	11/20/02	20:00	Gaza	SW-846 1311
Initial Volume of Extr. Fluid	1000	ml	11/20/02	20:00	Gaza	SW-846 1311
Initial pH	9.40		11/20/02	20:00	Gaza	SW-846 1311
Final pH	5.60		11/20/02	20:00	Gaza	SW-846 1311
Organics						
1-Methyl naphthalene	11	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
2-Methyl naphthalene	20	mg/kg	11/21/02	21:00	Lata	SW-846 8270C

Polynuclear Aromatic Hydrocarbons (PAH's)

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Certificate Of Analysis

Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

Date Received 11/20/02
Time Received:
Delivered By: Customer

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P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-8 **Client's Sample ID:** Bailey #8 Grab
Date Sampled: 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Organics (Continued)						
Polynuclear Aromatic Hydrocarbons (PAH's) (Continued)						
Acenaphthene	0.3	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Acenaphthylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Anthracene	0.4	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)anthracene	0.5	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)pyrene	0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(b)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(ghi)perylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(k)fluoranthene	0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Chrysene	0.5	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Dibenz(a,h)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluoranthene	0.7	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluorene	0.7	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Indeno(1,2,3-cd)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Naphthalene	14	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Phenanthrene	3.8	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Pyrene	0.8	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Metals						
Selenium (Se)	<4	mg/kg	11/23/02	11:50	Kozakovsky	SW-846 6010B
General Chemistry						
Prep: TPH, Soxhlet Extraction			11/21/02	08:00	Buttray	SW-846 9071A
Solids, %	68.9	%	11/20/02	13:00	Gaza	SM 2540 G
Petroleum Hydrocarbons, Total	1100	mg/kg	11/25/02	08:00	Buttray	EPA 418.1

Results expressed as mg/kg are calculated on a dry weight basis.

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Certificate Of Analysis

Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

Date Received 11/20/02
Time Received:
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11548 Cotton Road
Meadville, PA 16335

P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-9 **Client's Sample ID:** Bailey #9 Grab
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			11/20/02	14:15	Gaza	SW-846 3050B
Prep: Semi-Volatile Soxhlet Extraction			11/20/02	16:30	Hindle	SW-846 3540C
SPLP Leachate	Completed		11/20/02	20:00	Gaza	SW-846 1312
TCLP Extraction						
Sample Mass Extracted	50.0	grams	11/20/02	20:00	Gaza	SW-846 1311
Initial Volume of Extr. Fluid	1000	ml	11/20/02	20:00	Gaza	SW-846 1311
Initial pH	9.20		11/20/02	20:00	Gaza	SW-846 1311
Final pH	6.80		11/20/02	20:00	Gaza	SW-846 1311
Organics						
1-Methyl naphthalene	0.4	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
2-Methyl naphthalene	0.5	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Polynuclear Aromatic Hydrocarbons (PAH's)						
Acenaphthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Acenaphthylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(b)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(ghi)perylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(k)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Chrysene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Dibenz(a,h)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluorene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Indeno(1,2,3-cd)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Naphthalene	0.5	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Phenanthrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C

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Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

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Date Received 11/20/02
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P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-9 **Client's Sample ID:** Bailey #9 Grab
Date Sampled: 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Metals						
Selenium (Se)	<3	mg/kg	11/23/02	11:50	Kozakovsky	SW-846 6010B
General Chemistry						
Prep: TPH, Soxhlet Extraction			11/21/02	08:00	Buttray	SW-846 9071A
Solids, %	85.6	%	11/20/02	13:00	Gaza	SM 2540 G
Petroleum Hydrocarbons, Total	40	mg/kg	11/25/02	08:00	Buttray	EPA 418.1

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0013856-10 **Client's Sample ID:** Bailey #10 Grab
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			11/20/02	14:15	Gaza	SW-846 3050B
Prep: Semi-Volatile Soxhlet Extraction			11/20/02	16:30	Hindle	SW-846 3540C
SPLP Leachate	Completed		11/20/02	20:00	Gaza	SW-846 1312
TCLP Extraction						
Sample Mass Extracted	50.0	grams	11/20/02	20:00	Gaza	SW-846 1311
Initial Volume of Extr. Fluid	1000	ml	11/20/02	20:00	Gaza	SW-846 1311
Initial pH	9.40		11/20/02	20:00	Gaza	SW-846 1311
Final pH	6.70		11/20/02	20:00	Gaza	SW-846 1311
Organics						
1-Methyl naphthalene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
2-Methyl naphthalene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Polynuclear Aromatic Hydrocarbons (PAH's)						

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Certificate Of Analysis

Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

11548 Cotton Road
Meadville, PA 16335

Date Received 11/20/02
Time Received:
Delivered By: Customer

P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-10 **Client's Sample ID:** Bailey #10 Grab
Date Sampled. 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Organics (Continued)						
Polynuclear Aromatic Hydrocarbons (PAH's) (Continued)						
Acenaphthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Acenaphthylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(b)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(ghi)perylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(k)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Chrysene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Dibenz(a,h)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluorene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Indeno(1,2,3-cd)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Naphthalene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Phenanthrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Metals						
Selenium (Se)	<4	mg/kg	11/23/02	11:50	Kozakovsky	SW-846 6010B
General Chemistry						
Prep: TPH, Soxhlet Extraction			11/21/02	08:00	Buttray	SW-846 9071A
Solids, %	76.5	%	11/20/02	13:00	Gaza	SM 2540 G
Petroleum Hydrocarbons, Total	180	mg/kg	11/25/02	08:00	Buttray	EPA 418.1

Results expressed as mg/kg are calculated on a dry weight basis.

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Certificate Of Analysis

Delivery Group ID: 2002:0013856

42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

11548 Cotton Road
Meadville, PA 16335

Date Received 11/20/02
Time Received:
Delivered By: Customer

P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-11 **Client's Sample ID:** Bailey #11 Grab

Date Sampled: 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			11/20/02	14:15	Gaza	SW-846 3050B
Prep: Semi-Volatile Soxhlet Extraction			11/20/02	16:30	Hindle	SW-846 3540C
SPLP Leachate	Completed		11/20/02	20:00	Gaza	SW-846 1312
TCLP Extraction						
Sample Mass Extracted	50.0	grams	11/20/02	20:00	Gaza	SW-846 1311
Initial Volume of Extr. Fluid	1000	ml	11/20/02	20:00	Gaza	SW-846 1311
Initial pH	9.20		11/20/02	20:00	Gaza	SW-846 1311
Final pH	5.10		11/20/02	20:00	Gaza	SW-846 1311
Organics						
1-Methyl naphthalene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
2-Methyl naphthalene	0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Polynuclear Aromatic Hydrocarbons (PAH's)						
Acenaphthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Acenaphthylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(b)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(ghi)perylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(k)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Chrysene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Dibenz(a,h)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluorene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Indeno(1,2,3-cd)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Naphthalene	0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Phenanthrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C

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Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

Date Received 11/20/02
Time Received:
Delivered By: Customer

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P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-11 **Client's Sample ID:** Bailey #11 Grab
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Metals						
Selenium (Se)	<3	mg/kg	12/12/02	10:30	Prutzman	SW-846 6010B
General Chemistry						
Prep: TPH, Soxhlet Extraction			11/21/02	08:00	Buttray	SW-846 9071A
Solids, %	89.9	%	11/20/02	13:00	Gaza	SM 2540 G
Petroleum Hydrocarbons, Total	60	mg/kg	11/25/02	08:00	Buttray	EPA 418.1

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0013856-12 **Client's Sample ID:** Bailey #12 Grab
Date Sampled. 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			11/20/02	14:15	Gaza	SW-846 3050B
Prep: Semi-Volatile Soxhlet Extraction			11/20/02	16:30	Hindle	SW-846 3540C
SPLP Leachate	Completed		11/20/02	20:00	Gaza	SW-846 1312
TCLP Extraction						
Sample Mass Extracted	50.0	grams	11/20/02	20:00	Gaza	SW-846 1311
Initial Volume of Extr. Fluid	1000	ml	11/20/02	20:00	Gaza	SW-846 1311
Initial pH	7.70		11/20/02	20:00	Gaza	SW-846 1311
Final pH	5.00		11/20/02	20:00	Gaza	SW-846 1311
Organics						
1-Methyl naphthalene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
2-Methyl naphthalene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Polynuclear Aromatic Hydrocarbons (PAH's)						

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Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

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Date Received 11/20/02
Time Received:
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P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-12 **Client's Sample ID:** Bailey #12 Grab
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Organics (Continued)						
Polynuclear Aromatic Hydrocarbons (PAH's) (Continued)						
Acenaphthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Acenaphthylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(b)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(ghi)perylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(k)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Chrysene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Dibenz(a,h)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluorene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Indeno(1,2,3-cd)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Naphthalene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Phenanthrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Metals						
Selenium (Se)	<4	mg/kg	12/12/02	10:30	Prutzman	SW-846 6010B
General Chemistry						
Prep: TPH, Soxhlet Extraction			11/21/02	08:00	Butray	SW-846 9071A
Solids, %	78.2	%	11/20/02	13:00	Gaza	SM 2540 G
Petroleum Hydrocarbons, Total	50	mg/kg	11/25/02	08:00	Butray	EPA 418.1

Results expressed as mg/kg are calculated on a dry weight basis.

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Certificate Of Analysis

Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

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P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-13 **Client's Sample ID:** Bailey #13 Grab
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			11/20/02	14:15	Gaza	SW-846 3050B
Prep: Semi-Volatile Soxhlet Extraction			11/20/02	16:30	Hindle	SW-846 3540C
SPLP Leachate	Completed		11/20/02	20:00	Gaza	SW-846 1312
TCLP Extraction						
Sample Mass Extracted	50.0	grams	11/20/02	20:00	Gaza	SW-846 1311
Initial Volume of Extr. Fluid	1000	ml	11/20/02	20:00	Gaza	SW-846 1311
Initial pH	7.00		11/20/02	20:00	Gaza	SW-846 1311
Final pH	4.90		11/20/02	20:00	Gaza	SW-846 1311
Organics						
1-Methyl naphthalene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
2-Methyl naphthalene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Polynuclear Aromatic Hydrocarbons (PAH's)						
Acenaphthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Acenaphthylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(b)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(ghi)perylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(k)fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Chrysene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Dibenz(a,h)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluoranthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluorene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Indeno(1,2,3-cd)pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Naphthalene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Phenanthrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Pyrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C

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Certificate Of Analysis

Delivery Group ID: 2002:0013856

42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

Date Received 11/20/02
Time Received:
Delivered By: Customer

11548 Cotton Road
Meadville, PA 16335

P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-13 **Client's Sample ID:** Bailey #13 Grab
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Metals						
Selenium (Se)	<4	mg/kg	11/23/02	11:50	Kozakovsky	SW-846 6010B
General Chemistry						
Prep: TPH, Soxhlet Extraction			11/21/02	08:00	Buttray	SW-846 9071A
Solids, %	76.0	%	11/20/02	13:00	Gaza	SM 2540 G
Petroleum Hydrocarbons, Total	100	mg/kg	11/25/02	08:00	Buttray	EPA 418.1

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0013856-14 **Client's Sample ID:** Bailey #14 Grab
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			11/20/02	14:15	Gaza	SW-846 3050B
Prep: Semi-Volatile Soxhlet Extraction			11/20/02	16:30	Hindle	SW-846 3540C
SPLP Leachate	Completed		11/20/02	20:00	Gaza	SW-846 1312
TCLP Extraction						
Sample Mass Extracted	50.0	grams	11/20/02	20:00	Gaza	SW-846 1311
Initial Volume of Extr. Fluid	1000	ml	11/20/02	20:00	Gaza	SW-846 1311
Initial pH	7.30		11/20/02	20:00	Gaza	SW-846 1311
Final pH	5.00		11/20/02	20:00	Gaza	SW-846 1311
Organics						
-Methyl naphthalene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
-Methyl naphthalene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C

Polynuclear Aromatic Hydrocarbons (PAH's)

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Certificate Of Analysis

Delivery Group ID: 2002:0013856

42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

Date Received 11/20/02
Time Received:
Delivered By: Customer

11548 Cotton Road
Meadville, PA 16335

P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-14 **Client's Sample ID:** Bailey #14 Grab
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Organics (Continued)						
Polynuclear Aromatic Hydrocarbons (PAH's) (Continued)						
Acenaphthene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Acenaphthylene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)anthracene	0.6	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(a)pyrene	0.5	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(b)fluoranthene	0.4	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(ghi)perylene	0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Benzo(k)fluoranthene	0.3	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Chrysene	0.5	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Dibenz(a,h)anthracene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluoranthene	1.4	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Fluorene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Indeno(1,2,3-cd)pyrene	0.3	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Naphthalene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Phenanthrene	<0.2	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Pyrene	1.0	mg/kg	11/21/02	21:00	Lata	SW-846 8270C
Metals						
Selenium (Se)	<3	mg/kg	11/23/02	11:50	Kozakovsky	SW-846 6010B
General Chemistry						
Prep: TPH, Soxhlet Extraction			11/21/02	08:00	Buttray	SW-846 9071A
Solids, %	83.6	%	11/20/02	13:00	Gaza	SM 2540 G
Petroleum Hydrocarbons, Total	70	mg/kg	11/25/02	08:00	Buttray	EPA 418.1

Results expressed as mg/kg are calculated on a dry weight basis.

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Selenium by Graphite Furnace

Certificate Of Analysis

Delivery Group ID: 2002:0014413 14 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

11548 Cotton Road
Meadville, PA 16335

Date Received 12/6/02
Time Received:
Delivered By: Customer

P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/11/2002 at 12:00PM

Sample ID: 2002:0014413-1 **Client's Sample ID:** Bailey #1 Org. #13856-1
Date Sampled: 11/19/02 **Time Sampled:** **Date Received:** 12/6/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			12/06/02	13:00	Gaza	SW-846 3050B
Metals						
Selenium (Se)	3.9	mg/kg	12/09/02	13:00	Kozakovsky	SW-846 7740

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0014413-2 **Client's Sample ID:** Bailey #2 Org. #13856-2
Date Sampled: 11/19/02 **Time Sampled:** **Date Received:** 12/6/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			12/06/02	13:00	Gaza	SW-846 3050B
Metals						
Selenium (Se)	4.5	mg/kg	12/09/02	13:00	Kozakovsky	SW-846 7740

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0014413-3 **Client's Sample ID:** Bailey #3 Org. #13856-3
Date Sampled: 11/19/02 **Time Sampled:** **Date Received:** 12/6/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			12/06/02	13:00	Gaza	SW-846 3050B

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Certificate Of Analysis

Delivery Group ID: 2002:0014413 14 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

Date Received 12/6/02
Time Received:
Delivered By: Customer

11548 Cotton Road
Meadville, PA 16335

P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/11/2002 at 12:00PM

Sample ID: 2002:0014413-3 **Client's Sample ID:** Bailey #3 Org. #13856-3
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 12/6/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Metals						
Selenium (Se)	3.1	mg/kg	12/09/02	13:00	Kozakovsky	SW-846 7740

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0014413-4 **Client's Sample ID:** Bailey #4 Org. #13856-4
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 12/6/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			12/06/02	13:00	Gaza	SW-846 3050B
Metals						
Selenium (Se)	5.4	mg/kg	12/09/02	13:00	Kozakovsky	SW-846 7740

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0014413-5 **Client's Sample ID:** Bailey #5 Org. #13856-5
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 12/6/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			12/06/02	13:00	Gaza	SW-846 3050B
Metals						
Selenium (Se)	3.4	mg/kg	12/09/02	13:00	Kozakovsky	SW-846 7740

Results expressed as mg/kg are calculated on a dry weight basis.

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EMAIL: service@free-col.com

Certificate Of Analysis

Delivery Group ID: 2002:0014413 14 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

Date Received 12/6/02
Time Received:
Delivered By: Customer

11548 Cotton Road
Meadville, PA 16335

P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/11/2002 at 12:00PM

Sample ID: 2002:0014413-6 **Client's Sample ID:** Bailey #6 Org. #13856-6
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 12/6/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			12/06/02	13:00	Gaza	SW-846 3050B
Metals						
Selenium (Se)	2.4	mg/kg	12/09/02	13:00	Kozakovsky	SW-846 7740

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0014413-7 **Client's Sample ID:** Bailey #7 Org. #13856-7
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 12/6/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			12/06/02	13:00	Gaza	SW-846 3050B
Metals						
Selenium (Se)	1.5	mg/kg	12/09/02	13:00	Kozakovsky	SW-846 7740

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0014413-8 **Client's Sample ID:** Bailey #8 Org. #13856-8
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 12/6/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			12/06/02	13:00	Gaza	SW-846 3050B

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Delivery Group ID: 2002:0014413 14 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

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Date Received 12/6/02
Time Received:
Delivered By: Customer

P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/11/2002 at 12:00PM

Sample ID: 2002:0014413-8 **Client's Sample ID:** Bailey #8 Org. #13856-8
Date Sampled: 11/19/02 **Time Sampled:** **Date Received:** 12/6/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Metals						
Selenium (Se)	0.91	mg/kg	12/09/02	13:00	Kozakovsky	SW-846 7740

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0014413-9 **Client's Sample ID:** Bailey #9 Org. #13856-9
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 12/6/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			12/06/02	13:00	Gaza	SW-846 3050B
Metals						
Selenium (Se)	0.98	mg/kg	12/09/02	13:00	Kozakovsky	SW-846 7740

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0014413-10 **Client's Sample ID:** Bailey #10 Org.#13856-10
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 12/6/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			12/06/02	13:00	Gaza	SW-846 3050B
Metals						
Selenium (Se)	0.80	mg/kg	12/09/02	13:00	Kozakovsky	SW-846 7740

Results expressed as mg/kg are calculated on a dry weight basis.

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Delivery Group ID: 2002:0014413 14 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

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Time Received:
Delivered By: Customer

P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/11/2002 at 12:00PM

Sample ID: 2002:0014413-11 **Client's Sample ID:** Bailey #11 Org. #13856-11
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 12/6/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			12/06/02	13:00	Gaza	SW-846 3050B
Metals						
Selenium (Se)	0.55	mg/kg	12/09/02	13:00	Kozakovsky	SW-846 7740

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0014413-12 **Client's Sample ID:** Bailey #12 Org. #13856-12
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 12/6/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			12/06/02	13:00	Gaza	SW-846 3050B
Metals						
Selenium (Se)	0.3	mg/kg	12/09/02	13:00	Kozakovsky	SW-846 7740

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0014413-13 **Client's Sample ID:** Bailey #13 Org. #13856-13
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 12/6/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			12/06/02	13:00	Gaza	SW-846 3050B

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Delivery Group ID: 2002:0014413 14 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

Date Received 12/6/02
Time Received:
Delivered By: Customer

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Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/11/2002 at 12:00PM

Sample ID: 2002:0014413-13 **Client's Sample ID:** Bailey #13 Org. #13856-13
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 12/6/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Metals						
Selenium (Se)	<0.2	mg/kg	12/09/02	13:00	Kozakovsky	SW-846 7740

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0014413-14 **Client's Sample ID:** Bailey #14 Org. #13856-14
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 12/6/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3050B Met Total			12/06/02	13:00	Gaza	SW-846 3050B
Metals						
Selenium (Se)	0.2	mg/kg	12/09/02	13:00	Kozakovsky	SW-846 7740

Results expressed as mg/kg are calculated on a dry weight basis.

John R Paraska
QUALITY ASSURANCE SUPERVISOR

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Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

Date Received 11/20/02
Time Received:
Delivered By: Customer

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P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-15 **Client's Sample ID:** Bailey #1 TCLP Leachate of 13856-1
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	05:30	Davis	SW-846 3010A
Metals						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

Sample ID: 2002:0013856-16 **Client's Sample ID:** Bailey #2 TCLP Leachate of 13856-2
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	05:30	Davis	SW-846 3010A
Metals						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

Sample ID: 2002:0013856-17 **Client's Sample ID:** Bailey #3 TCLP Leachate of 13856-3
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	05:30	Davis	SW-846 3010A
Metals						

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Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

Date Received 11/20/02
Time Received:
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P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-17 **Client's Sample ID:** Bailey #3 TCLP Leachate of 13856-3
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Metals (Continued)						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

Sample ID: 2002:0013856-18 **Client's Sample ID:** Bailey #4 TCLP Leachate of 13856-4
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	05:30	Davis	SW-846 3010A
Metals						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

Sample ID: 2002:0013856-19 **Client's Sample ID:** Bailey #5 TCLP Leachate of 13856-5
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	05:30	Davis	SW-846 3010A
Metals						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

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Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

Date Received 11/20/02
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P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

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Sample ID: 2002:0013856-20 **Client's Sample ID:** Bailey #6 TCLP Leachate of 13856-6
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	05:30	Davis	SW-846 3010A
Metals						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

Sample ID: 2002:0013856-21 **Client's Sample ID:** Bailey #7 TCLP Leachate of 13856-7
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	05:30	Davis	SW-846 3010A
Metals						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

Sample ID: 2002:0013856-22 **Client's Sample ID:** Bailey #8 TCLP Leachate of 13856-8
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	05:30	Davis	SW-846 3010A
Metals						

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Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

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Date Received 11/20/02
Time Received:
Delivered By: Customer

P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-22 **Client's Sample ID:** Bailey #8 TCLP Leachate of 13856-8
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Metals (Continued)						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

Sample ID: 2002:0013856-23 **Client's Sample ID:** Bailey #9 TCLP Leachate of 13856-9
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	05:30	Davis	SW-846 3010A
Metals						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

Sample ID: 2002:0013856-24 **Client's Sample ID:** Bailey #10 TCLP Leachate of 13856-10
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	05:30	Davis	SW-846 3010A
Metals						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

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Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

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P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-25 **Client's Sample ID:** Bailey #11 TCLP Leachate of 13856-11
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	05:30	Davis	SW-846 3010A
Metals						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

Sample ID: 2002:0013856-26 **Client's Sample ID:** Bailey #12 TCLP Leachate of 13856-12
Date Sampled. 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	05:30	Davis	SW-846 3010A
Metals						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

Sample ID: 2002:0013856-27 **Client's Sample ID:** Bailey #13 TCLP Leachate of 13856-13
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	05:30	Davis	SW-846 3010A
Metals						

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Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

Date Received 11/20/02
Time Received:
Delivered By: Customer

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P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-27 **Client's Sample ID:** Bailey #13 TCLP Leachate of 13856-13
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Metals (Continued)						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

Sample ID: 2002:0013856-28 **Client's Sample ID:** Bailey #14 TCLP Leachate of 13856-14
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	05:30	Davis	SW-846 3010A
Metals						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

Sample ID: 2002:0013856-29 **Client's Sample ID:** Bailey #1 SPLP Leachate of 13856-1
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	14:00	Davis	SW-846 3010A
Metals						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

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Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

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Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-30 **Client's Sample ID:** Bailey #2 SPLP Leachate of 13856-2
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	14:00	Davis	SW-846 3010A
Metals						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

Sample ID: 2002:0013856-31 **Client's Sample ID:** Bailey #3 SPLP Leachate of 13856-3
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	14:00	Davis	SW-846 3010A
Metals						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

Sample ID: 2002:0013856-32 **Client's Sample ID:** Bailey #4 SPLP Leachate of 13856-4
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	14:00	Davis	SW-846 3010A
Metals						

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Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

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Time Received:
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P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-32 **Client's Sample ID:** Bailey #4 SPLP Leachate of 13856-4
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Metals (Continued)						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

Sample ID: 2002:0013856-33 **Client's Sample ID:** Bailey #5 SPLP Leachate of 13856-5
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	14:00	Davis	SW-846 3010A
Metals						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

Sample ID: 2002:0013856-34 **Client's Sample ID:** Bailey #6 SPLP Leachate of 13856-6
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	14:00	Davis	SW-846 3010A
Metals						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

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Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

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P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

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Sample ID: 2002:0013856-35 **Client's Sample ID:** Bailey #7 SPLP Leachate of 13856-7
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	14:00	Davis	SW-846 3010A
Metals						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

Sample ID: 2002:0013856-36 **Client's Sample ID:** Bailey #8 SPLP Leachate of 13856-8
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	14:00	Davis	SW-846 3010A
Metals						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

Sample ID: 2002:0013856-37 **Client's Sample ID:** Bailey #9 SPLP Leachate of 13856-9
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	14:00	Davis	SW-846 3010A
Metals						

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Certificate Of Analysis

Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

Date Received 11/20/02
Time Received:
Delivered By: Customer

11548 Cotton Road
Meadville, PA 16335

P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-37 **Client's Sample ID:** Bailey #9 SPLP Leachate of 13856-9
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Metals (Continued)						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

Sample ID: 2002:0013856-38 **Client's Sample ID:** Bailey #10 SPLP Leachate of 13856-10
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	14:00	Davis	SW-846 3010A
Metals						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

Sample ID: 2002:0013856-39 **Client's Sample ID:** Bailey #11 SPLP Leachate of 13856-11
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	14:00	Davis	SW-846 3010A
Metals						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

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Delivery Group ID: 2002:0013856 42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

Date Received 11/20/02
Time Received:
Delivered By: Customer

11548 Cotton Road
Meadville, PA 16335

P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-40 **Client's Sample ID:** Bailey #12 SPLP Leachate of 13856-12
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	14:00	Davis	SW-846 3010A
Metals						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

Sample ID: 2002:0013856-41 **Client's Sample ID:** Bailey #13 SPLP Leachate of 13856-13
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	14:00	Davis	SW-846 3010A
Metals						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

Sample ID: 2002:0013856-42 **Client's Sample ID:** Bailey #14 SPLP Leachate of 13856-14
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Prep Group						
Prep: 3010A Met Total			11/22/02	14:00	Davis	SW-846 3010A
Metals						

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Delivery Group ID: 2002:0013856

42 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

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Date Received 11/20/02
Time Received:
Delivered By: Customer

P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/18/2002 at 11:16AM

Sample ID: 2002:0013856-42 **Client's Sample ID:** Bailey #14 SPLP Leachate of 13856-14

Date Sampled: 11/19/02 **Time Sampled:** **Date Received:** 11/20/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
Metals (Continued)						
Selenium (Se)	<0.05	mg/L	11/23/02	09:30	Kozakovsky	SW-846 6010B

Supplemental Revision on 12/18/02 to Report 2002:0013856 printed on 11/27/02.

John R Paraska
QUALITY ASSURANCE SUPERVISOR

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Delivery Group ID: 2002:0014098 14 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

Date Received 11/26/02
Time Received:
Delivered By: Customer

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P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/10/2002 at 01:48PM

Sample ID: 2002:0014098-1 **Client's Sample ID:** Bailey #1 Org. #13856-1
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/26/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
General Chemistry						
Total Organic Carbon	14800	mg/kg	12/04/02	14:30	Pearson	SW-846 9060

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0014098-2 **Client's Sample ID:** Bailey #2 Org. #13856-2
Date Sampled. 11/19/02 **Time Sampled:** **Date Received:** 11/26/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
General Chemistry						
Total Organic Carbon	20200	mg/kg	12/04/02	14:30	Pearson	SW-846 9060

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0014098-3 **Client's Sample ID:** Bailey #3 Org. #13856-3
Date Sampled. 11/19/02 **Time Sampled:** **Date Received:** 11/26/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
General Chemistry						
Total Organic Carbon	21100	mg/kg	12/04/02	14:30	Pearson	SW-846 9060

Results expressed as mg/kg are calculated on a dry weight basis.

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Delivery Group ID: 2002:0014098 14 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

Date Received 11/26/02
Time Received:
Delivered By: Customer

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P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/10/2002 at 01:48PM

Sample ID: 2002:0014098-4 **Client's Sample ID:** Bailey #4 Org. #13856-4
Date Sampled: 11/19/02 **Time Sampled:** **Date Received:** 11/26/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
General Chemistry						
Total Organic Carbon	9570	mg/kg	12/05/02	14:30	Pearson	SW-846 9060

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0014098-5 **Client's Sample ID:** Bailey #5 Org. #13856-5
Date Sampled: 11/19/02 **Time Sampled:** **Date Received:** 11/26/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
General Chemistry						
Total Organic Carbon	33000	mg/kg	12/04/02	14:30	Pearson	SW-846 9060

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0014098-6 **Client's Sample ID:** Bailey #6 Org. #13856-6
Date Sampled: 11/19/02 **Time Sampled:** **Date Received:** 11/26/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
General Chemistry						
Total Organic Carbon	12400	mg/kg	12/04/02	14:30	Pearson	SW-846 9060

Results expressed as mg/kg are calculated on a dry weight basis.

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Certificate Of Analysis

Delivery Group ID: 2002:0014098 14 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

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Date Received 11/26/02
Time Received:
Delivered By: Customer

P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/10/2002 at 01:48PM

Sample ID: 2002:0014098-7 **Client's Sample ID:** Bailey #7 Org. #13856-7
Date Sampled: 11/19/02 **Time Sampled:** **Date Received:** 11/26/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
General Chemistry						
Total Organic Carbon	25200	mg/kg	12/05/02	14:30	Pearson	SW-846 9060

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0014098-8 **Client's Sample ID:** Bailey #8 Org. #13856-8
Date Sampled: 11/19/02 **Time Sampled:** **Date Received:** 11/26/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
General Chemistry						
Total Organic Carbon	183000	mg/kg	12/05/02	14:30	Pearson	SW-846 9060

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0014098-9 **Client's Sample ID:** Bailey #9 Org. #13856-9
Date Sampled: 11/19/02 **Time Sampled:** **Date Received:** 11/26/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
General Chemistry						
Total Organic Carbon	58200	mg/kg	12/05/02	14:30	Pearson	SW-846 9060

Results expressed as mg/kg are calculated on a dry weight basis.

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Delivery Group ID: 2002:0014098

14 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

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Meadville, PA 16335

Date Received 11/26/02
Time Received:
Delivered By: Customer

P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/10/2002 at 01:48PM

Sample ID: 2002:0014098-10 **Client's Sample ID:** Bailey #10 Org. #13856-10
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/26/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
General Chemistry						
Total Organic Carbon	12200	mg/kg	12/05/02	14:30	Pearson	SW-846 9060

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0014098-11 **Client's Sample ID:** Bailey #11 Org. #13856-11
Date Sampled: 11/19/02 **Time Sampled:** **Date Received:** 11/26/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
General Chemistry						
Total Organic Carbon	12800	mg/kg	12/05/02	14:30	Pearson	SW-846 9060

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0014098-12 **Client's Sample ID:** Bailey #12 Org. #13856-12
Date Sampled 11/19/02 **Time Sampled:** **Date Received:** 11/26/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
General Chemistry						
Total Organic Carbon	6990	mg/kg	12/05/02	14:30	Pearson	SW-846 9060

Results expressed as mg/kg are calculated on a dry weight basis.

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Delivery Group ID: 2002:0014098

14 Sample(s) are included in this Delivery Group.

Company Name: Moody & Associates

11548 Cotton Road
Meadville, PA 16335

Date Received 11/26/02
Time Received:
Delivered By: Customer

P.O. Bailey

Project Name: Bailey Mine Stream Sediment/02-406BS

Printed on 12/10/2002 at 01:48PM

Sample ID: 2002:0014098-13 **Client's Sample ID:** Bailey #13 Org. #13856-13
Date Sampled: 11/19/02 **Time Sampled:** **Date Received:** 11/26/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
General Chemistry						
Total Organic Carbon	5450	mg/kg	12/05/02	14:30	Pearson	SW-846 9060

Results expressed as mg/kg are calculated on a dry weight basis.

Sample ID: 2002:0014098-14 **Client's Sample ID:** Bailey #14 Org. #13856-14
Date Sampled: 11/19/02 **Time Sampled:** **Date Received:** 11/26/02

Analyte	Result	Units	Date Analyzed	Start Time	Analyst	Method Source
General Chemistry						
Total Organic Carbon	4610	mg/kg	12/05/02	14:30	Pearson	SW-846 9060

Results expressed as mg/kg are calculated on a dry weight basis.

John R Paraska

QUALITY ASSURANCE SUPERVISOR

Moody and Associates Inc.
1 Cotton Rd., Meadville, PA 16335
Phone 814/724-4970 Fax 814/724-4973

CHAIN OF CUSTODY RECORD

No. 8377

1898

PROJECT: BAILEY MINE STREAM SEDIMENTS DATE: 11/19/02

02-406 BS

3856

BILL TO: ☐ CLIENT ☐ MOODY'S

SAMPLE DESCRIPTION	SAMPLING METHOD	DATE	TIME	COLLECTOR
1. BAILEY #1	GRAB	11/19/02	—	MIOLA / SUTHRIN
Parameters: SEE ATTACHED SHEET				(4 JARS)
2. BAILEY #2	GRAB	11/19/02	—	MIOLA / SUTHRIN
Parameters: SEE #1				(4 JARS)
3. BAILEY #3	GRAB	11/19/02	—	MIOLA / SUTHRIN
Parameters: SEE #1				(4 JARS)
4. BAILEY #4	GRAB	11/19/02	—	MIOLA / SUTHRIN
Parameters: SEE #1				(3 JARS)
5. BAILEY #5	GRAB	11/19/02	—	MIOLA / SUTHRIN
Parameters: SEE #1				(3 JARS)
6. BAILEY #6	GRAB	11/19/02	—	MIOLA / SUTHRIN
Parameters: SEE #1				(3 JARS)
7. BAILEY #7	GRAB	11/19/02	—	MIOLA / SUTHRIN
Parameters: SEE #1				(3 JARS)
8. BAILEY #8	GRAB	11/19/02	—	MIOLA / SUTHRIN
Parameters: SEE #1				(3 JARS)

Signature	Title	Organization	Inclusive Dates
1. [illegible]	GEO TECH	MOODY'S	11/19/02
2. [illegible]	GEOLOGIST	MOODY	11/19/02
3. [illegible]	ENV SCI	MOODY'S	11/19/02
4. [illegible]	[illegible]		11-20-02
[illegible]	Director	[illegible]	11-20-02
[illegible]	QA		11/20-12/20/02

White - Office Canary - Client Pink - Lab

Moody and Associates Inc.
1 Cotton Rd., Meadville, PA 16335
Phone 814/724-4970 Fax 814/724-4973

CHAIN OF CUSTODY RECORD

No. 3378

PROJECT: BAILEY MINE STREAM SEDIMENTS DATE: 11/19/02
02-406 BS
3856
BILL TO: ☐ CLIENT ☐ MOODY'S

SAMPLE DESCRIPTION	SAMPLING METHOD	DATE	TIME	COLLECTOR
1. BAILEY #9	GRAB	11/19/02	—	MEDLA / SUTPHIN
Parameters: SEE ATTACHED SHEET			(3 JARS)	
2. BAILEY #10	GRAB	11/19/02	—	MEDLA / SUTPHIN
Parameters: SEE #1			(3 JARS)	
3. BAILEY #11	GRAB	11/19/02	—	MEDLA / SUTPHIN
Parameters: SEE #1			(3 JARS)	
4. BAILEY #12	GRAB	11/19/02	—	MEDLA / SUTPHIN
Parameters: SEE #1			(3 JARS)	
5. BAILEY #13	GRAB	11/19/02	—	MEDLA / SUTPHIN
Parameters: SEE #1			(3 JARS)	
6. BAILEY #14	GRAB	11/19/02	—	MEDLA / SUTPHIN
Parameters: SEE #1			(4 JARS)	
7.				
Parameters				
8.				
Parameters				

Signature	Title	Organization	Inclusive Dates
1. Brendan Medla	GEO TECH	MOODY'S	11/19/02
2. [illegible]	GEOLOGIST	MOODY	11/19/02
3. [illegible]	ENV SCI	MOODY'S	11/19/02
4. [illegible]	TECH. CAL		11-20-02
Laura Gregoire	Chemist		11-20-02
[illegible]	FL	QA	11/20 - 12/10/02

White - Office Canary - Client Pink - Lab

CONSOL ENERGY™

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phone: 412/831-4679
fax: 412/831-4513
e-mail: Jonathanpachter@consolenergy.com
web: www.consolenergy.com

CERTIFIED MAIL
RETURN RECEIPT REQUESTED

February 10, 2003

Mr. Albert H. Rogalla
Chief, Regulatory Branch
Operations and Readiness Division
Department of the Army
Pittsburgh District, Corps of Engineers
1000 Liberty Avenue
Pittsburgh, PA 15222-4186

RE: Proposed Bailey Mine Coal Refuse Disposal Areas
Consol Pennsylvania Coal Company
Richhill Township, Greene County, PA

Dear Mr. Rogalla:

On January 10, 2003, Consol Pennsylvania Coal Company (CPCC) personnel (CPCC; Jonathan Pachter and Tom Jageman) and Civil & Environmental Consultants, Inc. personnel (CEC; Mark Haibach and Jim Mudge) met in State College, Pennsylvania with Christina Neubert and Marcia Haberman from your office (COE), Cindy Tibbott, Mark Roberts and Jennifer Kagel of the United States Fish & Wildlife Service (FWS) and David Rider of the United States Environmental Protection Agency, Region III (USEPA) to discuss the selenium (Se) and polycyclic aromatic hydrocarbon (PAH) concentrations measured in Enlow Fork downstream of the proposed facility and future monitoring efforts. Prior to the meeting we forwarded additional information and analysis regarding the selenium and PAH issues discussed during our December 5, 2002 conference call. Attachment A to this letter is a list of references and/or documents most of which were previously provided to representatives of COE, FWS and EPA or have been provided by the agencies.

CPCC is very concerned about proceeding with the monitoring program proposed by the agencies at the January 10, 2003 meeting for the following eight reasons:

Rec'd 2/11/2003

1. The unsupported presumption that the proposed facility will result in pollutant discharges (e.g., Se, PAHs) to the streams that are comparable to or greater than those attributed by the agencies to the existing facility when in fact the proposed facility will have lined sedimentation ponds and only discharge in accordance with NPDES criteria. In fact December 2002 analysis of the ponds at the existing facility and nearby streams for Se resulted in all values being non-detect at 2 μg/L.

2. The agencies' assumption that monitoring the effects of current stream conditions will be reflective of the future operation of the proposed facility and will result in a cumulative impact assessment is questionable at best. We question and do not understand how the results from the monitoring of the existing impoundment, designed and constructed differently than the proposed facility, can serve as a basis for approval or denial of the proposed facility.

3. The agencies' perception that any concentration of Se and PAH downstream that is greater than upstream levels warrants further study. In addition, the lack of agency definition on what concentration of Se is acceptable in freshwater sediments for ecological risk screening purposes. Furthermore, the use of USEPA (1997) ecological risk assessment (ERA) guidance would not support the position that adverse effects to ecological receptors would be expected based on the selenium concentrations measured in sediments downstream from the existing facility (see discussion in Attachment B).

4. At the January 10 meeting, CPCC proposed to do monitoring after the proposed facility was installed, based on the discharge limits imposed in the NPDES permit. If the results of the monitoring indicated exceedences of regulatory limits, then CPCC offered that further evaluations would be performed to determine the ecological effects associated with the discharges. CPCC then offered to install engineering controls if adverse effects to aquatic life were determined. Agency personnel felt that an assessment was required now and rejected this alternative for post-construction monitoring. CPCC believes the monitoring proposed by the agencies may address current operations and other contributing sources of the Se and PAH in the streams near the existing and proposed facilities but is not going to be definitive and will not provide the cumulative impact assessment desired by the COE to assess the effects of the new impoundment and the existing complex. CPCC is very concerned that the proposed agency will not be conclusive and will instead result in indecision and delays in the issuance of the Section 404 permit. As we advised the agencies at our meeting in December 2002, the continuing operation of the Bailey Central Processing Plant, the Bailey Mine, and the Enlow Fork Mine – as well as the continued employment of all of the people who work tat these facilities – depend on CPCC's ability to start construction of the new refuse disposal areas in early fall 2003.

5. The elevated PAH levels identified in Enlow Fork downstream of the facility may or may not be attributable to the operation of the current facility and it is questionable whether this can be definitively determined because the PAH composition in the environment changes through time due to a number of processes.

6. The FWS stated that a reasonable freshwater sediment screening criteria for total PAHs (TPAH) was the probable effect concentration (PEC) of 22.8 ppm suggested by CPCC in our December 5, 2002 presentation and based on the work of Ingersoll et al. (2000). However, agency representatives stated at the January 10, 2003 meeting that the FWS samples (EF-012 and EF-012 duplicate) with elevated PAH measurements should not be adjusted because of the elevated total organic carbon (TOC) values associated with each sample (i.e., about 14 and 18%). Subsequent discussions with Dr. Ingersoll indicated that that the PEC was established using sediment toxicity testing and sediment samples that ranged in TOC content from 1-3%. Dr. Ingersoll stated that it would be appropriate to adjust or normalize the sample results to 1-2% TOC and then direct comparisons to the PEC would be appropriate. The FWS sample results for total PAHs based on 13 representative compounds were normalized to 2% TOC using the approach described by FWS in their letter to COE dated October 23, 2002. The resultant total PAH values are about 17 and 4.8 ppm (Table 1). Since both of these values are less than the 22.8 PEC screening value, it does not appear that further study is warranted.

7. Naphthalene and phenanthrene values in two and one FWS sediment samples, respectively, exceed the Ingersoll et al. (2000) PEC values. However, we do not believe this necessitates further study for the following reasons: a) DiToro and McGrath (2002) indicate the PECs overestimate toxicity because they do not accurately account for bioavailability (see PAH discussion in Attachment B); and b) Swartz (1999) states that "guidelines for individual PAHs seem inappropriate regardless of whether they are derived from correlative, experimental or theoretical methods. Because of the mixture paradox, they will be either be ecologically irrelevant or create the false impression that the individual compounds has caused the observed effects. Because the effects are actually caused by multiple co-varying PAHs, it seems reasonable to define the guideline in the mixture context. In particular, a guideline based on TPAH would resolve the mixture paradox and reduce the variability among guidelines for individual compounds. "

8. FWS stated that lower PAH guidelines like 1 ppm could be used for the screening and provided the article by Johnson et al. (2002) to support this position. However, this work is not appropriate in this particular case for the following reasons: a) it relies on an estuarine species, English sole, which is a species that would not be found in the freshwater environs of the proposed facility; b) the endpoints of the assessment are liver lesion prevalence, DNA adduct levels and impacts on growth and reproduction which are not the population and community assessment endpoints that the individuals at the meeting agreed were the most relevant to making practical decisions on the ecological effects in Enlow Fork; and c) the samples used in the assessment contained "significant

concentrations of higher molecular weight PAHs" which is not true of the samples collected in Enlow Fork. Johnson et al. (2002) state "...sediment PAH effects thresholds generated with these data may not be fully applicable at sites where sediments contain primarily low molecular weight PAHs..."

CEC has provided additional discussion of the issues associated with the selenium and PAHs detected in Enlow Fork in Attachment B to this letter. Based on the information contained in this letter and its attachments, CPCC still questions the ecological risk posed by the observed concentrations of selenium and PAHs in Enlow Fork sediments and, therefore, the need for the further studies requested by the agencies. I would welcome the opportunity to further discuss the need for further monitoring at this time. As stated above, CPCC would be amenable to post-operational monitoring to support the positions stated above in regard to the proposed facility. Please call me at (412) 831-4679 to schedule a meeting with you and your staff.

Very truly yours,

Jonathan M. Pachter

Jonathan. M. Pachter
Manager, Environmental Permits

Enclosures

cc: Mark Haibach, CEC
Jim Mudge, CEC
Tom Jageman, CPCC

Table 1. Polycyclic aromatic hydrocarbons(PAHs) in Enlow Fork adjusted to 2% total organic carbon and compared to the consensus-based probable effect concentration (PEC), Greene County, Pennsylvania. September 4, 2001.

		Sediment Station			
	PEC	EF012[1]	EF012[2]	EF014[1]	EF014[2]
Organics					
Anthracene	0.845	1.32	0.177	0.497	0.055
Fluorene	0.536	1.2	0.161	0.674	0.074
Naphthalene	0.561	43.5	5.839	13.6	1.503
Phenanthrene	1.17	11.4	1.530	4.44	0.491
Benz(a)anthracene	1.05	1.21	0.162	0.593	0.066
Benzo(a)pyrene	1.45	0.866	0.116	0.377	0.042
Chrysene	1.29	1.04	0.140	0.449	0.050
Fluoranthene	2.23	3.37	0.452	1.04	0.115
Pyrene	1.52	3.28	0.440	1.1	0.122
Acenaphthene	NV	0.0459	0.006	0.0231	0.003
Acenaphthalene	NV	0.250	0.034	0.133	0.015
2-methylnaphthalene	NV	59.1	7.933	20	2.210
Dibenz(a,h)anthracene	NV	0.0865	0.012	0.0422	0.005
Percent TOC		14.9	2	18.1	2
Total PAHs (13 common)	22.8	126.67	17.00	42.97	4.75

[1]Original data; [2]Data adjusted to 2% TOC.
All values in µg/g dry weight and adjusted to 2% TOC per FWS letter dated October 23, 2002.
NV - no value
Shading indicates a value greater than consensus-based PEC identified by Ingersoll et al. (2000).

ATTACHMENT A

References

1. Scientific references on selenium toxicology:

- Lemly, D.A. 1998. A Position Paper on Selenium Ecotoxicology: A Procedure for Deriving Site-Specific Water Quality Criteria. *Ecotox. Env. Safety* 39: 1-9.

- Lemly, D.A. 2002. A Procedure for Setting Environmentally Safe Total Maximum Daily Loads (TMDLs) for Selenium. *Ecotox. Env. Safety* 52: 123-127.

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- Lohner, T.W., R.J. Reash, V.E. Willet, and L.A. Rose. 2001. Assessment of Tolerant Sunfish Populations (*Lepomis* sp.) Inhabiting Selenium-Laden Coal Ash Effluents. 1. Hematological and Population Level Assessment. *Ecotox. Env. Safety* 50: 203-216.

- Lohner, T.W., R.J. Reash, and M. Williams. 2001. Assessment of Tolerant Sunfish Populations (*Lepomis* sp.) Inhabiting Selenium-Laden Coal Ash Effluents. 2. Tissue Biochemistry Evaluations. *Ecotox. Env. Safety* 50: 217-224.

- Lohner, T.W., R.J. Reash, V.E. Willet, and J. Fletcher. 2001. Assessment of Tolerant Sunfish Populations (*Lepomis* sp.) Inhabiting Selenium-Laden Coal Ash Effluents. 3. Serum Chemistry and Fish Health Indicators. *Ecotox. Env. Safety* 50: 203-216.

- United States Environmental Protection Agency (USEPA). 2002. Aquatic Life Water Quality Criteria for Selenium. March 2002 Draft. Office of Water. Washington, D.C. (Not attached).

- United States Environmental Protection Agency (USEPA). 2002. National Recommended Water Quality Criteria: 2002. EPA-822-R-02-047. Office of Water. Washington, D.C. (Not attached).

2. Reference on ecological risk assessment:

- USEPA. 1997. Ecological risk assessment guidance for Superfund: Process for designing and conducting ecological risk assessments, interim final. EPA 540-R-97-006. Environmental Response Team. Edison, New Jersey.

3. Scientific references on PAHs:

- Chapman, P.M., J. Downie, A. Maynard, and L.A. Taylor. 1996. Coal and Deodorizer Residues in Marine Sediments – Contaminants or Pollutants? *Env. Tox. Chem.* 15(5): 638-642.

- Ingersoll, C.G., D.D. MacDonald, N. Wang, J.L. Crane, L.J. Field, P.S. Haverland, N.E. Kimble, R.A. Lindskoog, C. Severn, and D.E. Smorong. 2000. Prediction of Sediment Toxicity using Consensus-based Freshwater Sediment Quality Guidelines. EPA 905/R-00/007. USEPA Great Lakes National Program Office. Chicago, IL. 25p.

- Paine, M.D., P.M. Chapman, P.J. Allard, M.H. Murdoch, and D. Minifie. 1996. Limited Bioavailability of Sediment PAH near an Aluminum Smelter: Contamination Does Not Equal Effects. *Env. Tox. Chem.* 15(11): 2003-2018.

- Talley, J.W., U. Ghosh, S.G. Tucker, J.S. Furey, and R.G. Luthy. 2002. Particle-Scale Understanding of Bioavailability of PAHs in Sediment. *Env. Sci. & Tech.* 36:477-483.

- DiToro, D.M. and J.A. McGrath. 2000. Technical Basis for Narcotic Chemicals and Polycyclic Aromatic Hydrocarbon Criteria. II. Mixtures and Sediments. *Env. Tox. Chem.* 19(8): 1971-1982.

- Zeng, E.Y. and C.L. Vista. 1995. Compositional Indices of Polycyclic Aromatic Hydrocarbon Sources off San Diego, California. Pages 38-52. In: Southern California Coastal Water Research Project Annual Report 1994-1995.

- Shorten, C.V., A.W. Elzerman, and G. White. 1990. Methods for the Determination of PAH Desorption Kinetics in Coal Fines and Coal Contaminated Sediments. *Chemosphere.* 20: 137-159.

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ATTACHMENT B

Below, the issues associated with the selenium and PAHs detected in Enlow Fork sediments are further discussed.

Selenium

The work of Lemly (2002) and Van Derveer and Canton (1997) suggest selenium (Se) concentrations in sediment not exceed 2 (effects predicted) to 4 μg/g (ppm; effects observed) dry weight. USEPA (2002) states that Se has the narrowest range of all the priority and non-priority pollutants in regard to the concentrations in water that are beneficial for biota and those that are detrimental (i.e., 0.5 ppm in water is required to maintain metabolism in many organisms and 5 ppm is toxic to some fish).

In the FWS study, the maximum Se concentration of 1.59 ppm was measured in Enlow Fork sediments downstream of Talley Run. The Moody 2002 data show that on the Bailey Mine site and at internal sediment and water treatment control pond sample locations 1 through 8 the Se concentrations ranged from 0.91 to 5.4 ppm. In contrast, at the off-site sample locations 9 through 14, the Se concentrations ranged from <0.02 to 0.98 ppm. None of the off-site (i.e., instream) measurements by FWS or Moody exceed either the predicted or observed Se concentrations for sediments recommended by Lemly (2002) and Van Derveer and Canton (1997).

In addition to total Se concentrations in sediments, the Moody samples were also tested for extractable Se, using the USEPA TCLP and the Pennsylvania SPLP extraction methods. For both techniques, Se was below detection limits indicating that the Se present in the sediments may not be readily biologically available.

Consol has also monitored the total selenium in surface water with samples collected upstream and downstream of the existing facility in December 2002. All values in Enlow Fork were below the detection limit of 2μg/L. In addition, Se was not detected in any of the surface water samples collected by FWS in May 2001. In summary, all values were less than the chronic water quality criterion for total selenium of 5 μg/L established by USEPA (2002) to protect aquatic life in freshwater streams.

These data indicate that the current Bailey Mine discharge control facility is working to control particulate-derived Se and the total Se concentrations in Enlow Fork sediments and surface water are below recommended levels.

USEPA's ecological risk assessment (ERA) guidance (1997) indicates that a hazard quotient method can be used to evaluate the exposure and risk to ecological receptors. This approach compares point estimates of screening ecotoxicity values and representative exposure conditions. A documented and/or best conservatively estimated no-observed-adverse-effect-level (NOAEL) should be used as a screening

ecotoxicity value. Thus, for a chemical of potential ecological concern (CPEC) identified in sediment at the site, the hazard quotient (HQ) can be expressed as the ratio of the exposure concentration (EC) at the site to the NOAEL.

$$HQ = EC/NOAEL$$

An HQ less than one indicates the CPEC alone is unlikely to cause adverse ecological effects (USEPA, 1997).

As discussed above, the NOAELs for the selenium HQ calculation were assumed to range from 2 to 4 ppm based on the predicted chronic effects described by Lemly (2002) and the observed effects reported by Van Derveer and Canton (1997). It should be noted that the use of the chronic effect values in concert with the maximum selenium concentration of 1.59 ppm measured by FWS in sediment is likely overprotective because it assumes species of concern will be exposed to the selenium for an extended period of time (i.e., weeks to months). In addition, mobile aquatic organisms have been documented to avoid toxic concentrations of many constituents.

The HQ is estimated to range from 0.4 to 0.8 using the maximum selenium concentration in Enlow fork sediments. The HQ is below the threshold value of 1.0 and indicates that the selenium in sediments is not likely to cause adverse effects to species of concern.

The results should be viewed as protective of aquatic resources because the following conservative assumptions were used to estimate potential ecological effects:

(1) The maximum selenium concentration in sediment was used for the HQ calculations when the remainder of the analyses by FWS and Moody were at concentrations less than the 1 ppm and would have resultant HQs of about 0.25 to 0.5; and

(2) As discussed above, use of the maximum concentration assumes continuous exposure to the selenium in sediments and does not take into account natural attenuation, bioavailability and exposure adjustments for habitat preference, seasonal use, or behavioral avoidance.

Based on this information, Consol believes the initial ecological risk screen for selenium is adequate to determine that the potential for risks to aquatic species of concern is unlikely.

PAHs

Consol still questions the source of the high PAH value measured by FWS and believes it might be attributable to another source (e.g. oil spill, treated sewage discharge) because the predominant PAHs detected are the low molecular weight (LMW) compounds (e.g., naphthalene, 2-methylnaphthlaene) which may be more indicative of a fuel spill or treated sewage and not unburned coal. Chapman et al. (1996) reported that unburned coal is dominated by higher molecular weight (HMW) compounds (e.g., phenanthrene, pyrene, fluoranthene, chrysene). Shorten et al. (1990) also reported that fresh coal fines from an unburned coal pile were dominated by PAHs with HMW: phenanthrene, pyrene, and chrysene. In contrast, Zeng and Vista (1995) reported that 90 to 100% of the PAHs measured in the effluent from the San Diego sewage treatment plant were LMW (i.e., 2,3 ring-PAHs) and that the samples had the highest total organic carbon (TOC) measurements (i.e., 34-36%) of the samples collected in their study. A sewage plant outfall is located on Enlow Fork and appears to discharge near the location where the sediment sample with the elevated PAH and TOC levels was collected by FWS in 2001.

Furthermore, studies by Chapman et al (1996) and Paine et al. (1996) indicate that unburned coal can be a source of high PAHs in the environment (i.e., contamination). However, they state that the available literature and their studies "indicate that coal and coal leachates are not acutely or chronically toxic to aquatic life, i.e., that these PAHs are not readily bioavailable." The work of Talley et al (2002) further supports this position and they state that "...PAHs associated with coal-derived materials are much less available, not biotreatable, and are apparently not significant with respect to bioaccumulation by earthworms."

In addition, DiToro and Grath (2000) have presented a target lipid narcosis method for developing PAH sediment quality guidelines (SQGs). The conclusion of their work was that the prior empirical guidelines for individual PAHs that are based on dry weight normalized and do not make a correction for bioavailability are one to two orders of magnitude smaller than the concentrations that are know to cause mortality, growth, or reproduction effects and therefore are not reflective of actual effect concentrations for these endpoints. The data presented by DiToro and Grath indicate that the current PAH sediment guidelines are overly conservative by 1-2 orders of magnitude.

Consol-COE/MKT/JEM

Baker
Engineering & Energy

Fax Transmittal Letter

Michael Baker Jr., Inc
A Unit of Michael Baker Corporation

100 Airside Drive
Moon Township, PA 15108
(412) 269-6000

Our Telefax No. Is: (412) 375-3986

Copies: **Jonathan Pachter**
Consol Pennsylvania Coal Company

Date: Date May 1, 2003

To: (Company) Recipient's Company U.S. Army Corps of Engineers

(Attention) Name of Recipient Christina Neubert and Scott Hans

Receiving Telecopier No: Fax # 412-644-4211

From: Name Michele Stewart

TOTAL NUMBER OF PAGES (INCLUDING THIS TRANSMITTAL PAGE) 4

Message:

Re: Consol Pennsylvania Coal Company
Bailey Central Mine Complex
Proposed Coal Refuse Disposal Areas No. 3 and No. 4

Christina and Scott,

See folder 2

Responses to PADEP Mining, PADEP Dams and Waterways, and MSHA comments on permit applications for the subject project are being mailed today. A complete copy is being forwarded to your office as well, to the attention of Albert Rogalla. Attached for your records are the transmittal letters that are being sent to those agencies.

see wetland folder

Note that the comment response submittal that is being forwarded to your office includes the proposed wetland mitigation plan. This plan addresses wetland mitigation comments that you provided in your November 5, 2002 comment letter. It is Consol's understanding that the information presented in this submittal, along with previous submittals to the Corps of Engineers, addresses all of your comments. Please contact me at 412-269-6022 or Jonathan Pachter of Consol at 412-831-4679 if you require additional information.

Michele Stewart

IF YOU **DO NOT** RECEIVE THE NUMBER OF PAGES INDICATED,
PLEASE CONTACT OUR OFFICE AS SOON AS POSSIBLE.

Challenge Us.

Baker

Engineering & Energy

Michael Baker Jr., Inc
A Unit of Michael Baker Corporation

Airside Business Park
100 Airside Drive
Moon Township, PA 15108

412-269-6300
FAX 412-375-3986

May 1, 2003

Mr. Joseph Szunyog, Hydrogeologist
Pennsylvania Department of Environmental Protection
District Mining Operations
3913 Washington Road
McMurray, PA 15317

Re: Consol Pennsylvania Coal Company
Bailey Central Mine Complex
Proposed Coal Refuse Disposal Areas No. 3 and No. 4
Coal Refuse Disposal Permit Application Number 30020701
Richhill Township, Greene County

Dear Mr. Szunyog:

Enclosed are four copies of responses to your February 21, 2003 comments on the subject permit application. Also enclosed are an original and three copies of permit application revision pages/drawings resulting from responses to your comments, as well as comments by other review agencies. Four copies of the revised wetland mitigation plan are included.

Please feel free to call me at (724) 269-6022 or Jonathan Pachter of CONSOL at (412) 831-4679 if you have any questions or comments or require additional information. We are providing replacement pages and drawings to other review agencies that received copies of the subject permit application as indicated below.

Sincerely,

MICHAEL BAKER JR., INC.

Michele Stewart

Michele Stewart, P.E.
Engineering Manager

cc: Jonathan M. Pachter, Consol Pennsylvania Coal Company – one copy
Edward Suter, Consol Pennsylvania Coal Company – two copies
Dennis R. Dickey, Division of Dam Safety - 3 copies, letter & comment response only
Cheryl McGill, Mine Safety and Health Administration – 3 copies, letter & comment response only
Albert H. Rogalla, U.S. Army Corps of Engineers – one copy
William J. Hoffman, U. S. EPA, Region III – one copy
David Densmore, U.S. Fish & Wildlife Service – one copy

Baker

Engineering & Energy

Michael Baker Jr., Inc
A Unit of Michael Baker Corporation

Airside Business Park
100 Airside Drive
Moon Township, PA 15108

412-269-6300
FAX 412-375-3986

May 1, 2003

Mr. Dennis R. Dickey, P.E.
Pennsylvania Department of Environmental Protection
Division of Dam Safety
Rachel Carson State Office Building
P.O. Box 8554
Harrisburg, PA 17105-8554

Re: Consol Pennsylvania Coal Company
Bailey Mine Area No. 3 Slurry Dam
Richhill Township, Greene County
DEP File No. D30-055
Technical Review No. 1

Dear Mr. Dickey:

Enclosed are three copies of responses to your February 13, 2003 comments on the subject dam permit application. Also enclosed are three copies of revision pages/drawings resulting from responses to your comments as well as comments by other review agencies. One copy includes my embossed seal on the first page of the replacement drawings and specifications as requested.

Please feel free to call me at (724) 269-6022 or Jonathan Pachter of CONSOL at (412) 831-4679 if you have any questions or comments or require additional information.

Sincerely,

MICHAEL BAKER JR., INC.

Michele Stewart

Michele Stewart, P.E.
Engineering Manager

cc: Jonathan M. Pachter, Consol Pennsylvania Coal Company – letter & comment response only
Edward Suter, Consol Pennsylvania Coal Company – 2 copies, letter & comment response only
Joseph Szunyog, PADEP District Mining Operations – 4 copies, letter 7 comment response only
Cheryl McGill, Mine Safety and Health Administration – 3 copies, letter & comment response only
Albert H. Rogalla, U.S. Army Corps of Engineers - letter & comment response only
William J. Hoffman, U. S. EPA, Region III - letter & comment response only
David Densmore, U.S. Fish & Wildlife Service - letter & comment response only

Baker

Engineering & Energy

Michael Baker Jr., Inc
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Airside Business Park
100 Airside Drive
Moon Township, PA 15108

412-269-6300
FAX 412-375-3986

May 1, 2003

Ms. Cheryl McGill
District Manager – Coal Mine Safety and Health District 2
U. S. Department of Labor
Mine Safety and Health Administration
New Stanton Office
RR1, Box 736
Hunker, PA 15639

Re: Consol Pennsylvania Coal Company
Bailey Central Mine Complex
Slurry Impoundment I.D. No 1211PA200107-08
Sedimentation Impoundment I.D. No 1211PA200107-09
Refuse Pile I.D. No 1211PA200107-10

Dear Ms. McGill:

Enclosed are three copies of responses to your March 27, 2003 comments on Consol Pennsylvania Coal Company's request for approval for the subject proposed disposal facilities. Also enclosed are three copies of Design Report revision pages/drawings resulting from responses to your comments as well as comments by other review agencies.

Please feel free to call me at (724) 269-6022 or Jonathan Pachter of CONSOL at (412) 831-4679 if you have any questions or comments or require additional information.

Sincerely,

MICHAEL BAKER JR., INC.

Michele Stewart, P.E.
Engineering Manager

cc: Jonathan M. Pachter, Consol Pennsylvania Coal Company – letter & comment response only
Edward Suter, Consol Pennsylvania Coal Company – 2 copies, letter & comment response only
Dennis R. Dickey, Division of Dam Safety – 3 copies, letter & comment response only
Joseph Szunyog, PADEP District Mining Operations – 4 copies, letter & comment response only
Albert H. Rogalla, U.S. Army Corps of Engineers - letter & comment response only
William J. Hoffman, U. S. EPA, Region III - letter & comment response only
David Densmore, U.S. Fish & Wildlife Service - letter & comment response only

1/29/03

Christy,

Enclosed find copies of Reprints that we sent to CEC, along with a copy of our cover letter.

I've also included a copy of the the paper that Tom Jagerman provided to us in the Meeting.

Most of the folks that conclude that coal-derived PAHs Are Not Bioavailable cite the work of Chapman et.al. (1996). As you can see from the few "effects" literature that we have included, coal-derived PAHs do express genotoxic responses in Both fish & Mammals.

Call if you have any questions or need any additional information!

Mark Robinson

Rec'd 2/7/2003

call to Jonathan Proctor - 1/28/03

1. 106 issues - Phase I in Spring.
2. PAH & selenium need baseline before permit is issued and for testing to be meaningful after permit.
3. Agreed to w/FWS - give us a plan in writing prior to meeting. What was agreed to & - effects of existing use
4. Reason that information previously collected not provided to COE & FWS.
5. P.I.R. factors. W. Quality is one of the factors.
6. Letter from FWS on thresholds of parameters.
7. Bio-availability & tissue sampling - project should not be increasing degradation of stream.

United States Department of the Interior

FISH AND WILDLIFE SERVICE

Pennsylvania Field Office
315 South Allen Street, Suite 322
State College, PA 16801-4850

January 21, 2003

Mr. Mark Haibach
Civil & Environmental Consultants, Inc.
333 Baldwin Road
Pittsburgh, Pennsylvania 15205-9702

Dear Mr. Haibach:

This responds to your letter of January 7, 2003, and is in follow-up to the meeting that was held at our office on January 10. Enclosed are copies of several scientific articles that we promised to send to you, many of which will be cited in our final report on the results of sediment and surface water sampling in Enlow Fork and its tributaries.

We found the exchange of technical information at the meeting beneficial; however, after reviewing the articles you provided, we maintain our position that the levels of PAHs and selenium found in sediments immediately downstream of Consol's existing coal refuse disposal and processing area warrant further investigations to determine their effects on fish and wildlife resources. All of the specific recommendations that we provided to you at the meeting (e.g., sediment chemistry, sediment bioassays, fish and benthic community evaluations and fish tissue residue analysis) will be included in our final report. These recommendations are clearly supported by scientific literature documenting that selenium is extremely bioaccumulative and that PAHs (including PAHs typically found in and derived from coal) can cause adverse responses in fish and wildlife resources.

We appreciate the offer by Jonathan Pachter of Consol to provide us with your PAH data that was analyzed concurrently with the 14 selenium locations. We look forward to receiving it at your earliest convenience.

We hope that you find the enclosed articles helpful, and if you have any questions regarding this matter, please contact Mark Roberts of my staff at 814-234-4090.

Sincerely,

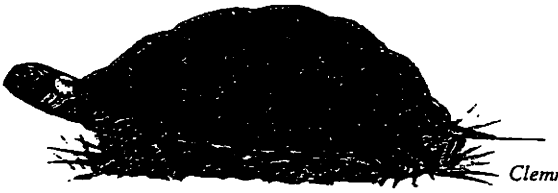
Cindy L. Tibbott

Cindy L. Tibbott
Assistant Supervisor, Environmental Quality

Enclosures

Rec'd 1/24/2003

U.S. Fish and Wildlife Service
Pennsylvania Field Office
315 South Allen Street, Suite 322
State College, Pennsylvania 16801-4850



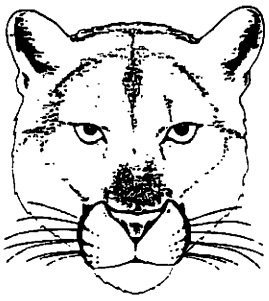
Clemmys muhlenbergii

Date: 1/15/03

To: TOM JAGEMAN 412-854-6753

From: MARK ROBERTS

No. of pages, including cover sheet: 6



Felis concolor couguar

Message: TOM –

Copies of source & abstracts for relevant literature as requested.

Hard copies of these will be included in the package sent out today to Mark Hanbach.

Call or email @ mark_roberts@fws.gov if you need anything else =

Mark

If there is a problem receiving this transmission, please contact our office at 814-234-4090 or by faxing to 814-234-0748.

Tue Jan 14 12:24:40 2003
Cambridge Scientific Abstracts
Database: Biological Sciences
Query: KW=(coal and PAHs and toxicity)
Your Comments:

Record 1 of 1

TI: Title
Local Impacts of Coal Mines and Power Plants across Canada. II. Metals, Organics and Toxicity in Sediments

AU: Author
Cheam, V; Reynoldson, T; Garbai, G; Rajkumar, J; Milani, D

AF: Affiliation
National Water Research Institute, Environment Canada, P.O. Box 5050, Burlington, Ontario L7R 4A6, Canada, [mailto:ven.cheam@cciw.ca]

SO: Source
Water Quality Research Journal of Canada [Water Qual. Res. J. Can.]. Vol. 35, no. 4, pp. 609-631. 2000.

IS: ISSN
1201-3080

AB: Abstract
A Canada-wide survey was undertaken to study local impacts of coal mines and coal-fired electrical generating stations. The first part dealt with thallium in waters and sediments. This, Part II, deals with metals and organics in sediments as well as sediment toxicity to four different organisms. Several elevated metal and PAH concentrations as well as high toxicity (based on biological sediment guidelines) were observed compared to uncontaminated sites. Based on Ontario's sediment guidelines, most of the studied sediments fell in the "marginally to significantly polluted" category of sediment quality, although two belonged to the "grossly polluted" class due to the extremely high concentrations of some metals. The observed diversity of PAHs and near-unity carbon preference indices indicate non-biological origins of the studied sediments. In this initial study, four different organisms, Chironomus riparius, Hyalella azteca, Hexagenia spp. (Hexagenia limbata) and Tubifex tubifex were used to determine sediment toxicity, which showed 50% of the tested sites were highly stressed.

LA: Language
English

SL: Summary Language
English

PY: Publication Year
2000

PD: Publication Date
20000000

PT: Publication Type
Journal Article

DE: Descriptors
Coal; Mining; Sediments; Heavy metals; Organic compounds; Thallium; Pollution; Soil; Canada; Power plants; Sediment pollution; Water pollution; Toxicity; Polycyclic aromatic hydrocarbons; Industrial pollution; Chironomus riparius; Hyalella azteca; Hexagenia limbata; Tubifex tubifex; Pollution effects; Organic matter; Mines; Coal Mines; Powerplants; Metals; Water Pollution Sources; Electric Power Production; Sediment Contamination; Hydrocarbons; Testing Procedures; Mines and mining;

Tue Jan 14 09:25:10 2003
Cambridge Scientific Abstracts
Database: Environmental Sciences and Pollution Mgmt
Query: KW=(coal AND pah)
Your Comments:

Record 1 of 1

TI: Title
Genotoxicity biomonitoring in coal regions using wild rodent Ctenomys torquatus by Comet assay and micronucleus test

AU: Author
da Silva, J; de Freitas, TRO; Heuser, V; Marinho, JR; Erdtmann, B
AF: Affiliation
Departamento de Genetica, Instituto de Biociencias, UFRGS, Av. Bento Goncalves 9500, CP 15053, CEP 91501-970, POA, RS, Brazil, [mailto:juliana@if.ufrgs.br]

SO: Source
Environmental and Molecular Mutagenesis [Environ. Mol. Mutag.]. Vol. 35, no. 4, pp. 270-278. 2000.
IS: ISSN
0893-6692
DO: DOI
10.1002/1098-2280(2000)35:4<270::AID-EM2>3.0.CO; 2-L

AB: Abstract
Coal is a mixture of a variety of chemicals, especially hydrocarbons, which may give rise to polycyclic aromatic hydrocarbons (PAH). Many PAH compounds produce mutagenic and carcinogenic effects. The quality of mineral coal in Rio Grande do Sul (RS) is low and it is typically obtained by stripping operations; it represents approximately 87% of the Brazil reserves. This report concerns the application of the Comet assay to Ctenomys torquatus to detect the effects of coal, comparing the results with a micronucleus (MN) assay, both using peripheral blood. This study was performed over a 2-year period in an attempt to evaluate seasonal patterns. The wild rodent is fossorial, and its geographic distribution in RS coincides with the distribution of coal reserves. Three localitions were studied: two coal fields, Butia (in a strip coal mine region) and Candiota (near a strip coal mine), and one control region, Pelotas (no coal). At the end of 2 years, 240 rodents had been analyzed. Our results showed that coal and derivatives induced DNA and chromosomal lesions in rodent cells that were demonstrated by Comet and MN assays. These tests also demonstrated quantitative differences between field exposures (Candiota > Butia). The Comet assay was more sensitive and also showed a direct relationship between age and damage, and an inverse relationship between temperature and damage index.

LA: Language
English
SL: Summary Language
English
PY: Publication Year
2000
PD: Publication Date
20000000
PT: Publication Type
Journal Article
DE: Descriptors
Mines; Genotoxicity testing; Coal; Comet assay; Micronuclei; Polycyclic aromatic hydrocarbons; Brazil; Genotoxicity; Ctenomys

Tue Jan 14 11:57:27 2003
Cambridge Scientific Abstracts
Database: ASFA: Aquatic Sciences and Fisheries Abstracts
Query: (coal and PAHs and toxicity)
Your Comments:

Record 1 of 1

TI: Title
Increased CYP1A1 and ribosomal protein L5 gene expression in a teleost: The response of juvenile chinook salmon to coal dust exposure

AU: Author
Campbell, PM; Devlin, RH
AF: Author Affilition
Department of Fisheries and Oceans, 4160 Marine Drive, West Vancouver, V7V 1N6, BC, Canada

SO: Source
Aquatic Toxicology [Aquat. Toxicol.], vol. 38, no. 1-3, pp. 1-15, May 1997
IS: ISSN
0166-445X
PB: Publisher
ELSEVIER SCIENCE B.V.

AB: Abstract
Molecular studies on the sublethal physiological effects of coal dust exposure in vertebrates are sparse. Coal dust contamination of the marine environment occurs, for example, around coal loading and storage terminals. To determine the potential impact of coal dust exposure on juvenile chinook salmon (Oncorhynchus tshawytscha), fish were exposed for an 8 day period to 60 mg L-1, 200 mg L-1 or 500 mg L-1 of coal dust in sea water and the levels of CYP1A1 mRNA quantitated using RT-cPCR. Two control groups were utilized; one `negative' control group was maintained in sea water only, whilst the second `positive' control group was i.p. injected with beta -naphthoflavone (BNF: 50 mg kg-1). There was a significant increase in CYP1A1 expression in fish exposed to coal dust (ANOVA; P<0.001), and in fish injected with BNF (t-test; P<0.001), relative to controls. In addition, RT-PCR analysis indicated increased expression of a second gene in the fish exposed to coal dust. Sequence analysis identified the second coal-dust-inducible gene as ribosomal protein L5. Both of these genes, CYP1A1 and L5, encode proteins vital in cellular metabolism. The enzyme encoded by CYP1A1 (P4501A1) plays an important role in the metabolic activation of PAHs to carcinogenic and mutagenic metabolites. L5 plays a crucial role in ribosome biogenesis. At present, the significance of the increased hepatic expression of L5 in coal dust exposed fish is unclear and warrants further investigation.

LA: Language
English
SL: Summary Language
English
PY: Publication Year
1997
PD: Publication Date
19970500
PT: Publication Type
Journal Article
DE: Descriptors
pollution effects; CYP1A1 gene; ribosomal protein L5; coal; Oncorhynchus tshawytscha; dust; water pollution; beta -naphthoflavone; L5 gene; cytochrome P4501A1; toxicity tests; cytochromes; fish physiology; liver; sublethal effects; contamination; marine environment; salmon; water pollution effects; physiology; Oncorhynchus tshawytscha

Tue Jan 14 12:17:03 2003
Cambridge Scientific Abstracts
Database: Environmental Sciences and Pollution Mgmt
Query: KW=(coal and PAHs and toxicity)
Your Comments:

Record 1 of 1

TI: Title
Chronic Effects of the Photoenhanced Toxicity of Anthracene on Daphnia magna Reproduction

AU: Author
Holst, LL; Giesy, JP
AF: Author Affiliation
Michigan State Univ. East Lansing. Pesticide Research Center

SO: Source
Environment Toxicology and Chemistry ETOCDK Vol. 8, No. 10, p 933-942, 1989. 5 fig, 5 tab, 27 ref. National Sea Grant College Program Grant MA-86AA-D-SG-043.

AB: Abstract
Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds consisting of two or more fused benzene rings with occasional inclusions of heteroatoms or cyclopentene rings. PAHs are of environmental concern not only because large quantities of them are released into the environment, but also because many PAHs are carcinogenic to mammals and phototoxic to aquatic organisms. Anthracene is a linear, three-ring PAH found in both oil and coal. In this study the chronic effects of exposure to anthracene and ultraviolet radiation (UVR) on Daphnia magna reproduction were investigated. D. Magna were exposed to anthracene in the presence or absence of ecologically relevant intensities of UVR for 21 d. Exposure to 8.2 micrograms/L anthracene in the absence of UVR significantly reduced the number of neonates produced by 13.8%; however, exposure the UVR in the absence of anthracene had no significant effect on the fecundity of D. magna. Concurrent exposure of D. magna to UVR and anthracene resulted in further reduced survival and fecundity. Exposure of D. magna to 7.2 micrograms/L anthracene and 117 microwatts/square cm UV-A radiation resulted in 70% mortality or a 69% decrease in production of neonates by D. magna that survived. The reduction in fecundity was proportional to both anthracene concentration and UVR intensity. Equations were developed that predict the relative percent reduction in production of neonates due to the photoenhanced toxicity of anthracene given a particular anthracene concentration and UVR intensity. This study has demonstrated that anthracene in the presence of UVR decreases the survival and fecundity of D. magna at concentrations well under aqueous solubility limits. (Author 's abstract)

PY: Publication Year
1989
DE: Descriptors
Reproduction; Anthracene; Synergistic effects; Daphnia; Aromatic compounds; Water pollution effects; Toxicity; Ultraviolet radiation; Embryonic growth stage; Aquatic animals; Organic compounds; Petroleum products; Polycyclic aromatic hydrocarbons
CL: Classification
SW 3030 Effects of pollution
SF: Subfile
Water Resources Abstracts
AN: Accession Number

Tue Jan 14 09:12:34 2003
Cambridge Scientific Abstracts
Database: ASFA: Aquatic Sciences and Fisheries Abstracts
Query: KW=(coal AND pah)
Your Comments:

Record 1 of 3

TI: Title
Suspended Solids, Trace Metal and PAH Concentrations and Loadings from Coal Pile Runoff to Hamilton Harbour, Ontario

AU: Author
Curran, KJ; Irvine, KN; Droppo, IG; Murphy, TP
AF: Affiliation
National Water Research Institute, Aquatic Ecosystem Protection Branch, Burlington, Ontario L7R 4A6, Canada, [mailto:ian.droppo@cciw.ca]

SO: Source
Journal of Great Lakes Research [J. Great Lakes Res.]. Vol. 26, no. 1, pp. 18-30. 2000.
IS: ISSN
0380-1330

AB: Abstract
The Kenilworth boatslip has been identified as a "hotspot" within the Hamilton Harbour Area of Concern because of highly contaminated bottom sediments. There are a variety of sources potentially contributing to this sediment contamination, including runoff from industrial coal piles. The objective of this study was to assess the contaminant characteristics associated with coal pile runoff and identify potential impacts that the runoff might have on sediment quality. Flow-proportioned samples of the coal pile runoff were collected from June through October, 1996 and analyzed for total suspended solids, trace metals, and PAHs. Loadings for selected metals and PAHs were determined using a volumetric approach that considered mean contaminant concentrations and measured or modeled flow volumes. The suspended solids and total trace metal concentrations (Al, Fe, Mn, V, Cd, Cr, Cu, Pb, Zn) often exceeded Canadian Water Quality Guidelines for the Protection of Aquatic Life. Concentrations of fluoranthene, phenanthrene, pyrene, and chrysene exceeded the provincial "Severe Effect Level" for sediment, although the bioavailability of these PAHs should be examined more thoroughly. In general, suspended solids concentration and coal pile volume were significantly correlated with the concentrations of trace metals in the coal pile runoff, while hydrometeorologic variables such as rainfall intensity, rainfall depth, and runoff volume were weakly correlated with metals concentrations. The ratios of various PAHs to naphthalene suggested that coal pile runoff could be an important contributing source to bed sediment contamination. Given the concentrations and loadings of solids, metals, and PAHs and the relatively low volume of runoff, it would be prudent to treat the coal pile discharge as a remedial action for the harbor.

LA: Language
English
SL: Summary Language
English
PY: Publication Year
2000
PD: Publication Date
20000000

1/10/03 meeting - Bailey Mine Refuse Area

Christina Neubert	USACE	412-395-7375
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Cindy Tibbott	US FWS	814-234-4090
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January 7, 2003

Ms. Cindy Tibbott
U.S. Department of the Interior
Fish and Wildlife Service
315 South Allen Street, Suite 322
State College, Pennsylvania 16801

Dear Ms. Tibbott:

Subject: Proposed Bailey Mine Refuse Areas
Consol Pennsylvania Coal Company
Greene County, Pennsylvania
CEC Project 221379

In advance of our meeting this Friday with you, David Rider, and Christina Neubert, we are forwarding additional information and analysis regarding the selenium and PAH issues discussed during our December 5, 2002 conference call. For your review and consideration, we are enclosing the following documents with this letter:

1. Sample location map and selenium data for sediment samples collected from Enlow Fork and the Bailey Mine Complex by Moody and Associates, Inc. on November 19, 2002.

2. Copies of the following scientific papers on selenium toxicology:

   - Lemly, D.A. 1998. A Position Paper on Selenium Ecotoxicology: A Procedure for Deriving Site-Specific Water Quality Criteria. *Ecotox. Env. Safety* 39: 1-9.

   - Lemly, D.A. 2002. A Procedure for Setting Environmentally Safe Total Maximum Daily Loads (TMDLs) for Selenium. *Ecotox. Env. Safety* 52: 123-127.

   - Van Derveer, W.D. and S. P. Canton. 1997. Selenium Sediment Toxicity Thresholds and Derivation of Water Quality Criteria for Freshwater Biota of Western Streams. *Env. Tox Chem.* 16(6):1260-1268.

   - Lohner, T.W., R.J. Reash, V.E. Willet, and L.A. Rose. 2001. Assessment of Tolerant Sunfish Populations (*Lepomis* sp.) Inhabiting Selenium-Laden Coal Ash Effluents. 1. Hematological and Population Level Assessment. *Ecotox. Env. Safety* 50: 203-216.

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Rec'd 1-8-2003

- Lohner, T.W., R.J. Reash, and M. Williams. 2001. Assessment of Tolerant Sunfish Populations (*Lepomis* sp.) Inhabiting Selenium-Laden Coal Ash Effluents. 2. Tissue Biochemistry Evaluations. *Ecotox. Env. Safety* 50: 217-224.

- Lohner, T.W., R.J. Reash, V.E. Willet, and J. Fletcher. 2001. Assessment of Tolerant Sunfish Populations (*Lepomis* sp.) Inhabiting Selenium-Laden Coal Ash Effluents. 3. Serum Chemistry and Fish Health Indicators. *Ecotox. Env. Safety* 50: 203-216.

- United States Environmental Protection Agency (USEPA). 2002. Aquatic Life Water Quality Criteria for Selenium. March 2002 Draft. Office of Water. Washington, D.C. (Not attached)

3. Copies of the following papers on PAH bioavailability and toxicology:

- Chapman, P.M., J. Downie, A. Maynard, and L.A. Taylor. 1996. Coal and Deodorizer Residues in Marine Sediments – Contaminants or Pollutants? *Env. Tox. Chem.* 15(5): 638-642.

- Paine, M.D., P.M. Chapman, P.J. Allard, M.H. Murdoch, and D. Minifie. 1996. Limited Bioavailability of Sediment PAH near an Aluminum Smelter: Contamination Does Not Equal Effects. *Env. Tox. Chem.* 15(11): 2003-2018.

- Talley, J.W., U. Ghosh, S.G. Tucker, J.S. Furey, and R.G. Luthy. 2002. Particle-Scale Understanding of Bioavailability of PAHs in Sediment. *Env. Sci. & Tech.* 36:477-483.

- DiToro, D.M. and J.A. McGrath. 2000. Technical Basis for Narcotic Chemicals and Polycyclic Aromatic Hydrocarbon Criteria. II. Mixtures and Sediments. *Env. Tox. Chem.* 19(8): 1971-1982.

Below, we discuss the enclosed information with regard to selenium and PAHs detected in Enlow Fork sediments.

Selenium

The work of Lemly (2002) and Van Derveer and Canton (1997) suggest selenium (Se) concentrations in sediment not exceed 2 (effects predicted) to 4 μg/g (ppm; effects observed)

dry weight. USEPA (2002) states that Se has the narrowest range of all the priority and non-priority pollutants in regard to the concentrations in water that are beneficial for biota and those that are detrimental (i.e., 0.5 ppm is required to maintain metabolism in many organisms and 5 ppm is toxic to some fish).

In the FWS study, the maximum Se concentration of 1.5 ppm was measured downstream of Talley Run. The Moody 2002 data show that on the Bailey Mine site and at internal sediment and water treatment control pond sample locations 1 through 8 the SE concentrations ranged from 0.91 to 5.4 ppm. In contrast, at the off-site sample locations 9 through 14, the SE concentrations ranged from <0.02 to 0.98 ppm. None of the off-site (i.e. instream) measurements by FWS or Moody exceed either the predicted or observed Se concentrations for sediments recommended by Lemly (2002) and Van Derveer and Canton (1997).

In addition to total Se concentrations in sediments, the Moody samples were also tested for extractable Se, using the USEPA TCLP and the Pennsylvania SPLP extraction methods. For both techniques, Se was below detection limits indicating that the Se present in the sediments may not be readily biologically available.

These data indicate that the Bailey Mine treatment facility is working to control particulate-derived Se and the Se concentrations in Enlow Fork sediments are below recommended levels.

PAHs

Consol still questions the source of the high PAH value measured by FWS and believes it might be attributable to another source (e.g. oil spill) because the predominant PAHs detected are the low molecular weight compounds (e.g., naphthalene, 2-methylnaphthlaene) which are more indicative of a fuel spill and not unburned coal. As reported by Chapman et al. (1996), unburned coal is dominated by higher molecular weight compounds (e.g., phenanthrene, pyrene, fluoranthene, chrysene).

Furthermore, studies by Chapman et al (1996) and Paine et al. (1996) indicate that unburned coal can be a source of high PAHs in the environment (i.e., contamination). However, they state that the available literature and their studies "indicate that coal and coal leachates are not acutely or chronically toxic to aquatic life, i.e., that these PAHs are not readily bioavailable." The work of Talley et al (2002) further supports this position and they state that "...PAHs associated with coal-derived materials are much less available, not biotreatable, and are apparently not significant with respect to bioaccumulation by earthworms."

In addition, DiToro and Grath (2000) have presented a target lipid narcosis method for developing PAH sediment quality guidelines (SQGs). The conclusion of their work was that the prior empirical guidelines for individual PAHs that are based on dry weight normalized and do not make a correction for bioavailability are one to two orders of magnitude smaller than the concentrations that are know to cause mortality, growth, or reproduction effects and therefore are not reflective of actual effect concentrations for these endpoints. The data presented by DiToro and Grath indicate that the current PAH sediment guidelines are overly conservative by 1-2 orders of magnitude.

CLOSING

Based on this information, we still question the ecological risk posed by the observed concentrations of selenium and PAHs in Enlow Fork sediments and, therefore, the need for the further studies requested by FWS. We look forward to discussing the enclosed information with you, Mr. Rider, and Ms. Neubert on Friday.

Very truly yours,

CIVIL & ENVIRONMENTAL CONSULTANTS, INC.

Mark Haibach

Mark R. Haibach, M.S.
Project Manager/ Ecologist

Mark Haibach for

James E. Mudge, Ph.D.
Principal Environmental Scientist

Enclosures

cc: Jonathan Pachter, Consol
Tom Jageman, Consol
David Rider, USEPA
Christina Neubert, USACOE

E-221379.Ja7/W

Objective: Determine source and extent of PAH and inorganic contamination of Enlow Fork, and biological effects.

1. Sediment sampling in Talley Run, existing coal refuse disposal area, sedimentation pond, upstream in Enlow Fork , upstream tributaries that may also have contaminant sources, and Enlow Fork downstream of Talley Run down to and including Pool 6C (at half-mile intervals).

   Analytes: TOC, grain size, inorganics and PAHs (including fingerprinting analyses, if appropriate)

2. Sediment bioassays (*Hyalella, Chironomus*)

3. Benthic invertebrate community, fish community, and habitat assessments in Talley Run, and upstream and downstream in Enlow Fork

4. Fish tissue analysis for inorganics (make sure analysis includes Hg, Sr, and Se).

Possible Phase II activities:

1. Histopathological evaluation of resident fish

2. Whole effluent toxicity testing of facility effluents

3. Residue analysis of benthic invertebrates

Table 1. Location and description of sediment and surface water samples collected in Enlow Fork and surrounding tributaries, Greene County Pennsylvania, September 4, 2001.

Sample Number	Matrix	Stream Name/Location	Latitude / Longitude	Number of Grabs	Comments	Percent TOC	Percent Moisture	Percent Sand	Percent Clay	Percent Silt
EF001	Water	Hewitt Run	N 39° 51' 11.2" / W 80° 28' 48.9"	1						
EF002	Sediment	Hewitt Run	N 39° 51' 11.2" / W 80° 28' 48.9"	4		0.9	36.4	80.7	3.8	15.5
EF003	Water	Chambers Run	N 39° 51' 26.1" / W 80° 28' 36.6"	1						
EF004	Sediment	Chambers Run	N 39° 51' 26.1" / W 80° 28' 36.6"	4		1.88	47.6	71.5	4.1	24.4
EF005	Water	Blank	NA	NA						
EF006	Sediment	Enlow Fork/Pool C	N 39° 57' 40.9" / W 80° 27' 42.3"	4	Lots of organic matter	1.96	48.5	69.6	3	27.4
EF007	Water	Enlow Fork/Pool C	N 39° 57' 40.9" / W 80° 27' 42.3"	1	Water level low					
EF008	Sediment	Duplicate of EF006	N 39° 57' 40.9" / W 80° 27' 42.3"	4	Lots of organic matter	2.17	48	64.7	6.8	28.5
EF009	Water	Templeton Fork	N 39° 59' 12.8" / W 80° 26' 34.6"	1						
EF010	Sediment	Templeton Fork	N 39° 59' 12.8" / W 80° 26' 34.6"	4	Sandy	1.18	38.3	80.8	2.3	16.9
EF011	Water	Enlow Fork/Downstream	N 39° 58' 18.9" / W 80° 25' 31.6"	1	Precipitate with acid					
EF012	Sediment	Enlow Fork/Downstream	N 39° 58' 18.9" / W 80° 25' 31.6"	7	Petroleum odor	14.9	51	27.6	18.8	53.6
EF013	Water	Duplicate of EF011	N 39° 58' 18.9" / W 80° 25' 31.6"	1	Precipitate with acid					
EF014	Sediment	Duplicate of EF012	N 39° 58' 18.9" / W 80° 25' 31.6"	7	Petroleum odor	18.1	49	35.1	15.4	49.5
EF015	Water	Enlow Fork/Upstream	N 39° 58' 36.7" / W 80° 24' 40.4"	1						
EF016	Sediment	Enlow Fork/Upstream	N 39° 58' 36.7" / W 80° 24' 40.4"	4		1.24	38.3	77	4.3	18.7

Table 2. Contaminants in Enlow Fork and surrounding tributary surface water compared to chronic ambient water quality criteria and wildlife benchmarks, Greene County, Pennsylvania. September 4, 2001.

	EPA 1995	Sample et al. 1996									
	Chronic AWQC	Mink	Belted Kingfisher	EF001	EF003	EF005	EF007	EF009	EF011	EF013	EF015
Aluminum	0.087	0.253	0.38	0.18	0.0888	<.0500	0.0993	0.0747	0.274	0.0955	0.136
Arsenic	0.15	0.216	0.846	<.00500	<.00500	<.00500	<.00500	<.00500	<.00500	<.00500	<.00500
Boron	na	na	na	<.100	<.100	<.100	0.132	0.128	0.206	0.197	0.141
Barium	na	na	na	0.0586	0.0506	<.00500	0.0856	0.0717	0.0777	0.0735	0.0801
Beryllium	0.0053	na	na	<.000500	<.000500	<.000500	<.000500	<.000500	<.000500	<.000500	<.000500
Cadmium	0.0011	0.0044	0.0032	<.000500	<.000500	<.000500	<.000500	<.000500	<.000500	<.000500	<.000500
Chromium	na	19.8	na	<.00300	<.00300	<.00300	<.00300	<.00300	<.00300	<.00300	<.00300
Copper	0.012	0.0387	0.42	<.00500	<.00500	<.00500	<.00500	<.00500	0.00606	<.00500	<.00500
Iron	1	na	na	0.299	0.101	<.100	0.135	0.142	0.614	0.218	0.29
Mercury	0.000012	0.0000045	0.0000065	<.00100	<.00100	<.00100	<.00100	<.00100	<.00100	<.00100	<.00100
Magnesium	na	na	na	6.02	5.4	<.100	10.2	6.59	19.2	18.4	8.72
Manganese	na	na	na	0.0214	0.0105	<.00500	0.0354	0.0361	0.158	0.118	0.0405
Molybdenum	na	na	na	<.0500	<.0500	<.0500	<.0500	<.0500	<.0500	<.0500	<.0500
Nickel	0.16	4.2	2	<.00500	<.00500	<.00500	<.00500	<.00500	0.00519	<.00500	<.00500
Lead	0.0032	9.823	0.493	<.0100	<.0100	<.0100	<.0100	<.0100	<.0100	<.0100	<.0100
Selenium	0.005	0.00071	0.00076	<.00500	<.00500	<.00500	<.00500	<.00500	<.00500	<.00500	<.00500
Strontium	na	na	na	0.157	0.136	0.0014	0.638	0.236	1.78	1.66	0.288
Vanadium	na	na	na	<.00100	<.00100	<.00100	<.00100	<.00100	<.00100	<.00100	<.00100
Zinc	0.11	1.86	0.268	0.0337	0.0386	0.0509	0.0454	0.0272	0.0519	0.0483	0.0313

All values in mg/L.
Light shading indicates value greater than EPA chronic AWQC (EPA 1995).

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Table 3. Contaminants in Enlow Fork and surrounding tributary sediment compared to the consensus-based probable effect concentration (PEC), Greene County, Pennsylvania. September 4, 2001.

		Sediment Station							
	PEC	EF002	EF004	EF006	EF008	EF010	EF012	EF014	EF016
INORGANICS									
Aluminum	na	13248	13171	9645	10047	7209	7837	7334	9498
Arsenic	33	9.84	8.95	8.12	7.61	5.65	10.5	12.2	7.28
Boron	na	<10.0	<10.0	<10.0	<10.0	<10.0	11.3	<10.0	<10.0
Barium	na	188	152	120	136	102	99.1	101	124
Beryllium	na	1.6	1.47	1.21	1.23	0.992	1.1	1.16	1.22
Cadmium	4.98	0.265	0.254	0.218	0.234	<.200	0.34	0.35	<.200
Chromium	na	26.4	23.9	21	21.7	15.1	22.6	22.9	19
Copper	149	22.9	21.7	28.1	18	11.7	19.7	20.1	14.9
Iron	na	34381	30568	26999	26877	22391	19581	19935	25200
Lead	128	22	23.7	15.9	16.3	12.2	15.6	16.7	16.1
Mercury	1.06	<.200	<.200	<.200	<.200	<.200	<.200	<.200	<.200
Magnesium	na	3255	2920	2586	2659	1870	2935	2939	2238
Manganese	na	792	668	601	721	464	753	792	579
Molybdenum	na	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00
Nickel	48.6	27.9	25.5	22.8	23.9	18.4	22.7	25	21.5
Selenium	na	<1.00	<1.00	<1.00	<1.00	<1.00	1.59	1.5	<1.00
Strontium	na	41.7	32	63.2	61.7	21.7	193	188	24.3
Vanadium	na	26.2	26.5	18.8	19.4	15.1	18.8	19.2	19.3
Zinc	459	81.9	86.2	66.7	67.7	50.9	89.6	94.9	65.9
ORGANICS									
Anthracene	0.845	<.00349	0.107	0.129	0.0592	0.0167	1.32	0.497	0.136
Fluorene	0.536	<.00349	0.0254	0.0438	0.0234	0.004	1.2	0.674	0.0228
Naphthalene	0.561	0.0229	0.0215	0.187	0.196	0.0257	43.5	13.6	0.0692
Phenanthrene	1.17	0.0193	0.131	0.206	0.126	0.0337	11.4	4.44	0.155
Benz[a]anthracene	1.05	0.0058	0.217	0.28	0.223	0.0514	1.21	0.593	0.232
Benzo(a)pyrene	1.45	0.0067	0.2	0.0074	0.193	0.0554	0.866	0.377	0.242
Chrysene	1.29	0.0087	0.139	0.194	0.16	0.0385	1.04	0.449	0.17
Fluoranthene	2.23	0.012	0.345	0.505	0.235	0.0742	3.37	1.04	0.429
Pyrene	1.52	0.0113	0.274	0.443	0.217	0.0689	3.28	1.1	0.334
Total PAHs (13 common)	22.8	0.11	1.56	2.31	1.76	0.41	126.67	42.97	1.93
Total PAHs (all)	na	0.3	2.76	5.23	4.44	0.9	340.05	129.88	3.65

All values in ug/g dry weight.
na indicates benchmark not available.
Shading indicates value greater than concensus-based PEC identified by MacDonald et al. 2000. enlowsedcriteria

Table 4. Contaminants in Enlow Fork and surrounding tributary sediment compared to values protective of wildlife species, Greene County, Pennsylvania. September 4, 2001.

	Sample et al. 1996		Sediment Station							
	Woodcock	Shrew	EF002	EF004	EF006	EF008	EF010	EF012	EF014	EF016
Aluminum	59	38	8419	6903	4971	5221	4147	3812	3740	5986
Arsenic	9.7	2.5	6.25	4.69	4.19	3.96	3.48	5.17	6.2	4.49
Boron	132	343	<6.36	<5.24	<5.15	<5.20	<6.17	5.54	<5.10	<6.17
Barium	55	72	119	79.5	61.7	70.9	62.8	48.6	51.4	67.1
Beryllium	na	na	1.02	0.771	0.623	0.641	0.612	0.538	0.592	0.756
Cadmium	26	35	0.168	0.133	0.112	0.122	<.123	0.167	0.178	<.123
Chromium	6.6	48	16.8	12.5	10.8	11.3	9.28	11.1	11.7	11.7
Copper	81	73	14.5	11.4	14.5	9.35	7.21	9.65	10.3	9.19
Iron	na	na	21849	16021	13916	13973	13811	9599	10167	15553
Mercury	0.08	0.57	<.127	<.105	<.103	<.104	<.123	<.0980	<.102	<.123
Magnesium	na	na	2069	1530	1333	1382	1153	1439	1499	1382
Manganese	na	1040	503	350	310	375	286	369	404	358
Molybdenum	46.6	5.2	<3.18	<2.62	<2.58	<2.60	<3.08	<2.45	<2.55	<3.09
Nickel	141	293	17.7	13.4	11.8	12.4	11.4	11.1	12.7	13.3
Lead	15	293	14	12.4	8.19	8.48	7.5	7.64	8.53	9.93
Selenium	1.1	1.2	<.636	<.524	<.515	<.520	<.617	0.78	0.764	<.617
Strontium	na	na	26.5	16.8	32.6	32.1	13.4	94.5	95.8	15
Vanadium	na	7.1	16.7	13.9	9.71	10.1	9.33	9.21	9.78	11.9
Zinc	173	1172	52.1	45.2	34.4	35.2	31.4	43.9	48.4	40.7

All values in ug/g wet weight.

na indicates benchmark unavailable.

Light shading indicates value greater than protective level for shrew.

Dark shading indicates value greater than protective level for woodcock.

Crosshatch indicates value greater than protective level for both shrew and woodcock.

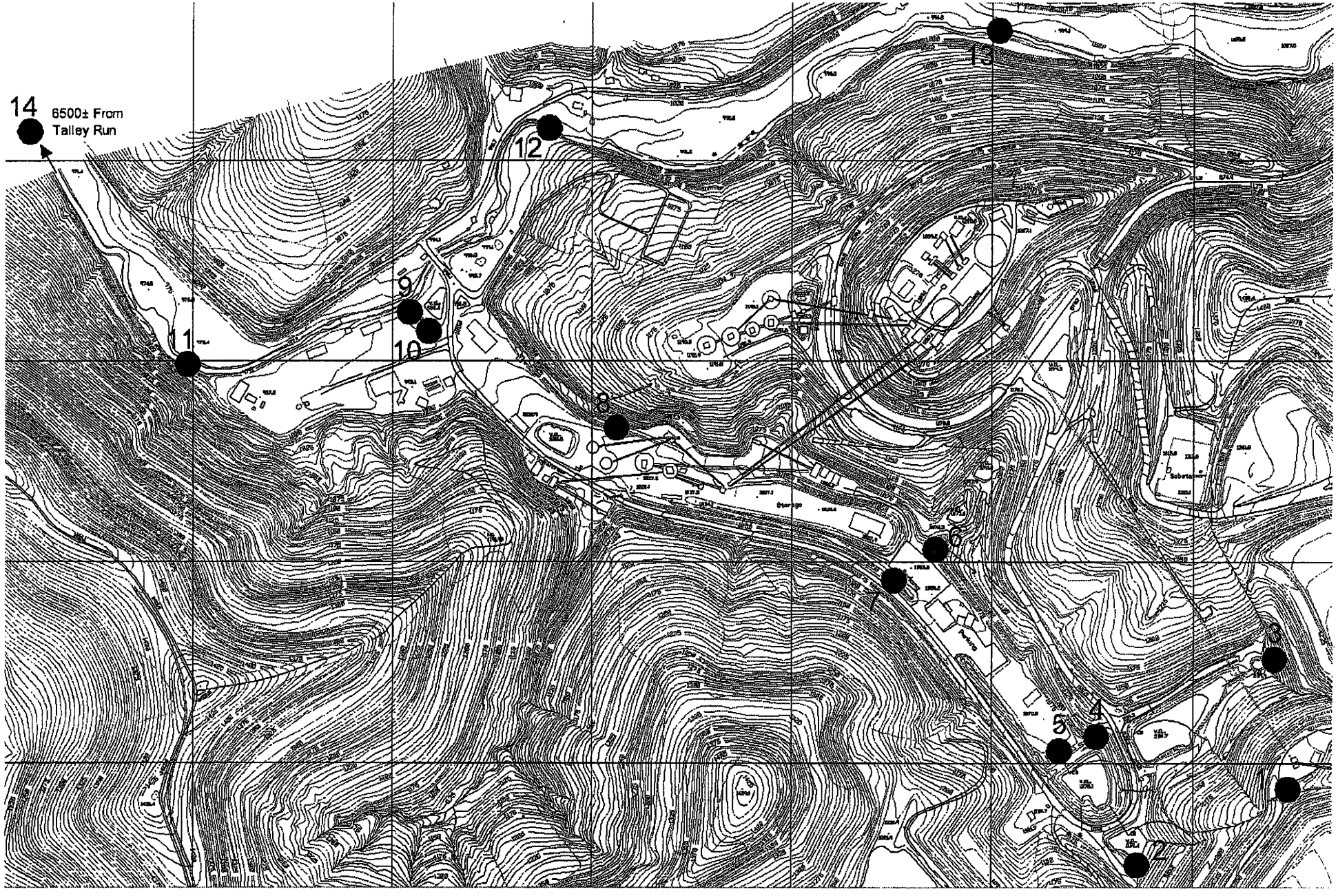
Appendix A. Polcyclic aromatic hydrocarbon concentrations in sediments of Enlow Fork and surrounding tributaties. All values are ug/g dry weight.

	EF002	EF004	EF006	EF008	EF010	EF012	EF014	EF016
acenaphthylene	<.00349	0.0445	0.0105	0.0078	<.00335	0.25	0.133	<.00353
acenaphthene	<.00349	0.0123	<.00432	<.00418	<.00335	0.0459	0.0231	0.00968
anthracene	<.00349	0.107	0.129	0.0592	0.0167	1.32	0.497	0.136
benzo(a)anthracene	0.00583	0.217	0.28	0.223	0.0514	1.21	0.593	0.232
benzo(a)pyrene	0.00668	0.2	0.0074	0.193	0.0554	0.866	0.377	0.242
benzo(b)fluoranthene	0.00995	0.234	0.302	0.262	0.0656	0.91	0.363	0.3
benzo(e)pyrene	0.00762	0.0869	0.112	0.105	0.028	0.579	0.276	0.106
benzo(g,h,i)perylene	0.00627	0.0777	0.0991	0.0916	0.027	0.464	0.215	0.0983
benzo(k)fluoranthene	<.00349	0.0674	0.0888	0.0736	0.0208	0.231	0.0851	0.0774
biphenyl	0.0062	0.00475	0.0225	0.017	0.0043	0.826	0.451	0.00642
C1-chrysenes	0.00754	0.0842	0.119	0.122	0.0167	2.28	1.34	0.106
C1-dibenzothiophenes	<.00349	0.00792	0.023	0.02	0.0036	2.41	0.905	0.0129
C1-fluoranthenes & pyrenes	0.0129	0.147	0.247	0.154	0.0399	7.43	2.91	0.171
C1-fluorenes	0.00581	0.0169	0.0524	0.0323	0.0069	1.52	0.899	0.02
C1-naphthalenes	0.0429	0.0387	0.482	0.518	0.0617	96.3	32.5	0.166
C1-phenanthrenes & anthracenes	0.0159	0.0792	0.179	0.141	0.03	15.5	5.97	0.111
C2-chrysenes	0.00444	0.0286	0.0567	0.0604	0.0084	2.47	1.34	0.0343
C2-dibenzothiophenes	<.00349	0.00588	0.0219	0.0188	<.00335	1.85	0.726	0.0107
C2-fluorenes	0.00806	0.0196	0.0587	0.0447	0.0137	2.18	1.26	0.028
C2-naphthalenes	0.0277	0.032	0.324	0.348	0.0502	54	19.5	0.117
C2-phenanthrenes & anthracenes	0.0102	0.0503	0.148	0.124	0.0215	15	5.74	0.077
C3-chrysenes	<.00349	<.00416	<.00432	<.00418	<.00335	0.174	0.0899	<.00353
C3-dibenzothiophenes	<.00349	<.00416	0.0151	0.014	<.00335	1.23	0.534	0.00699
C3-fluorenes	0.00402	0.0129	0.0803	0.0802	0.0145	2.3	1.51	0.0181
C3-naphthalenes	0.0199	0.0291	0.247	0.277	<.00335	28.6	14.2	0.0957
C3-phenanthrenes & anthracenes	0.00786	0.0236	0.0958	0.0858	0.0122	11.4	4.32	0.0412
C4-chrysenes	<.00349	0.0138	0.0169	0.0168	0.0042	0.103	0.0533	0.0153
C4-naphthalenes	0.00942	0.0175	0.173	0.18	0.0353	15.9	8.47	<.00353
C4-phenanthrenes & anthracenes	0.00494	0.00697	0.0468	0.0376	0.0056	7.34	2.69	0.0156
chrysene	0.00869	0.139	0.194	0.16	0.0385	1.04	0.449	0.17
dibenz(a,h)anthracene	<.00349	0.0236	0.0272	0.0243	0.0067	0.0865	0.0422	0.0303
dibenzothiophene	<.00349	0.00729	0.0159	0.0118	<.00335	1.15	0.448	0.0102
fluoranthene	0.012	0.345	0.505	0.235	0.0742	3.37	1.04	0.429
fluorene	<.00349	0.0254	0.0438	0.0234	0.004	1.2	0.674	0.0228
indeno(1,2,3-cd)pyrene	0.00493	0.107	0.13	0.11	0.0341	0.292	0.0964	0.133
naphthalene	0.0229	0.0215	0.187	0.196	0.0257	43.5	13.6	0.0692
perylene	<.00349	0.0215	0.0434	0.0293	0.0219	0.0456	0.0211	0.0439
phenanthrene	0.0193	0.131	0.206	0.126	0.0337	11.4	4.44	0.155
pyrene	0.0113	0.274	0.443	0.217	0.0689	3.28	1.1	0.334
INDIVIDUAL ISOMERS								
1,6,7-Trimethyl-naphthalene	0.00718	0.00901	0.0879	0.0638	0.0114	3.82	2.17	0.0221
1-methylnaphthalene	0.019	0.0174	0.201	0.219	0.0309	37.1	12.6	0.0707
1-methylphenanthrene	0.0066	0.0232	0.0615	0.051	0.011	5.43	2.16	0.0373
2,6-dimethylnaphthalene	0.00723	0.00998	0.105	0.0772	0.0112	5.22	2.88	0.0247
2-methylnaphthalene	0.0239	0.0213	0.281	0.3	0.0309	59.1	20	0.0953
Total PAHs	0.30326	2.76101	5.2332	4.4396	0.9013	340.05	129.88	3.65199
Total naphthalenes	0.12282	0.1388	1.413	1.519	0.1729	238.3	88.27	0.4479
Total phenanthrenes & anthracenes	0.06403	0.61507	1.0846	0.7966	0.1711	63.17	24.25	0.7678
Total of 13 common parent PAHs	0.1106	1.5616	2.3139	1.7647	0.4061	126.67	42.968	1.92528

Selenium in Sediment Samples Collected at Bailey Mine Complex
Consol Pennsylvania Coal Company
Greene County, Pennsylvania
November 19, 2002

Sampling Station	Sampling Station Location	Total Selenium (mg/Kg)	TCLP Selenium (mg/L)	SPLP Selenium (mg/L)
CRDA 1	Intersection of east groin drain, bench drain, and bench gravel drain at mid-level bench face of slurry pond	3.9	<0.05	<0.05
CRDA 2	West groin drain at toe of slurry pond face	4.5	<0.05	<0.05
CRDA 3	Seepage zone at toe of coarse refuse face	3.1	<0.05	<0.05
CRDA 4	Pond 2 outlet (coarse refuse area sediment control pond)	5.4	<0.05	<0.05
CRDA 5	Pond 10 outlet (combined coarse refuse area and face/seeps of slurry pond)	3.4	<0.05	<0.05
CRDA 6	Discharge from Ponds 7 and 8 and blackwater pond (thickener dump and prep plant sediment controls)	2.4	<0.05	<0.05
CRDA 7	Discharge channel, downstream of CRDA 5 and upstream of CRDA 6	1.5	<0.05	<0.05
CRDA 8	Bottom of flume from coal loadout collection ditches, adjacent to raw coal silos	0.91	<0.05	<0.05
CRDA 9	Discharge channel (Talley Run) at discharge from Pond 5 (normally sediment control for loadout area and shop), with occasional contribution from Pond 6; just upstream of confluence with Enlow Fork	0.98	<0.05	<0.05
CRDA 10	Discharge channel (Talley Run) upstream of CRDA 9; essentially all drainage from facilities excepting clean coal silos and loadout	0.8	<0.05	<0.05
CRDA 11	Enlow Fork, about 1200 feet downstream of Talley Run confluence, just below discharges from sanitary plant and storage yards	0.55	<0.05	<0.05
CRDA 12	Enlow Fork about 1400 feet above Talley Run confluence	0.3	<0.05	<0.05
CRDA 13	Enlow Fork about 4000 feet above Talley Run confluence	<0.02	<0.05	<0.05
CRDA 14	Enlow Fork about 6500 feet below Talley Run confluence	0.2	<0.05	<0.05

Notes:
1. Samples collected by Moody and Associates, Inc. and analyzed by Free-col Laboratories


14
6500± From
Talley Run
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Neubert, Christina L LRP

From: Mark Haibach [mhaibach@cecinc.com]
Sent: Thursday, December 05, 2002 10:45 AM
To: 'Christina Neubert'
Subject: FW: Consol Response to Regulatory Agency Comments-Bailey Mine Refuse Area
Follow Up Flag: Review
Flag Status: Flagged

Christina,

Sorry, I misspelled your name/e-mail address the first time.

Mark

-----Original Message-----
From: Mark Haibach [mailto:mhaibach@cecinc.com]
Sent: Thursday, December 05, 2002 10:38 AM
To: 'Christina Newbert'; 'Cindy Tibbott'; 'Scott Hans (home)'
Subject: Consol Response to Regulatory Agency Comments-Bailey Mine Refuse Area

Christina, Cindy, and Scott,

Here is the power point presentation. Cindy, the file size looked small enough (<2MB), so I hope it arrives OK and doesn't cause problems for your server (I will fax a copy to you also). Scott, I will try to insert the slides into a second e-mail to you.

Exemption #6 -privacy

The call-in numbers for the conference call are as follows: (1) dial the toll-free number [redacted] (the star key must be pressed before and after the number; (3) you will then be in the conference room; wait until others join the call.

I left a message for Jack Kreider with the call-in numbers for the 11:00 call, but haven't heard back from him yet.

We (Consol and their consultants) will be calling in from CEC's office for the meeting, rather than trying to drive into downtown.

Please call me (800-365-2324, ext. 156) with any questions or problems. If you get my voice mail, dial 0 or 125 and ask the receptionist to page me.

Thank you.

Mark

12/5/02 Conference Call/meeting for Bailey Refuse Area:

1. Jonathan Pachter Consol
2. Tom Jageman Consol
3. Michelle Stewart Baker Engineering
4. Burt Waite Moody Associates
5. Barry Sutphin Moody Associates
6. Dr. Jim Mudge CEC
7. Mark Haibach CEC
8. Dr. Brad Owen ecological consultant

Meeting Between Consol and Regulatory Agencies to Discuss Bailey Mine Refuse Area Permit Application

December 5, 2002

Meeting Agenda

1. Introductions
2. Response to FWS Comments on Chemical Contamination of Enlow Fork
3. Stream Mitigation Proposal
4. Wetland Mitigation Options
5. Conclusions
6. Discussion

FWS: Potential Impacts of the Expansion on the Chemical Water Quality of Enlow Fork

- Sediment downstream of Talley Run has strong petroleum like odor
- Polycyclic Aromatic Hydrocarbons (PAHs); 310 ppm downstream of Talley Run or 18.8 ppm adjusted for 1% organic carbon (OC)
- No regulatory criteria for sediment contamination
- Compared PAH results to NOAA and Canadian guidelines

FWS: Potential Impacts of the Expansion on the Chemical Water Quality of Enlow Fork (Continued)

- Selenium (Se) 1.5 ppm downstream of Talley Run
- Concern about current and future chemical loading to Enlow Fork
- Need additional sampling to determine loading and whether technology is available to prevent releases
- No expansion until investigations are completed

Consol Response to FWS Comments on Potential Impacts of the Expansion on the Chemical Water Quality of Enlow Fork

- Sediment sample from upstream is predominately (77%) sand and has total organic carbon (TOC) content of 1.24%
- Sediment samples from downstream are predominately silt (50-54%) with TOCs of 14.9 and 18.1%
- Inappropriate to directly compare samples from different habitats (appears area sampled downstream are depositional while area upstream is not)

Consol Response to FWS Comments (Continued)

- Sediment sample results for selenium should be compared to levels of concern observed in freshwater:

1. "Aquatic cycling of selenium: implications for fish and wildlife."1987. Lemly and Smith. U.S. Fish and Wildlife Leaflet 12.
2. " Guidelines for evaluating selenium data from aquatic monitoring and assessment. 1993. Lemly. Enviro. Monit. Assessment 28: 83-100.
3. "Selenium toxicity to aquatic life: an argument for sediment-based water quality criteria."1997. Canton and Van Derveer. ET&C 16(6): 1255-1259.
4. "Guidelines for conducting TMDL consultations on selenium." 2000. Lemly. USFWS Technical Report.

Consol Response to FWS Comments (Continued)

- Lemly and Smith: $\geq 4\mu g/g$ (ppm) Se causes reproductive failure or mortality due to food-chain bioconcentration
- Lemly: Se biological effect thresholds, ppm, dry weight

Plankton & forage fish	30-370
Some freshwater and anadromous fish	4
Some aquatic birds & benthic invertebrates	3-10

- Canton and Van Derveer: "predicted" effect Se level 2.5
  "observed" effect Se level 4.0
- The 1.5 ppm value reported by FWS is below these sediment threshold concentrations, therefore adverse effects are not indicated

Consol Response to FWS Comments (Continued)

- Sediment sample results for PAHs should be compared to more recent United States sponsored Sediment Quality Guidelines (SQGs):

"Prediction of sediment toxicity using consensus based freshwater sediment guidelines." (2000) Ingersoll et al. EPA 905/R-00/007

Consol Response to FWS Comments (Continued)

- Probable Effects Concentration (PEC)-level above which adverse effects are expected to occur frequently
- PEC estimated by Ingersoll et al. (2000) for Total PAH is 22.8 ppm

Consol Response to FWS Comments (Continued)

- Inappropriate to directly compare FWS results to NOAA (1999) and Canadian SQGs (CCME 1999) for the following reasons:

1. CCME does not present a total PAH value of 7.1 ppm but rather 13 individual PAH values that FWS apparently totaled.
2. The Enlow Fork samples had more than the 13 PAHs listed quantified.
3. If the appropriate 13 PAHs for the two downstream samples are averaged and adjusted to 1% OC the total PAH value is 5.1 ppm, which is below both the NOAA and Canadian values of 12 and 7.1 ppm, respectively.
4. Swartz (1999) and Ingersoll et al. both note the importance of evaluating the "mixture" and state addition of individual SQGs may be inappropriate.

Consol Response to FWS Comments (Continued)

- Other sources could contribute PAHs to the stream:

  FWS (1987); petroleum spillage primary source of PAHs in the aquatic environment

  Menzie et al. (1992); road dusts, 8-336 ppm

Consol Response to FWS Comments (Continued)

- Other sources could contribute PAHs to the stream:

  Discharge of hydrostatic test water from natural gas pipelines can contribute PAHs (primarily naphthalene's)

  Unburned coal and coal leachates – Chapman et al. (1996) indicate these PAHs are not readily bioavailable, therefore not toxic to aquatic life.

Conclusions

- Sediments collected downstream are not comparable to upstream; therefore direct comparison of results do not appear appropriate
- Selenium concentrations downstream of Talley Run do not exceed relevant SQGs
- PAH concentrations downstream of Talley Run may not be attributable to refuse disposal activities and do not exceed a recent and relevant SQG

Discussion

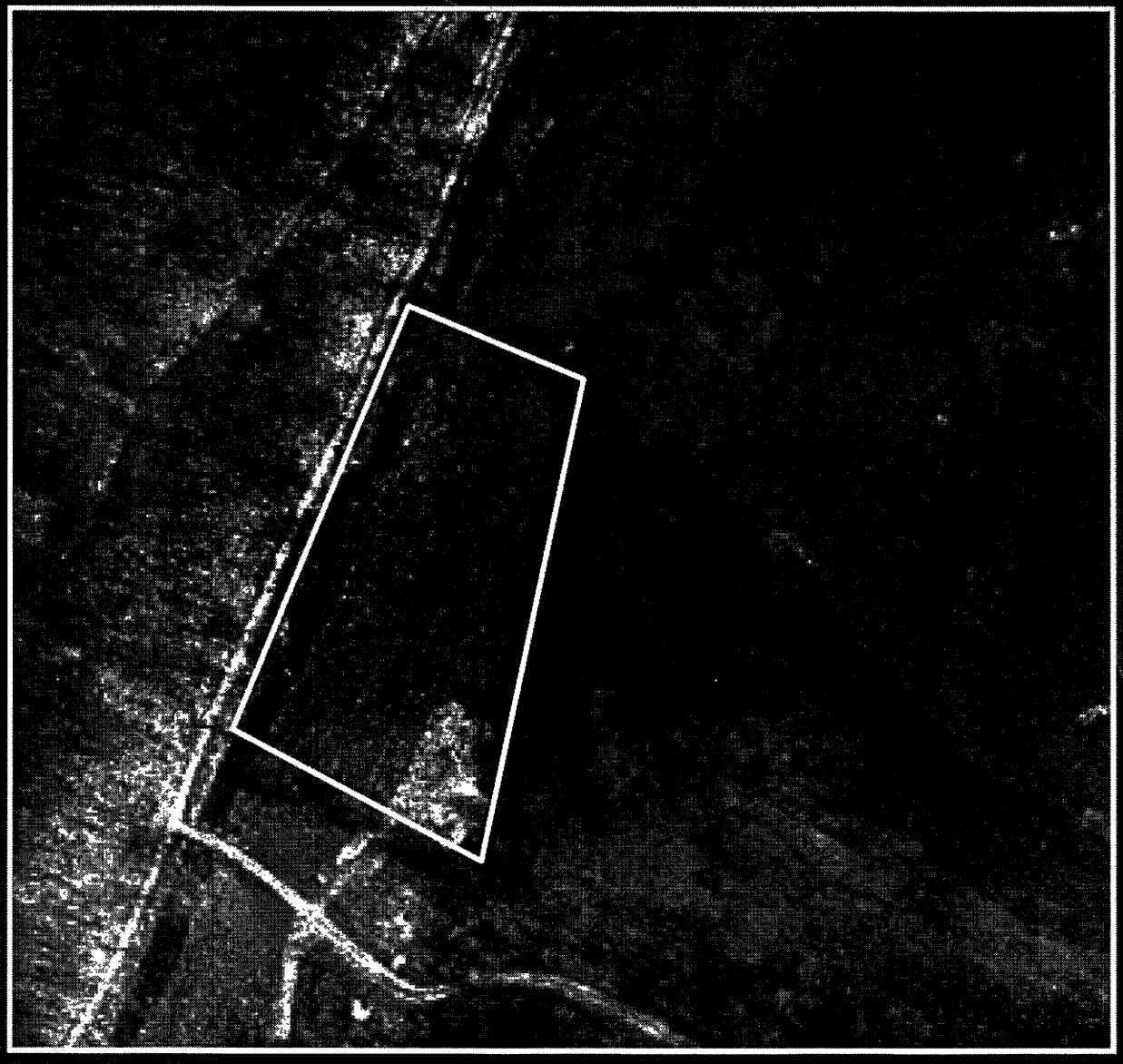
Bailey Mine Refuse Areas
Wetland Mitigation Requirements

	Ratio	Acres
A. Wetland Impact Acreage		1.37
B. COE Mitigation Requirements		
1. Minimum Mitigation Required	1.5:1	2.06
2. Minimum Creation/Restoration	1:1	1.37
3. Balance of Mitigation:		
a. Creation/Restoration	1:1	0.69
b. Enhancement	5:1	3.45
c. Preservation	10:1	6.90

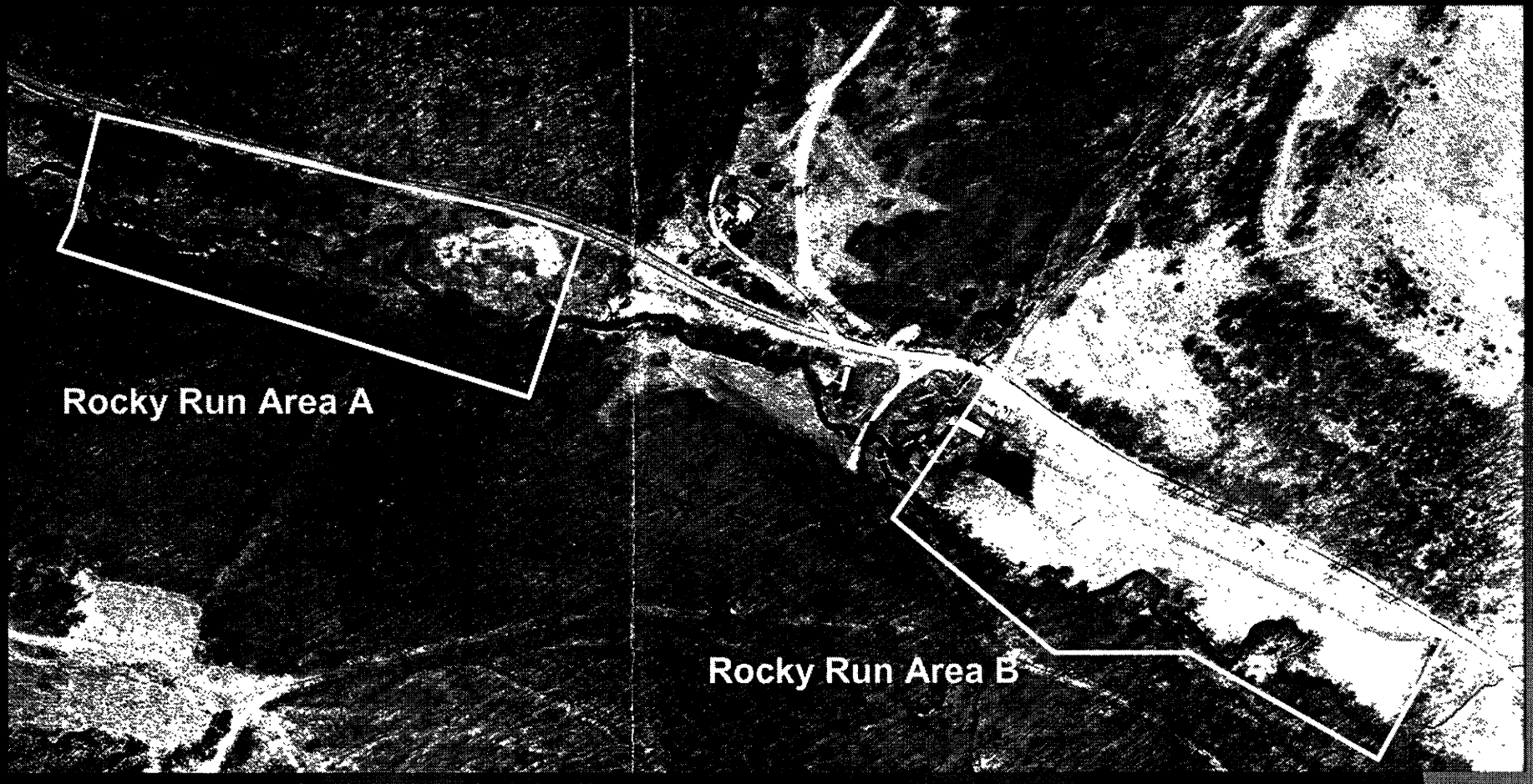
Bailey Mine Refuse Areas
Wetland Mitigation Options

Mitigation Proposals	Create	Enhance	Preserve	Total
A. Creation/Enhancement				
1. Rocky Run A				
2. Rocky Run B	1.54	1.00		2.54
3. Templeton		1.64		1.64
Total	1.54	2.64		4.18
Mitigation Credit	1.54	0.53		2.07
B. Creation/Preservation				
1. Rocky Run A			2.34	2.34
2. Rocky Run B	1.47		1.00	2.47
3. Templeton			1.64	1.64
Total	1.47		5.98	7.45
Mitigation Credit	1.47		0.60	2.07

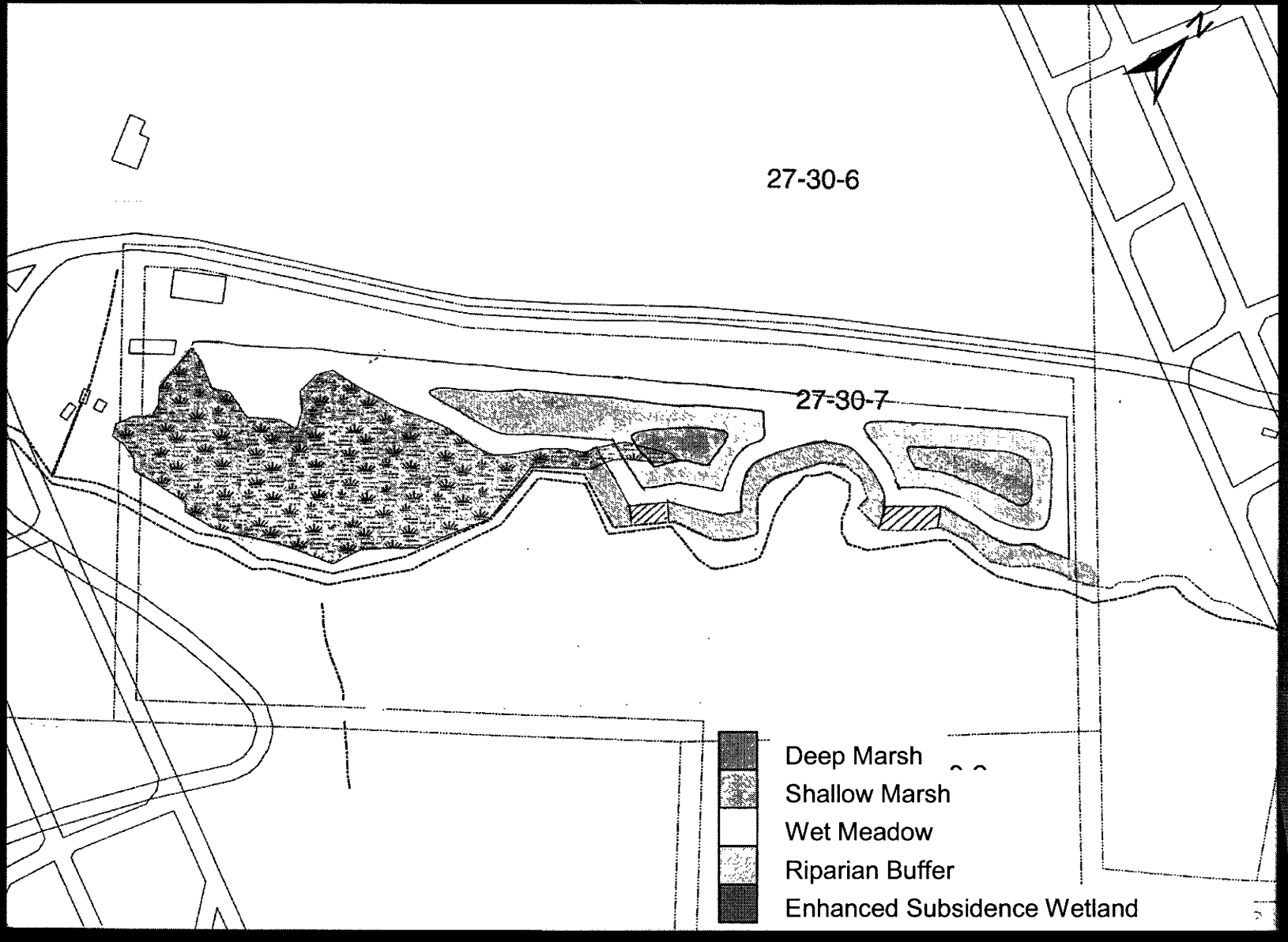
Templeton Fork Area



Rocky Run Areas A and B



Wetland Creation at Rocky Run Area B



Neubert/7375

November 5, 2002

Operations and Readiness Division
Regulatory Branch
200200371

Mr. Jonathan M. Pachter
Manager, Permits & Compliance
CNX Coal Operations
172 Route 519
P.O. Box 355
Eighty Four, PA 15330

Dear Mr. Pachter:

This letter is in reference to your Bailey Mine coal refuse disposal facility application. On October 7, 2002, you met in our office with Scott Hans, Nancy Mullen, and Christina Neubert to respond to our correspondence dated September 19, 2002.

In this meeting, you and your consultants presented information to support your proposal to preserve wetlands that may have been created by longwall mining subsidence. My staff said they would take this additional information into consideration along with any comment letters and give you a final answer as to whether or not your mitigation proposal is acceptable after the comment period for your public notice ended.

The goals of the Corps Regulatory program includes protecting the chemical, physical and biological integrity of all waters of the U.S., and providing for a no net loss of aquatic resources. While enhancing and preserving wetlands created by subsidence may meet this first goal, such actions do not provide for a no net loss of aquatic resources.

In consideration of the cumulative and secondary impacts associated with the proposed action, the existing resource quality, and difficulty of creating successful wetland replacement sites, your wetland mitigation proposal should replace the resources being impacted at a minimum rate of **1.5:1**. Your proposed wetland impacts total 1.37 acres, so you will be responsible for a minimum total of 2.05 acres of mitigation. A revised mitigation proposal should be submitted which includes not less than **1:1 creation or restoration** of wetland habitats. In other words, you must create at least 1.37 acres of wetland, but you have the option to mitigate for the other 0.685 acres using enhancement or preservation measures. Enhancement and preservation measures will be considered for the remaining mitigation requirements at not less than **5:1 for enhancement and 10:1 for preservation**. If you wish to mitigate for your wetland

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impacts by creating 2.05 acres of wetlands, that is also an acceptable option.

The following information will help us review your mitigation proposal: A map/drawing with cross sections of the proposed wetland mitigation site that shows current and proposed grading, photographs of proposed wetland mitigation site in its current condition with the photograph locations indicated on the drawing, a planting schematic, piezometer locations, and a monitoring plan. In addition, if your mitigation proposal includes any enhancement or preservation of existing wetlands, please provide a drawing to scale that identifies the delineated wetland boundaries, photographs with locations indicated on the map, wetland data forms, and details of any proposed enhancement measures.

At this time we also request more specific details on the stream mitigation plan so we can review and make comments. These details should include the measures to be undertaken, the quantity of resource to be enhanced and preserved, and a monitoring plan which includes measurable criteria.

If you have any questions, please contact Scott Hans at (412) 395-7154, Nancy Mullen at (412) 395-7170, or Christina Neubert at (412) 395-7375.

Sincerely,

Albert H. Rogalla
Chief, Regulatory Branch

Copy Forwarded:

William Plassio, McMurray District Mining Office

Mark Haibach, CEC

Neubert/7375

September 19, 2002

Operations and Readiness Division
Regulatory Branch
200200371

Mr. Jonathan M. Pachter
Consolidation Coal Company
1800 Washington Road
Pittsburgh, Pennsylvania 15241-1421

Dear Mr. Pachter:

This letter is in reference to your Bailey Mine application for the new refuse disposal areas. We have reviewed your response to our May 17, 2002 comment letter and concluded that your wetland mitigation as proposed is unacceptable for the following reasons:

(1) Consol has not provided any pre-mining documentation showing the areas adjacent to Rocky Run were field surveyed for the presence of wetlands. The soil maps and aerial photographs are not conclusive evidence to prove the presence or absence of wetlands.

(2) It is evident that stream habitat along Rocky Run has been impacted as a result of Consol's longwall mining activities. Pool, run, and riffle complexes are critical components to healthy stream ecology. Subsidence from longwall mining has altered these components in Rocky Run. As a regulatory agency responsible for protecting aquatic habitat, we can not endorse the creation of wetlands at the expense of another aquatic resource.

(3) Attached is a letter from Gary Camus, Game Land Officer Manager, representing the Pennsylvania Game Commission. He does not support your mitigation as currently proposed, and outlines documentation measures which would be necessary to claim credit for such wetland development.

In summary, Consol proposes to impact 1.27 acres of shrub/scrub wetland and 0.10 acres of forested wetland. Mitigation should adequately offset the functions and values lost by the filling of these aquatic resources. We can advertise your mitigation plan as currently proposed, however, it is unlikely that a permit will be issued unless the plan is revised and improved. The report submitted by CEC does not adequately substantiate a net gain of wetland habitat from the pre-mining conditions of Rocky Run. We recommend that you explore other

record file copy

mitigation options which should include creation or restoration of additional wetland habitats and may include stream corridor restoration measures.

If you have any questions, please contact Nancy Mullen at (412) 395-7170, Scott Hans at (412) 395-7154, or Christina Neubert at (412) 395-7375.

Sincerely,

SIGNED

Albert H. Rogalla
Chief, Regulatory Branch

Enclosure

CF:
Gary Camus, Pennsylvania Game Commission

AHR

Mullen/7170

May 17, 2002

Operations and Readiness Division
Regulatory Branch
200200371

Mr. Jonathan M. Pachter
Consolidation Coal Company
1800 Washington Road
Pittsburgh, Pennsylvania 15241-1421

Dear Mr. Pachter:

This letter is to confirm the discussions that resulted from our May 8, 2002, site visit for the Bailey Central Mine Complex Coal Refuse Disposal Areas No. 3 and No. 4 and Sedimentation Pond, Greene County, Pennsylvania. The following information is needed in writing for us to advertise a Public Notice for your proposal:

1 - Three different acreages of wetland impacts were indicated in the application. Please provide us with the correct acreage.

2 - Please justify how the enhancement of existing wetlands will provide proper replacement mitigation for the loss of the impacted areas and result in a no net loss of aquatic resources.

3 - Please re-evaluate the possibility of additional wetlands in the coarse coal valley disposal site. You will need to submit the data sheets to us so the presence or absence of additional wetlands can be verified.

Additionally, you have proposed to mitigate for stream impacts by installing 12.5 miles of cattle fencing. It is likely we will require additional site specific details and conservation easements for the entire 12.5 miles of stream, prior to permit issuance. We will also need to know what alternative will be implemented if landowners are unwilling to sign these conservation agreements.

If you have any questions, please contact Nancy Mullen at (412) 395-7170 or Christina Neubert at (412) 395-7375.

Sincerely,

Albert H. Rogalla
Chief, Regulatory Branch

Copy Furnished:

Michele Stewart
Michael Baker, Jr. Inc.
Airport Office Park, Building 3
420 Rouser Road
Coraopolis PA 15108

MULLEN OR-F

NEUBERT OR-F

HANS OR-F

ROGALLA OR-F

CONSOL ENERGY™

CONSOL Energy Inc.
Consol Plaza
1800 Washington Road
Pittsburgh, PA 15241-1421

phone: 412/831-4679
fax: 412/831-4513
e-mail: Jonathanpachter@consolenergy.com
web: www.consolenergy.com

CERTIFIED MAIL
RETURN RECEIPT REQUESTED

July 22, 2002

Mr. Albert H. Rogalla
Chief, Regulatory Branch
Department of the Army
Pittsburgh District, Corps of Engineers
William S. Moorhead Federal Building
1000 Liberty Avenue
Pittsburgh, PA 15222-4186

RE: Consol Pennsylvania Coal Company
Bailey Mine – New Refuse Disposal Area
Richhill Township, Greene County

Dear Mr. Rogalla:

In reference to your May 17, 2002 comment letter, enclosed please find the following additions and/or revisions. The Corps of Engineers (the Corps)'s comments are shown *in italics*, followed by Consol Pennsylvania Coal Company (CPCC)'s responses. Please note that CPCC is a subsidiary of CONSOL Energy Inc.

1. Three different acreages of wetland impacts were indicated in the application. Please provide us with the correct acreage.

CPCC has reviewed the information contained in the application. The following parts of Module 15 of the PA DEP's Coal Refuse Disposal Application have been revised and are included with this correspondence as Enclosure 1: Module 15, Attachment 15.1, and Attachment 15.5 (minus photographs and drawings which remain unchanged). The correct acreages are 1.267 acres in Area No. 3 and 0.102 acre in Area No. 4.

2. Please justify how the enhancement of existing wetlands will provide proper replacement mitigation for the loss of the impacted areas and result in no net loss of aquatic resources.

CPCC proposes to use wetlands created by subsidence as the basis for the wetland mitigation plan for the new refuse area. As shown in Enclosure 2, Civil and Environmental Consultants,

Scott 200200371 199.660042

10 feed 7/25/2002 R

Inc. (CEC) has addressed this issue. Enclosure 2 presents information that addresses the following two comments as voiced to us by your staff during our May 8, 2002 site visit.

- Provide information documenting that the proposed wetland mitigation areas were recently created and did not exist prior to longwall mining; and,
- The mitigation plan proposes to provide and enhance recently created wetlands at a 2:1 ration to offset impacts for the proposed mine refuse areas. The Corps typically requires a 5:1 to 10:1 ration for enhancement of existing wetlands as mitigation for wetland impacts. Justify the proposed 2:1 mitigation ration.

CEC's letter, as transmitted to you in Enclosure 2, should provide you with the information you need to better understand how our proposed wetland mitigation plan provides proper replacement for the loss of impacted areas and results in a no net loss of aquatic resources. CPCC welcomes the opportunity to meet with the Corps and discuss this issue as well as any other approaches that you may have for wetland mitigation.

3. Please re-evaluate the possibility of additional wetlands in the coarse coal valley disposal site. You will need to submit the data sheets to us so the presence or absence of additional wetlands can be verified.

Enclosure 3, "Re-examination of a Candidate Wetland Area of the Proposed Bailey Mine Refuse Hollow, Greene County, Pennsylvania", provides the documentation needed to prove that there are no additional wetlands in the coarse coal valley disposal site.

In regard to the general comment regarding the stream fencing mitigation plan, CPCC is working with California University of PA to prepare that plan. After we identify specific stream segments to be fenced and after we talk about this plan with the property owners, we will provide you with a more detailed stream-fencing plan. The plan will include alternatives in case landowners are unwilling to sign the conservation agreements or easements.

Please note that I have enclosed for your files single copies of letters transmitting these revisions to the PA Department of Environmental Protection (McMurray District Mining Office), the PA DEP - Bureau of Waterways Engineering, Division of Dam Safety, the US EPA, and the US Department of the Interior (U. S. Fish and Wildlife Service). Submission of these additions and/or revisions should allow the Corps to continue with the processing of the above referenced application. Any priority that you can place upon completing your completeness review of this application is greatly appreciated. Please call me at (412) 831-4679 with any questions regarding this correspondence and its enclosures.

Sincerely,

Jonathan M. Pachter

Jonathan M. Pachter
Manager, Environmental Permits

Enclosures

cc w/ enc.: PA Department of Environmental Protection (McMurray District Mining Office)
PA DEP - Bureau of Waterways Engineering, Division of Dam Safety
US EPA
US Department of the Interior - U. S. Fish and Wildlife Service

COMMONWEALTH OF PENNSYLVANIA
PENNSYLVANIA GAME COMMISSION
2001 ELMERTON AVENUE, HARRISBURG, PA 17110-9797

June 27, 2002

Mr. Joseph Szunyog
Mr. Craig Burda
Department of Environmental Protection
McMurry District Office
3913 Washington Road
McMurray, PA 15317-2532

Re: CMAP #30020701
Bailey CRDA No. 3 and No. 4
Richhill and Gray Townships
Greene County, PA

Gentlemen:

Thank you for forwarding the above referenced application to our office for review and comment.

We have completed an office review and determined that except for occasional transient individuals, this project should not affect any endangered or threatened species of bird or mammal recognized by the Pennsylvania Game Commission.

We do realize, however, that the selection of sites for the coal refuse and coal slurry disposal areas will negatively impact approximately 1.5 acres (1.462 listed in Module 5 and 1.369 shown on mapping provided) of wetland area currently providing seasonally critical habitat in winter and early spring to wildlife utilizing this area. While a review of the wetland analysis data indicates low functions and values for these wetland areas due to agricultural disturbances and lack of vegetative species diversity, loss of the existing functions and values must be mitigated for.

It appears it is the intention of the applicant to propose wetlands it claims to have created due to subsidence from past mining as mitigation wetlands. This is only acceptable under the following conditions:

1.) While there is no question some wetlands created in the nearby Rocky Run and Templeton Fork watersheds were the direct result of subsidence damage to streams caused by mining operations by Consol, additional wetland acreage has also been created by natural causes such as beavers damming the streams. To

Christy & Nancy rec'd 7/1/2002

ADMINISTRATIVE BUREAUS:
PERSONNEL: 717-787-7836 ADMINISTRATION: 717-787-5670 AUTOMOTIVE AND PROCUREMENT DIVISION: 717-787-6594
LICENSE DIVISION: 717-787-2084 WILDLIFE MANAGEMENT: 717-787-5529 INFORMATION & EDUCATION: 717-787-6286 LAW ENFORCEMENT: 717-787-574
LAND MANAGEMENT: 717-787-6818 REAL ESTATE DIVISION: 717-787-6568 AUTOMATED TECHNOLOGY SYSTEMS: 717-787-4076 FAX: 717-772-2411
WWW.PGC.STATE.PA.US
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st Scott

assume credit for all wetland acreage that has been created and occurring over the past 3 years is a bit presumptuous on the part of Consol, since not one dollar was spent on plans or proposals for/and activities creating these wetland areas. However, in a spirit of fairness to Consol for being responsible for causing the hydrologic changes to Rocky Run and Templeton Fork which have resulted in wetland formation through natural processes, the Commission would find for partial wetland creation credit on behalf of Consol if the company can show and prove a net gain of wetland acreage in the Rocky Run and Templeton Fork watersheds as a result of their mining. The entire area mined in these watersheds must include detailed, dated field surveys and mapping showing all wetlands present prior to mining occurring and a re-evaluation of these wetland areas following mining. If this information is available and it can be determined by the Commission that Consol's mining has resulted in a net increase in wetland acreage in the Rocky Run and Templeton Fork watersheds, we are willing to accept this fact as mitigation for proposed impacts in the adjacent slurry and coarse coal refuse disposal areas. The actual rate of accepted wetland mitigation would have to be established based on a functions and values analysis and mitigation would have to provide at least a 1:1 acreage replacement for all impacted/eliminated wetland areas.

2.) The Department of Environmental Protection , the US Army Corps of Engineers and the Pennsylvania Fish and Boat Commission must establish a wetland banking system protocol similar to that being utilized by PennDOT. While this specific case may be addressed as stated above in item #1 for resolution with the Pennsylvania Game Commission, all affected parties (resources agencies) must approve.

3.) If this situation cannot be addressed according to items 1 and 2 listed above, please provide a mitigation plan which shows and provides for an acreage increase of 1.5 acres of wetland area adjacent to existing wetlands along Rocky Run and/or Templeton Fork. Proposals to increase functions and values alone in existing wetland areas do not fullfill all requirements of Chapter 105 regulations; acreage replacement at a minimum ratio of 1:1 impacted/replaced wetland areas must also occur.

If you have any questions regarding this information, feel free to contact me at (717) 783-1728.

Sincerely,

Gary R. Camus

Gary R. Camus
Game Land Officer Manager
Section Oil/Gas and Mineral Development
Bureau of Land Management

GRC/pfb

Cc: File
Camus
Capouillez
Kepler, PFBC
Hans, S., USACOE

ENCLOSURE 2
LETTER REPORT
CIVIL AND ENVIRONMENTAL CONSULTANTS, INC.

June 26, 2002

Mr. Jonathan M. Pachter
Manager, Environmental Permits
CONSOL Energy, Inc.
1800 Washington Road
Pittsburgh, Pennsylvania 15241-1421

Dear Mr. Pachter:

Subject: Wetland Mitigation Plan
Coal Refuse Disposal Areas No. 3 and No. 4
Bailey Central Mine Complex
Consol Pennsylvania Coal Company
Greene County, Pennsylvania
CEC Project 220806.0004

Civil & Environmental Consultants, Inc. (CEC) has prepared the following analysis and responses to comments by the U.S. Army Corps of Engineers (Corps) regarding the proposed wetland mitigation for the Bailey Mine Coal Refuse Disposal Areas No. 3 and No. 4. Each of the Corps' comments is listed below followed by our response.

1. Comment: *Provide information documenting that the proposed wetland mitigation areas were recently created and did not exist prior to longwall mining.*

Response: Consol has documented the creation of riparian wetlands along streams following longwall mine activities (CEC 2000, Pike 2000). These studies refute unsupported claims by the Raymond Proffitt Foundation (Schmidt and Kuntz 2000) that longwall mining in southwestern Pennsylvania has destroyed wetlands. Wetlands created by longwall mining are typically depressional-type wetlands that form adjacent to perennial streams. The fact that these wetlands were created as a result of longwall mining does not minimize the benefits that they afford nor does it detract from the role that they play in the overall ecosystem.

Three such wetlands have recently developed over portions of the Enlow Fork Mine, within the Enlow Fork watershed and in close proximity to the proposed refuse disposal areas. These wetlands are identified in the mitigation plan as the Rocky Run Wetland Mitigation Areas A and B and the Templeton Fork Wetland Mitigation Area. The Rocky Run Wetland Mitigation Area A is located over the Enlow Fork Mine F1 Longwall Mine Panel and was created following completion of mining in 2000. The Rocky Run Wetland Mitigation Area A is located over the Enlow Fork Mine F2 Longwall Mine Panel and was created following completion of mining in

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E-mail info@cecinc.com

Chicago 877/963-6026
Cincinnati 800/759-5614
Columbus 888/598-6808
Export 800/899-3610
Indianapolis 877/746-0749
Nashville 800/763-2326
St. Louis 866/250-3679

Corporate Web Site http://www.cecinc.com

2001. The Templeton Fork Wetland Mitigation Area is located over the Enlow Fork Mine A6 Longwall Mine Panel and was created following completion of mining in 1994.

To document the pre-mining condition of the three proposed mitigation areas, CEC examined USDA soil maps from the county soil survey (USDA SCS 1983) and pre-mining aerial photographs for each site. The Rocky Run Wetland Mitigation Areas A and B are both mapped in the county soil survey as Newark silt loam. Newark silt loam is not identified as a hydric soil on the county hydric soils list, but can contain inclusions of hydric soils (USDA NRCS). Examination of Consol 1999 aerial photography (Figure 1) and mid-1990s USGS digital ortho quarter-quadrangle (DOQQ) aerial photography (Figure 2) of the Rocky Run sites shows no wetland signatures at Mitigation Area B and a small existing wetland at the upstream end of Mitigation Area A. Based on interpretation of vegetation signatures on the aerial photography, the Rocky Run Wetland Mitigation Site A appears to have been comprised predominantly of non-wetland bottomland forest and pasture and Rocky Run Wetland Mitigation Site B appears to consist of non-wetland pasture and a small graded parking area adjacent to an outbuilding. The county soil survey maps the soil at the Templeton Fork Wetland Mitigation Area as Huntington silt loam. Like the Newark soil series, the Huntington soils are not hydric, but can include smaller areas of hydric soils. The mid-1990s USGS digital ortho quarter-quadrangle (DOQQ) aerial photography of the Templeton Fork Wetland Mitigation Area (Figure 3) shows vegetative signatures characteristic of fallow pasture. The vegetative signatures are similar to those of the upstream adjacent property, which currently consists of non-wetland pasture.

In conclusion, the available evidence provided by the county soil survey and pre-mining aerial photography indicates that almost all of the land area within the three proposed wetland mitigation sites was non-wetland pasture and forest prior to the recent longwall mining. The creation of extensive wetlands at these sites occurred as the result of recent ground subsidence and ponding/flooding from longwall mining. Longwall mining by Consol has created significant new wetland resources adjacent to Rocky Run and Templeton Fork.

2. <u>Comment</u>: *The mitigation plan proposes to provide and enhance recently created wetlands at a 2:1 ratio to offset impacts for the proposed mine refuse areas. The Corps typically requires a 5:1 to 10:1 ratio for enhancement of existing wetlands as mitigation for wetland impacts. Justify the proposed 2:1 mitigation ratio.*

<u>Response</u>: Mitigation ratios vary between states and between state and federal regulatory agencies. In general, wetland mitigation ratios are reflective of the level of impacts to the aquatic resource. In Pennsylvania, the Corps and the Pennsylvania Department of

Environmental Protection (PADEP) typically require a minimum wetland replacement ratio of 1:1 – i.e., 1 acre of replacement (i.e., restoration or creation) for every acre of wetlands disturbed or destroyed. For higher quality wetlands (i.e., forested wetlands), or wetlands filled without a permit, the mitigation ratio can be 2:1 or higher. Other forms of mitigation include enhancing existing wetlands (ratios of 5:1 to 10:1, depending of the level of effort and benefits gained) and, in special cases, preservation of exceptional quality wetlands and wetland/riparian buffers (ratios of 10:1 and higher), although a minimum of 1:1 replacement through restoration or creation is usually required to meet national and state "no net loss of wetlands" goals.

To mitigate for filling 1.37 acres of wetlands within the refuse and slurry disposal areas, Consol has purchased and proposes to preserve and enhance and expand the newly created wetlands within the Rocky Run Wetland Mitigation Area B and the Templeton Fork Wetland Mitigation Area to meet a 2:1 wetland replacement goal of 2.74 acres. As currently proposed in the mitigation plan submitted with the Coal Refuse Disposal Permit application, dated March 2002, these two mitigation areas would provide a total of 2.30 acres of wetland replacement. Consol proposes to further expand wetlands at these two sites or to include additional newly created wetlands at the Rocky Run Wetland Mitigation Area A to provide an additional 0.44 acre of wetlands to meet the 2:1 replacement goal. Additional non-wetland area is present at the Rocky Run B and Templeton Fork sites that can be used to expand the newly created subsidence wetlands at these locations.

The following justification is provided for the proposed 2:1 wetland replacement ratio using recently created, enhanced, and expanded subsidence wetlands: First, it is appropriate that wetlands created by longwall mining be used to offset the proposed wetland losses associated with coal mining and production, since these activities are linked by a common project purpose. Second, the recent creation of wetlands on properties underlain by coal mining cannot be taken for granted as an unavoidable consequence of mining anymore than the necessary filling of wetlands for the refuse areas. Consol requests that reasonable consideration and credit be given for creating *and responsibly enhancing, managing and maintaining* wetlands caused by longwall mining. Property owners whose land has become ponded or flooded by longwall mining have petitioned mining companies and regulatory agencies to drain these areas to restore their property to its former non-wetland condition. Emergency permits have been issued in the past authorizing drainage activities to eliminate subsidence-induced ponding and flooding, with the corresponding removal of newly created wetland hydrology and potential for wetland development. Consol has purchased the property encompassing the proposed mitigation areas and is committed to taking appropriate measures to protect these wetland resources in perpetuity, as required under the 105 and 404 permits. Furthermore, Consol has proposed

enhancement measures to further increase the value and function of the wetlands, and will monitor and maintain these wetlands through the wetland success monitoring period specified under the permit. Third, the newly created wetland hydrology and wetland plant community development in the mitigation areas should be considered a positive indication of the high probability of wetland mitigation success for these sites. In a sense, Consol has demonstrated wetland mitigation in advance of wetland impacts, which is usually considered a desirable condition in providing agencies with assurance of mitigation success and often warrants a lower mitigation ratio. Finally, the 2:1 ratio proposed by Consol exceeds the minimum 1:1 ratio typically required for many other non-enforcement 105/404 permits in Pennsylvania. Consol recognizes that the proposed mitigation sites do contain existing, although recently created, wetlands and is willing to provide a reasonable wetland replacement ratio above the typically required 1:1 ratio. For the reasons listed above, however, a greater ratio is not warranted given the mining-related origin and potential vulnerability of these recently created wetlands and Consol's proposed efforts to improve, expand, and manage these wetlands.

CEC concurs with the conclusion stated in the mitigation plan prepared by Dr. Brad Owen that these wetland mitigation areas will substantially increase the amount and diversity of, otherwise regionally scarce, wetland habitats in southwestern Pennsylvania.

REFERENCES

Civil & Environmental Consultants, Inc (CEC). 2000. *Second Jurisdictional Wetland Delineation Report for the Enlow Fork Riparian Zone, Bailey Mine Panels 8C, 9C, and 10C, West Finley Township, Washington County and Richhill Township, Greene County, Pennsylvania.* Prepared for Consol Pennsylvania Coal Company. 31 pp. + Appendices.

Pike, D.E. 2000. *An Investigation of Wetlands and Underground Mining in Greene and Washington Counties, Pennsylvania.* Prepared for the Pennsylvania Coal Association. 68 pp.

Schmidt, J.A. and S.P. Kuntz. 2000. *Wetlands and Longwall Mining.* Prepared for the Raymond Proffitt Foundation.

U.S. Department of Agriculture, Natural resources Conservation Service (NRCS). *Hydric Soils – Greene and Washington Counties, Pennsylvania.* 1p.

U.S. Department of Agriculture, Soil Conservation Service (USDA SCS). 1983. *Soil Survey of Greene and Washington Counties, Pennsylvania.* Washington D.C. 93 pp. + maps.

CLOSING

CEC appreciates the opportunity to continue to provide service to Consol. Please contact us if you have any questions regarding this letter. We look forward to continuing to work with you on this project.

Very truly yours,

CIVIL & ENVIRONMENTAL CONSULTANTS, INC.

Mark Haibach

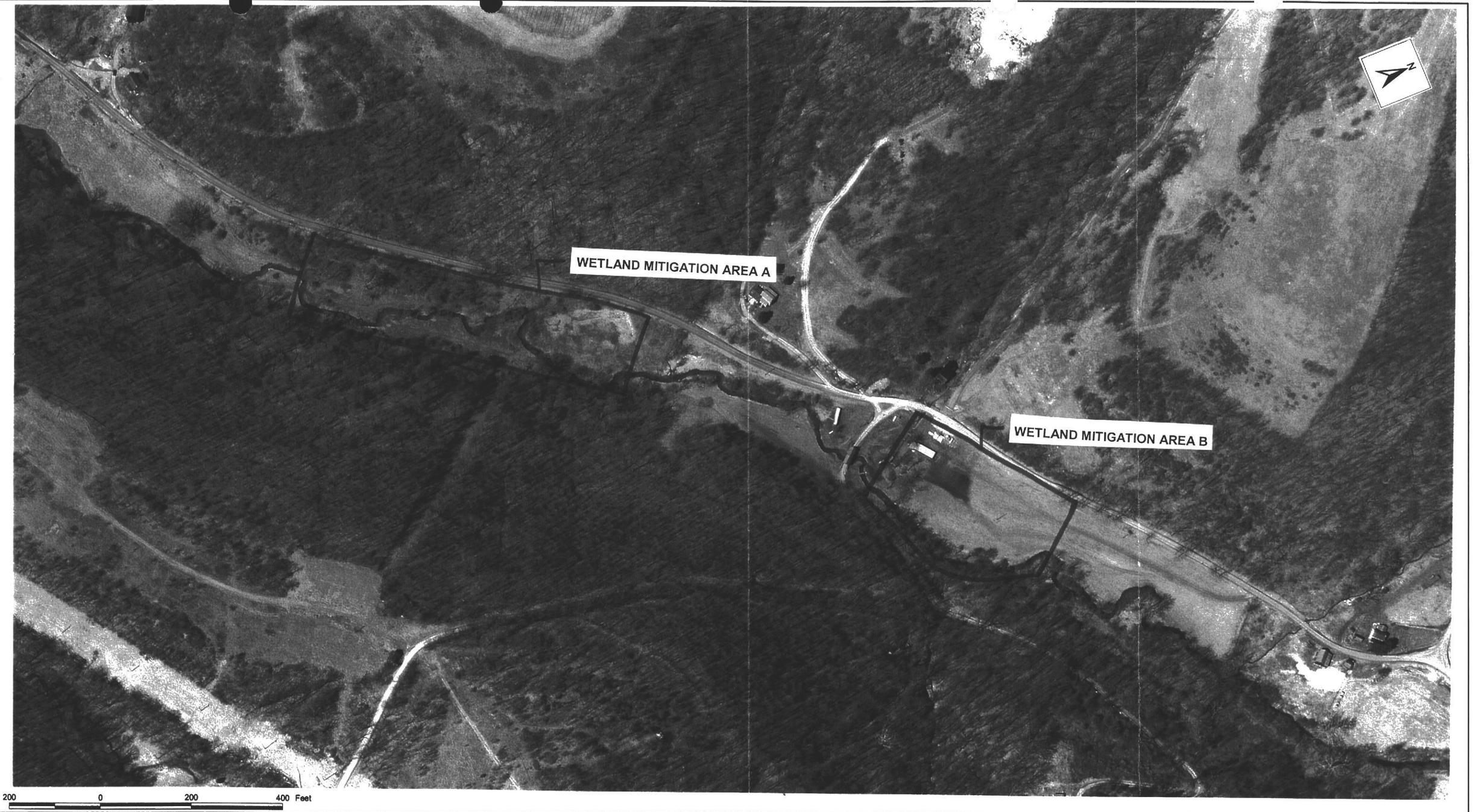
Mark R. Haibach, M.S.
Project Manager/ Environmental Scientist

Daniel A. Maltese

Daniel A. Maltese
Project Manager/Environmental Scientist

Attachments

RC-220806.0004.JN26/I



REFERENCE:

Source:
Aerial Photograph
by Keddal Aerial Mapping
Pittsburgh, PA (3/21/99)

LEGEND:

Wetland Mitigation Areas

CIVIL & ENVIRONMENTAL CONSULTANTS, INC.
Pittsburgh, PA 15205 - 9702
Columbus, OH * Cincinnati, OH * Indianapolis, IN * Nashville, TN * St. Louis, MO * Chicago, Ill

ROCKY RUN WETLAND MITIGATION AREAS A and B
BAILEY MINE REFUSE DISPOSAL AREAS NO. 3 and NO. 4
CONSOL PENNSYLVANIA COAL COMPANY
GREENE COUNTY, PENNSYLVANIA

DWN. BY: JEFF MIHALIK	SCALE: AS SHOWN	DATE: 06/25/02	PROJECT NO.: 220806.0004	FIGURE 1
CHK. BY: MRH				

J:\Projects\220806\bailey_mine.apr\Rocky_run

REFERENCE:

USGS Digital Ortho Quarter Quad
Claysville PA. SE 1995
(download from PASDA website)

LEGEND:

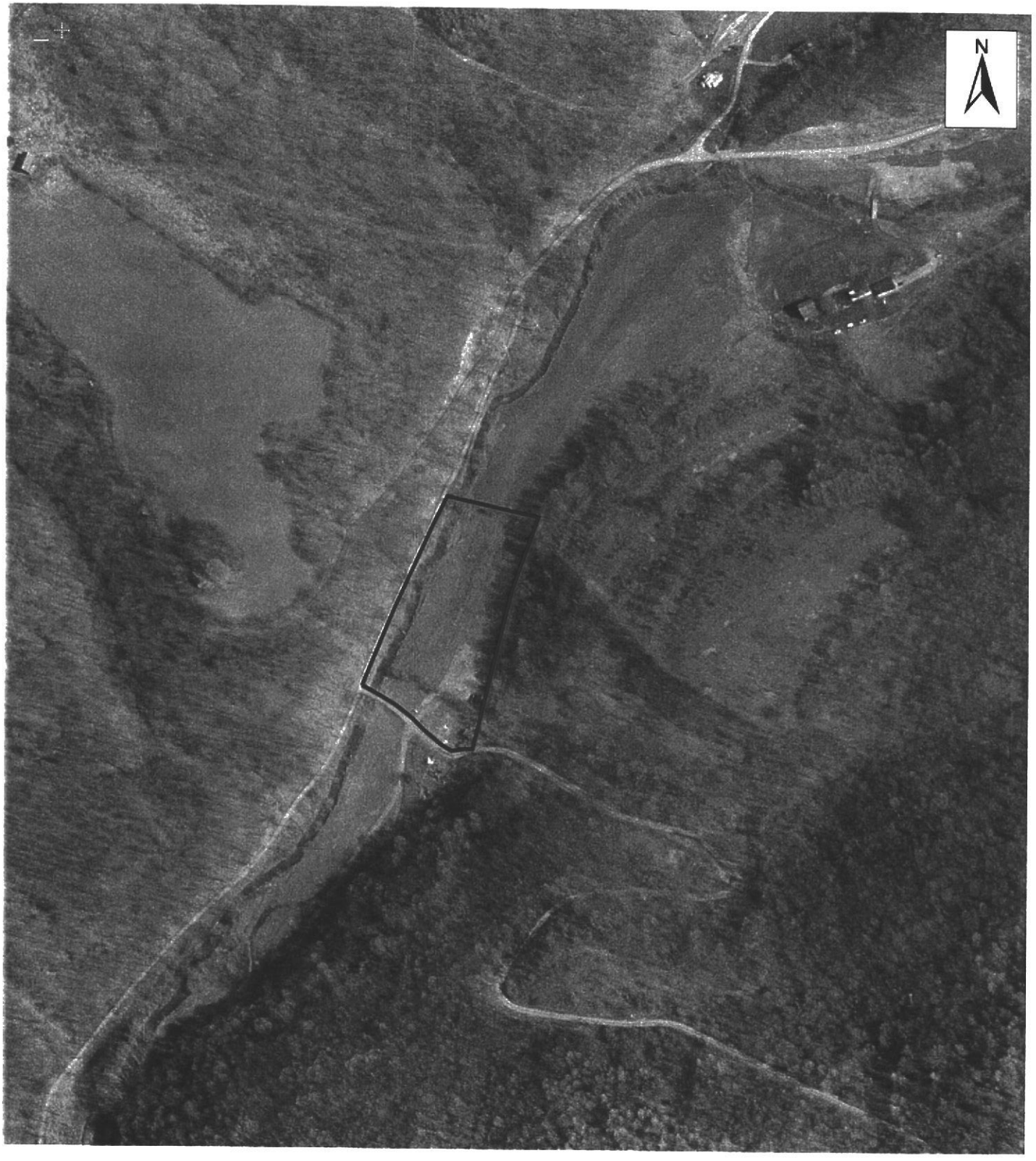
Wetland Mitigation Areas

CEC

CIVIL & ENVIRONMENTAL CONSULTANTS, INC.
Pittsburgh, PA 15205 - 9702
Columbus, OH.* Cincinnati, OH. * Indianapolis, IN. * Nashville, TN. * St. Louis, MO. * Chicago, ILL. * Export, PA

ROCKY RUN WETLAND MITIGATION AREAS A and B
BAILEY MINE REFUSE DISPOSAL AREAS NO. 3 and NO. 4
CONSOL PENNSYLVANIA COAL COMPANY
GREENE COUNTY, PENNSYLVANIA

DWN. BY: JEFF MIHALIK	SCALE:	DATE:	PROJECT NO.:	
CHK. BY: MRH	1" = 400'	06/25/02	220806.0004	FIGURE 2



J:\Projects\220806\bailey_mine\templetonfork_wetland

REFERENCE:

USGS Digital Ortho Quarter Quad
Claysville PA. SE 1995
(download from PASDA website)

LEGEND:

Wetland Mitigation Area

CEC

CIVIL & ENVIRONMENTAL CONSULTANTS, INC.
Pittsburgh, PA 15205 - 9702

Columbus, OH.* Cincinnati, OH. * Indianapolis, IN. * Nashville, TN. * St. Louis, MO. * Chicago, ILL.

TEMPLETON FORK
WETLAND MITIGATION AREA
BAILEY MINE REFUSE DISPOSAL
AREAS NO. 3 and NO. 4
CONSOL PENNSYLVANIA COAL COMPANY
GREENE COUNTY, PENNSYLVANIA

DWN. BY: Jeff Mihalik	SCALE:	DATE:	PROJECT NO.:	
CHK. BY: MRH	1" = 400'	06/25/02	220806.0004	FIGURE 3

ENCLOSURE 1
MODULE 15
ATTACHMENT 15.1
ATTACHMENT 15.5

Module 15: Streams/Wetlands

15.1 Surface Activities Within 100 Feet of a Stream

If surface mining activities, including haul road crossings, are proposed within 100 feet of any intermittent or perennial stream provide the following information: (Note: Variance request must be included in the proof of publication.)

a) Name and location of the stream; and location, length, and acreage disturbed by the proposed activities: (Identify the location of the proposed activities on Exhibits 9.1 and 18.1);

Coal Refuse Disposal Areas No. 3 and No. 4 and associated sedimentation pond will be located within the valley of an unnamed tributary to Enlow Fork of Wheeling Creek and the valley of a major side branch to that tributary. The project site is situated primarily in Richhill Township and a minor part in Gray Township both in Greene County, Pennsylvania. The site is located approximately 3,300 feet south of the intersection of State Routes 4009 (Grinnage Road) and 4013 (Dogtown Road) and is bordered on the west by the existing slurry impoundment for CPCC's Bailey Central Mine Complex. Refer to Figure 1 of Attachment 15.1.

Development of the sites for coal refuse disposal will encroach on 13,198 feet of perennial and intermittent stream channel - 9,898 feet within the mainstream valley and 3,300 feet within the major side branch valley. Refer to Exhibits 6.2 and 9.1.

b) A narrative giving a description and the purpose and justification of the proposed activities;

Consol Pennsylvania Coal Co. is proposing to construct a new slurry impoundment (Coal Refuse Disposal Area No. 3) and new coarse coal refuse disposal area (Coal Refuse Disposal Area No. 4) for disposal of coal refuse generated by the Bailey Central Mine Complex. Existing disposal areas that currently service the mine complex are nearing full capacity.

c) A hydrologic and hydraulic analysis which shall include: data on size, shape and characteristics of the watershed; the size and frequency of the design storm; the hydraulic capacity of any structures; the hydraulic capacity of the channel upstream and downstream; and, where flooding is a problem, flood damage and backwater analysis;

Hydrologic and hydraulic analyses developed for the disposal facility and sedimentation pond designs include details of watershed size, shape and characteristics. These analyses are presented in Appendix G of the Module 21 Design Report.

Stream base flow will be carried under the disposal facilities in a rock drain constucted along the same approximate alignment as the stream channels. Refer to Appendix G of the Module 21 Design Report for calculations demonstrating the capacity of the rock drain and drain outlet pipes.

Hydrologic and hydraulic analyses for the slurry impoundment, sedimentation pond, and channels that will carry storm flows within the watershed are included in Appendix G of the Module 21 Design Report. Design Storms for these structures are presented in the Design Report calculations as well as report narrative.

d) A description of the character of the stream bed and banks, and a profile of the stream for a reasonable distance above and below the proposed site showing bed slopes, normal and flood water surfaces; and a description of the riparian vegetation;

Refer to the Biological Resources report presented as Attachment 15.1 for a description of the character of the stream bed and banks and a description of the riparian vegetation. No stream sections will extend above the proposed site. The stream section immediately below the site is the invert of an existing culvert under the railroad embankment. The slope of this culvert is 2.1%. Calculations showing the capacity of this culvert are included in Appendix G of the Module 21 Design Report.

e) A plan and typical cross sections showing stream channel and existing ground, activities proposed, barriers to be maintained, and normal and flood water surfaces;

Plans and cross sections showing the existing stream channel, existing ground, and proposed activity are include in the Module 21 Construction Drawings. Stream barrier and variance areas are shown on Exhibit 9.1.

f) Where a bridge or culvert is proposed provide the following information:

1) Plans and details showing the location, type, size, and height of the structure;

2) Calculations showing the hydraulic capacity of the structure;

3) A profile of the stream bed for a reasonable distance above and below the proposed location showing normal and flood water surface elevations and backwater effects of the structure;

4) Cross sections upstream, downstream, and at the proposed location of the structure showing normal and flood water surface elevations and other topographic features, elevations, etc., necessary for an appraisal of the hazard potential of the structure;

5) A narrative description of the construction methods and sequence including water handling during construction, and erosion and sedimentation controls;

6) Indicate if the structure will be temporary or permanent (include plans for removal of temporary structures.)

No bridges or culverts are proposed. Stream base flow will be carried under the disposal facilities in a rock drain constructed along the same approximate alignment as the stream channels. Refer to Appendix G of the Module 21 Design Report for calculations demonstrating the capacity of the rock drain and drain outlet pipes.

g) A characterization of the existing water quality and quantity of the stream, including downstream water uses and 25 PA Code Chapter 93 Protected Water Use Classification.

Both unnamed tributaries are classified as Warm Water Fishery (WWF, 25 PA code chapter 93). Within the site the streams are used for cattle grazing and for wildflife water supply. Downstream of the site is a culvert carrying the stream under the railroad. Below the culvert, the stream serves as a water source for area wildlife.

Stream flow rate and water quality data are presented in Forms 8.3B and 8.4A.

15.2 Stream Relocation and Channel Changes

If the proposed surface activities involve a relocation or channel change of a stream provide the information outlined in (a) through (g) below. All plans for stream relocations and channel changes must be certified by a qualified registered professional engineer. (Note: Stream variance request must be included in the proof of publication.)

a) Name and location of stream and location and length of the proposed channel change (identify the location of the proposed activities on Exhibits 9.1 and 18.1);

Refer to Module 15.1.a.

b) A narrative giving a description and the purpose and justification of the proposed relocation or channel change;

Refer to Module 15.1.b.

c) A characterization of the resident aquatic community, a description of the riparian vegetation and an assessment of the probable hydrologic consequences of the proposed activities on the water quality and quantity, and the resident aquatic communities. Provide the name(s), address(es) and telephone number(s) of the individual(s) responsible for the collection and analysis of this data and provide a description of the methodologies used to collect and analyze the data;

Refer to the Biological Resources report presented as Attachment 15.1 for a characterization of the resident aquatic community, a description of the riparian vegetation, and a description of methodologies used to collect and analyze the data. This report was prepared by:

Dale E. Pike, PhD and Bradford B. Owen Jr., PhD
Pike Environmental Consulting
784 Craynes Run Road
Waynesburg, PA 15370-2766
(724) 627-9691

Hydrologic performance of the proposed facility is expected to be at least the same as that of the existing Bailey Central Mine Complex disposal facility, especially since the hydrogeologic setting of both sites are similar. In fact, performance of the proposed facility should exceed that of the existing facility since the proposed facility, unlike the existing facility, will be provided with an on-site soil liner. More detailed discussion of expected water quality impacts from Coal Refuse Disposal Areas No. 3 and No. 4 are presented in Module 8.

Proposed Coal Refuse Disposal Areas No. 3 and No. 4, like the existing Bailey disposal facility, are not expected to adversely impact water quantity. Stream base flow will be carried under the disposal areas in a rock drain and site runoff ultimately will be discharged into the unnamed tributary after passing through the sedimentation pond. Proposed site development will not increase but should decrease flood flows; runoff will be controlled by the slurry impoundment and sedimentation ponds. CPCC plans to recycle slurry impoundment supernatant to the preparation plant, through the existing disposal facility. Based on CPCC's experience at the existing disposal facility, recycling of process water should have no detrimental impact on downstream water quantity.

CPCC proposes to mitigate the impacts of the stream loss by implementing the attached mitigation plan (Attachment 15.2.c). This plan proposes to fund the enhancement of fish and wildlife habitat in a nearby watershed in Greene County and to fund biological monitoring of these habitat improvements to mitigate stream losses. Mitigation will begin prior to site development and will continue concurrent with Stage I development. The mitigation plan provides for stream monitoring to document improvement levels that are achieved. Remedial action will be initiated for this mitigation plan if improvement goals outlined in the plan have not been achieved within 5 years.

d) A hydrologic and hydraulic analysis which includes;

1) Data on size, shape and characteristics of the watershed;

2) The size and frequency of the design storm;

3) The hydraulic capacity of the proposed replacement channel;

4) The hydraulic capacity of the stream channel upstream and downstream of the proposed relocation or channel change.

Refer to Module 15.1.c.

e) A stream profile for the existing and proposed channel for a reasonable distance upstream, downstream and within the proposed change, showing bed slopes, pool-riffle ratios, normal and flood water surfaces, and existing obstructions;

A profile of the main unnamed tributary and the major side branch tributary is presented as Attachment 15.2.e Stream conditions are described in the Biological Resources Report (Attachment 15.1). Pool-riffle ratios are not applicable.

f) A detailed plan and cross sections of the existing and proposed channel upstream, downstream and within the proposed channel change showing the limits and configuration of the proposed activities, dimensions, channel linings, and normal and flood water surfaces;

Refer to the Construction Drawings presented in Module 21.

g) A description of the construction methods and sequence including: water handling during construction, erosion and sedimentation controls, and measures to be taken to prevent adverse impacts to water quality and quantity, water users and the aquatic communities, and measures for environmental enhancement if practicable.

Refer to the Construction Drawings presented in Module 21.

h) A characterization of the existing water quality and quantity of the stream, including downstream water uses and 25 PA Code Chapter 93 Protection Water Use Classification.

Refer to Module 15.1.g.

15.3 Wetland Related Information. Provide the name, address, and phone no. of person conducting the wetland delineation.

a) Complete Form 15A to provide inventory and classification information on all wetlands which occur on or within the permit area of surface mining activity sites. In completing the form, answer "yes" or "no" to the following questions as they pertain to each wetland.

Exceptional Value Wetland Characteristics

1) Does the wetlands serve as habitat for flora and fauna listed as "threatened" or "endangered" under the Endangered Species Act of 1973, or Wild Resource Conservation Act, Fish and Boat Code, or Game and Wildlife Code?

2) Is the wetland hydrologically connected to or located within 1/2 mile of another wetland which serves as habitat of "threatened" or "endangered" species, and does it serve to maintain the habitat in that wetland?

3) Is the wetland located in or along the floodplain of a wild trout stream (as designated by the Pennsylvania Fish and Boat Commission), or the floodplain of a tributary to a wild trout stream?

4) Is the wetland located in or along the floodplain of a stream listed as exceptional value (under Chapter 93) or the floodplain of a tributary to an exceptional value stream?

5) Is the wetland within the corridor of a waterway which has been designated as a wild or scenic river in accordance with the Wild and Scenic Rivers Act of 1968 or the PA Scenic Rivers Act?

6) Is the wetland part of, or located along, an existing public or private drinking water supply and does it maintain the quality or quantity of the drinking water supply?

7) Is the wetland located in an area designated by the Department as "natural" or "wild" area within state forest, game or park lands?

8) Is the wetland located in an area designated as a Federal Wilderness Area under the Wilderness Act or the Federal Eastern Wilderness Act of 1975?

9) Is the wetland located in an area designated as a National Natural Landmark by the Secretary of the Interior under the Historic Sites Act of 1935?

NOTE: If a "yes" response is indicated for any question in (1) through (9) above, the wetlands would be "exceptional value"(as defined in 25 PA Code Section 105.17) and a demonstration must be made that the requirements of subsection (a) of 25 PA Code Section 105.18(a) have been met (See copy of Section 105.18(a) at the end of this Module).

Wetland Functions

10) Does the wetland serve natural biological functions, including food chain production; general habitat; and nesting, spawning, rearing or resting sites for aquatic or land species?

11) Does the wetland provide areas for study of the environment, or as sanctuaries or refuges?

12) Does the wetland aid in, or maintain natural drainage characteristics, natural water filtration processes, current (flow) patterns or other environmental characteristics?

13) Does the wetland serve as a storage area for flood and storm waters, or does it shield other areas from erosion or storm damage?

14) Does the wetland provide recharge to local streams that maintains minimum baseflows?

15) Does the wetland serve as a prime natural discharge area where surface water and groundwater are directly connected?

16) Does the wetland aid in the prevention of pollution?

17) Is the wetland used for, or does it provide the opportunity to be used for recreation?

15.4 Wetland Impact Analysis/Assessment

a) Describe the alternatives to the proposed surface mining activities that have been considered to avoid or minimize impacts on wetlands. An alternative analysis should include alternatives to the proposed surface mining activities, including alternative locations, routings or designs to avoid adverse impacts on the wetlands (i.e. relocating spoil/topsoil storage areas, rerouting haul roads).

Refer to the Alternatives Analysis that was submitted for this project to PADEP McMurray District Mining Office and approved on August 1, 2001.

b) Discuss whether any of the alternatives considered in (a) are practical to achieve the basic purposes of the project taking into account availability, cost, technology and logistics of the other possible project sites which would not affect wetlands?

Wetland impacts at the site are unavoidable. Refer to the Alternatives Analysis that was submitted for this project to PADEP McMurray District Mining Office and approved on August 1, 2001.

c) If any wetlands will be directly affected, provide the following:

1) Identify the wetland and the areal extent of the impact.

All of the wetlands listed on Form 15A will be completely impacted and removed by the proposed activities. Figure 2 of Attachment 15.1 shows the location and approximate extent of the existing wetland areas.

2) Submit a cross-sectional view showing the wetland and the proposed disturbed area.

Cross sectional views of valley bottom areas where the wetlands are located are included with the Module 21 Construction Drawings

3) Explain how the proposed activities will directly affect the hydrology, functions and values of the wetlands.

i) If the proposed surface mining activities will affect less than 1.0 acre of wetland and the wetland is not an exceptional value wetland (in accordance with 25 PA Code Section 105.17), provide a description and probable degree of impact to the wetland functions and values which will be impacted by the proposed mining activities. NOTE: If a "yes" response is indicated for any question in 15.3 (a)(1)-(9), the wetlands would be exceptional value (as defined in Section 105.17).

ii) If the proposed surface mining activities will affect 1.0 or more acres of wetlands or may affect an exceptional value wetland, provide a detailed assessment of the wetland functions and values identified in 15.3 (a)(10)-(17). Provide extent or degree of impact to each function and value.

A detailed assessment of wetland functions is included in Attachment 15.5. As indicated by that report and the Attachment 15.1 report, very few of the Area No. 3 wetlands are in

a natural state and most have been highly disturbed by cattle traffic. Wetland areas encompassing springs and seeps serve as groundwater discharge areas. Proposed construction provides for spring and seep flow to be intercepted and carried under the project site in an underdrain. Erosion and sedimentation and flood control provided by the wetlands will be replaced by proposed facilities detailed in the Module 21 Construction Drawings.

d) If any wetlands will be indirectly affected by surface mining activities (e.g. altering the wetland hydrology):

1) Identify the wetland and provide an estimate of the total wetland acreage affected. Describe the functions or values to be impacted and the degree of impact.

2) Provide a description of how the proposed surface mining activities will indirectly affect the wetlands' functions and values.

No indirect wetland impacts are anticipated.

e) Indicate whether the cumulative impact of the proposed and anticipated surface mining activities result in a major impairment of the wetland resource in the general area, provide an explanation of the determination and identify any contacts with state or federal agencies involved in making the determination.

Cumulative impacts of the proposed surface mining activities will not result in a major impairment of wetland resources in the general area. Any wetland impacts will be mitigated/replaced as described in Module 15.5. The proposed activity will be primarily contained within the watershed of the two unnamed tributaries. Recharge contributed by wetlands and streams within the project site to areas downstream will be maintained by discharge from the proposed sedimentation pond.

f) Where a wetland's hydrology is at risk of being altered by underground coal extraction, as determined by the assessment under Module 8.5, information concerning wetland delineation ad functions must be provided as outlined in Sections 15.3 and 15.4 of this module.

Not Applicable.

15.5 Wetland Mitigation/Replacement. (Sites where less than 0.5 acres of wetland is affected may qualify for mitigation options provided under the Pennsylvania Wetland Replacement Project. Contact the DEP permitting office for details.)

a) If wetland mitigation measures or wetland replacement are proposed, address the following items:

1) Identify the wetlands where mitigation measures will be employed, wetlands that will be replaced, and sites where replacement wetlands will be constructed along with the respective area of each.

2) Provide a plan for mitigation/replacement following the guidelines in the DEP's technical guidance document, entitled "Design Criteria for Wetlands Replacement". (This guidance is available from DEP's Bureau of Water Quality Protection, Post Office Box 8465, Harrisburg, Pennsylvania 17105-8465, telephone 717-787-2666 or through the Department's web site under Technical Guidance # 363-0300-001.

3) Show all affected wetlands, mitigation areas, and replacement sites on Exhibit 9.1; and, in addition, show replacement sites on Exhibit 18.1.

4) Provide a wetlands functions and values comparison of current vs. replacement wetland acreage. In the case of mitigation, a comparison of the known wetlands functions and values and degree of impact to each must be compared to the functions and values of the proposed mitigation site when completed. This comparison of "currently existing" to "probable replacement" allows for a basis of the 1:1 replacement ratio.

Refer to the Attached Wetland Mitigation Plan (Attachment 15.5) for descriptions of affected wetlands and replacement wetlands, including a comparison of functions and values. Affected wetlands also are shown on Exhibit 9.1 and 18.1.

NOTES: At a minimum, wetland replacement must be at a 1:1 ratio (replacement acres:affected acres), although the Department may require the ratio to exceed 1:1 based on the functions and values of the wetlands to be affected.

Wetland replacement sites will generally not be approved unless the site is located within the same general area as the existing wetland to be be replaced.

FORM 15A - WETLAND INVENTORY

Surface Site I.D.	Wetland I.D.	Acreage (acres)	Provide a positive (Y) or negative response (N) to each question under 15.3 as it applies to each wetland. (Column numbers correspond to question numbers).																
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Area No. 3	S-1	0.055	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	S-2	0.008	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	S-3	0.067	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	S-4	0.209	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	N	Y	N
	S-5	0.050	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	S-6	0.022	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	S-7	0.090	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	S-8	0.013	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	S-9	0.020	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	S-10	0.435	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	S-11	0.048	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	S-12	0.004	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	S-13	0.048	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	S-14	0.021	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	S-15	0.080	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	S-16	0.031	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	S-17	0.009	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	S-18	0.045	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	S-19	0.012	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	Total	**1.267**																	

Surface Site I.D.	Wetland I.D.	Acreage (acres)	Provide a positive (Y) or negative response (N) to each question under 15.3 as it applies to each wetland. (Column numbers correspond to question numbers).																
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Area No. 4	R-1	0.026	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	R-2	0.009	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	R-3	0.014	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	R-4	0.033	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	R-5	0.004	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	R-6	0.012	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	R-7	0.004	N	N	N	N	N	N	N	N	N	N	N	Y	Y	N	Y	Y	N
	Total	**0.102**																	

Rev. 6/22/02

ATTACHMENT 15.1

BIOLOGICAL RESOURCES REPORT

BIOLOGICAL RESOURCES

OF

THE PROPOSED BAILEY MINE REFUSE

AND SLURRY VALLEYS,

GREENE COUNTY, PENNSYLVANIA

By

Dale E. Pike, Ph.D.

and

Bradford B. Owen Jr., Ph.D.

for

Consol Pennsylvania Coal Company

August 8, 2001

INTRODUCTION

Consol Pennsylvania Coal Company is planning to develop new coal refuse disposal and slurry impoundment facilities for the Bailey Mine in the valley of an unnamed tributary to Enlow Fork of Wheeling Creek southeast of the mine's existing facilities (Figure 1). The site consists of the mainstem of the unnamed tributary where the slurry impoundment will be constructed and a major side branch of that tributary in which coal refuse will be disposed. Biological evaluations were made of each valley during May and June, 2001 to locate and delineate wetlands, determine the length of non-ephemeral stream channels that could be impacted by construction and to informally assess aquatic macroinvertebrate populations of the project sites.

METHODS

Each valley was walked to locate wetlands in the floodplain. All tributary drainages were walked to their sources, since wetlands are often located in spring or seep origins of tributaries. Terraces and slumps at the elevation of the tributary sources were checked for possible wetlands.

The mainstream channel in each valley and all of its tributaries were walked to determine where flows became ephemeral. Prior to the visits there had been a period of rain heavy enough to wash out leaf litter normally found in ephemeral channels during the spring, making the distinction between ephemeral and non-ephemeral channels difficult. Therefore, portions of channels with defined substrates and the presence of aquatic organisms normally requiring at least subsurface flow to complete their lifecycles were considered non-ephemeral. The intermittent and perennial portions of the stream channels were measured and lengths recorded.

Macroinvertebrates were collected from the main stem of each valley and selected points in the tributaries. In the main stem streams composite samples were made from stream segments than appeared to have similar substrates and flows. Where major tributaries entered the main stem new composite samples were taken. A total of five samples were collected from each valley

(Figure 1). Collections were made with a D-frame kick-net and by hand picking specimens from leaf-packs and stream substrates. The samples were preserved and returned to the lab for sorting of specimens from sample debris and identification to the lowest practical taxon. Identifications were made with the aid of taxonomic keys found in Merritt and Cummins (1996); Peckarsky, et al. (1990); Stewart and Stark (1993) and Jezerinac, et al. (1995).

Each valley was surveyed in the field in detail according to the Routine Wetland Determination methods of the Army Corps of Engineers Manual (Environmental Laboratory, 1987). Jurisdictional wetlands were staked by the author and surveyed by Blue Mountain Engineering. Plant identification was primarily according to Strausbaugh and Core (undated) with assistance from other plant guides, and nomenclature was updated according to the synonymy in Reed (1997). Plant indicator categories were taken from the Revision of the National List of Plant Species that Occur in Wetlands (ibid). Soils were classified according to the soil survey of Greene and Washington Counties (U.S. Dept. of Agriculture et al., 1983) and their hydric classification was according to the list of hydric soils of the United States (U. S. Dept. of Agriculture, 1991). Detailed field data and the plant indicator categories are summarized on the attached "Standard Data Form 1" from the Army Corps of Engineers Manual (Environmental Laboratory, 1987). Locations of jurisdictional wetlands are shown in Figure 2.

RESULTS – JURISDICTIONAL WETLANDS

REFUSE VALLEY

With few exceptions, the wetlands of the refuse valley were streamside or seep areas with relatively heavy forest cover.

Wetland R-1 is a small wetland (0.026acres) resulting partly from ATV traffic. It had an inundated area about two meters square, while the rest of the wetland varied from saturated soils to dryer areas, resulting in a variety of plants being common. *Bidens frondosa* was dominant around the inundated area, while *Poa trivialis* and *Glyceria striata* dominated the spring flora in surrounding areas.

Wetlands R-2 and R-3 are relatively small somewhat marginal streamside and seep wetlands (0.009 and 0.014 acres, respectively). Wetland R-3 has a number of *Lindera benzoin*, typical of much of the flood plain in this area.

Wetland R-4 is a somewhat larger streamside wetland (0.033 acres), with shallow soils over gravel. Its spring flora was dominated by *Poa trivialis* while *Impatiens capensis* (as in all future references, could be *I. Pallida* – couldn't be determined in spring collections) was appearing likely to be the late season dominant.

Wetland R-5 is a very small seep wetland (0.004 acres) in heavy forest, and its spring flora was dominated by *Carex prasina*, with *Impatiens capensis* likely to become the late season dominant. Wetlands R-6 and R-7 are two spring-seep wetlands (0.012 and 0.004 acres, respectively) at the headwaters of the Refuse Valley. Both are in heavy forest cover, but had different dominant spring herbs. *Carex prasina* dominated Wetland R-6, while *Impatiens capensis* dominated Wetland R-7.

SLURRY VALLEY

Jurisdictional wetlands of the Slurry Valley varied greatly in size, cover and plant composition. The valley was only partially wooded and most of it was heavily impacted by cattle grazing.

Wetlands S-1 and S-2 are small (0.055 and 0.008 acres, respectively) wetlands recently created by the adjacent railroad embankment. Both are in completely open areas and are heavily dominated by *Typha latifolia* with lesser amounts of other wetland and transitional species. These are low quality wetlands.

Wetland S-3 is another small wetland (0.067 acres) in an open area, with spring vegetation dominated by grasses with a few sedges and other taxa mixed in.

Wetland S-4 is a fairly large wetland (0.209 acres) in a mostly open area. It has areas with almost an inch of water standing between vegetation clumps, but the majority of this wetland is a wet meadow with soil saturation a few inches below the surface. A great variety of herbs grow in this wetland, with some areas dominated in the spring by *Glyceria striata* and others by *Typha latifolia* or *Poa trivialis.* Late season vegetation will find *Aster puniceus*, *Carex* species and *Polygonum sagittatum* becoming the dominants in most of the areas where spring grasses were dominant.

Wetland S-5 is a small wetland (0.050 acres) that includes a small pooled area and surrounding wet areas dominated by a sparse cover of *Glyceria striata, Bidens frondosa* and a few other taxa. This wetland appears to be the result of an old channel that has been abandoned by the stream, while still maintaining water by virtue of a nearby seep.

Wetland S-6 is a seep area (0.022 acres) in a power line right of way. Having almost no cover it supports a dense herbaceous layer dominated by *Polygonum hydropiperoides* and *Carex frankii*, with a large spring season representation of *Poa trivialis. Impatiens capensis* and *Bidens frondosa* will likely dominate some of the wetland in late season.

Wetlands S-7 and S-8 (0.090 and 0.013 acres, respectively) are streamside areas heavily impacted by cattle. Most of the soils were dug up and much of the vegetation either grazed or mashed by cattle. Wetland 7 was dominated in the spring sampling by a mixture of *Leersia virginica, Bidens frondosa* and *Poa trivialis.* Wetland S-8 is a seep area near Wetland S-7 that was dominated by *Poa trivialis* and *Pilea pumila* in the spring sampling. Late season vegetation will be dominated by *P. pumila* and possibly *Polygonum hydropiperoides.*

Wetland S-9 (0.020 acres) is an area where the stream spread over a large flat area and created an island of gravely soils that supported some wetland vegetation. *Poa trivialis* and *Pilea pumila* dominated the spring vegetation and again late season vegetation will likely be dominated by *P. pumila* and *Polygonum hydropiperoides.*

Wetland S-10 is the largest wetland of the Slurry Valley (0.435 acres). It encompassed a large relatively flat wet meadow with some areas saturated to the surface, grading to transitional areas. Spring vegetation was dominated by a number of grasses and sedges and smooth rush, depending on the specific area.

Wetland S-11 is a small wetland (0.048 acres) in an open area below an abandoned pond. Its spring flora was dominated by *Carex frankii* with the grasses *Bromus inermis* and *Glyceria striata* also very common. *B. inermis* is a UPL rated grass that dominated the adjacent grazed pasture and despite its rating seemed to be thriving in the wetland environment – possibly because it withstands grazing better than its would – be competitors.

Wetland S-12 is a tiny (0.004 acres) wetland at the headwaters of a small tributary. It was heavily impacted by cattle and had spring vegetation dominated by *Poa trivialis* with *Polygonum hydropiperoides* likely to dominate latter in the season.

Wetland S-13 is a wet area (0.048 acres) within the old abandoned and breached impoundment. A small area of standing water was surrounded by mud flats with sparse vegetation dominated in the spring by *Poa trivialis* and a few wetland plants with *Bromus inermis* again quite common.

Wetland S-14 is a small seep area (0.021 acres) adjacent to the main stream. It was an open area dominated by two sedges and smooth rush, despite the heavy grazing by cattle.

Wetlands S-15 and S-16 are areas (0.080 and 0.031 acres, respectively) very heavily disturbed by cattle loafing, with much of the vegetation destroyed and soils a mass of deep hoof prints. Wetland S-15 was in an area partially shaded by a *Craetagus* thicket. It had scattered vegetation often dominated by *Bidens frondosa.* Wetland S-16 was mostly bare mud with a scattering of plants, *Pilea pumila* being the most abundant.

Wetlands S-17, S-18 and S-19 are headwater wetlands (0.009, 0.045 and 0.012 acres, respectively) that were in mostly open areas. Despite the heavy grazing by cattle, a variety of

vegetation remained, with each area having its own dominant wetland plant, but all areas again having a fair amount of *Bromus inermis* that had invaded from adjacent pasture.

RESULTS—AQUATIC RESOURCES

Spring fed streams in southwest Pennsylvania often have perennial or intermittent flows for a short distance from their source and then become ephemeral to some point downstream where flows once again become at least intermittent. This was the case encountered in the drainages visited during this investigation.

Figure 1 shows the non-ephemeral stream channels in the project area. From the existing Bailey Railroad grade culvert upstream through the valley that is the site of the proposed slurry disposal facility approximately 9898 feet of non-ephemeral stream channel were identified. The valley proposed for coarse refuse disposal had about 3300 feet of non-ephemeral stream channel from its confluence with the main stem channel to its headwaters.

Substrates were quite variable over the entire length of stream investigated. No effort was made to quantitatively characterize stream substrates, but it was noted that there were areas of fine substrates in the headwater and some downstream sections of the streams. Large stretches of channel had gravels and cobble size materials. Shortly after stream measurements and macroinvertebrate collections were made the project area experienced an extremely heavy storm event resulting in major scouring of streambeds in the drainage. Gravel and finer size materials were washed out and deposited across the valley floodplain. Larger size materials were repositioned in the streambed with a large percentage of the aquatic biota disturbed or likely destroyed.

The slurry disposal valley is currently used for cattle grazing resulting in stream banks and some riparian areas being heavily damaged. Several areas used for resting or congregation within the floodplain are devoid of vegetation and have soils churned up due to cattle activity. The

proposed refuse disposal valley has not been recently grazed, but sections of the streambed have been disturbed by four-wheelers crossing or running in the stream channel.

Macroinvertebrate survey results for the proposed slurry impoundment and refuse disposal valleys are presented in Tables 1 and 2, respectively. Sampling of aquatic organisms was qualitative, so the Tables only show the presence of a particular taxon at a sampling station. The streams in both valleys had relatively diverse aquatic communities consistent with those found in southwest Pennsylvania. The larger number of taxa found in the proposed slurry impoundment valley is probable due to that stream being larger and providing more habitat types than the smaller valley proposed for coal refuse disposal.

CONCLUSIONS

Both the Refuse and Slurry valleys had a number of small wetlands associated with the streams in each valley - typical of southwestern Pennsylvania watersheds. The Refuse Valley contained seven discrete Jurisdictional Wetlands totaling only 0.102 acres, while the Slurry Valley contained 19 Jurisdictional Wetlands totaling 1.267 acres. The wetlands of the Refuse Valley were mostly very small streamside or seep wetlands under heavy woodland cover. Most were relatively undisturbed natural wetlands of the sort commonly seen associated with stream origins and flood plains in southwestern Pennsylvania. Wetlands of the Slurry Valley ranged from wet meadows to headwater seep wetlands. Only Wetlands S-1 to S-3 were not impacted by cattle traffic and grazing. Very few of the Slurry Valley wetlands were in a natural state and most were so highly disturbed that it is difficult to say what the natural vegetation should have been.

The macroinvertebrate fauna of the streams in the proposed project site were typical of small streams in this part of Pennsylvania. Many of the stream channels had been disturbed to some degree. The Refuse Valley had some disturbance from four-wheeler traffic, while the stream channel in the Slurry Valley was heavily impacted by pastured cattle. The aquatic biota of the latter stream, relative to a similar size stream in an un-grazed valley, is probably reduced in numbers of individuals, if not in numbers of taxa, due to cattle activity. In addition, extremely

heavy late spring rains had washed out or repositioned most substrates in both valleys impacting the aquatic communities at least for the short term.

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Table 1. Macroinvertebrates Collected From the Proposed Slurry Impoundment Site, Bailey Mine, Greene County, Pennsylvania, June 4, 2001

Taxon	STA 1	STA 2	STA 3	STA 4	STA 5
Oligochaeta					
Enchytraeidae			✔	✔	
Lumbriculidae	✔		✔	✔	✔
Bivalvia					
Pisidium	✔				✔
Gastropoda					
Fossaria					✔
Gyraulus	✔				
Physella	✔	✔			✔
Ephemeroptera					
Ameletus			✔		
Baetis	✔	✔	✔		
Eurylophella	✔				
Stenonema	✔	✔	✔	✔	✔
Odonata					
Cordulegaster	✔	✔		✔	
Plecoptera					
Amphinemura	✔	✔	✔	✔	✔
Beloneuria	✔	✔			✔
Diploperla		✔			
Isoperla	✔	✔	✔	✔	✔
Hemiptera					
Microvelia		✔		✔	

Table 1. Macroinvertebrates Collected From the Proposed Slurry Impoundment Site, Bailey Mine, Greene County, Pennsylvania, June 4, 2001 (continued)

Taxon	STA 1	STA 2	STA 3	STA 4	STA 5
Trichoptera					
Chimarra					✔
Eocosmoecus		✔			
Ironoquia				✔	
Lepidostoma				✔	
Limnephilidae (pupa)					✔
Limnephilus	✔	✔			
Neophylax		✔		✔	✔
Lepidoptera					
Acentria			✔		
Coleoptera					
Agabetes				✔	✔
Hydrobius					✔
Hydroporus		✔			✔
Laccobius				✔	✔
Stenus		✔			
Megaloptera					
Nigronia	✔				
Diptera					
Brachypremna	✔	✔		✔	✔
Chironomidae	✔	✔	✔	✔	✔
Chrysops				✔	
Dicranota				✔	
Limnophila		✔			
Pedicia				✔	
Scatella	✔				
Tipula	✔	✔		✔	✔

Table 1. Macroinvertebrates Collected From the Proposed Slurry Impoundment Site, Bailey Mine, Greene County, Pennsylvania, June 4, 2001 (continued)

Taxon	STA 1	STA 2	STA 3	STA 4	STA 5
Amphipoda					
Crangonyx	✔				
Decapoda					
♀ *Cambarus*					✔
juv. *Cambarus*	✔	✔			✔
Total Taxa	19	21	9	17	19

Table 2. Macroinvertebrates Collected From the Proposed Refuse Disposal Site, Bailey Mine, Greene County, Pennsylvania, May 22, 2001

Taxon	STA 6	STA 7	STA 8	STA 9	STA 10
Oligochaeta					
Lumbriculidae			✔		
Ephemeroptera					
Ephemerella	✔	✔			✔
Paraleptophlebia	✔		✔		✔
Stenacron	✔	✔	✔		
Stenonema	✔				
Plecoptera					
Amphinemura	✔	✔			✔
Diploperla	✔	✔	✔		
Diura		✔			
Isoperla	✔	✔	✔	✔	✔
Peltoperla	✔		✔	✔	✔
Sweltsa		✔			
Trichoptera					
Diplectrona	✔	✔	✔	✔	
Ironoquia		✔			
Lepidostoma		✔			
Pycnopsyche			✔	✔	

Table 2. Macroinvertebrates Collected From the Proposed Refuse Disposal Site, Bailey Mine, Greene County, Pennsylvania, May 22, 2001 (continued)

Taxon	STA 6	STA 7	STA 8	STA 9	STA 10
Coleoptera					
Anchytarus				✔	
Megaloptera					
Nigronia	✔		✔	✔	
Diptera					
Chironomidae		✔			✔
Chrysops	✔				
Cryptolabis	✔			✔	
Limnophila	✔	✔		✔	✔
Pedicia				✔	✔
Pseudolimnophila				✔	
Tipula		✔	✔		
Amphipoda					
Crangonyx		✔			
Decapoda					
Cambarus bartonii		✔	✔		
juv. *Cambarus*	✔	✔		✔	
Total Taxa	14	15	11	11	8

ATTACHMENT 15.5

WETLAND MITIGATION PLAN

WETLAND MITIGATION FOR

BAILEY MINE SLURRY AND REFUSE HOLLOWS

GREENE COUNTY, PENNSYLVANIA

Prepared for

Consol Pennsylvania Coal Company

by

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Dale E. Pike, Ph.D.

December 22, 2001

INTRODUCTION

Consol Pennsylvania Coal Company has proposed the use of two adjacent valleys for the disposal of coarse coal refuse and fine coal refuse from the Bailey Central Preparation Plant, hereafter referred to as the refuse valley and slurry valley; (locations shown in Figure 1). These two valleys were surveyed for wetlands in June, 2001. A total of 0.102 acres of wetlands were found in the proposed refuse disposal valley and 1.267 acres were found in the proposed slurry disposal valley. Thus a total loss of 1.369 acres would have to be mitigated. The following report details the wetlands that would be lost in the proposed disposal valleys and proposes mitigation for these losses at a ratio of 1:1.5 by enhancing three new wetlands created by recent longwall mining-related subsidence in the nearby Rocky Run and Templeton Fork watersheds (locations shown in Figure 1).

METHODS

The wetlands of the proposed slurry and refuse valleys, as well as the newly created wetlands the Rocky Run and Templeton Fork watersheds were surveyed in the field in detail according to the Routine Wetland Determination methods of the Army Corps of Engineers Manual (Environmental Laboratory, 1987). Plant identification was primarily according to Strausbaugh and Core (undated) with assistance from other plant guides and nomenclature was updated according to the synonymy in Reed (1997). Plant indicator categories were taken from the Revision of the National List of Plant Species that Occur in Wetlands (ibid). Soils were classified according to the soil survey of Greene and Washington Counties (U.S. Dept. of Agriculture et al., 1983) and their hydric classifications were checked in the list of hydric soils of the United States (U. S. Dept. of Agriculture, 1991). Detailed field data and the plant indicator categories for Jurisdictional Wetlands were summarized on Standard Data Form 1C from the Army Corps of Engineers Manual (Environmental Laboratory, 1987). These forms and photographs of each wetland are included in Appendices A - D.

Wetlands of the proposed slurry and refuse valleys were delineated in July, 2001, while final delineation of the subsidence - created wetlands was postponed until fall, 2001 in order to allow wetland plants to become well established, especially in the Rocky Run wetlands which were essentially new as of the 2001 growing season.

RESULTS

WETLANDS OF THE PROPOSED REFUSE VALLEY

With few exceptions, the wetlands of the refuse valley (Figure 2, Appendix A) were small streamside or seep areas with relatively heavy forest cover. Seven Jurisdictional Wetlands were delineated, totaling 0.102 acres.

Wetland R-1 is a small wetland (0.026 acres) resulting partly from ATV traffic. It had an inundated area about two meters square, while the rest of the wetland varied from saturated soils to dryer areas, resulting in a variety of plants being common. *Bidens frondosa* was dominant around the inundated area, while *Poa trivialis* and *Glyceria striata* dominated the spring flora in surrounding areas.

Wetlands R-2 and R-3 are relatively small somewhat marginal streamside and seep wetlands (0.009 and 0.014 acres, respectively). Wetland R-3 supported a number of *Lindera benzoin*, typical of much of the flood plain in this area.

Wetland R-4 is a somewhat larger streamside wetland (0.033 acres), with shallow soils over gravel. Its spring flora was dominated by *Poa trivialis* while *Impatiens capensis* (as in all future references, could be *I. Pallida* couldn t be determined in spring collections) was appearing likely to be the late season dominant.

Wetland R-5 is a very small seep wetland (0.004 acres) in heavy forest, and its spring flora was dominated by *Carex prasina*, with *Impatiens capensis* likely to become the late season dominant.

Wetlands R-6 and R-7 are two spring-seep wetlands (0.012 and 0.004 acres, respectively) at the headwaters of the refuse valley. Both are in heavy forest cover, but had different dominant spring herbs. *Carex prasina* dominated Wetland R-6, while *Impatiens capensis* dominated Wetland R-7.

WETLANDS OF THE PROPOSED SLURRY VALLEY

Most of the Jurisdictional Wetlands of the slurry valley (Figure 3, Appendix B) were also streamside or seep areas, but they varied greatly in size, cover and plant composition. This

valley was only partially wooded and most of it was heavily impacted by cattle grazing. Nineteen Jurisdictional Wetlands were delineated, totaling 1.267 acres.

Wetlands S-1 and S-2 are small (0.055 and 0.008 acres, respectively) wetlands recently created by the adjacent railroad embankment. Both are in completely open areas and were heavily dominated by *Typha latifolia* with lesser amounts of other wetland and transitional species.

Wetland S-3 is another small wetland (0.067 acres) in an open area, with early season vegetation dominated by grasses with less abundant sedges and a few other taxa.

Wetland S-4 is a fairly large wetland (0.209 acres) in a mostly open, streamside area. It has areas with almost an inch of water standing between vegetation clumps, but the majority of this wetland is a wet meadow with soil saturation a few inches below the surface. A great variety of herbs grow in this wetland, with some areas dominated in the spring by *Glyceria striata* and others by *Typha latifolia* or *Poa trivialis.* Late season vegetation will find *Aster puniceus*, *Carex* species and *Polygonum sagittatum* becoming the dominants in most of the areas where spring grasses were dominant.

Wetland S-5 is a small wetland (0.050 acres) that includes a small pooled area and surrounding wet areas dominated by a sparse cover of *Glyceria striata, Bidens frondosa* and a few other taxa. This wetland appears to be the result of an old channel that has been abandoned by the stream, while still maintaining water by virtue of a nearby seep.

Wetland S-6 is a seep area (0.022 acres) in a power line right of way. Having almost no overstory cover, it supported a dense herbaceous layer dominated by *Polygonum hydropiperoides* and *Carex frankii*, with a large spring season representation of *Poa trivialis*. *Impatiens capensis* and *Bidens frondosa* will likely dominate some of the wetland in late season.

Wetlands S-7 and S-8 are small streamside areas heavily impacted by cattle. Most of the soils were dug up and much of the vegetation either grazed or trampled by cattle. Wetland S-7 (0.090 acres) was dominated in the spring sampling by a mixture of *Leersia virginica, Bidens frondosa* and *Poa trivialis*. Wetland S-8 (0.013 acres) is a seep area near Wetland S-7 that was dominated by *Poa trivialis* and *Pilea pumila* in the spring sampling. Late season vegetation will be dominated by *P. pumila* and possibly *Polygonum hydropiperoides.*

Wetland S-9 (0.020 acres) is an area where the stream spread over a large flat area and created an island of gravely soils that supported some wetland vegetation. *Poa trivialis* and *Pilea pumila* dominated the spring vegetation and again late season vegetation will likely be dominated by *P. pumila* and *Polygonum hydropiperoides.*

Wetland S-10 is the largest wetland of the slurry valley (0.435 acres). It encompassed a large relatively flat, wet meadow with some areas saturated to the surface, grading to transitional areas. Spring vegetation was dominated by a number of grasses and sedges and smooth rush, depending on the specific area.

Wetland S-11 is a small wetland (0.048 acres) in an open area below an abandoned pond. Its spring flora was dominated by *Carex frankii,* with the grasses *Bromus inermis* and *Glyceria striata* also very common. *B. inermis* is a UPL rated grass that dominated the adjacent grazed pasture and despite its rating, it seemed to be thriving in the wetland environment possibly because it withstands grazing better than its competitors.

Wetland S-12 is a tiny (0.004 acres) wetland at the headwaters of a small tributary. It was heavily impacted by cattle and had spring vegetation dominated by *Poa trivialis* with *Polygonum hydropiperoides* likely to dominate later in the season.

Wetland S-13 is a wet area (0.048 acres) within the abandoned and breached impoundment. A small area of standing water was surrounded by mud flats with sparse vegetation dominated in the spring by *Poa trivialis* and a few wetland plants with *Bromus inermis* again quite common.

Wetland S-14 is a small seep area (0.021 acres) adjacent to the main stream. It was an open area dominated by two sedges and smooth rush, despite the heavy grazing by cattle.

Wetlands S-15 and S-16 are areas (0.080 and 0.031 acres, respectively) very heavily disturbed by cattle, with much of the vegetation destroyed and soils a mass of deep hoof prints. Wetland S-15 was in an area partially shaded by a *Craetagus* thicket. It had scattered vegetation often dominated by *Bidens frondosa.* Wetland S-16 was mostly bare mud with a scattering of plants, *Pilea pumila* being the most abundant.

Wetlands S-17, S-18 and S-19 are headwater wetlands (0.009, 0.045 and 0.012 acres, respectively) that were in mostly open areas. Despite the heavy grazing by cattle, a variety of vegetation remained, with each area having its own dominant wetland plant, but all areas again having a fair amount of *Bromus inermis* that had invaded from adjacent pasture.

SUBSIDENCE - CREATED WETLANDS

Subsidence has created several wetlands by lowering land relative to the water table and/ or adjacent stream. This report describes three such wetlands that are proposed to be enhanced for mitigation for the loss of wetlands due to the proposed construction of the slurry and refuse disposal areas in the valleys discussed above. The three newly created wetlands are less than four miles from the proposed disposal valleys and are all within a short distance of each other, near the confluence of Rocky Run and Templeton Fork in southern Washington County (Figure 4). Once mitigated, the three wetlands together will constitute a significant net increase in valuable wetland habitat (open water and emergent wetland habitat) that is currently a scarce resource in this region. Two are within sight of each other and adjacent to Rocky Run, and one is adjacent to Templeton Fork close to the confluence of Rocky Run and Templeton Fork.

Rocky Run Wetland A

The extensive wetland created by recent subsidence under Rocky Run contains a variety of habitats ranging from pooled areas up to about four feet in depth to wet meadows (Figure 5; also see photographs in Appendix C). Since the wetland was a result of subsidence in late 2000, wetland vegetation was in successional stages during the 2001 sampling year. Plant abundance for this growing season was heavily influenced by propagule availability. The wetland communities will undoubtedly look somewhat different after a few more growing seasons as certain species out compete others. Due to the newness of this wetland, final delineation was not done until the end of this first growing season. Although the following descriptions are based on several visits to the area during the 2001 growing season, the final delineation was done on October 1, 2001. In order to better describe the variety of habitats created, the wetland was divided into six areas which are separately described below and shown in photographs in Appendix C. Five of the habitats are also described on Data Form 1Cin Appendix C. The sixth area, the area of open water, generally lacked emergent vegetation and therefore was not separately described on a Data Form 1. A number of plants that were never dominant or abundant in any one of the areas described below were nevertheless found scattered throughout the wetland and contributed to the biodiversity (Table 1). These plants will become more, or less abundant as the wetland matures over the next few years. It must be kept in mind that the following description of the wetland are as it was observed in late 2001, and that the extensive damming by beavers was partially responsible for the size of the impounded area (this will be discussed later in the section on mitigation).

Area 1 - an extensive area heavily dominated by *Phalaris arundinacea* at the northeastern, upstream end of the created wetland. Much of the area was an almost monoculture of *P. arundinacea* and a good proportion of this area was inundated up to six inches. At the outer dryer fringes of this wetland area *Dichanthelium clandestinum* and *Agrimonia parvifloria* dominated. Towards the southern part of this area there were less densely vegetated mud flats which had large stands of *Eragrostis hypnoides*, *Polygonum* spp. and scattered individuals of *Cyperus strigosus*, *Mimulus ringens* and *Verbena urticifolia* (the latter, rated FACU, may not persist as this wetland matures).

Area 2 - an area adjacent to area 1 and on the banks of the original stream channel. Much of this area was also somewhat dominated by *P. arundinacea*, but a fairly large area was more sparsely vegetated and contained a mixture of *Polygonum* species *M. ringens, V. urticifolia* and scattered clumps of *E. hypnoides*. As above, peripheral areas were heavily populated with *A. parviflora* and *D. clandestinum.*

Area 3- wetlands on the southern edge of the old stream channel, containing one large peninsula extending out into the open water areas of the created wetland. Much of this area was somewhat open and relatively sparsely vegetated with newly established herbs. *Ludwigia palustris* and *M. ringens* were the most common of the taller vegetation and lower vegetation included patches of *E. hypnoides* and *Polygonum* species. Somewhat less abundant were *P. Arundinacea, Cyperus strigosus* and *Leersia oryzoides*.

Area 4 - is a very complex part of this wetland, containing beaver structures and land ranging from inundated to borderline wetlands. A great diversity of plants were found in this area, and only a fraction of them are shown in Appendix A. There were no dominant taxa, although *P. sagittatum* was perhaps the most widespread plant at this time of year. Plants that were relatively common in this area but not listed in Appendix A include *Eupatorium perfoliatum*, Carex cf. *prasina, Mimulus ringens, Cyperus strigosus, Juncus effusus* and along the edges of the delineated area, *Dichanthelium clandestinum*. This area may change as beaver activities change, and only a portion of this area is expected to remain wetland over the longterm without mitigation.

Table 1. Common plants of the subsidence created Rocky Run A Wetland as of October 1, 2001.

Taxon	Overall abundance (1 - 4)*	Wetland rating

Dichanthelium clandestinum	2	FAC+
Leersia virginica	3	FACW
Phalaris arundinacea	1	FACW
Muhlenbergia frondosa	4	FAC
Agrostis stolonifera	4	FACW
Eragrostis hypnoides	2	OBL
Cyperus strigosus	3	FACW
Eleocharis obtusa	3	OBL
Scirpus tabernaemontani	3	OBL
Carex cf. prasina	4	OBL
Acoris calamis	4	OBL
Juncus effusus	4	FACW+
Polygonum sagittatum	2	OBL
Polygonum hydropiperoides	2	OBL
Phytolacca americana	4	FACU+
Agrimonia parviflora	3	FACW
Impatiens capensis	4	FACW
Ludwigia palustris	3	OBL
Epilobium coloratum	3	FACW+
Lysimachia nummularia	3	FACW-
Verbina urticifolia	3	FACU
Lycopus unifloris	4	OBL
Mentha spicata	4	FACW+
Mimulus ringens	4	OBL
Eupatorium perfoliatum	4	FACW+

* 1 is most abundant, or dominant in at least one area, while 4 is scattered and least common.

Area 5 - is a very small area along the northwestern shore of the inundated portion of the wetland. It had been heavily grazed by deer by the time it was sampled and thus the common grass species could not be identified. Other common species included a mixture of wetland and non-wetland species.

Area 6 - is the open water habitat resulting from the subsidence and subsequent flooding by Rocky Run. The original stream channel of Rocky Run is not visible due to the inundation from subsidence and beaver dams. This area had a few patches of emergents, the most prominent being the fairly extensive shoreline of Area 1, which had *Phalaris arundinacea* growing in up to 4 - 6 inches of water. The only other plant commonly seen was *Lemna minor*, which was present in protected areas of the open water habitat.

Despite the newness of this wetland, a viable and complex hydrophytic community had developed in the full one year growing season. Furthermore, a number of wetland dependant animal species used the wetland habitats in 2001. When first visited in the spring, inundated areas, especially those associated with emergent growth of *Phalaris arundinacea*, were so heavily used by American toads that the water was virtually boiling with activity and breeding pairs were barely a foot apart. At this same time a Canada goose was occupying a nest in the same area, ducks were heard, but not seen and redwing blackbirds were in abundance. Beaver activity was quite evident, and their embankments in Area 4 caused the area of inundation to be even greater than it would have been due to the recent subsidence alone. During later visits to the wetland, ducks were again heard, an unidentifiable shorebird was seen at a distance foraging in shallows, a great blue heron was seen feeding in the wetland and kingfishers were seen cruising the open waters. Numerous trails and footprints showed that deer used the area heavily (Area 5 described above was one point of deer entry to the open water and was heavily grazed).

We did not sample the open water habitat for fish or macroinvertebrates, but it is certain that both have taken advantage of this habitat that is relatively scarce in the region. The area will serve as a nursery area for certain fish species and the deeper water habitat should allow certain sport fish (bass especially) to thrive. Amphibians other than the American toad either are or will be using the area - wood frogs, spring peepers, green frogs, leopard frogs and bullfrogs are expected to reproduce in this habitat. Macroinvertebrates preferring the wetland or lentic

conditions will proliferate - in particular it is expected that dragonflies will abound, as was evidenced by the large number of adults seen in the summer.

Rocky Run Wetland B

This wetland was within sight of Rocky Run Wetland A, being just above the Sprowls Covered Bridge (Figure 6; also see photographs in Appendix D). It has an extensive area of shallow standing water as well as a sizeable wet fringe. Subsidence occurred during the 2001 growing season, not allowing a typical wetland community to become fully established to date. However, a number of wetland plants did become abundant in the short growing season. Most of the wetland is in a floodplain field that was previously used for hay production and for parking during the annual Covered Bridge Festival. Much of the delineated area is currently covered with shallow water - up to about 1.5 feet deep. This wetland also was influenced by beavers and three separate dams that were built on Rocky Run caused the water to impound to even greater depths than would have resulted from subsidence alone. The delineation discussed below and shown in Appendix B (the data were combined onto one Data Form 1 since the wetland had not matured enough to separate plant communities) is based on water levels at the end of November 2001, and thus describes a system partially dependant on the beaver impoundments.

Open water area - the largest habitat in this wetland as of November, 2001 was the area of shallow water, which was somewhat dominated by *Phalaris arundinacea* and *Ranunculus hispidis*. *Typha latifolia*, *Juncus effusus* and *Leersia oryzoides* were also abundant and were seen to be increasing in importance as the growing season progressed. Other hydrophytic species were also moving in and it is expected that if the current water levels continue *R. hispidis* will largely be displaced by other taxa such as *T. Latifolia*. However, if the current level of muskrat activity is maintained, *T. Latifolia* may be controlled and other less palatable rush, bulrush and sedge species may become dominant. The November sampling revealed the presence of a number of non-wetland species that had grown to maturity in 2001 (such as *Rumex crispis* and *Prunella vulgaris*), but these taxa will not be present next year if water levels are maintained.

Emergent and wet meadow areas - most of the shore transitional area surrounding the open water of this wetland and extending upstream for a short distance is currently dominated by *R. hispidis* and *P. arundinacea*. Several plants which had undoubtedly been important when the field was dryer, such as *Dactylis glomerata,* still were alive in these areas of saturated soils, but will be replaced by hydrophytes within another growing season if the water levels are maintained.

Because of the very limited growing season, this wetland was not nearly as well developed as Rocky Run Wetland A. However, a number of hydrophytes were becoming established by the end of the growing season, and soils had already developed hydric characteristics. If the current water levels are maintained, next growing season s vegetation will undoubtedly be more like that of Wetland A. The proximity of Rocky Run and its supply of wetland propagules assures that a more typical wetland will develop next year. There was some evidence that despite the newness of the wetland, it was already being used by some animals. A few amphibians were seen in the water in late fall and there was ample evidence of heavy muskrat and beaver use. There was an active muskrat hutch in the middle of the inundated part of the wetland and evidence of a lot of recent cutting of vegetation, especially cattails. Beaver were also actively cutting and building in and around the wetland.

Templeton Fork Wetland

The Templeton Fork wetland was more typical of the wetlands of the region. It was primarily a wet meadow wetland with only very limited areas with any inundation, and those were dried up by October (Figure 7). Unlike the Rocky Run wetlands there was no direct connection with the stream, instead, this wetland was the result of subsidence bringing much of the land down to the permanent water table. The barn in the corner of the field that this wetland developed in, and evidence that this field was used for hay production prior to subsidence lend credence that most, if not all of this wetland was created from subsidence in 1994 when the area was undermined. The ages of the willows and sycamores that have colonized parts of the wetland provide further evidence of its age.

Although far from uniform, this wetland didn't have the dramatically different zones that were present in the Rocky Run A wetland. This was due to the lack of significant open water habitat as well as the length of time that the wetland had to develop. A few young black willows and sycamores were present in one small area towards the southeastern edge of the wetland, but the vast majority of this wetland had only herbaceous growth. There was one fairly sizeable area towards the center of the wetland that was dominated by *Typha latifolia* and a small area adjacent to Templeton Fork was dominated by *Phalaris arundinacea*, but most of the wetland was densely vegetated by a diverse mixture of herbaceous plants, the most abundant of which in this late part of the growing season was *Polygonum sagittatum*. Plant communities were well developed in this wetland and are likely to remain much the same over the next few years, unlike the communities of the newly formed Rocky Run wetlands which were dominated in some areas by pioneer species. Table 2 lists the plants most commonly seen in this wetland in order of their relative abundance as of October 1, 2001.

Wildlife use of this wetland was more limited than that of the newly formed Rocky Run wetlands due to the lack of any significant open water or emergent areas. Redwing blackbirds were common in the spring and later in the season there were obvious signs of muskrat use. Non - wetland species such as whitetail deer and various birds also use this wetland, and probably to a much greater degree than when it was a managed field.

FUNCTIONS AND VALUES OF THE ORIGINAL AND MITIGATION WETLANDS

Wetlands are multiple value systems and unfortunately the most valuable products of wetlands are public amenities that often have no value to the property owner. Currently popular systems of valuation of wetlands tend to stress the importance of use by fish and game species, physical attributes such as wetland contributions to the hydrologic cycle, control of flooding, water quality, and human uses. There are three wetland assessment methods that are currently accepted by many wetland scientists and regulatory authorities. The first, and probably still the most universally applicable assessment method was the Wetland Evaluation Technique (WET) developed by Adamus et al. (1987). This method of assessment evaluates the following wetland functions:

Table 2. Common plants of the subsidence Templeton Fork Wetland as of October 1, 2001.

Taxon	Overall abundance (1 - 4)*	Wetland rating
Typha latifolia	1	OBL
Dichanthelium clandestinum	3	FAC+
Leersia virginica	4	FACW
Leersia oryzoides	2	OBL
Phalaris arundinacea	1	FACW
Eragrostis hypnoides	4	OBL
Cyperus strigosus	4	FACW
Cyperus esculentus	3	FACW
Eleocharis obtusa	3	OBL
Scirpus tabernaemontani	4	OBL
Scirpus cyperinus	2	FACW+
Carex sp. 1	2	-
Carex sp. 2	3	-
Juncus effusus	2	FACW+
Polygonum sagittatum	2	OBL
Polygonum hydropiperoides	2	OBL
Ranunculus hispidus	4	FAC
Agrimonia parviflora	2	FACW
Impatiens capensis	4	FACW
Ludwigia palustris	3	OBL
Epilobium coloratum	4	FACW+
Lycopus unifloris	4	OBL
Mentha spicata	3	FACW+
Mimulus ringens	4	OBL
Eupatorium perfoliatum	4	FACW+

* 1 is most abundant, or dominant in at least one area, while 4 is scattered and least common.

Ground water recharge
Ground water discharge
Floodflow alteration
Sediment stabilization
Sediment and toxicant retention
Aquatic diversity and abundance
Nutrient removal or transformation
Recreation
Product export
Uniqueness and heritage
Wildlife diversity and abundance

These functions are valued in terms of social significance, and the technique can be used to evaluate any wetland. WET allows a rapid assessment of wetland functions and values and assesses the suitability of wetland habitat for waterfowl and other water dependent vertebrates and invertebrates. A second wetland evaluation technique, EMAP, was developed primarily to evaluate wetland condition, where condition is defined as the state of a set of characteristics which are associated with wetlands and which are valued by society. It evaluates biological diversity, harvestable productivity, flood reduction and shoreline protection, groundwater conservation and water quality improvement.

A third wetland evaluation technique, the hydrogeomorphic or HGM technique was developed by the US Army Corps of Engineers to evaluate wetlands using similar criteria as those of WET to assess the degree to which a wetland functions in comparison to regional reference wetland functions. .

WET is the technique best suited to provide an analysis of all wetlands in a region of interest, as opposed to both EMAP and HGM, which only allow comparisons within wetland classes. Thus, for the purposes of the subject analysis WET functions have been considered (Table 3).

The wetlands to be replaced have minimal functions (Table 3) except for groundwater discharge (many were actual seep areas or produced by seeps). The value of this function may be questioned in this area of abundant springs and seeps. The mitigation wetlands will probably not

function as either groundwater discharge or recharge areas, since their presence is determined by their interception of existing water tables, with no discharge of the intercepted water. Flood flow alteration is not very effective in headwater wetlands as compared to downstream wetlands (Mitch and Gosselink, 1993). None of the wetlands will be particularly effective in sediment stabilization (this is more a function of shoreline wetlands). Sediment and toxicant retention will probably only be significant in the mitigation wetlands where flood flow of Rocky Run and Templeton Fork will likely overtop the stream banks at least annually and allow the wetlands to trap sediments. Nutrient removal or transformation will not occur to a significant degree except in the downstream mitigation wetlands where flooding will allow some deposition and residence time in a significant area of wetland; the upstream refuse and slurry valley wetlands will not likely receive significant nutrients under natural conditions (currently, however, the wetlands of the slurry valley do receive a lot of nutrients due to heavy cattle grazing). None of the refuse or slurry valley wetlands offer any significant recreation, product export, uniqueness or heritage.

The most significant function in terms of capabilities of wetlands in this region are their ability to offer aquatic habitat and foster wildlife use. The small upland wetlands of the refuse and slurry valleys have virtually no standing water even in the wettest seasons and thus have little to no aquatic diversity and abundance. By contrast, the proposed mitigation wetlands will have significant open shallow water habitat that will foster biotic diversity of organisms not usually found in the adjacent lotic and upland habitats. This is evidenced in Rocky Run Wetland A, where aquatic life has already successfully moved into a wetland less than a year old, as discussed above. Similarly, wildlife is not visibly using the small headwater wetlands of the refuse and slurry valleys, but is already using the new wetlands created by subsidence, even before mitigation.

Since it is evident that the slurry and refuse valley wetlands cannot begin to offer the functions and values that the proposed mitigation wetlands will, we have not attempted to produce a more formal model comparing the functions. In addition, it would be difficult to accurately rate particular functions before the mitigation wetlands are in place and fully functional. However, as shown in the following pages, we feel safe in saying that the mitigation wetlands will produce functions of considerably greater value to society than the small headwater wetlands of the refuse and slurry valleys.

Table 3. Estimates of WET functions for the Slurry Valley Wetlands, Refuse Valley Wetlands, and the three proposed Mitigation Wetlands.*

Function	R-1...R-7	S-1....S-19 except S-4	S-4	Mitigation Wetlands
Ground water recharge	0	0	0	0
Ground water discharge	2	2	0	0
Flood flow alteration	1	1	2	3
Sediment stabilization	0	0	0	1
Sediment and toxicant retention	1	1	1	2
Aquatic diversity and abundance	0	0	0	3
Nutrient removal or transformation	1	1	2	2
Recreation	0	0	0	2
Product export	0	0	0	0
Uniqueness and heritage	0	0	0	0
Wildlife diversity and abundance	1	1	1	3

* 0 = no significant function
1 = minimal function
2 = moderate function
3 = high function

MITIGATION PLANS

The overall philosophy of our plan is to enhance the three newly created subsidence wetlands to 1) make them permanent and 2) provide habitat that will foster the maximum possible diversity of aquatic and wildlife species, and 3) make them naturally fit into the regional landscape. In order to do this each wetland will be generally modified to provide a combination of open shallow water habitat with islands and a complex shoreline with a surrounding area of emergent, wet meadow and transitional habitat. Gradients will be gentle, allowing ecotones to develop and making the wetlands blend into the landscape (Mitsch and Cronk 1992). These wetlands have already been more or less established prior to our proposed modifications, and with the exception of Rocky Run Wetland B, they already have extensive naturally established hydrophytic communities that are obviously best suited to the area. Therefore, revegetation will be unnecessary except possibly in Wetland B. This wetland has some hydrophytic vegetation established, but to enhance the revegetation after the completion of mitigation earthwork, the seed bank method will be used. This commonly accepted practice uses freshly removed soils, preferably from nearby wetlands to provide a source of hydrophyte propagules best suited to the area. Wetland soils have been found to hold from 21,455 to 42,615 seeds per square meter of the top 10 cm of soil (van der Valk and Davis 1978). As discussed by numerous authors in Kusler and Kentula (1990) and other references, it is advantageous to revegetate with indigenous species, or at least to supply soils with the necessary tubers, seeds and other propagules as opposed to planting species which may or may not compete well with local plants - a common cause of constructed wetland failure. The following discussion also draws upon engineering discussions in Dunne et al., 1998, Interagency Workgroup on Wetland Restoration, 2001, USDA 1992 and Hayes et al., 2000.

ROCKY RUN WETLAND A

This new subsidence wetland (Figure 5) is artificially large due to several beaver dams. The purpose of this plan is to essentially keep this wetland intact by contouring the site such that it will remain wet after the beavers have left the area. The final mitigated wetland area will be a little smaller than the current beaver-enhanced size, due to Rocky Run being returned to its original channel. Additional features such as a more complex shoreline and several islands have

been included in this plan in order to encourage aquatic biota and wildlife diversity and production.

The proposed modification to Rocky Run Wetland A is shown in Figure 8. The final wetland areas would be: open water - 0.77 acres; islands - 0.018 acres; emergent and wet meadow - 0.852 acres. To achieve the configuration of open shallow water habitat, islands and surrounding emergent wetland habitat, shallow observation wells would be established prior to construction of the wetland to provide ground water level information to assist in determining the necessary final elevations. It is proposed to drain the large open water area from the existing wetland by breaching the existing beaver dams, pumping water from the pool area during low flow conditions, or by using a siphon to drain water from the pool area. After the area is drained sufficiently for access by low ground pressure equipment, the area would be contoured to provide for the deeper standing water areas, islands and higher wetland areas. Slope transitions of the ground surface will be gentle and variable from 3H:1V to as gradual as 20H:1V. As much of the existing wetland soils as possible would be used on site for the contouring, but it is estimated there will be 1000 cubic yards of waste soils would be suitably disposed of offsite at an approved area. Evidenced by the vibrant growth of wetland vegetation that was seen during the delineation, the existing wetland soils should have a more than adequate propagule availability to establish native wetland vegetation to recolonize the areas.

It is felt that disturbance to the area could be kept to a minimum by the use of smaller low ground pressure equipment, limiting movement of the equipment to small areas at a time and the use of proper erosion and sediment control techniques during construction. It would be proposed to perform this work during low flow conditions. Detailed specifications, plans and cross sections would be required for the contractor to perform this work. These specifications would address items such as soil excavation, hauling and placement methods, dewatering, allowable work dates and construction sequence. The specifications, construction sequence and best methods for performing this work have not been detailed for this report, but will be provided to the PADEP for approval prior to construction initiation.

After construction of the project is completed, initial site conditions will be documented to provide baseline information, which the site can be evaluated against during the subsequent

monitoring phase. A monitoring program would be implemented during the initial years of the wetland development (see below). During this time, disturbance to the site will be avoided unless necessary to correct any obvious problems. The shallow observation wells established during the construction of the wetland would continue to provide ground water level information during the wetland monitoring phase.

Judging from the wetland vegetation that has developed in one growing season (see above descriptions), there will be no need to seed or plant this wetland after earthwork in completed. This wetland developed in the flood plain of Rocky Run and because of this there is obviously a good supply of viable hydrophyte propagules.

ROCKY RUN WETLAND B

This new subsidence wetland (Figure 6) is also artificially large due to several beaver dams. The purpose of this plan is to essentially keep the same wetland area by contouring the site such that it will remain wet after the beavers have left the area. Additional features such as a more complex shoreline and an island have been included in this plan in order to encourage aquatic biota and wildlife diversity and abundance.

Figure 9 shows the proposed modifications for Rocky Run Wetland B. The final size of this wetland would be: open water - 0.342 acres; island - 0.013 acres; emergent and wet meadow - 0.563 acres. To achieve the configuration of open shallow water habitat, islands and surrounding emergent wetland habitat, shallow observation wells would be established prior to construction of the wetland to provide ground water level information to assist in determining the necessary final elevations. Wetland soils will be brought into Rocky Run Wetland area B to provide the seed, organics and root mat that will expedite the propagation of diverse hydrophytic plant communities. An estimated 700 cubic yards of soils will be imported from the Templeton Fork Wetland (see following section) in order to provide about a four inch depth of hydric soils in the disturbed areas. Some of the existing soils (as well as an unknown amount of fill material that has been placed in the area) will require removal to allow for the desired open water areas and higher wetland areas before the imported wetland soils are brought into the site. The imported wetland soils will be loosely placed and firmed to a depth of about four inches (see above

discussion of seed banks), but will not be compacted or rolled. Once placed, no equipment or vehicle access will be permitted on the area. A variety of gentle slopes will be created for transition between the different areas. It is proposed that the existing beaver dams be breached and the area dewatered of standing water before the work would begin. During construction, any areas of the stream bank that have been breached into the wetland area by beaver activity will be plugged with earth fill to eliminate direct connection between the stream water and the wetland area. Low ground pressure equipment would be used for work within the wetland creation area and movement will be limited to small areas to minimize disturbance.

After contour grading is completed and the wetland soils placed, the drainage ditch from the unnamed tributary to Rocky Run, which is located to the west of the proposed wetland area, will be diverted into the newly created wetland to provide additional water to the site. As previously discussed, detailed plans, specifications and construction sequence will be required to perform this work. The specifications will be provided to the PADEP for approval prior to construction initiation. The specifications should focus on the quick placement of the excavated Templeton Fork wetland soils so as not to expose the soils to excess drying or the need for stockpiling. Excess drying or exposure may destroy the seed bank, cause premature germination of the seed bank, or cause premature establishment of vegetative propagules.

As with Rocky Run Wetland A, a wetland monitoring program would be implemented after construction and the shallow observation wells established during construction would be used to monitor ground water levels (see discussion below).

TEMPLETON FORK MITIGATION WETLAND

This subsidence wetland (Figure 7) is well established after almost eight years of existence. The purpose of this plan is to keep the same wetland area but provide increased habitat diversity by developing an open water area. A complex shoreline and an island have been included in this plan in order to encourage aquatic biota and wildlife diversity and abundance.

Figure 10 shows the proposed modification to the Templeton Fork Wetland. The final size of this wetland would be: open water - 0.322 acres; island - 0.014 acres; emergent and wet meadow

- 1.03 acres. Unlike the Rocky Run Wetland A and B areas, the Templeton Fork wetland is not influenced by any beaver dams, which will make construction of the proposed open water area easier. To achieve the configuration of open shallow water habitat and islands, shallow observation wells would be established prior to construction of the wetland to provide ground water level information to assist in determining the necessary final elevations. To achieve the desired contouring, low ground pressure equipment will be used to excavate up to 1.5 ft. of material from the existing wetland. The equipment operating area will be limited to the outline of the proposed open water area, so that no disturbance to the wetland area outside the open water will occur (except for a construction entrance access to the south, which will be reclaimed to approximate original conditions after the excavation is completed). An estimated 700 cubic yards of wetland soils removed from the Templeton Fork wetland will be immediately transported and placed at the Rocky Run Area B wetland as described above. The well-established vegetation from this wetland will provide for a good seed base to establish vegetation in the newly created Rocky Run Wetland B Area. Any excess wetland soils that are not used at the Rocky Run Wetland B Area will be suitably disposed of offsite at an approved area. The specifications, construction sequence and best methods for this work have not been detailed for this report, but will be given to the PADEP for approval prior to construction initiation.

As previously discussed, detailed plans, specifications and construction sequence will be required to perform this work. The specifications will include schedules that allow the immediate placement of the removed wetland soils in the contoured areas of Rocky Run Wetland B, as discussed above. After excavation of the wetland soils from the Templeton Fork area, as-built conditions will be documented as baseline information for evaluation of the site during the subsequent monitoring phase. Proposed monitoring will include water levels in the monitoring wells installed prior to construction.

POST - CONSTRUCTION MONITORING

Post construction monitoring plans will be submitted to PADEP for approval prior to construction. There will be three monitoring plans; one to monitor hydrology, one to monitor vegetation success and one to monitor wildlife use. The hydrologic monitoring plan will consist of periodic monitoring of the observation wells installed prior to construction. This will continue

until there is sufficient evidence that the wetlands are successful under varied natural hydrologic conditions. Should there be a need to further modify the wetlands to change water or saturation levels, the monitoring well data will provide the necessary information for designing such modifications.

Monitoring wetland success will be based on two elements. First, vegetation will be monitored annually to assess the species and community composition of each wetland and its components, as well as to estimate the cover density or plant productivity. This monitoring plan will be similar to the one used at Consol's successful Kirby Shaft wetland replacement, where vegetation quadrants were permanently located and monitored annually for species composition, relative abundance and density. Second, wildlife use of the wetlands will be monitored by field observations conducted during appropriate seasons.

CONCLUSIONS

Typical of southwestern Pennsylvania watersheds, both the refuse and slurry valleys had a number of small headwater wetlands associated with the streams in each valley. The refuse valley contained seven discrete Jurisdictional Wetlands totaling only 0.102 acres, while the slurry valley contained 19 Jurisdictional Wetlands totaling 1.267 acres. The wetlands of the refuse valley were mostly very small streamside or seep wetlands under heavy woodland cover. Most were relatively undisturbed natural wetlands of the sort commonly seen associated with stream origins and headwater flood plains in southwestern Pennsylvania and due to their sizes and headwater placement, they had low levels of wetland functions and values. Wetlands of the slurry valley ranged from wet meadows to headwater seep wetlands. Only wetlands S-1 to S-3 were not impacted by cattle traffic and grazing. Very few of the slurry valley wetlands were in a natural state and most were so highly disturbed that it is difficult to say what the natural vegetation should have been. As discussed above only wetland S-4 was judged to have more than very minimal wetland functions and values.

Due to the proximity of the three proposed mitigation wetlands, their inclusion of significant open shallow water habitat, the diversity of wetland habitats provided and their downstream watershed positions, they stand to provide a significant addition of this regionally scarce resource in southwestern Pennsylvania. Once wetland communities are reestablished in the mitigated

wetlands, they will provide a much higher level of wetland functions and values than the wetlands they will replace. At a ratio of 1:1.5, the mitigation wetlands will also greatly exceed the required replacement, with a total of 3.924 acres to mitigate the proposed loss of 1.369 acres of wetlands (a ratio of over 3:1). Furthermore, the success of the proposed mitigation wetlands is highly likely in view of the current post subsidence levels of wetland vegetation development and wildlife use.

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APPENDIX A

Data Forms and Photographs of the Jurisdictional Wetlands of the Proposed Bailey Mine Refuse Valley

APPENDIX B

Data Forms and Photographs of the Jurisdictional Wetlands of the Proposed Bailey Mine Slurry Valley

APPENDIX C

Data Forms and Photographs of the Subsidence Created Rocky Run Wetland A

APPENDIX D

Data Forms and Photographs of the Subsidence Created Rocky Run Wetland B

APPENDIX E

Data Forms and Photographs of the Subsidence Created Templeton Fork Wetland

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Refuse Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No R-1** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Poa trivialis***	**FACW**
2.		8. ***Glyceria striata***	**OBL**
3.		9. ***Bidens frondosa***	**FACW**
Saplings/shrubs		10 ***Aster puniceus***	**OBL**
4.		11. ***Carex lurida***	**OBL**
5.		12. ***Scirpus microcarpus***	**OBL**
6.		13.	

% of species that are OBL, FACW, and/or FAC: **100**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No____. Basis: **Dominant plants are all rated FACW to OBL**.

Soil
Series and phase: **Fluvaquents, loamy** On hydric soils list? Yes___ No **X**
Mottled: Yes____; No **X**. Mottle color:_____; Matrix color: **N5/**
Gleyed: Yes **X**; No____. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Low chroma, gleyed, saturation**

Hydrology
Inundated: Yes **X**; No____. Depth of standing water: **up to 3 inches**
Saturated soils: Yes **X**; No____. Depth to saturated soil: **+3 to -3 inches**
Other indicators:_____Wetland hydrology: Yes **X**; No____. Basis: **saturated soils and an area of inundation**
Atypical situation: Yes____; No **X**.

Normal Circumstances: Yes **X** No____.
Wetland Determination: Wetland **X**; Nonwetland
Comments:_____.

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Refuse Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No R-2** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Impatiens capensis***	**FACW**
2.		8. ***Pilea pumila***	**FACW**
3.		9. ***Poa trivialis***	**FACW**
Saplings/shrubs		10. ***Leersia virginica***	**FACW**
4.		11. ***Ranunculus recurvatus***	**FAC**
5.		12.	
6.		13.	

% of species that are OBL, FACW, and/or FAC: **100**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No___.Basis: ***I. Capensis* (FACW) totally dominated the vegetation.**

Soil
Series and phase: **Fluvaquents, loamy** On hydric soils list? Yes **X** No
Mottled: Yes **X**; No____. Mottle color: **5YR 5/6**; Matrix color: **10YR 5/2**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Low matrix chroma, mottles**

Hydrology
Inundated: Yes____; No **X**. Depth of standing water:
Saturated soils: Yes **X**; No____. Depth to saturated soil: **0-4 inches**
Other indicators:
Wetland hydrology: Yes **X**; No____. Basis: **Soils saturated to near surface**
Atypical situation: Yes____; No **X**.

Normal Circumstances: Yes **X** No____.
Wetland Determination: Wetland **X**; Nonwetland
Comments:_____.

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Refuse Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No R-3** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Poa trivialis***	**FACW**
2.		8. ***Pilea pumila***	**FACW**
3.		9. ***Impatiens capensis***	**FACW**
Saplings/shrubs		10. ***Leersia virginica***	**FACW**
4. ***Lindera benzoin***	**FACW-**	11. ***Polygonum virginianum***	**FAC**
5. ***Acer negundo***	**FAC+**	12. ***Ranunculus recurvatus***	**FAC**
6.		13.	

% of species that are OBL, FACW, and/or FAC: **100**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No____. Basis: **Most abundant plants rated FACW**.

Soil
Series and phase: **Fluvaquents, loamy** On hydric soils list? Yes____ No **X**
Mottled: Yes **X**; No____. Mottle color: **2.5YR 5/8**; Matrix color: **10YR 6/1**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Low chroma, mottles**

Hydrology
Inundated: Yes____; No **X**. Depth of standing water:
Saturated soils: Yes **X**; No____. Depth to saturated soil: **4-6 inches**
Other indicators:
Wetland hydrology: Yes **X**; No___. Basis: **Saturation to 4-6 inches, mottles and low chroma soils**
Atypical situation: Yes____; No **X**.

Normal Circumstances: Yes **X** No____.
Wetland Determination: Wetland **X**; Nonwetland
Comments:_____.

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Refuse Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No R-4** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Poa trivialis***	**FACW**
2.		8. ***Impatiens capensis***	**FACW**
3.		9. ***Lysimachia nummularia***	**FACW-**
Saplings/shrubs		10. ***Aster punicius***	**OBL**
4. ***Lindera benzoin***	**FACW-**	11. ***Leersia virginica***	**FACW**
5.		12. ***Ranunculus recurvatus***	**FAC**
6.		13. ***Carex prasina***	**OBL**

% of species that are OBL, FACW, and/or FAC: **100**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No____. Basis: **Most abundant plants are rated FACW**.

Soil
Series and phase: **Fluvaquents, loamy** On hydric soils list? Yes___ No **X**
Mottled: Yes____; No **X**. Mottle color:_____; Matrix color: **10YR 3/2**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Low soil chroma and saturation to near surface**

Hydrology
Inundated: Yes____; No **X**. Depth of standing water:
Saturated soils: Yes **X**; No____. Depth to saturated soil: **0-3 inches**
Other indicators:
Wetland hydrology: Yes **X**; No____. Basis: **Soils saturated to near surface**
Atypical situation: Yes____; No **X**.

Normal Circumstances: Yes **X** No____.
Wetland Determination: Wetland **X**; Nonwetland
Comments:_____.

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Refuse Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No R-5** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Impatiens capensis***	**FACW**
2.		8. ***Carex prasina***	**OBL**
3.		9. ***Poa trivialis***	**FACW**
Saplings/shrubs		10. ***Cardomine rotundifolia***	**OBL**
4. ***Acer negundo***	**FAC+**	11. ***Leersia virginica***	**FACW**
5. ***Lindera benzoin***	**FACW-**	12. ***Pilea pumila***	**FACW**
6.		13.	

% of species that are OBL, FACW, and/or FAC: **100**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No____. Basis: **Dominant plants are rated FACW or OBL**.

Soil
Series and phase: **Fluvaquents, loamy** On hydric soils list? Yes___ No **X**
Mottled: Yes____; No **X**. Mottle color:_____; Matrix color: **N3/**
Gleyed: Yes **X**; No____. Other indicators: **saturation to near surface**
Hydric soils: Yes **X**; No____. Basis: **Soil color, gleyed, saturation to near surface**

Hydrology
Inundated: Yes____; No **X**. Depth of standing water:
Saturated soils: Yes **X**; No____. Depth to saturated soil: **0.5-3 inches**
Other indicators:
Wetland hydrology: Yes **X**; No____. Basis: **Soils saturated to near surface**
Atypical situation: Yes____; No **X**.

Normal Circumstances: Yes **X** No____.
Wetland Determination: Wetland **X**; Nonwetland
Comments:_____.

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Refuse Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No R-6** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Carex prasina***	**OBL**
2.		8. ***Impatiens capensis***	**FACW**
3.		9. ***Poa trivialis***	**FACW**
Saplings/shrubs		10. ***Pilea pumila***	**FACW**
4.		11. ***Leersia virginica***	**FACW**
5.		12.	
6.		13.	

% of species that are OBL, FACW, and/or FAC: **100**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No____. Basis: **All common plants are rated OBL or FACW**.

Soil
Series and phase: **Dormont-Culleoka silt loams** On hydric soils list? Yes____ No **X**
Mottled: Yes____; No **X**. Mottle color:_____; Matrix color: **5YR 4/1**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Low chroma, saturation to near surface**

Hydrology
Inundated: Yes____; No **X**. Depth of standing water:
Saturated soils: Yes **X**; No____. Depth to saturated soil: 0-3 inches
Other indicators:
Wetland hydrology: Yes **X**; No____. Basis: **Saturated soils**
Atypical situation: Yes____; No **X**.

Normal Circumstances: Yes **X** No____.
Wetland Determination: Wetland **X**; Nonwetland
Comments:

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Refuse Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No. R-7** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Impatiens capensis***	**FACW**
2.		8. ***Poa trivialis***	**FACW**
3.		9. ***Carex prasina***	**OBL**
Saplings/shrubs		10 ***Pilea pumila***	**FACW**
4.		11. ***Laportea canadensis***	**FAC**
5.		12. ***Cryptotaenia canadensis***	**FAC**
6.		13.	

% of species that are OBL, FACW, and/or FAC: **100**. Other indicators:
Hydrophytic vegetation: Yes **X**; No____. Basis: **dominant vegetation is FACW or OBL**

Soil
Series and phase: **Dormont-Culleoka silt loams** On hydric soils list? Yes____; No **X**.
Mottled: Yes____; No **X**. Mottled color:_____; Matrix color: **5PB 5/1** Gleyed: Yes **X**; No____. Other indicators:_____ Hydric soils: Yes **X**; No____. Basis: **Gleyed, saturated soil**

Hydrology
Inundated: Yes____; No **X**. Depth of standing water:
Saturated soils: Yes **X**; No____. Depth to saturated soil: **0 - 2 inches** Other indicators:_____ Wetland hydrology: Yes **X**; No____. Basis: **Soils saturated to surface or near-surface** Atypical situation: Yes____; No **X**.

Normal Circumstances: Yes **X** No____.
Wetland Determination: Wetland **X**; Nonwetland
Comments: **Typical headwater seep wetland**

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Slurry Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No S-1** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Typha latifolia***	**OBL**
2.		8. ***Carex lurida***	**OBL**
3.		9. ***Carex vulpinoidea***	**OBL**
Saplings/shrubs		10. ***Agrimonia parviflora***	**FACW**
4.		11. ***Carex granularis***	**FACW+**
5.		12. ***Carex frankii***	**OBL**
6.		13.	

% of species that are OBL, FACW, and/or FAC: **100**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No____. Basis: **Dominant plants are all rated FACW to OBL**.

Soil
Series and phase: **Fluvaquents, loamy** On hydric soils list? Yes___ No **X**
Mottled: Yes____; No **X**. Mottle color:_____; Matrix color: **N5/**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Low chroma, saturation**

Hydrology
Inundated: Yes____; No **X**. Depth of standing water:
Saturated soils: Yes **X**; No____. Depth to saturated soil: **1-4 inches**
Other indicators:
Wetland hydrology: Yes **X**; No____. Basis: **saturated soils**
Atypical situation: Yes **X**; No___.

Normal Circumstances: Yes___ No **X**.
Wetland Determination: Wetland **X**; Nonwetland
Comments: **This wetland appears to have resulted from adjacent railroad construction**.

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Slurry Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No S-2** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Typha latifolia***	**OBL**
2.		8. ***Carex scoparia***	**FACW**
3.		9. ***Poa trivialis***	**FACW**
Saplings/shrubs		10. ***Mentha spicata***	**FACW+**
4.		11. ***Impatiens capensis***	**FACW**
5.		12. ***Agrimonia parviflora***	**FACW**
6.		13.	

% of species that are OBL, FACW, and/or FAC: **100**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No____. Basis: ***T. Latifolia* (OBL) totally dominated**

Soil
Series and phase: **Fluvaquents, loamy** On hydric soils list? Yes____ No **X**
Mottled: Yes____; No **X**. Mottle color:_____; Matrix color: **N5/**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Low chroma, saturation**

Hydrology
Inundated: Yes **X**; No____. Depth of standing water: **up to 3 inches**
Saturated soils: Yes **X**; No____. Depth to saturated soil: **+3 to -3 inches**
Other indicators:
Wetland hydrology: Yes **X**; No____. Basis: **saturated soils and an area of inundation**
Atypical situation: Yes____; No **X**.

Normal Circumstances: Yes **X** No____.
Wetland Determination: Wetland **X**; Nonwetland
Comments:_____.

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Slurry Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No S-3** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Glyceria striata***	**OBL**
2.		8. ***Leersia virginica***	**FACW**
3.		9. ***Poa trivialis***	**FACW**
Saplings/shrubs		10. ***Impatiens capensis***	**FACW**
4.		11. ***Carex lurida***	**OBL**
5.		12. ***Carex frankii***	**OBL**
6.		13. ***Polygonum sagittatum***	**OBL**

% of species that are OBL, FACW, and/or FAC: **100**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No____. Basis: **Dominant plants are all rated FACW to OBL**.

Soil
Series and phase: **Fluvaquents, loamy** On hydric soils list? Yes____ No **X**
Mottled: Yes **X**; No____. Mottle color: **5YR 5/6**; Matrix color: **5N/**
Gleyed: Yes **X**; No____. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **gleyed**

Hydrology
Inundated: Yes____; No **X**. Depth of standing water:
Saturated soils: Yes **X**; No____. Depth to saturated soil: **0-4 inches**
Other indicators:
Wetland hydrology: Yes **X**; No____. Basis: **saturated soils**
Atypical situation: Yes____; No **X**.

Normal Circumstances: Yes **X** No____.
Wetland Determination: Wetland **X**; Nonwetland
Comments:_____.

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Slurry Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No S-4** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Glyceria striata***	**OBL**
2.		8. ***Typha latifolia***	**OBL**
3.		9. ***Poa trivialis***	**FACW**
Saplings/shrubs		10. ***Onoclea sensibilis***	**FACW**
4.		11. ***Aster puniceus***	**OBL**
5.		12. ***Carex lurida***	**OBL**
6.		13. ***Carex laevivaginata***	**OBL**

% of species that are OBL, FACW, and/or FAC: **100**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No____. Basis: **Dominant plants are all rated FACW to OBL**.

Soil
Series and phase: **Fluvaquents, loamy** On hydric soils list? Yes____ No **X**
Mottled: Yes **X**; No____. Mottle color: **5YR 5/6**; Matrix color: **10YR 5/2**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Low chroma, mottles, saturation**

Hydrology
Inundated: Yes **X**; No____. Depth of standing water: **up to 1 inch**
Saturated soils: Yes **X**; No____. Depth to saturated soil: **+1 to -3 inches**
Other indicators:
Wetland hydrology: Yes **X**; No____. Basis: **saturated soils and an some inundation**
Atypical situation: Yes____; No **X**.

Normal Circumstances: Yes **X** No____.
Wetland Determination: Wetland **X**; Nonwetland
Comments:_____.

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Slurry Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No S-5** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Glyceria striata***	**OBL**
2.		8. ***Bidens frondosa***	**FACW**
3.		9. ***Cardamine rotundifolia***	**OBL**
Saplings/shrubs		10. ***Poa trivialis***	**FACW**
4.		11. ***Carex frankii***	**OBL**
5.		12.	
6.		13.	

% of species that are OBL, FACW, and/or FAC: **100**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No____. Basis: **Sparsely vegetated by FACW and OBL plants**.

Soil
Series and phase: **Fluvaquents, loamy** On hydric soils list? Yes___ No **X**
Mottled: Yes **X**; No____. Mottle color: **5YR 5/8**; Matrix color: **10YR 5\1**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes X; No____. Basis: **Low chroma, mottles, saturation**

Hydrology
Inundated: Yes **X**; No____. Depth of standing water: **up to 4 inches**
Saturated soils: Yes **X**; No____. Depth to saturated soil: **+4 to -4 inches**
Other indicators:
Wetland hydrology: Yes **X**; No____. Basis: **saturated soils and an area of inundation**
Atypical situation: Yes____; No **X**.

Normal Circumstances: Yes **X** No____.
Wetland Determination: Wetland **X**; Nonwetland
Comments:_____.

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Slurry Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No S-6** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Polygonum hydropiperoides***	**OBL**
2.		8. ***Carex frankii***	**OBL**
3.		9. ***Poa trivialis***	**FACW**
Saplings/shrubs		10. ***Impatiens capensis***	**FACW**
4.		11. ***Leersia oryzoides***	**OBL**
5.		12. ***Carex vulpinoidea***	**OBL**
6.		13. ***Bidens frondosa***	**FACW**

% of species that are OBL, FACW, and/or FAC: **100**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No____. Basis: **Dominant plants are all rated FACW to OBL**.

Soil
Series and phase: **Fluvaquents, loamy** On hydric soils list? Yes___ No **X**
Mottled: Yes____; No **X**. Mottle color:_____; Matrix color: **N5/**
Gleyed: Yes **X**; No____. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Gleyed, saturation**

Hydrology
Inundated: Yes____; No **X**. Depth of standing water:
Saturated soils: Yes **X**; No____. Depth to saturated soil: **0 to 3 inches**
Other indicators:
Wetland hydrology: Yes **X**; No____. Basis: **saturated soils**
Atypical situation: Yes____; No **X**.

Normal Circumstances: Yes **X** No____.
Wetland Determination: Wetland **X**; Nonwetland
Comments:_____.

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Slurry Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No S-7** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Leersia virginica***	**FACW**
2.		8. ***Bidens frondosa***	**FACW**
3.		9. ***Poa trivialis***	**FACW**
Saplings/shrubs		10. ***Impatiens capensis***	**FACW**
4.		11. ***Glyceria striata***	**OBL**
5.		12. ***Pilea pumila***	**FACW**
6.		13. ***Carex vulpinoidea***	**OBL**

% of species that are OBL, FACW, and/or FAC: **100**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No____. Basis: **Dominant plants are all rated FACW to OBL**.

Soil
Series and phase: **Fluvaquents, loamy** On hydric soils list? Yes____ No **X**
Mottled: Yes____; No **X**. Mottle color:_____; Matrix color: **N4/**
Gleyed: Yes **X**; No____. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Gleyed, saturated**

Hydrology
Inundated: Yes **X**; No____. Depth of standing water: **up to 1 inches**
Saturated soils: Yes **X**; No____. Depth to saturated soil: **+1 to -3 inches**
Other indicators:
Wetland hydrology: Yes **X**; No____. Basis: **saturated soils and very minor inundation**
Atypical situation: Yes____; No **X**.

Normal Circumstances: Yes____ No **X**.
Wetland Determination: Wetland **X**; Nonwetland
Comments: **Very heavily impacted by cattle**.

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Slurry Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No S-8** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Poa trivialis***	**FACW**
2.		8. ***Pilea pumila***	**FACW**
3.		9. ***Impatiens capensis***	**FACW**
Saplings/shrubs		10. ***Leersia virginica***	**FACW**
4. ***Fraxinus americana***	**FACU**	11. ***Polygonum hydropiperoides***	**OBL**
5.		12.	
6.		13.	

% of species that are OBL, FACW, and/or FAC: **83**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No____. Basis: **Dominant herbs are all rated FACW or OBL; only a few saplings of F. Americana**.

Soil
Series and phase: **Fluvaquents, loamy** On hydric soils list? Yes____ No **X**
Mottled: Yes____; No **X**. Mottle color:_____; Matrix color: **10YR 4/2**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Low chroma, saturation**

Hydrology
Inundated: Yes____; No____. Depth of standing water:
Saturated soils: Yes **X**; No____. Depth to saturated soil: **0 to 3 inches**
Other indicators:
Wetland hydrology: Yes **X**; No____. Basis: **saturated soils**
Atypical situation: Yes____; No **X**.

Normal Circumstances: Yes **X** No____.
Wetland Determination: Wetland **X**; Nonwetland
Comments: **Spring - seep area**.

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Slurry Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No S-9** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Poa trivialis***	**FACW**
2.		8. ***Pilea pumila***	**FACW**
3.		9. ***Leersia virginica***	**FACW**
Saplings/shrubs		10. ***Polygonum hydropiperoides***	**OBL**
4.		11. ***Onoclea sensibilis***	**FACW**
5.		12.	
6.		13.	

% of species that are OBL, FACW, and/or FAC: **100**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No____. Basis: **Dominant plants are all rated FACW to OBL**.

Soil
Series and phase: **Dormont-Culleoka silt loam** On hydric soils list? Yes____ No **X**
Mottled: Yes **X**; No____. Mottle color: **2.5YR 4/8**; Matrix color: **10YR 5/1**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Low chroma, mottles, saturation**

Hydrology
Inundated: Yes____; No **X**. Depth of standing water:
Saturated soils: Yes **X**; No____. Depth to saturated soil: **0 to 3 inches**
Other indicators:_____ Wetland hydrology: Yes **X**; No____. Basis: **saturated soils**
Atypical situation: Yes____; No **X**.

Normal Circumstances: Yes **X** No____.
Wetland Determination: Wetland **X**; Nonwetland
Comments:_____.

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Slurry Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No S-10** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Glyceria striata***	**OBL**
2.		8. ***Carex lurida***	**OBL**
3.		9. ***Poa trivialis***	**FACW**
Saplings/shrubs		10. ***Juncus effusus***	**FACW+**
4.		11. ***Pilea pumila***	**FACW**
5.		12. ***Carex vulpinoidea***	**OBL**
6.		13. ***Carex stipata***	**OBL**

% of species that are OBL, FACW, and/or FAC: **100**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No____. Basis: **Dominant plants are all rated FACW to OBL**.

Soil
Series and phase: **Dormont-Culleoka silt loam** On hydric soils list? Yes___ No **X**
Mottled: Yes **X**; No____. Mottle color: **10YR 5/6**; Matrix color: **10YR 5/1**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Low chroma, mottles**

Hydrology
Inundated: Yes____; No **X**. Depth of standing water:
Saturated soils: Yes **X**; No____. Depth to saturated soil: **0 to 6 inches**
Other indicators:
Wetland hydrology: Yes **X**; No____. Basis: **saturated soils**
Atypical situation: Yes____; No **X**.

Normal Circumstances: Yes **X** No____.
Wetland Determination: Wetland **X**; Nonwetland
Comments:_____.

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Slurry Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No S-11** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Carex frankii***	**OBL**
2.		8. ***Bromus inermis***	**UPL**
3.		9. ***Glyceria striata***	**OBL**
Saplings/shrubs		10. ***Poa trivialis***	**FACW**
4.		11. ***Carex vulpinoidea***	**OBL**
5.		12. ***Carex stipata***	**OBL**
6.		13. ***Mentha piperita***	**FACW+**

% of species that are OBL, FACW, and/or FAC: **86**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No____. Basis: **Most plants are all rated FACW to OBL; *B. innermis* is an invader from adjacent pasture**.

Soil
Series and phase: **Dormont-Culleoka silt loam** On hydric soils list? Yes____ No **X**
Mottled: Yes **X**; No____. Mottle color:_____; Matrix color: **N5/**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Low chroma, mottles**

Hydrology
Inundated: Yes____; No **X**. Depth of standing water:
Saturated soils: Yes **X**; No____. Depth to saturated soil: **3 to 6 inches**
Other indicators:_____ Wetland hydrology: Yes **X**; No____. Basis: **saturated soils; soil colors**
Atypical situation: Yes____; No **X**.

Normal Circumstances: Yes____ No **X**.
Wetland Determination: Wetland **X**; Nonwetland
Comments: **Area heavily impacted by cattle**.

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Slurry Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No S-12** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Poa trivialis***	**FACW**
2.		8. ***Polygonum hydropiperoides***	**OBL**
3.		9. ***Bromus inermis***	**UPL**
Saplings/shrubs		10. ***Carex frankii***	**OBL**
4.		11. ***Polygonum cespitosum***	**FACU-**
5.		12.	
6.		13.	

% of species that are OBL, FACW, and/or FAC: **60**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No____. Basis: ***P. trivialis* (FACW) was the total dominant**

Soil
Series and phase: **Dormont-Culleoka silt loam** On hydric soils list? Yes____ No **X**
Mottled: Yes **X**; No____. Mottle color: **10YR 5/6**; Matrix color: **10YR 5/1**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Low chroma, mottles**

Hydrology
Inundated: Yes____; No____. Depth of standing water:
Saturated soils: Yes **X**; No____. Depth to saturated soil: **0 to 4 inches**
Other indicators:_____ Wetland hydrology: Yes **X**; No____. Basis: **saturated soils**
Atypical situation: Yes____; No **X**.

Normal Circumstances: Yes **X** No____.
Wetland Determination: Wetland **X**; Nonwetland
Comments: **Spring-seep area heavily impacted by cattle**.

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Slurry Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No S-13** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Poa trivialis***	**FACW**
2.		8. ***Bromus inermis***	**UPL**
3.		9. ***Eleocharis* sp.**	**OBL?**
Saplings/shrubs		10. ***Carex frankii***	**OBL**
4.		11. ***Phalaris arundinacea***	**FACW**
5.		12. ***Polygonum hydropiperoides***	**OBL**
6.		13.	

% of species that are OBL, FACW, and/or FAC: **83**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No____. Basis: **All plants are all rated FACW to OBL except for B. inermis which invaded from adjacent heavily grazed meadow.**

Soil
Series and phase: **Dormont-Culleoka silt loam** On hydric soils list? Yes____ No **X**
Mottled: Yes **X**; No____. Mottle color: **2.5YR 4/8**; Matrix color: **10YR 5/1**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Low chroma, mottles**

Hydrology
Inundated: Yes **X**; No____. Depth of standing water: **up to 1 inch**
Saturated soils: Yes **X**; No____. Depth to saturated soil: **+1 to 3 inches**
Other indicators:
Wetland hydrology: Yes **X**; No____. Basis: **saturated soils and an area of inundation**
Atypical situation: Yes **X**; No____.

Normal Circumstances: Yes____ No **X**.
Wetland Determination: Wetland **X**; Nonwetland
Comments: **This wetland is the remnants of a partially drained manmade pond**.

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Slurry Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No S-14** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Carex vulpinoidea***	**OBL**
2.		8. ***Carex frankii***	**OBL**
3.		9. ***Juncus effusus***	**FACW+**
Saplings/shrubs		10. ***Eupatorium perfoliatum***	**FACW+**
4.		11. ***Bromus inermis***	**UPL**
5.		12. ***Polygonum hydropiperoides***	**OBL**
6.		13.	

% of species that are OBL, FACW, and/or FAC: **83**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No____. Basis: **Dominant plants are all rated FACW to OBL; *B. inermis* is an invader from adjacent pasture**.

Soil
Series and phase: **Dormont-Culleoka silt loams** On hydric soils list? Yes____ No **X**
Mottled: Yes **X**; No____. Mottle color: **5YR 5/1**; Matrix color: **10YR5/1**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Low chroma, mottles**

Hydrology
Inundated: Yes___; No **X**. Depth of standing water:
Saturated soils: Yes **X**; No____. Depth to saturated soil: **0 - 4 inches**
Other indicators:
Wetland hydrology: Yes **X**; No____. Basis: **saturated soils**
Atypical situation: Yes____; No **X**.

Normal Circumstances: Yes **X** No____.
Wetland Determination: Wetland **X**; Nonwetland
Comments: **Area is heavily impacted by cattle**.

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Slurry Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No S-15** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Bidens frondosa***	**FACW**
2.		8. ***Poa trivialis***	**FACW**
3.		9. ***Polygonum hydropiperoides***	**OBL**
Saplings/shrubs		10. ***Echinochloa crus-galli***	**FACU**
4.		11. ***Bromus inermis***	**UPL**
5.		12.	
6.		13.	

% of species that are OBL, FACW, and/or FAC: **60**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No____. Basis: **Dominant plants are all rated FACW to OBL**.

Soil
Series and phase: Dormont-Culleoka silt loam On hydric soils list? Yes____ No **X**
Mottled: Yes **X**; No____. Mottle color: **7.5Y 6/6**; Matrix color: **10YR 6/2**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes X; No____. Basis: **Low chroma, mottles**

Hydrology
Inundated: Yes____; No **X**. Depth of standing water:
Saturated soils: Yes **X**; No____. Depth to saturated soil: **0 to 4 inches**
Other indicators:
Wetland hydrology: Yes **X**; No____. Basis: **saturated soils**
Atypical situation: Yes____; No **X**.

Normal Circumstances: Yes **X** No____.
Wetland Determination: Wetland **X**; Nonwetland
Comments: **Area is very heavily impacted by cattle; little vegetation remaining**.

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Slurry Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No S-16** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Pilea pumila***	**FACW**
2.		8. ***Leersia virginica***	**FACW**
3.		9. ***Poa trivialis***	**FACW**
Saplings/shrubs		10. ***Polygonum cespitosum***	**FACU-**
4.		11.	
5.		12.	
6.		13.	

% of species that are OBL, FACW, and/or FAC: **75**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No____. Basis: **Dominant plants are rated FACW**.

Soil
Series and phase: Dormont-Culleoka silt loams On hydric soils list? Yes___ No **X**
Mottled: Yes **X**; No____. Mottle color: **5YR 4/6**; Matrix color: **10YR 6/1**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Low chroma, mottles**

Hydrology
Inundated: Yes____; No **X**. Depth of standing water:
Saturated soils: Yes **X**; No____. Depth to saturated soil: **0 - 3 inches**
Other indicators:
Wetland hydrology: Yes **X**; No____. Basis: **saturated soils**
Atypical situation: Yes____; No **X**.

Normal Circumstances: Yes **X** No____.
Wetland Determination: Wetland **X**; Nonwetland
Comments: **Area is so heavily impacted by cattle that few plants survive**.

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Slurry Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No S-17** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Mentha piperita***	**FACW+**
2.		8. ***Bromus inermis***	**UPL**
3.		9. ***Agrominia parviflora***	**FACW**
Saplings/shrubs		10. ***Carex vulpinoidea***	**OBL**
4.		11. ***Polygonum hydropiperoides***	**OBL**
5.		12.	
6.		13.	

% of species that are OBL, FACW, and/or FAC: **80**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No____. Basis: **Dominant plants are rated FACW to OBL except for *B. inermis* which invaded from adjacent pasture**.

Soil
Series and phase: Dormont-Culleoka silt loam On hydric soils list? Yes____ No **X**
Mottled: Yes **X**; No____. Mottle color: **7.5YR 5/8**; Matrix color: **10YR 5/1**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Low chroma, mottles**

Hydrology
Inundated: Yes____; No **X**. Depth of standing water:
Saturated soils: Yes **X**; No____. Depth to saturated soil: **0 to 4 inches**
Other indicators:
Wetland hydrology: Yes **X**; No____. Basis: **saturated soils**
Atypical situation: Yes____; No **X**.

Normal Circumstances: Yes **X** No____.
Wetland Determination: Wetland **X**; Nonwetland
Comments: **Area impacted by cattle**.

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Slurry Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No S-18** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Polygonum hydropiperoides***	**OBL**
2.		8. ***Bromus inermis***	**UPL**
3.		9. ***Carex frankii***	**OBL**
Saplings/shrubs		10. ***Veronica americana***	**OBL**
4.		11. ***Juncus effusus***	**FACW+**
5.		12. ***Carex vulpinoidea***	**OBL**
6.		13.	

% of species that are OBL, FACW, and/or FAC: **83**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No____. Basis: **Dominant plants are all rated FACW to OBL, excepting *B. inermis* which invaded from adjacent pasture**.

Soil
Series and phase: **Dormont-Culleoka silt loam** On hydric soils list? Yes____ No **X**
Mottled: Yes____; No **X**. Mottle color:_____; Matrix color: **10YR 5/1**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Low chroma, saturation**

Hydrology
Inundated: Yes____; No **X**. Depth of standing water:
Saturated soils: Yes **X**; No____. Depth to saturated soil: **0 to 4 inches**
Other indicators:
Wetland hydrology: Yes **X**; No____. Basis: **saturated soils**
Atypical situation: Yes____; No **X**.

Normal Circumstances: Yes **X** No____.
Wetland Determination: Wetland **X**; Nonwetland
Comments: **Area impacted by cattle grazing**.

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Slurry Valley**
State: **PA** County: **Greene** Legal Description: Township:_____ Range:
Date: **July 20, 2001** Plot No.: **Wetland No S-19** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Carex vulpinoidea***	**OBL**
2.		8. ***Bromus inermis***	**UPL**
3.		9. ***Scirpus cyperinus***	**FACW+**
Saplings/shrubs		10. ***Carex frankii***	**OBL**
4.		11. ***Agrimonia parviflora***	**FACW**
5.		12.	
6.		13.	

% of species that are OBL, FACW, and/or FAC: **80**. Other indicators:_____.
Hydrophytic vegetation: Yes **X**; No____. Basis: **Dominant plants are rated FACW to OBL, except for B. inermis which invaded from adjacent pasture**.

Soil
Series and phase: **Dormont-Culleoka silt loam** On hydric soils list? Yes____ No **X**
Mottled: Yes **X**; No____. Mottle color: **7.5YR 4/6**; Matrix color: **10YR 6/1**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Low chroma, mottles**

Hydrology
Inundated: Yes____; No **X**. Depth of standing water:
Saturated soils: Yes **X**; No____. Depth to saturated soil: **1 - 4 inches**
Other indicators:
Wetland hydrology: Yes **X**; No____. Basis: **saturated soils**
Atypical situation: Yes____; No **X**.

Normal Circumstances: Yes **X** No____.
Wetland Determination: Wetland **X**; Nonwetland
Comments: **Area is impacted by cattle**.

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company**. Application Number:_____ Project Name: **Bailey Mine Mitigation**
State: **PA** County: **Washington** Legal Description: Township:_____ Range:_____ Date: **October 1, 2001** Plot No.: **Rocky Run Subsidence Wetland A** Section: **1**

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Phalaris arundinacea***	**FACW**
2.		8. ***Polygonum sagittatum***	**OBL**
3.		9. ***Eragrostis hypnoides***	**OBL**
Saplings/shrubs		10. ***Polygonum hydropiperoides***	**OBL**
4.		12. ***Dichanthelium clandestinum***	**FAC+**
5.		13. ***Agrimonia parviflora***	**FACW**
6.		14. ***Scirpus tabernaemontani***	**OBL**

% of species that are OBL, FACW, and/or FAC: **100**. Other indicators:
Hydrophytic vegetation: Yes **X**; No____. Basis: **Dominant taxon is FACW; next three most abundant are OBL.**

Soil
Series and phase: **Newark Silt Loam** On hydric soils list? Yes____; No **X**.
Mottled: Yes **X**; No____. Mottled color: **2.5YR 4/8**; Matrix color: **N5/**
Gleyed: Yes____; No **X**. Other indicators: **root channel staining** Hydric soils: Yes **X**; No____. Basis: **Low matrix color, mottles, root channel staining**

Hydrology
Inundated: Yes **X**; No____. Depth of standing water: **Portions of areas dominated by *Phalaris Arundinacea* were up to 4-6 inches deep.** Saturated soils: Yes **X**; No___. Depth to saturated soil: **0-6 inches**
Other indicators: **Soil indicators listed above** Wetland hydrology: Yes **X**; No____. Basis: **Several visits throughout the season indicate almost constant inundation levels** Atypical situation: Yes **X**; No____.

Normal Circumstances: Yes____ No **X**.
Wetland Determination: Wetland **X**; Nonwetland
Comments: **This is a portion of a new wetland created from mine subsidence**

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company**. Application Number:_____ Project Name: **Bailey Mine Mitigation**
State: **PA** County: **Washington** Legal Description: Township:_____ Range:_____ Date: **October 1, 2001** Plot No.: **Rocky Run Subsidence Wetland A** Section: **2**

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1. ***Salix nigra***	**FACW+**	7. ***Phalaris arundinacea***	**FACW**
2.		8. ***Agrimonia parviflora***	**FACW**
3.		9. ***Dichanthelium clandestinum***	**FAC+**
Saplings/shrubs		10. ***Polygonum hydropiperoides***	**OBL**
4.		11. ***Acoris calamis***	**OBL**
5.		12. ***Polygonum sagittatum***	**OBL**
6.		13. ***Eragrostis hypnoides***	**OBL**

% of species that are OBL, FACW, and/or FAC: **100**. Other indicators:
Hydrophytic vegetation: Yes **X**; No____. Basis: **Most taxa are FACW or OBL**

Soil
Series and phase: **Newark Silt Loam** On hydric soils list? Yes____; No **X**.
Mottled: Yes____; No **X**. Mottled color:_____; Matrix color: **4GY 4/1**
Gleyed: Yes____; No **X**. Other indicators: **root channel staining**
Hydric soils: Yes **X**; No____. Basis: **Low chroma, root channel staining**

Hydrology
Inundated: Yes **X**; No____. Depth of standing water: **up to six inches at edges**
Saturated soils: Yes **X**; No____. Depth to saturated soil: **0 - 4 inches** Other indicators: **streamside location, likely flooded seasonally** Wetland hydrology: Yes **X**; No____. Basis: **Several visits throughout the season indicate almost constant inundation levels** Atypical situation: Yes **X**; No____.

Normal Circumstances: Yes____ No **X**.
Wetland Determination: Wetland **X**; Nonwetland
Comments: **This is a portion of a new wetland created from mine subsidence**

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company**. Application Number:_____ Project Name: **Bailey Mine Mitigation**
State: **PA** County: **Washington** Legal Description: Township:_____ Range:_____ Date: **October 1, 2001** Plot No.: **Rocky Run Subsidence Wetland A** Section: **3**

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Ludwigia palustris***	**OBL**
2.		8. ***Mimulus ringens***	**OBL**
3.		9. ***Eragrostis hypnoides***	**OBL**
Saplings/shrubs		10. ***Polygonum hydropiperoides***	**OBL**
4.		11. ***Cyperus strigosus***	**FACW**
5.		12. ***Leersia virginica***	**FACW**
6.		13. ***Phalaris arundinacea***	**FACW**

% of species that are OBL, FACW, and/or FAC: **100**. Other indicators:
Hydrophytic vegetation: Yes **X**; No____. Basis: **Most abundant plants are all rated OBL**

Soil
Series and phase: **Newark Silt Loam** On hydric soils list? Yes____; No **X**.
Mottled: Yes **X**; No____. Mottled color: **2.5YR 5/1**; Matrix color: **2.5YR 4/8**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Low chroma matrix and mottles**

Hydrology
Inundated: Yes **X**; No____. Depth of standing water: **up to 6 inches at edges**
Saturated soils: Yes **X**; No____. Depth to saturated soil: **0 - 6 inches** Other indicators: **Streamside location, likely seasonally flooded** Wetland hydrology: Yes **X** No____. Basis :**Several visits throughout the season indicate almost constant inundation levels** Atypical situation: Yes **X**; No____.

Normal Circumstances: Yes____ No **X**.
Wetland Determination: Wetland **X**; Nonwetland
Comments: **This is a portion of a new wetland created from mine subsidence**

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company**. Application Number:_____ Project Name: **Bailey Mine Mitigation**
State: **PA** County: **Washington** Legal Description: Township:_____ Range:_____ Date: **October 1, 2001** Plot No.: **Rocky Run Subsidence Wetland A** Section: **4**

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Polygonum sagittatum***	**OBL**
2.		8. ***Phalarus arundinacea***	**FACW**
3.		9. ***Verbena urticifolia***	**FACU**
Saplings/shrubs		10. ***Epilobium coloratum***	**FACW+**
4.		11. ***Impatiens capensis***	**FACW**
5.		12. ***Muhlenbergia frondosa***	**FAC**
6.		13. ***Eragrostis hypnoides***	**OBL**

% of species that are OBL, FACW, and/or FAC: **86**. Other indicators:
Hydrophytic vegetation: Yes **X**; No____. Basis: **Most common plants rated FAC to OBL**

Soil
Series and phase: **Newark Silt Loam** On hydric soils list? Yes____; No **X**.
Mottled: Yes **X**; No____. Mottled color: **5YR 5/6**; Matrix color: **7.5YR 5/1** Gleyed: Yes____; No **X**. Other indicators:_____ Hydric soils: Yes **X**; No____. Basis: **Low chroma and mottles**

Hydrology
Inundated: Yes **X**; No____. Depth of standing water: **Up to 6 inches**
Saturated soils: Yes **X**; No____. Depth to saturated soil: **0 - 6 inches** Other indicators:_____ Wetland hydrology: Yes **X**; No____. Basis: **Several visits throughout the season indicate almost constant inundation levels** Atypical situation: Yes **X**; No____.

Normal Circumstances: Yes____ No **X**.
Wetland Determination: Wetland **X**; Nonwetland
Comments: **This is a portion of a new wetland created from mine subsidence**

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company**. Application Number:_____ Project Name: **Bailey Mine Mitigation**
State: **PA** County: **Washington** Legal Description: Township:_____ Range:_____ Date: **October 1, 2001** Plot No.: **Rocky Run Subsidence Wetland A** Section: **5**

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Ludwigia palustris***	**OBL**
2.		8. ***Phytolacca americana***	**FACU+**
3.		9. **unidentifiable Graminae**	**-**
Saplings/shrubs		10. ***Cyperus strigosus***	**FACW**
4.		11. ***Agrimonia parviflora***	**FACW**
5.		12. ***Dichanthelium clandestinum***	**FAC+**
6.		13.	

% of species that are OBL, FACW, and/or FAC: **66**. Other indicators:
Hydrophytic vegetation: Yes **X**; No____. Basis: **Marginally hydrophytic; couldn t identfy common grass due to heavy deer grazing.**

Soil
Series and phase: **Newark Silt Loam** On hydric soils list? Yes____; No **X**.
Mottled: Yes **X**; No____. Mottled color: **2.5YR 4/8**; Matrix color: **10YR 4/1**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Low chroma matrix and mottles**

Hydrology
Inundated: Yes **X**; No____. Depth of standing water: **up to 6 inches at edges**
Saturated soils: Yes **X**; No____. Depth to saturated soil: **0 - 6 inches** Other indicators:_____ Wetland hydrology: Yes **X**; No____. Basis: **Several visits throughout the season indicate almost constant inundation levels**
Atypical situation: Yes **X**; No____.

Normal Circumstances: Yes____ No **X**.
Wetland Determination: Wetland **X**; Nonwetland
Comments: **This is a portion of a new wetland created from mine subsidence**

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company**. Application Number:_____ Project Name: **Bailey Mine Mitigation**
State: **PA** County: **Washington** Legal Description: Township:_____ Range:_____ Date: **October 1, 2001** Plot No.: **Rocky Run Subsidence Wetland B** Section: **1**

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Ranunculus hispidis***	**FACW+**
2.		8. ***Phalaris arundinacea***	**FACW**
3.		9. ***Juncus effusus***	**FACW+**
Saplings/shrubs		10. ***Leersia oryzoides***	**OBL**
4.		11. ***Typha latifolia***	**OBL**
5.		12. ***Rumex crispis***	**FACU**
6.		13. ***Eleocharis obtusa***	**OBL**

% of species that are OBL, FACW, and/or FAC: **86**. Other indicators:
Hydrophytic vegetation: Yes **X**; No____. Basis: **Dominant species are FACW to OBL**

Soil
Series and phase: **Newark Silt Loam** On hydric soils list? Yes____; No **X**.
Mottled: Yes____; No **X**. Mottled color:_____; Matrix color: **10YR 4/1**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Low chroma (despite young age of wetland)**

Hydrology
Inundated: Yes **X**; No____. Depth of standing water: **0 - 1.5 feet**
Saturated soils: Yes **X**; No____. Depth to saturated soil: **surface** Other indicators:_____ Wetland hydrology: Yes **X**; No____. Basis: **inundation observed in late summer and fall** Atypical situation: Yes **X**; No____.

Normal Circumstances: Yes____ No **X**.
Wetland Determination: Wetland **X**; Nonwetland
Comments: **This wetland was created by mine subsidence and further enhanced by beaver dams**

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company**. Application Number:_____ Project Name: **Bailey Mine Mitigation**
State: **PA** County: **Washington** Legal Description: Township:_____ Range:_____ Date: **October 1, 2001** Plot No.: **Rocky Run Subsidence Wetland B** Section: **2**

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Phalaris arundinacea***	**FACW**
2.		8. ***Ranunculus hispidis***	**FACW+**
3.		9. ***Leersia oryzoides***	**OBL**
Saplings/shrubs		10. ***Dactylis glomerata***	**FACU**
4.		11. ***Prunella vulgaris***	**FACU+**
5.		12. ***Carex* sp 1**	**-**
6.		13. ***Carex* sp 2**	**-**

% of species that are OBL, FACW, and/or FAC: **66**. Other indicators:
Hydrophytic vegetation: Yes **X**; No____. Basis: **The two dominant taxa were FACW and FACW+**

Soil
Series and phase: **Newark Silt Loam** On hydric soils list? Yes____; No **X**.
Mottled: Yes____; No **X**. Mottled color:_____; Matrix color: **10YR 4/1**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Low chroma (despite young age of wetland)**

Hydrology
Inundated: Yes____; No **X**. Depth of standing water:
Saturated soils: Yes **X**; No____. Depth to saturated soil: **0 - 4 inches** Other indicators:_____ Wetland hydrology: Yes **X**; No____. Basis: **Appears to have shallow soil saturation for much of growing season**
Atypical situation: Yes **X**; No____.

Normal Circumstances: Yes____ No **X**.
Wetland Determination: Wetland **X**; Nonwetland
Comments: **This wetland was created by mine subsidence and further enhanced by beaver dams**

Determined by:

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company**. Application Number:_____ Project Name: **Bailey Mine Mitigation**
State: **PA** County: **Washington** Legal Description: Township:_____ Range:_____ Date: **October 1, 2001** Plot No.: **Templeton Fork Subsidence Wetland** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1. ***Salix nigra***	**FACW+**	7. ***Polygonum sagittatum***	**OBL**
2. ***Platanus occidentalis***	**FACW-**	8. ***Phalaris arundinacea***	**FACW**
3.		9. ***Typha latifolia***	**OBL**
Saplings/shrubs		10. ***Carex sp***	-
4.		11. ***Cyperus esculentus***	**FACW**
5.		12. ***Juncus effusus***	**FACW+**
6.		13. ***Ludwigia palustris***	**OBL**

% of species that are OBL, FACW, and/or FAC: **100**. Other indicators:
Hydrophytic vegetation: Yes **X**; No____. Basis: **Identifiable taxa are OBL or FACW**

Soil
Series and phase: **Huntington silt loam** On hydric soils list? Yes____; No **X**.
Mottled: Yes **X**; No____. Mottled color: **7.5YR 5/1**; Matrix color: **2.5YR 4/8**
Gleyed: Yes____; No **X**. Other indicators:
Hydric soils: Yes **X**; No____. Basis: **Low chroma, mottles**

Hydrology
Inundated: Yes **X**; No____. Depth of standing water: **up to 3 inches in limited areas**
Saturated soils: Yes **X**; No____. Depth to saturated soil: **0 - 6 inches** Other indicators: **Adjacency to Templeton Fork and elevation assure some flooding** Wetland hydrology: Yes **X**; No____. Basis: **Saturated soils and inundation in some places** Atypical situation: Yes **X**; No____.

Normal Circumstances: Yes____ No **X**.
Wetland Determination: Wetland **X**; Nonwetland
Comments : **This is a wetland created by subsidence of flood plain field**

Determined by:

ENCLOSURE 3
RE-EXAMINATION OF A CANDIDATE WETLAND
BAILEY MINE REFUSE HOLLOW
GREENE COUNTY, PA

RE- EXAMINATION OF A CANDIDATE WETLAND

AREA OF THE PROPOSED

BAILEY MINE REFUSE HOLLOW

GREENE COUNTY, PENNSYLVANIA

Prepared for

Consol Pennsylvania Coal Company

by

Bradford B. Owen Jr., Ph.D.

Consulting Ecologist

June 15, 2002

INTRODUCTION

This report is in response to the May 17, 2002 US Army Corps of Engineers letter sent to Jonathan Pachter, Consol Pennsylvania Coal Company concerning the May 8, 2002 site visit to the proposed Bailey Mine Complex Refuse Disposal Areas. This letter formally requested the evaluation of the "possibility of additional wetlands in the coarse coal refuse valley disposal site." This formalized the concerns expressed in the field by Scott Hans that an area near an old building foundation (where the main stream of the valley had cut a new channel since the time of the original wetland delineations) was developing into a Jurisdictional Wetland.

METHODS

The candidate wetland of the proposed refuse valley was surveyed in the field on June 11, 2002 in detail according to the Routine Wetland Determination methods of the Army Corps of Engineers Manual (Environmental Laboratory, 1987). Plant identification was primarily according to Strausbaugh and Core (undated) with assistance from other plant guides and nomenclature was updated according to the synonymy in Reed (1997). Plant indicator categories were taken from the Revision of the National List of Plant Species that Occur in Wetlands (ibid). Soils were classified according to the soil survey of Greene and Washington Counties (U.S. Dept. of Agriculture et al., 1983) and their hydric classifications were checked in the list of hydric soils of the United States (U.S. Dept. of Agriculture, 1991). Detailed field data and the plant indicator categories for Jurisdictional Wetlands were summarized on "Standard Data Form 1" from the Army Corps of Engineers Manual (Environmental Laboratory, 1987).

RESULTS AND DISCUSSION

The subject area of the proposed Coarse Refuse Disposal Valley was surveyed on June 11, 2002 in order to maximize the opportunity to identify plants accurately. While some plants had not flowered yet, this was the earliest possible date to find the dominant grass in bloom, thus enabling the author to verify its suspected identification as *Poa trivialis*.

The candidate area found by Scott Hans of the US Army Corps of Engineers had been quite wet in

May when the field inspection was conducted, due to the change in stream flow patterns since the original delineations were done. However, when the author returned on June 11, the stream had not only returned to its original channel, but as a result of two very significant precipitation events that occurred in the interim, the stream had scoured a much deeper channel. As a consequence of this the candidate area will be unable to maintain wetland hydrology. None of the soil boreholes developed any water during the sampling, indicating that the stream channels were draining the area, despite the recent heavy precipitation.

VEGETATION

On June 11 the vegetation of the candidate area (Table 1) was dominated by *Poa trivialis*, the same grass species that dominated the late spring vegetation of much of the shaded stream floodplain and adjacent land. The dominance of this species marginally qualifies the vegetation of this site as hydrophytic. However, this FACW species is a spring ephemeral that will be succeeded in dominance by some of the other species listed in Table 1 as the season progresses. The two woody species present on and around the site are the same taxa dominating most of the alluvial plane of this area. Unlike typical wetlands of this region, there were no OBL plants present in any stage of development. Normally in this environment one would expect to at least see some *Carex* species and seedlings of other hydrophytes such as *Polygonum* and *Bidens* species. The presence of large numbers of UPL and FACU plants also seem to point to this area not being a true wetland at this point.

SOILS

Soils of the candidate site were relatively crumbly,10YR 3/3 or 10YR 3/2 with no mottling over the first six inches, and 10YR 4/2 from six to ten inches, but still lacking any significant mottling. In a few very isolated locations (where the stream had eroded the land to a somewhat lower level), there was some faint root channel staining and below ten inches some soil chromas were close to one. Thus, most of the soils appear to not quite qualify as hydric at this time. Had the stream retained the new channel it exhibited on the May 8, 2002 field trip, the soils would undoubtedly have become hydric at some future date.

HYDROLOGY

The candidate area showed signs of recent stream inundation. There were flattened grasses in the lower channel areas where the water had flowed in May and in subsequent precipitation events. However, there were no saturated soils within the first twelve inches and there was no free water in any of the soil samples boreholes after an hour. The defining hydrologic events in the area were the two major precipitation events in the three weeks prior to the June 11 sampling. While there are no on site precipitation data it was obvious that there had been serious flooding that resulted in the main stream of the valley returning to its original channel and eroding it deeply into new substrates. This has resulted in the candidate site becoming perched considerably above the drainage. If this condition continues it is virtually certain that the candidate area cannot develop a hydric regime. Thus the present evidence indicates that the area does not have wetland hydrology.

CONCLUSIONS

Based on the marginally hydric vegetation, the marginal soils and the evidence of the present and probable future lack of wetland hydrology of the candidate site, it is the authors opinion that this area is not a Jurisdictional Wetland and that unless there is another change in the stream channel in the area, it should remain in a transitional to upland condition.

Table 1. Plants of the Candidate Wetland Area of the Bailey Mine Refuse Valley, June 11, 2002

Taxon	Abundance (1 - 4)*	Wetland Rating
Herbs		
Poa trivialis	1	FACW
Galium concinnum	2	UPL
Impatiens capensis/pallida	2	FACW
Glechoma hederacea	2	FACU
Viola sororia	3	FAC
Viola canadensis	3	NI
Cryptotaenia canadensis	3	FAC
Pilea pumila	3	FACW
Monarda didyma	4	FAC+
Geum laciniatum	4	FAC+
Lysimachia nummularia	4	FACW-
Ranunculus recurvatus	4	FAC+
Woody Vegetation		
Lindera benzoin	2	FACW-
Acer negundo	2	FAC+

* "1" is dominant; "4" is scattered or rare within the site

DATA FORM 1
WETLAND DETERMINATION

Applicant Name: **Consol Pennsylvania Coal Company** Application Number:_____ Project Name: **Bailey Mine Refuse Valley** State: **PA** County: **Greene** Legal Description: Township: _____ Range: _ Date: **June 11, 2002** Plot No.: **Candidate Wetland No. 1** Section:

Vegetation [list the three dominant species in each vegetation layer (5 if only 1 or 2 layers)]. Indicate species with observed morphological or known physiological adaptations with an asterisk.

Species	Indicator Status	Species	Indicator Status
Trees		Herbs	
1.		7. ***Poa trivialis***	**FACW**
2.		8. ***Galium concinnum***	**UPL**
3.		9. ***Impatiens capensis/pallida***	**FACW**
Saplings/shrubs		10. ***Glechoma hederacea***	**FACU**
4. **Lindera benzoin**	**FACW-**	11. ***Viola sorora***	**FAC**
5. **Acer negundo**	**FAC+**	12. ***Viola canadensis***	**NI**

% of species that are OBL, FACW, and/or FAC: **50**. Other indicators:
Hydrophytic vegetation: Yes **X**; No__. Basis: **The dominant plant was P. Trivialis (FACW)**

Soil
Series and phase: Fluvaquents, loamy On hydric soils list? Yes___; No **X**
_Mottled: Yes___; No **X**. Mottle color:_____; Matrix color: 10YR 3/2 to 10YR 4/2
_Gleyed: Yes___; No **X**. Other indicators:
Hydric soils: Yes___; No **X**. Basis: **Low chroma, but no mottling above 10 inches**

Hydrology
Inundated: Yes___; No **X**. Depth of standing water:
Saturated soils: Yes___; No **X**. Depth to saturated soil:
Other indicators: **Signs of recent flooding**
Wetland hydrology: Yes__; No **X**. Basis: **Recent flooding due to unusual circumstances ;no free water above 12 inches on June 11.** Atypical situation: Yes___; No **X**.

Normal Circumstances: Yes **X** No___.
Wetland Determination: Wetland_____; Nonwetland **X**
Comments: **Only two of the criteria are met, and the deeply incised stream channel will prevent future development of hydric conditions (see text for further explanation)**

Determined by:_____

REFERENCES

Environmental Laboratory. 1987. Corps of Engineers Wetland Delineation Manual. Technical Report. Y-87. U. S. Army Engineer Waterways Experiment Station, Vicksburg, Miss.

Strausbaugh, P. D., and E. L. Core. Undated. Flora of West Virginia. Seneca Books, Inc. Grantville, WV. 1079 pp.

Reed, P. B., Jr. 1997. Revision of the national list of plant species that occur in wetlands. U.S. Dept. of Interior, Fish and Wildlife Service. January 15, 1997. 462pp.

U. S. Department of Agriculture Soil Conservation Service, and Pennsylvania State University . 1983. Soil survey of Greene and Washington Counties, Pennsylvania. 93pp. plus maps.

U. S. Department of Agriculture Soil Conservation Service. 1991. Hydric soils of the United States. U.S. Dept. of Agriculture Misc. Publ. No. 1491. Unpaged.

Neubert/7375

October 31, 2002

Operations and Readiness Division
Regulatory Branch
200200371

Mr. Jonathan M. Pachter
Manager, Permits & Compliance
CNX Coal Operations
172 Route 519
P.O. Box 355
Eighty Four, PA 15330

Dear Mr. Pachter:

This letter is in reference to your Bailey Mine coal refuse disposal facility application. On October 7, 2002, you met in our office with Scott Hans, Nancy Mullen, and Christina Neubert to respond to our correspondence dated September 19, 2002.

In this meeting, you and your consultants presented information to support your proposal to preserve wetlands that may have been created by longwall mining subsidence. My staff said they would take this additional information into consideration along with any comment letters and give you a final answer as to whether or not your mitigation proposal is acceptable after the comment period for your public notice ended.

The goals of the Corps Regulatory program includes protecting the chemical, physical and biological integrity of all waters of the U.S., and providing for a no net loss of aquatic resources. While enhancing and preserving wetlands created by subsidence may meet this first goal, such actions do not provide for a no net loss of aquatic resources.

In consideration of the cumulative and secondary impacts associated with the proposed action, the existing resource quality, and difficulty of creating successful wetland replacement sites, your wetland mitigation proposal should replace the resources being impacted at a minimum rate of **1.5:1**. A revised mitigation proposal should be submitted which includes not less than **1:1 creation or restoration** of wetland habitats. Enhancement and preservation measures will be considered for the remaining mitigation requirements at not less than **5:1 for enhancement and 10:1 for preservation**.

The following information will help us review your mitigation proposal: A map/drawing with cross sections of the proposed wetland mitigation site that shows current and proposed grading, photographs of proposed wetland mitigation site in its current condition with the photograph locations indicated on the

record file copy

drawing, a planting schematic, piezometer locations, and a monitoring plan. In addition, if your mitigation proposal includes any enhancement or preservation of existing wetlands, please provide a drawing to scale that identifies the delineated wetland boundaries, photographs with locations indicated on the map, wetland data forms, and details of any proposed enhancement measures.

At this time we also request more specific details on the stream mitigation plan so we can review and make comments. These details should include the measures to be undertaken, the quantity of resource to be enhanced and preserved, and a monitoring plan which includes measurable criteria.

If you have any questions, please contact Scott Hans at (412) 395-7154, Nancy Mullen at (412) 395-7170, or Christina Neubert at (412) 395-7375.

Sincerely,

Albert H. Rogalla
Chief, Regulatory Branch

Copy Forwarded:

William Plassio, McMurray District Mining Office

Mark Haibach, CEC

Commonwealth of Pennsylvania
Pennsylvania Historical and Museum Commission
Bureau for Historic Preservation
Commonwealth Keystone Building, 2nd Floor
400 North Street
Harrisburg, PA 17120-0093

October ~~September~~ 2, 2003

Christine Davis
560 Penn Street
Verona, PA 15147

Re: ER# **2002-1693-059-D (1985-0390-059-VVV)**
COE: Interim Draft Report, Phase II Archaeological Survey,
Bailey Disposal Facility, Greene County, PA

Dear Ms. Davis:

The Bureau for Historic Preservation (the State Historic Preservation Office) has reviewed the above named project in accordance with Section 106 of the National Historic Preservation Act of 1966, as amended in 1980 and 1992, and the regulations (36 CFR Part 800) of the Advisory Council on Historic Preservation. These requirements include consideration of the project's potential effect upon both historic and archaeological resources.

Thank you for the interim report on your evaluation measures thus far for archaeological sites 36GR268, 36GR269, 36GR270, 26GR271, 36GR272, 36GR273, and 36GR274 which were identified and reported to this office in July of 2003. At that time, we agreed with your recommendations and proposed work plan to conduct Phase II National Register evaluation testing at these sites. We also thank you for taking time from your schedule on September 24, 2003 to visit our office and explain the complex nature of the undertaking and your preliminary findings.

Your efforts to date have demonstrated that significant resources are located within the project area. Due to the complex nature of the proposed undertaking and the significance of the resources, we recommend that a complete Phase II report be submitted for review in order to properly evaluate their significance and determine their eligibility for listing to the National Register of Historic Places. Please address regional context and the evaluation criteria outlined in our July 2003 response to the Phase I report.

Please send four copies of the final Phase I report (one unbound and all with original photographs) for our files and distribution to the various repositories. Append a signed gift agreement for archaeological collections to the final report and state where and when the collection will be permanently curated. The curated collections are an important part of the data that make archaeological sites significant. Making collections accessible enables future research to build on the discoveries of the past, makes research replicable, and allows us to share the information we learn from cultural resource management projects with the public through exhibits. If the State Museum in Harrisburg will not be the final repository for collections, then additional documentation in the form of detailed photographs and measurements will be required to facilitate future research.

If you need further information in this matter please consult Chan Funk at (717) 772-0924 or pfunk@state.pa.us.

Sincerely,

Kurt W. Carr, Chief
Division of Archaeology & Protection

cc: Christine Neubert, USACOE, Pittsburgh District, Regulatory Branch

KWC/DNS

Bureau for Historic Preservation
Commonwealth Keystone Building, 2nd Floor
400 North Street
Harrisburg, PA 17120-0093
(717)783-8947

FAX TRANSMITTAL SHEET

DATE 10/2/03

ATTENTION CHRISTY NEUBERT / CHRISTINE DAVIS

ORGANIZATION

FAX NUMBER

FROM CHAD FUNK **TELEPHONE** 717-772-0924

FAX NUMBER (717) 772-0920

NUMBER OF PAGES (INCLUDING COVER SHEET): 3

Bureau for Historic Preservation
Commonwealth Keystone Building, 2nd Floor
400 North Street
Harrisburg, PA 17120-0093
(717)783-8947

FAX TRANSMITTAL SHEET

DATE 15/7/03

ATTENTION CDC, INC & COE, PITT

ORGANIZATION

FAX NUMBER

FROM CHAD FUNK **TELEPHONE** 717-772-0924

FAX NUMBER (717) 772-0920

NUMBER OF PAGES (INCLUDING COVER SHEET): 4

Neubert, Christina L LRP

From: Pachter, Jonathan [JonathanPachter@consolenergy.com]
Sent: Friday, July 19, 2002 2:53 PM
To: 'Neubert, Christina L LRP'
Subject: RE: Shoemaker Nationwide Application & Bailey Questions

Christy - I can answer your questions now.

SHOEMAKER
1. There will be an underdrain and other drains in the coarse refuse fill areas, including but not limited to the structural porti ns of the dam. Of course, there will not be an underdrain beneath the slurry impoundment (pool) area.

2. We think that Scott visited the site on August 31, 2000.

3. The pond and the fill will be in place for more than 1 year.

BTW, we called the WV DEP about the 401 certification. They told us that they are waiting for you guys to issue the Nationwide before they issue the individual 401 Certification. They will issue the 401 after receiving the proper written notifications from you.

BAILEY
I am finishing the information that Nancy requested for the new refuse area. It will be forwarded to you on Monday. And we are are preparing a response to the PA Game Commission's letter - I will FAX a copy to you when it is sent to Harrisburg.

Call with questions. Have a good weekend.

Jonathan

-----Original Message-----
From: Neubert, Christina L LRP [mailto:Christina.L.Neubert@LRP02.USACE.ARMY.MIL]
Sent: Tuesday, July 16, 2002 4:31 PM
To: 'jonathanpachter@consolenergy.com'
Subject: Shoemaker Nationwide Application

Hi, Jonathan.

I just have a few questions regarding this project.

1. Will there be any underdrain used for this disposal site? If not, why?

2. Do you have the date Scott visited this site for the j.d.?

3. How long will the temporary fill be in place? I can't find anything specific in the Regs, but Scott said that anything over a year would be considered permanent.

I think that is all. I will keep you posted on the status. I am still waiting to hear from USFWS.

What's going on with the Bailey mine? We received a copy of the PA fish and boat commission letter. I think Nancy is still waiting for a reply to her letter also.

Thanks,

Neubert, Christina L LRP

From: Pachter, Jonathan [JonathanPachter@consolenergy.com]
Sent: Tuesday, July 16, 2002 4:46 PM
To: 'Neubert, Christina L LRP'
Subject: RE: Shoemaker Nationwide Application

Christy - no problem with the hold. I am getting answers to your Shoemaker questions, and will relay them to you ASAP. Re the Bailey questions - I am finalizing our responses to Nancy's letter and will forward that information to you all this week. But, so far as I know, the PA Fish and Boat people did not comment on any applications; the PA Game Commission sent in a letter, however. Talk to you soon, and thanks for the information on Shoemaker.

Jonathan Pachter

-----Original Message-----
From: Neubert, Christina L LRP [mailto:Christina.L.Neubert@LRP02.USACE.ARMY.MIL]
Sent: Tuesday, July 16, 2002 4:31 PM
To: 'jonathanpachter@consolenergy.com'
Subject: Shoemaker Nationwide Application

Hi, Jonathan.

I just have a few questions regarding this project.

1. Will there be any underdrain used for this disposal site? If not, why?

2. Do you have the date Scott visited this site for the j.d.?

3. How long will the temporary fill be in place? I can't find anything specific in the Regs, but Scott said that anythin over a year would be considered permanent.

I think that is all. I will keep you posted on the status. I am still waiting to hear from USFWS.

What's going on with the Bailey mine? We received a copy of the PA fish and boat commission letter. I think Nancy is still waiting for a reply to her letter also.

Thanks,
Christy Neubert
P.S. Sorry again for keeping you on hold so long today.

Neubert, Christina L LRP

From: Pachter, Jonathan [JonathanPachter@consolenergy.com]
Sent: Wednesday, September 18, 2002 10:53 AM
To: 'Neubert, Christina L LRP'
Subject: RE: Bailey Mine Coal Refuse Disposal Site Application

Christy - that survey has not yet been done. We hoped to wait until the fields are mowed this fall or wait until early in the spring before the vegetation grows back. Would that be a problem from your perspective?

Jonathan

-- --Original Message-----
From: Neubert, Christina L LRP [mailto:Christina.L.Neubert@LRP02.USACE.ARMY.MIL]
Sent: Tuesday, September 17, 2002 1:09 PM
To: 'Pachter, Jonathan'
Subject: Bailey Mine Coal Refuse Disposal Site Application

Hi, Jonathan.

We are hoping to have the Public Notice ready and sent out this week. I wanted to know the status of the PHMC phase I survey. Please let me know what has transpired.
Thanks,
Christy Neubert

Schroeder, Christina L LRP

From: Pachter, Jonathan [JonathanPachter@consolenergy.com]
Sent: Thursday, January 29, 2004 10:00 AM
To: 'Hans, Scott A LRP'; Christy Schroeder - COE Pittsburgh (E-mail)
Cc: Jose Taracido CUP (E-mail)
Subject: RE: Meeting on Thursday 1/29/04 at 2:00 p.m. about Bailey Refuse Perm it Conditions

Scott and Christy - here is a tentative list of topics that I would like to discuss at our status update meeting this afternoon.

1. Status of work at new Bailey refuse area
   a. Construction
   b. Archeology
   c. Wetlands mitigation, including conservation easements
   d. Selenium and PAH sampling
2. Stream fencing - Jose Taracido, California University of PA
3. General discussion

I don't see this meeting taking longer than an hour but I really wanted to go over these items face-to-face with you. See you at 2:00 p.m.

Jonathan Pachter

---Original Message-----
From: Hans, Scott A LRP [mailto:Scott.A.Hans@lrp02.usace.army.mil]
Sent: Tuesday, January 27, 2004 3:13 PM
To: 'Pachter, Jonathan'
Subject: RE: Meeting on Thursday 1/29/04 at 2:00 p.m. about Bailey Refuse Perm it Conditions

See you Thursday
Scott

-----Original Message-----
From: Pachter, Jonathan [mailto:JonathanPachter@consolenergy.com]
Sent: Tuesday, January 27, 2004 3:01 PM
To: Scott Hans USACE - Pgh. (E-mail); Christy Schroeder - COE Pittsburgh (E-mail)
Cc: Jose Taracido CUP (E-mail)
Subject: Meeting on Thursday 1/29/04 at 2:00 p.m. about Bailey Refuse Perm it Conditions

Scott and Christy - just a note to confirm our meeting on Thursday 1/29/04 at your office starting at 2:00 p.m. to review the status of our efforts to comply with the permit conditions for the Corps of Engineers permit for the new Bailey refuse area. Jose Taracido of California University of PA will join us for the meeting - Jose manages the stream fencing being done as part of the mitigation plan. Please feel free to call me with questions about the meeting.

Sincerely,
Jonathan
Jonathan M. Pachter
Manager, Environmental Permitting
CONSOL Energy Inc.

Consol Plaza
1800 Washington Road
Pittsburgh, PA 15241-1421

phone: 412/831-4679
fax: 412/831-4774
e-mail: jonathanpachter@consolenergy.com
web: www.consolenergy.com

Cindy Tibbott 12/09/2003 02:34 PM

To: Christina.L.Neubert@LRP02.USACE.ARMY.MIL
cc:

Subject: consol conditions

Christy, I just received the consol permit. I still don't understand condition 10. Why aren't you requiring sampling upstream and downstream of the new facility, or is there something I'm missing here?

Thanks!

Cindy

OPTIONAL FORM 99 (7-90)

FAX TRANSMITTAL

# of pages ▶ 4

To Christy Schroeder	From Cindy Tibbott
Dept./Agency	Phone # 814-234-4090
Fax #	Fax #

NSN 7540-01-317-7368 5099-101 GENERAL SERVICES ADMINISTRATION

Cindy Tibbott
11/24/2003 08:29 AM

To: Christina.L.Neubert@LRP02.USACE.ARMY.MIL
cc:
Subject: consol conditions

Christy, you're right -- I should have just responded by e-mail earlier, when it was obvious we were going to keep missing each other. I've placed my comments in "bold" font. Please give me a call when you've had a chance to look this over -- I'm in all day today!

consol special conditions.dc

1. PHMC conditions
2. The wetland mitigation proposal, dated April 28, 2003, which outlines the creation of 1.54 acres of replacement wetlands and the enhancement of 0.30 acre of riparian habitat, must be performed prior to or within one year of the start of the fill placement.
3. The monitoring plan submitted by CEC, dated April 28, 2003 must be implemented with copies of all monitoring reports provided to this office within 60 days of each monitoring event.
4. Surveyed as-built drawings of the wetland mitigation must be provided to this office with the first, third, and final monitoring report.
5. The conservation easement for the preservation of 4.86 acres of existing wetland must be provided to this office prior to the start of construction. **This office will review the terms of the conservation easement, in coordination with the U.S. Fish and Wildlife Service. Following written notification of approval by the Pittsburgh District, Consol must have the easement recorded on the applicable deed(s) at the county courthouse within 60 days.**
6. The stream mitigation proposal, revised March, 2003, which included a minimum of 12.5 miles of streambank fencing with controlled crossings, establishment of 100-acres of native grasslands, creation of 20 border-edge cuts, and monitoring, must be implemented as proposed. Copies of the final comprehensive mitigation plan and monitoring reports must be submitted to the Corps for final approval within 60 days of permit issuance or prior to the start of construction. **All stream mitigation projects must be completed within one year of permit issuance.**
7. The monitoring parameters must show a 20% improvement either by increasing species diversity or improving water quality in the restored segments of stream channel verses pre-project conditions or reference reaches. If these improvements are not met additional corrective measures must be required. **[Christy – "improving water quality" is not adequate; one could decrease the fecal coliform county by 20% and call it a success. The point of the 20% improvement was to increase biological production by that much. Also, I don't know how the biological monitoring has been described in other permits, but I think it would be appropriate to have Consol use RBP metrics that are used by the southwest region of DEP. Suggested rewording of this item: "Stream mitigation reaches will be monitored before and after construction using the same Rapid Bioassessment Protocol metrics established by the PA DEP Southwest Region for use in assessing streams for the State-wide Surface Waters Assessment Program. The biological score for each mitigation reach must show a 20% improvement over pre-project conditions, or additional corrective measures or mitigation will be required.]**
8. Not less than 50% of the stream mitigation measures must be established within the Enlow Fork watershed. **[ALL of the mitigation must be accomplished in the Enlow Fork watershed]**

9. A minimum of five miles of successfully restored reaches of stream channel must be placed under conservation easement by the end of the streambank monitoring period as outlined in the mitigation proposal revised March, 2003. **This office will review the terms of the conservation easement, in coordination with the U.S. Fish and Wildlife Service. Following written notification of approval by the Pittsburgh District, Consol must have the easement recorded on the applicable deed(s) at the county courthouse within 60 days.**

10. Sediment sampling and testing for selenium and PAH's must be performed at sampling locations 9 through 14 as identified on the map provided by CEC dated February 25, 2003. The sediment samples should be taken quarterly from the start of construction and until two years after the existing coal refuse disposal facility is closed and reclaimed. An analysis and summary of the results must be provided to the Corps after each monitoring event. If the levels of selenium and/or PAH values increase by greater than 10% from the samples collected on November 19, 2002, immediate corrective measures will be required. **[Christy – This is an excellent condition. However, in all fairness to Consol, sampling location and even laboratory variations could result in a 10% difference in analytical results. 20% would probably be more fair (and there's research that backs 20% as an appropriate value). Also, sample locations 9 through 14 are are the existing facility, aren't they? We should be asking for this sampling at the new facility (the one you'll be permitting)]**

Review of
Review of "Sediment Evaluation of Enlow Fork and Tributaries for the First through Fourth Quarters of 2004, Bailey Mine-New Refuse Disposal Facility, Consol Pennsylvania Coal Company, CEC Project 040-148, February 10, 2005"

BACKGROUND/ METHODS

Sampling, testing, and evaluation of the sediments of Enlow Fork and tributaries of Enlow Fork were required by Special Condition 10 of USACE Section 401 Permit No. 200200371, issued on November 26, 2003.

Sampling Sites and Parameters Analyzed

Samples were collected at 7 sites (Table 1). Sampling at five of these sites was initiated prior to 2004 (#14, 11, 10, 12, & 13). During the 2004, samples were also collected at 2 control sites assumed to be representative of background conditions, located upstream of all Consol activity: one on Enlow Fork and a second located on the North Fork of Enlow Fork in Simpson Creek, PA (sampling sites 16 and 15, respectively). Although sampling sites 12 and 13 were located upstream of the Talley run discharge, they cannot be considered representative of background conditions since they are located adjacent to, and could possibly receive drainage from, the Consol site.

Table 1
Sediment Sampling Sites

Site #	Stream	Location
14	Enlow Fork	6500 feet downstream of the Talley Run discharge
11	Enlow Fork	1200 feet downstream of the Talley Run discharge
10	Talley Run	Talley Run discharge
12	Enlow Fork	400 feet upstream of the Talley Run discharge, adjacent to the Consol site
13	Enlow Fork	4000 feet upstream of the Talley Run discharge, adjacent to Consol site
15	North Fork Enlow	upstream of all Consol activity in the town of Simpson Creek, PA
16	Enlow Fork	upstream of all Consol activity

Surface sediment samples were collected at each sampling site (0 to 4 inches) and were analyzed for total Selenium, TCLP selenium, PAHs, Total organic carbon (TOC), grain size, and percent solids. Companion water samples were analyzed for specific conductivity, pH, dissolved oxygen (DO), and water temperature.

Sampling Frequency

On September 4, 2001, pre construction sediment data were collected by the US Fish and Wildlife Service (USFWS) at two of the 7 sites, one located upstream and the other downstream of the Talley Run discharge (sites 12 and 14, respectively). On November 19, 2002, Consol (Moody and Associates Inc.) collected samples from all sites except the two control sites (16 and 15). From the start of construction in 2004, sediment samples were collected quarterly by Moody and Associates Inc: March 24, June 22, September 16, and December 15, 2004.

DATA REVIEW/ RESULTS

Data Quality

Duplicate samples were collected at site 10 on June 22 & at site 14 on Dec 15, 2004. Results of duplicate samples for selenium analyses were acceptable. However, results of

analyses of PAH duplicate samples were questionable. The percent difference between duplicate PAHs ranged between 59 and 273%. This may be an indication of inconsistent sampling techniques, laboratory protocol, or accuracy may have been limited by low detection limits.

PAHs

Total PAH concentrations by stream mile are presented in **Figure 1.** As can be seen in this Figure, there is a definite trend towards increasing concentrations downstream of the control sites (Sites #15 and #16).

PAH results are also presented by sampling site in **Figure 2.** Trend lines for each sampling site over time are also shown in Figure 2. As can be seen in this figure, while there was no change in the trend line at the 2 control sites, there was a decreasing trend was observed at sites 12 and 14, an increasing trend at sites 10 and 11, and a decreasing trend at site 14. However, these data show extreme variation in concentrations observed at all sampling sites throughout the study period (particularly on 6/22/04). As demonstrated in **Figure 3**, because organic compounds bind to fine sediments but not to coarser sands and gravels, analyses of 2004 samples with the higher the % fines also have the highest concentrations of PAHs, no matter where the samples were collected. Therefore, it is likely that erratic PAH concentrations observed over the study period were likely attributable to the % fines and clay in the samples.

Results of the USFW preconstruction survey were orders of magnitude greater than those of Consol's (Moody) 2004 surveys at the same locations. For example 170,353 ug/kg and 1300 ug/kg total PAH were documented at sampling site 12 by the USFWS in 2001 and by Moody in 2004, respectively. Of note, USFWS' TOC concentrations ranged between 14 to 18% while Consol's results from the same sites ranged between 1 and 3%. Differences observed in the data sets could be related to % fines or could also be related to which side of the stream the samples were collected.

Because the goal of Special Condition 10 is to assure compliance with NEPA (no environmental degradation), if data are to be compared to available criteria, it would be more appropriate to use the Lowest Effects Level (**LEL**) guidelines rather than the Severe Effects Level (**SEL**) guidelines. While the SEL guidelines "provide an accurate basis for **predicting the absence sediment toxicity**", the SEL provide an "...accurate basis for **predicting sediment toxicity"** (MacDonald et. al.). LEL = clean to marginally polluted and SEL = heavily polluted.

Sediment data are compared to LEL and SEL guidelines in **Table 2**. While no exceedences of the SEL guidelines were observed in the 2004 data, the total PAH concentrations observed by the USFWS in 2001 at site 12 (400 feet upstream of the Talley Run discharge) did exceed the SEL criteria. In addition, the LEL sediment quality guideline for total PAHs was exceeded at sampling sites located downstream of the 2 control sites, showing a trend towards degradation.

Table 2

Comparison of Total PAH Concentrations (ug/kg) with Sediment Quality Guidelines

Exceeded Lowest Effects Level (LEL) Criteria 4000 ug/kg = Yellow Highlight

Exceeded Consensus based Threshold Effects Concentration TEC (harmful Effects Unlikely) 1610 ug/kg = Green Highlight

Exceeded Severe Effects Level (SEL) Criteria 100000 ug/kg (unadjusted) = Orange Highlight

Exceeded Probable Effect Concentration (PEC) (Harmful Effects Likely) Criteria 22800 ug/kg (unadjusted) = Red Highlight

Total PAH ug/kg

Site #	9/4/01	11/19/02				3/24/04	6/22/04	6/22/04	9/16/04	12/15/04
	T. PAH	T. PAH	TOC	TOC adjusted SEL	TOC adjusted PEC	T. PAH	T. PAH	T. PAH	T. PAH	T. PAH
14		4800	0.46	460	52.44	1190	1545		2693	2918
11		1500	1.28	1280	291.84	5355	926		4029	1634
10		1300	1.22	1220	278.16	4122	268	616	2587	8838
12		1300	0.7	700	159.6	2275	490		606	708
13		1300	0.55	550	125.4	1588	1117		363	1083
15						544	87		272	466
16						73	103		132	84

Selenium

As suggested in Appendix B of Consol's February 3, 2005 letter to the District, results of selenium analyses do not show a clear increase in concentrations in Enlow Fork downstream of existing treatment facility when compared to upstream values **(Figure 4).**

Again, comparison with SQGs is not recommended but some discussion is pertinent. While there are no regulatory guidelines for selenium in sediments, 4.0 mg/kg is frequently cited for the potential for bioaccumulation (http://ks.water.usgs.gov/Kansas/pubs/abstracts/vg.030100.html). In addition, site specific criteria can be even more stringent depending on aquatic life impacts. For example, the selenium SQG recommended for San Francisco Bay is 1.4 mg/kg (http://www.sfei.org/rmp/1997/c0401.htm). As can be seen in **Figure 4**, selenium spikes as high as 3.2 mg/kg were documented downstream of the Talley Run discharge. It is therefore recommended that selenium monitoring be continued to assure documentation of trends over time.

RECOMMENDATIONS/ CONCLUSIONS:

- Continue the PAH and selenium sediment sampling program as agreed, with modifications suggested below. The trigger (a 20% increase) should not be modified based on the results of the first year of study since four sets of data are insufficient for trend analyses.
- Encourage consistency in sampling techniques to assure comparability of results. Samples should be collected from the top few inches rather than the top 4 inches and from the side of the stream that is adjacent to the Consol site (the left descending bank for Enlow Fork, for example) to assure that only new depositional material is collected. Also, as demonstrated in **Table 4** and discussed above, it is easy to bias results simply by collecting coarser material. Recommend that all samples collected have the same % fines (>40%).
- Request a map showing:

1. all streams (Enlow Fork, the North Fork of Enlow Fork, Talley Run, Fletcher Run, Grinnage Run, Owens Run, unnamed tributary to Owens Run, and any other unnamed tributaries mentioned in correspondences)
2. all existing and/or proposed coal slurry dams and sedimentation and/or treatment ponds
3. outfalls from sedimentation and/or treatment ponds
4. seeps draining into Enlow Fork from areas with old or recent fill
5. new and old coal refuse disposal facilities
6. sediment and water sampling sites
7. mitigation wetlands

- Because Consol questioned the ability to identify sources of elevated concentrations of PAHs and selenium (more specifically, activity at their new facility, Feb 2003) with the existing sampling site network, recommend that an additional sampling site on Enlow Fork be added. This site should be located upstream of the North Fork and all Simpson Store, PA municipal outfalls, and downstream of the most upstream edge of the new fill site. It is expected that data from this site would capture impacts from outfalls and runoff from the new fill areas. Once a map showing all streams, activities and outfalls is provided, the location of the new sampling site location can be refined.
- Request a copy of all of Consol's 2004 TOC results of analyses.
- For future reviews, conduct all statistical analyses on raw, not adjusted data.
- Utilize only sampling sites 15 and 16 as representative of background conditions
- Request a description of coal slurry treatment (sedimentation only or chemical treatment?) ponds, including sizes and flow from outfalls.
- Comparison of results with sediment quality guidelines (SQGs) is not recommended since the intent of this Special Condition 10 sediment quality survey is to provide assurance of non-degradation (compliance with NEPA) and effectiveness of treatment. However, since Consol did compare results to SQGs:
    1. Request an explanation /specific reference for adjustment of the **data** rather than the **criteria** by % TOC. I was unable to find reference to data adjustment in MacDonald, Ingersoll, and Berger's paper, "Development and Evaluation of Consensus-based Sediment Quality Guidelines for Freshwater Ecosystems", referenced by Consol. However, adjustment of the SEL **criteria** by % TOC is recommended for the Ontario Sediment Quality standards. These recommended adjustments for TOC will **decrease the criteria value** the lower the % TOC of the sample, rather than **decrease the concentration of contaminants in the sample**.
    2. Encourage comparison with the Low Effects Level (LEL) rather than the Severe Effects Level (SEL) sediment quality guidelines.
- Request from PA copies of Section 401 NPDES permit quarterly data submissions to keep tabs on water quality trends (conductivity, metals, sulfate, and suspended solids), including locations of ground and surface water quality sampling sites.
- Request from the USFWS their 2001 sediment quality data (sample location, units, sample protocol, % fines, etc.).

Figure 1
Total PAHs by Stream Mile
From the Most Downstream Sampling Site (# 14) to the Most Upstream (#16)
2001, 2002, and 2004

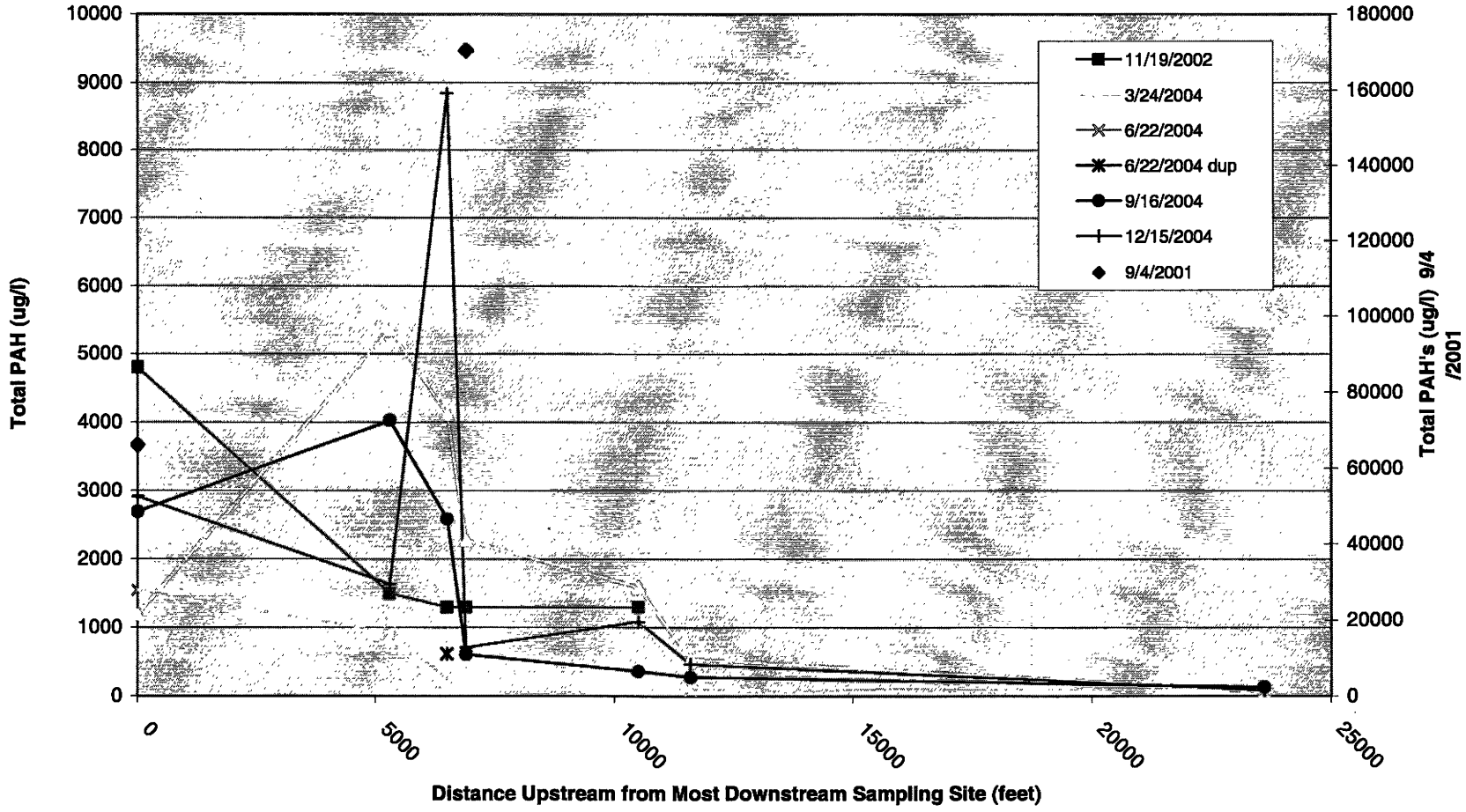


Figure 2
Total PAHs by Site and Date With Trend Lines (dotted lines)
2002 to 2004

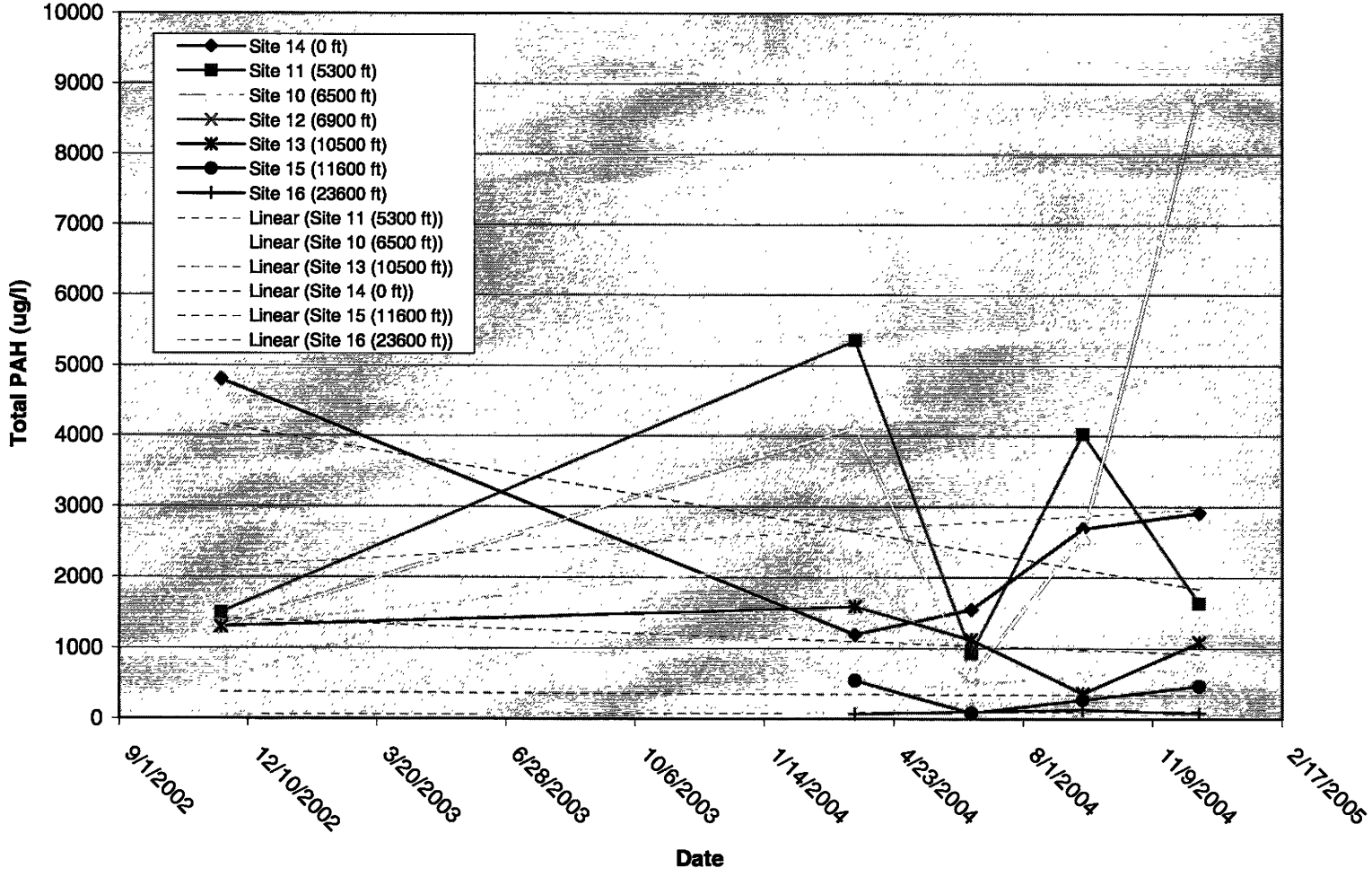


Figure 3
Enlow Fork Consol Coal
% Silt, % clay and Total PAH at Sampling Sites 11 and 12

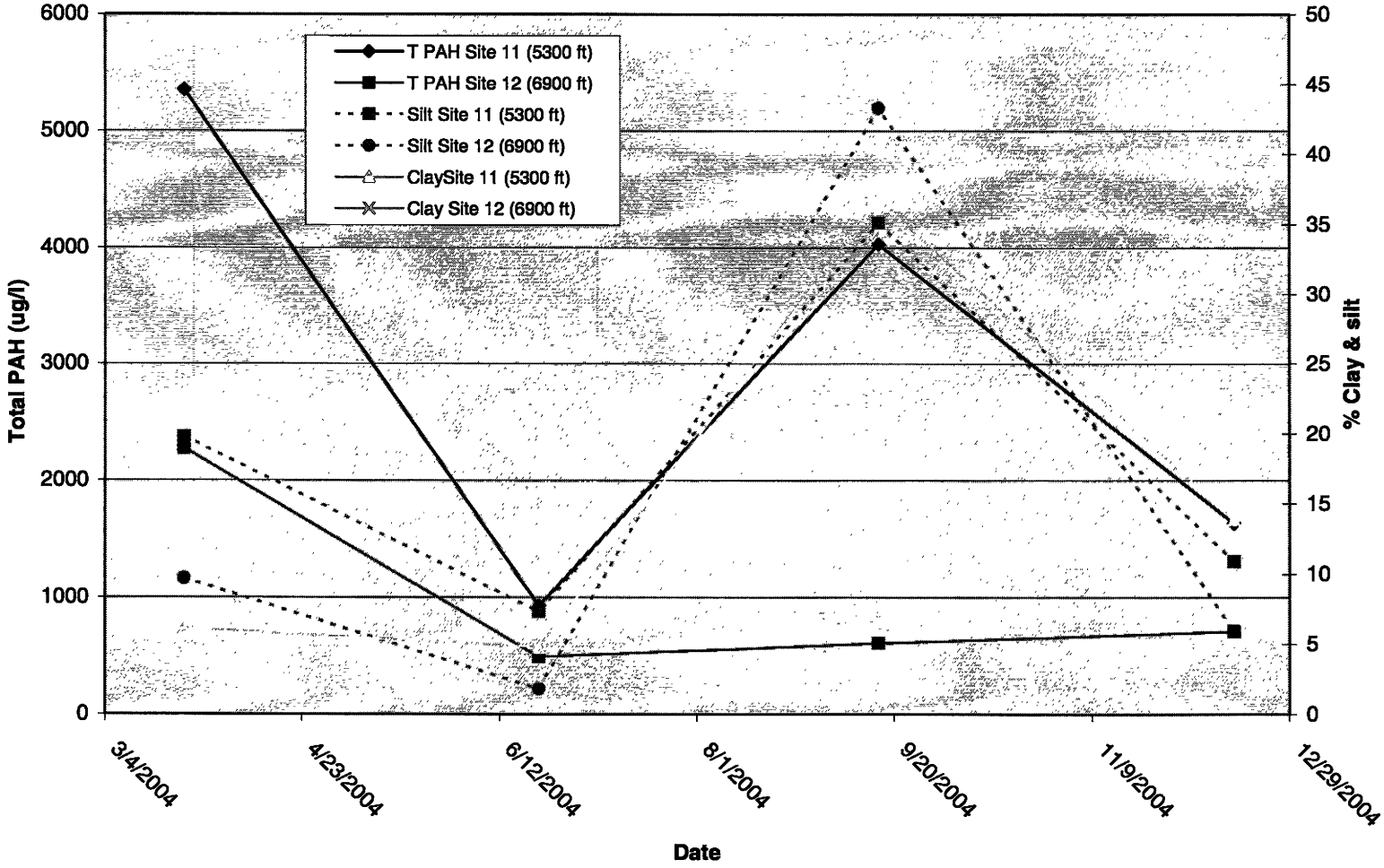
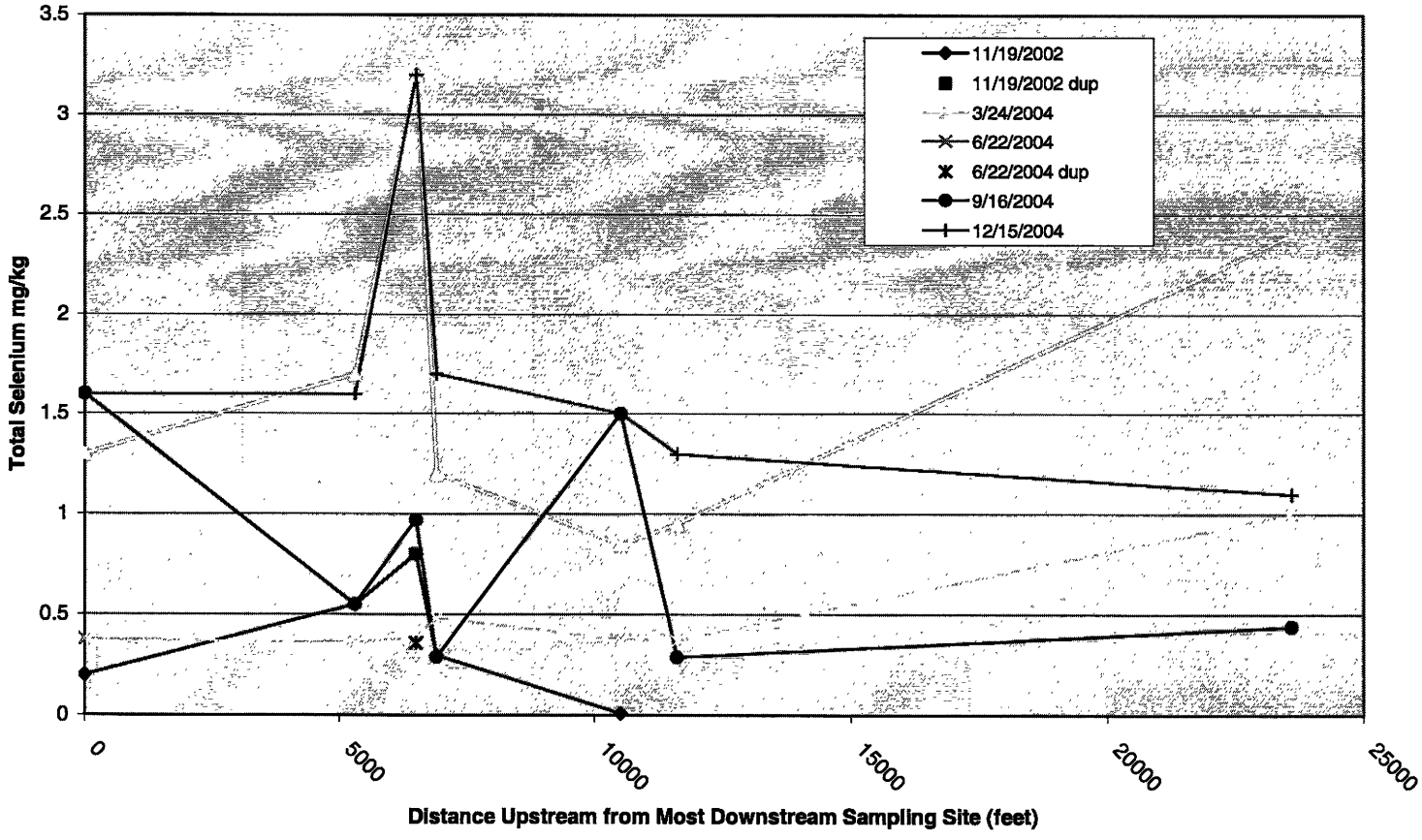


Figure 4
Total Selenium by Stream Mile
From the Most Downstream Sampling Site (#11) to the Most Upstream (#16)
2002 and 2004



REFERENCES

McDonald, D.D. and C. G. Ingersoll, T.A. Berger, 2000. Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Ecosystems. Environmental Contamination and Toxicity, 39, 20-31

Schroeder, Christina L LRP 8:30 a.m. @ Claysville Office

From: Shumaker, Todd [ToddShumaker@consolenergy.com]
Sent: Friday, September 23, 2005 12:49 PM
To: Schroeder, Christina L LRP
Subject: RE:

From Pittsburgh, take I-79 South to Washington, from Washington take I-70 West towards Wheeling. Take the Claysville exit off of I-70. At the stop sign at the end of the exit ramp take a right. At the next stop sign take a right onto S.R. 40. Travel about 1 mile and make a right hand turn onto S.R. 231 (there is a Catholic Church on the right hand side of the road at the corner of this turn). Travel 4 to 5 miles on S.R. 231 until you come to a stop sign. Turn left at the stop sign onto Pleasant Grove Road. Travel 300 feet and turn left into the Claysville Office Parking lot. The office is an old elementary school building.

What time would you like to meet?

From: Schroeder, Christina L LRP [mailto:Christina.L.Schroeder@lrp02.usace.army.mil]
Sent: Friday, September 23, 2005 10:36 AM
To: Shumaker, Todd
Subject: RE:

No, I'll need directions.

From: Shumaker, Todd [mailto:ToddShumaker@consolenergy.com]
Sent: Friday, September 23, 2005 8:57 AM
To: Schroeder, Christina L LRP
Cc: mike@habitatsolutions.net; mhaibach@cecinc.com; Stanley, Mark
Subject: RE:

Christina,

October 18 will work. We could meet here at the Claysville Office and go from there. Let me know what time and I will arrange with the others. Jose Taracido from Cal. U (stream fencing, etc.), Mark Haibach from CEC and possibly Mike Mooney from Habitat Solutions (wetlands mitigation), Mark Stanley, and I will be present. Do you know where the Claysville Office is?

Todd

From: Schroeder, Christina L LRP [mailto:Christina.L.Schroeder@lrp02.usace.army.mil]
Sent: Friday, September 16, 2005 9:16 AM
To: Shumaker, Todd
Subject: RE:

Ok, Todd. Thanks. I would like to schedule a compliance visit for the month of October and take a look at all of the different aspects of the mitigation (streambank fencing, wetland creation, etc.) I am waiting to see this year's PAH and selenium monitoring before I forward the recommendations to you that I mentioned during our meeting. In the mean time, let's pick a tentative date for October. Will the 18th work for you? If Mark Stanley or someone else needs to be involved with the compliance monitoring, please coordinate with them also.
I'll be in touch.
Christina

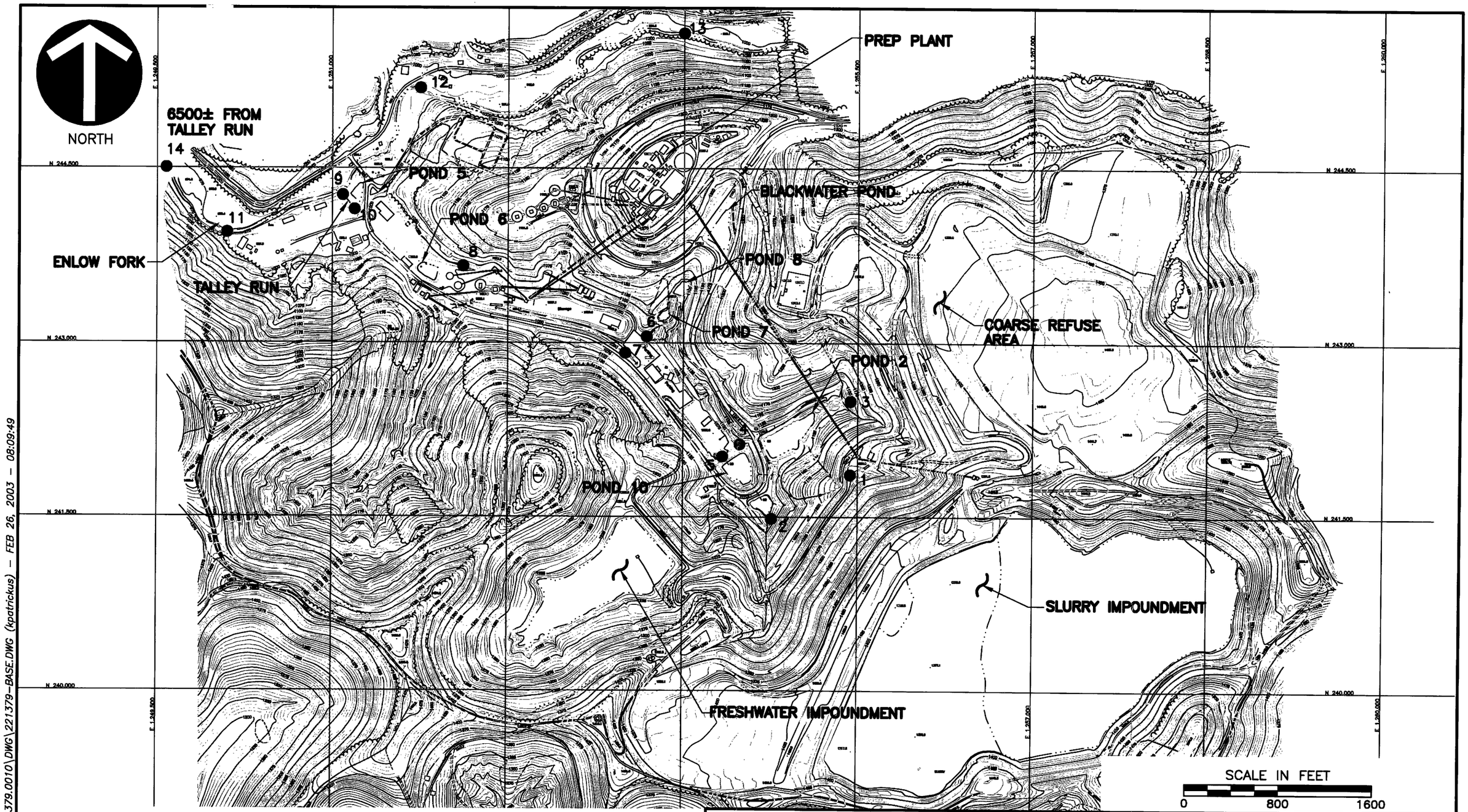
From: Shumaker, Todd [mailto:ToddShumaker@consolenergy.com]
Sent: Friday, September 16, 2005 9:07 AM
To: Schroeder, Christina L LRP
Subject:

Christina,

I am placing in the mail today the items that you requested at our September 6 meeting. There are two copies each of the 1st and 2nd Quarter Enlow Fork Sediment Evaluation Reports, one copy each of the Quarterly Progress Reports of the Wildlife Habitat Restoration Mitigation (stream fencing project) as submitted by The Foundation for California University, and two maps showing the old and new refuse areas along the streams and outfalls. I apologize for you not receiving these items previously. I will send them to your attention via certified mail. As for the wetlands mitigation project, all of the stream bank work has been completed, the dirt work to develop the wet lands has been completed and about half of the planting was performed. When the dry weather hit we placed the planting on hold, but will be starting again next week in order to complete this project. It should be done by the end of the month, at which time we will perform the as-built survey. If you need anything else please let me know.

Thanks

Todd M. Shumaker
Environmental Engineer
CNX Coal - PA Operations
1525 Pleasant Grove Road
PO Box J
Claysville, PA 15323
(724)663-3039
toddshumaker@consolenergy.com



LEGEND

8 ● SEDIMENT SAMPLING LOCATIONS

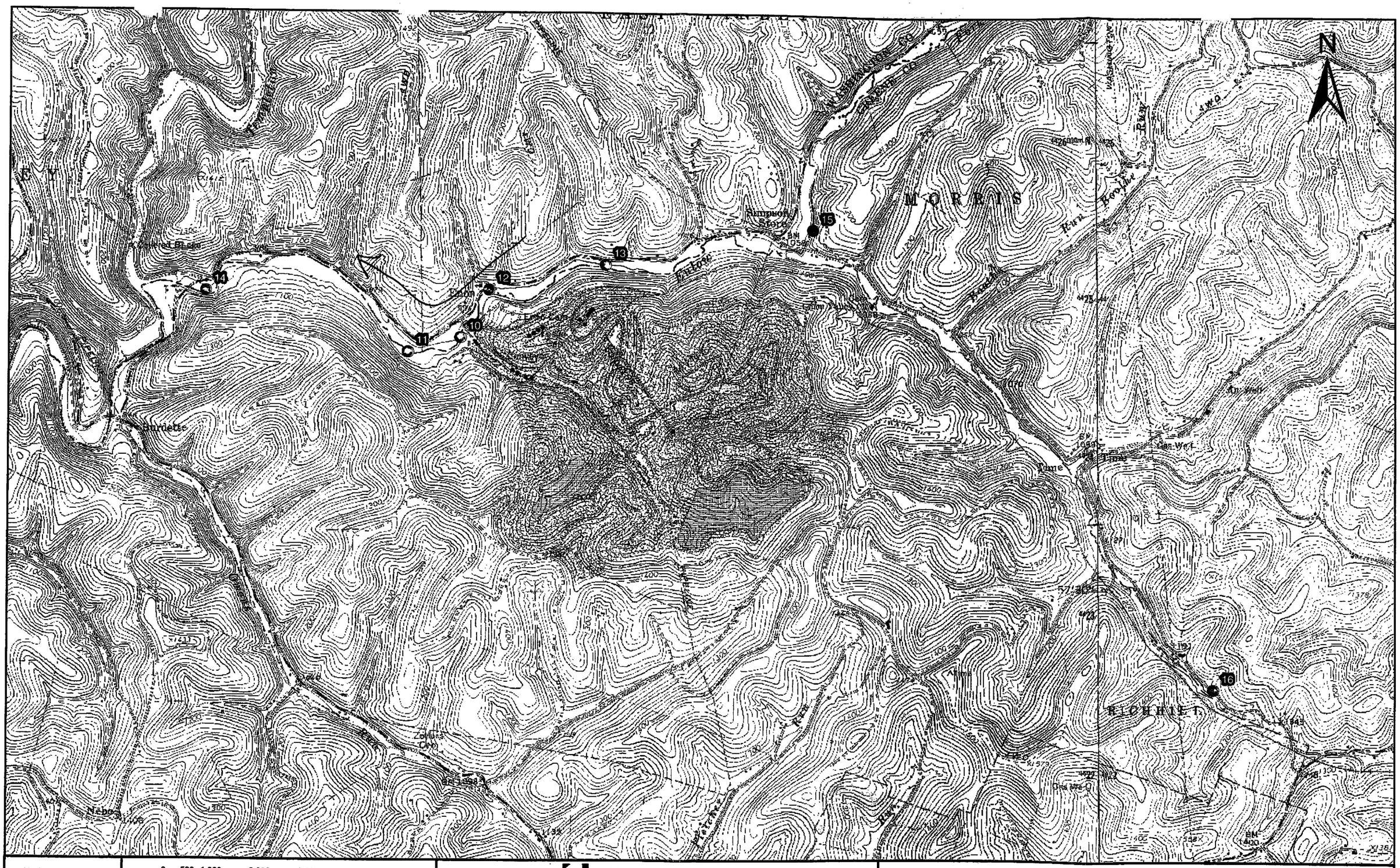
REFERENCE:
ELECTRONIC COPY OF SITE LAYOUT PROVIDED BY CONSOL PENNSYLVANIA COAL COMPANY FROM UPDATED AERIAL PHOTOGRAPHY DATED 08/05/03 BY TOPOTECH, INC., EAST LIVERPOOL, OHIO

CEC
Civil & Environmental Consultants, Inc.
Pittsburgh, PA 15205
(412) 429-2324 • (800) 365-2324
Cincinnati, OH • Columbus, OH • Indianapolis, IN • Nashville, TN

SEDIMENT SAMPLING LOCATIONS
BAILEY MINE COMPLEX
CONSOL PENNSYLVANIA COAL COMPANY
GREENE COUNTY, PENNSYLVANIA

DWN. BY: KAP	SCALE:	DATE:	PROJECT NO.:	
CHKD. BY: MRH	AS NOTED	02/25/03	221379.0010	FIGURE 1

G:\PROJECTS\2002\221379.0010\DWG\221379-BASE.DWG (kpatrickus) – FEB 26, 2003 – 08:09:49



USGS Windridge, and Rogersville, PA Quadrangles

0 500 1,000 2,000 3,000 4,000 Feet

● Sediment Sampling Stations

DWN. BY: Jeff Mihalik	CHK. BY: Bob Ventorini
SCALE: 1:24000	
DATE: 4/16/04	

ISSUED FOR: CONSOLENERGY

ISSUED BY:

CIVIL & ENVIRONMENTAL CONSULTANTS, INC.
333 Baldwin Road
Pittsburgh, PA 15205-9702
1-800-365-2324
Columbus, OH * Cincinnati, OH * Indianapolis, IN * Nashville, TN * Chicago, IL * St. Louis, MO * Export, PA

SEDIMENT SAMPLING LOCATIONS

CONSOL PENNSYLVANIA COAL COMPANY
GREENE COUNTY, PENNSYLVANIA

PROJECT NO.: 04-0148

FIGURE 1

Schroeder, Christina L LRP

From: Jageman, Tom [TomJageman@consolenergy.com]
Sent: Wednesday, September 07, 2005 1:51 PM
To: Schroeder, Christina L LRP
Cc: Shumaker, Todd; jmudge@cecinc.com
Subject: FW: Precision Data for Method 200.7
Attachments: 20050907095223166.pdf

Christina,
Attached are scanned pages indicating the precision that can be expected for low level selenium determinations in solid matrices when using US EPA's Method 200.7 - analysis by ICP-AES, the method that we used for analyzing the Bailey CRDA stream sediment samples. EPA's data indicate that when two environmental standards, EPA Hazardous Soil #884 and NBS 1645 River Sediment, were spiked with selenium at 20 mg/kg the relative percent difference between duplicate spikes was 52.4 % and 27.1 % respectively.

Because the 200.7 precision data was generated from duplicate analyses of a spiked standard; the data reflect only the variability associated with a single lab, single analyst for sample prep and instrument response. The sediment samples collected at the Bailey CRDA are grab samples collected at three month intervals from a dynamic stream bed and contain much lower concentrations of selenium than the spiked standards - as such, it should be expected that the measured selenium content of the sediments would display even greater variability than is documented in the 200.7 precision data. I believe the precision data contained in 200.7 indicate that the criteria for corrective action at the Bailey CRDA (+20% from the single Moody sample) is not workable. The variability in low level selenium in a solid matrix is not unique to analysis by ICP-AES - precision data from Method 200.8 (analysis by ICP-MS) and Method 200.9 (analysis by graphite furnace) indicate similar variability.

I will forward similar information for the PAH analysis as soon as I identify the extraction procedure that was used.

Tom

<<20050907095223166.pdf>>

METHOD 200.7

DETERMINATION OF METALS AND TRACE ELEMENTS IN WATER AND WASTES BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY

Revision 4.4
EMMC Version

USEPA-ICP Users Group (Edited by T.D. Martin and J.F. Kopp) - Method 200.7, Revision 1.0, (Printed 1979, Published 1982)

T.D. Martin and E.R. Martin - Method 200.7, Revision 3.0 (1990)

T.D. Martin, C.A. Brockhoff, J.T. Creed, and S.E. Long (Technology Applications Inc.) - Method 200.7, Revision 3.3 (1991)

T.D. Martin, C.A. Brockhoff, J.T. Creed, and EMMC Methods Work Group - Method 200.7, Revision 4.4 (1994)

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

TABLE 7: PRECISION AND RECOVERY DATA IN SOLID MATRICES

EPA HAZARDOUS SOIL #884

ANALYTE	SAMPLE CONC mg/kg	LOW+ SPIKE mg/kg	AVERAGE RECOVERY R(%)	S(R)	RPD	HIGH+ SPIKE mg/kg	AVERAGE RECOVERY R(%)	S(R)	RPD
Ag	1.1	20	98	0.7	1.0	100	96	0.2	0.6
Al	5080	20	*	*	7.2	100	*	*	5.4
As	5.7	20	95	5.4	10.6	100	96	1.4	3.6
B	20.4	100	93	2.7	5.3	400	100	2.1	5.5
Ba	111	20	98	71.4	22.2	100	97	10.0	1.0
Be	0.66	20	97	0.7	2.0	100	99	0.1	0.2
Ca	85200	-	-	-	-	-	-	-	-
Cd	2	20	93	0.7	1.0	100	94	0.2	0.4
Co	5.5	20	96	3.5	7.7	100	93	0.8	2.1
Cr	79.7	20	87	28.8	16.5	100	104	1.3	1.1
Cu	113	20	110	16.2	4.4	100	104	4.0	4.2
Fe	16500	-	-	-	-	-	-	-	-
Hg	<1.4	10	92	2.5	7.7	40	98	0.0	0.0
K	621	500	121	1.3	0.0	2000	107	0.9	1.8
Li	6.7	10	113	3.5	4.4	40	106	0.6	0.6
Mg	24400	500	*	*	8.4	2000	*	*	10.1
Mn	343	20	*	*	8.5	100	95	11.0	1.6
Mo	5.3	20	88	5.3	13.2	100	91	1.4	4.1
Na	195	500	102	2.2	2.4	2000	100	1.5	3.7
Ni	15.6	20	100	1.8	0.0	100	94	1.5	3.6
P	595	500	106	13.4	8.0	2000	103	3.2	2.7
Pb	145	20	88	51.8	17.9	100	108	15.6	17.4
Sb	6.1	20	83	3.9	7.5	100	81	1.9	5.9
Se	<5	20	79	14.7	52.4	100	99	0.7	2.1
Sn	16.6	20	91	34.6	5.8	80	112	8.7	2.8
Sr	102	100	84	9.6	10.8	400	94	2.5	4.6
Tl	<4	20	92	4.8	14.6	100	91	1.5	4.6
V	16.7	20	104	4.2	5.4	100	99	0.8	1.7
Zn	131	20	103	31.2	7.3	100	104	7.2	6.4

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.
- Not spiked.
+ Equivalent

TABLE 7: PRECISION AND RECOVERY DATA IN SOLID MATRICES (Cont.)

NBS 1645 RIVER SEDIMENT

ANALYTE	SAMPLE CONC mg/kg	LOW+ SPIKE mg/kg	AVERAGE RECOVERY R(%)	S(R)	RPD	HIGH+ SPIKE mg/kg	AVERAGE RECOVERY R(%)	S(R)	RPD
Ag	1.6	20	92	0.4	1.0	100	96	0.3	0.9
Al	5160	20	*	*	8.4	100	*	*	2.4
As	62.8	20	89	14.4	9.7	100	97	2.9	5.0
B	31.9	100	116	7.1	13.5	400	95	0.6	1.5
Ba	54.8	20	95	6.1	2.8	100	98	1.2	1.3
Be	0.72	20	101	0.4	1.0	100	103	1.4	3.9
Ca	28000	-	-	-	-	-	-	-	-
Cd	9.7	20	100	1.1	0.0	100	101	0.7	1.8
Co	9.4	20	98	3.8	4.8	100	98	0.9	1.8
Cr	28500	20	*	*	0.4	100	*	*	0.7
Cu	109	20	115	8.5	0.0	100	102	1.8	1.0
Fe	84800	-	-	-	-	-	-	-	-
Hg	3.1	10	99	4.3	7.7	40	96	0.7	1.0
K	452	500	98	4.1	2.0	2000	106	1.4	2.3
Li	3.7	10	101	2.0	0.7	40	108	1.3	3.0
Mg	6360	500	*	*	1.8	2000	93	2.7	1.0
Mn	728	20	*	*	3.5	100	97	12.4	2.2
Mo	17.9	20	97	12.5	18.5	100	98	0.6	0.0
Na	1020	500	92	2.6	0.0	2000	97	1.1	1.7
Ni	36.2	20	94	5.9	4.0	100	100	1.1	1.5
P	553	500	102	1.4	0.9	2000	100	0.8	1.6
Pb	707	20	*	*	0.8	100	103	5.9	0.4
Sb	22.8	20	86	2.3	0.0	100	88	0.6	0.9
Se	6.7	20	103	14.3	27.1	100	98	3.1	7.6
Sn	309	20	*	*	1.0	100	101	7.9	2.7
Sr	782	100	91	12.3	3.0	400	96	3.3	2.6
Tl	<4	20	90	0.0	0.0	100	95	1.3	4.0
V	20.1	20	89	5.4	5.8	100	98	0.7	0.0
Zn	1640	20	*	*	1.8	100	*	*	1.1

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.
- Not spiked.
+ Equivalent

TABLE 9 : PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES (Cont).

SEWAGE TREATMENT PRIMARY EFFLUENT

Element	Sample Concn. (µg/L)	Low Spike (µg/L)	Average Recovery R (%)	S(R)	RPD	High Spike (µg/L)	Average Recovery R (%)	S(R)	RPD
Al	1150	50	*	*	3.5	200	100.0	13.8	1.5
Sb	1.5	10	95.7	0.4	0.9	100	104.5	0.7	1.9
As	<1.4	50	104.2	4.5	12.3	200	101.5	0.7	2.0
Ba	202	50	79.2	9.9	2.5	200	108.6	4.6	5.5
Be	<0.3	10	110.5	1.8	4.5	100	106.4	0.4	0.9
Cd	9.2	10	101.2	1.3	0.0	100	102.3	0.4	0.9
Cr	128	10	*	*	1.5	100	102.1	1.7	0.4
Co	13.4	10	95.1	2.7	2.2	100	99.1	1.1	2.7
Cu	171	10	*	*	2.4	100	105.2	7.1	0.7
Pb	17.8	10	95.7	3.8	1.1	100	102.7	1.1	2.5
Mn	199	10	*	*	1.5	100	103.4	2.1	0.7
Mo	136	10	*	*	1.4	100	105.7	2.4	2.1
Ni	84.0	10	88.4	16.3	4.1	100	98.0	0.9	0.0
Se	<7.9	50	112.0	10.9	27.5	200	108.8	3.0	7.8
Ag	10.9	50	97.1	0.7	1.5	200	102.6	1.4	3.7
Tl	<0.3	10	97.5	0.4	1.0	100	102.0	0.0	0.0
Th	0.11	10	15.4	1.8	30.3	100	29.3	0.8	8.2
U	0.71	10	109.4	1.8	4.3	100	109.3	0.7	1.8
V	<2.5	50	90.9	0.9	0.6	200	99.4	2.1	6.0
Zn	163	50	85.8	3.3	0.5	200	102.0	1.5	1.9

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

TABLE 10 : PRECISION AND RECOVERY DATA IN SOLID MATRICES (Cont).

NBS 1645 RIVER SEDIMENT

Element	Sample Concn. (mg/kg)	Low+ Spike (mg/kg)	Average Recovery R (%)	S(R)	RPD	High+ Spike (mg/kg)	Average Recovery R (%)	S(R)	RPD
Al	5060	20	*	*	-	100	*	*	-
Sb	21.8	20	73.9	6.5	9.3	100	81.2	1.5	3.9
As	67.2	20	104.3	13.0	7.6	100	107.3	2.1	2.9
Ba	54.4	20	105.6	4.9	2.8	100	98.6	2.2	3.9
Be	0.59	20	88.8	0.2	0.5	100	87.9	0.1	0.2
Cd	8.3	20	92.9	0.4	0.0	100	95.7	1.4	3.9
Cr	29100	20	*	*	-	100	*	*	-
Co	7.9	20	97.6	1.3	2.6	100	103.1	0.0	0.0
Cu	112	20	121.0	9.1	1.5	100	105.2	2.2	1.8
Pb	742	20	*	*	-	100	-	-	-
Mn	717	20	*	*	-	100	-	-	-
Mo	17.1	20	89.8	8.1	12.0	100	98.4	0.7	0.9
Ni	41.8	20	103.7	6.5	4.8	100	102.2	0.8	0.0
Se	<3.2	20	108.3	14.3	37.4	100	93.9	5.0	15.1
Ag	1.8	20	94.8	1.6	4.3	100	96.2	0.7	1.9
Tl	1.2	20	91.2	1.3	3.6	100	94.4	0.4	1.3
Th	0.90	20	91.3	0.9	2.6	100	92.3	0.9	2.8
U	0.79	20	95.6	1.8	5.0	100	98.5	1.2	3.5
V	21.8	20	91.8	4.6	5.7	100	100.7	0.6	0.8
Zn	1780	20	*	*	-	100	*	*	-

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.
- Not determined.
+ Equivalent.

TABLE 10 : PRECISION AND RECOVERY DATA IN SOLID MATRICES

EPA HAZARDOUS SOIL #884

Element	Sample Concn. (mg/kg)	Low+ Spike (mg/kg)	Average Recovery R (%)	S(R)	RPD	High+ Spike (mg/kg)	Average Recovery R (%)	S(R)	RPD
Al	5170	20	*	*	-	100	*	*	-
Sb	5.4	20	69.8	2.5	4.7	100	70.4	1.8	6.5
As	8.8	20	104.7	5.4	9.1	100	102.2	2.2	5.4
Ba	113	20	54.9	63.6	18.6	100	91.0	9.8	0.5
Be	0.6	20	100.1	0.6	1.5	100	102.9	0.4	1.0
Cd	1.8	20	97.3	1.0	1.4	100	101.7	0.4	1.0
Cr	83.5	20	86.7	16.1	8.3	100	105.5	1.3	0.0
Co	7.1	20	98.8	1.2	1.9	100	102.9	0.7	1.8
Cu	115	20	86.3	13.8	3.4	100	102.5	4.2	4.6
Pb	152	20	85.0	45.0	13.9	100	151.7	25.7	23.7
Mn	370	20	*	*	12.7	100	85.2	10.4	2.2
Mo	4.8	20	95.4	1.5	2.9	100	95.2	0.7	2.0
Ni	19.2	20	101.7	3.8	1.0	100	102.3	0.8	0.8
Se	<3.2	20	79.5	7.4	26.4	100	100.7	9.4	26.5
Ag	1.1	20	96.1	0.6	0.5	100	94.8	0.8	2.3
Tl	0.24	20	94.3	1.1	3.1	100	97.9	1.0	2.9
Th	1.0	20	69.8	0.6	1.3	100	76.0	2.2	7.9
U	1.1	20	100.1	0.2	0.0	100	102.9	0.0	0.0
V	17.8	20	109.2	4.2	2.3	100	106.7	1.3	2.4
Zn	128	20	87.0	27.7	5.5	100	113.4	12.9	14.1

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.
- Not determined.
+ Equivalent.

Schroeder, Christina L LRP

From: Jageman, Tom [TomJageman@consolenergy.com]
Sent: Tuesday, September 13, 2005 5:16 PM
To: Schroeder, Christina L LRP
Cc: jmudge@cecinc.com; Shumaker, Todd
Subject: Precision Data for SW 846 8270C
Attachments: 20050913164758173.pdf

Christina,
Attached are scanned pages indicating the precision that can be expected for low level PAH determinations in solid matrices when using SW 8270C - analysis of extracted PAH by GC-MS, the method we used for analyzing the Bailey CRDA stream sediment samples. EPA's data indicated that when two environmental standards (EC-1 and

HS-3) were extracted by Method 3561 and analyzed four times each the average recovery for the various PAH compounds ranged from 85 to 148 % of the 'known' values for EC-1 and from 82 to 133 % for HS-3. The RSD for individual PAH compounds in the four replicate analyses ranged from 0.05 to 18.2 % for EC-1 and 8.1 to 27.3 % for HS-3.

As with the selenium precision data previously provided, the variability demonstrated in EPA's tables indicates only the variability associated with a single lab, single analyst for sample prep and instrument response for a single environmental standard. Because the Bailey sediment samples are collected at three month intervals from a dynamic stream bed, it should be expected that they will have even greater variability than is documented in the 8270C precision tables. As with the selenium data, I believe the 8270C precision data indicates the PAH criteria for corrective action at the Bailey CRDA (+20 % from the single Moody sample) is not workable.

Thanks for considering this data in your evaluation.

Tom

<<20050913164758173.pdf>>

TABLE 13

SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SEDIMENT EC-1, USING METHOD 3561 (SFE - SOLID TRAP)

Compound	Certified Value (mg/kg)	SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	(27.9)[b]	41.3 ± 3.6	(148)	8.7
Acenaphthylene	(0.8)	0.9 ± 0.1	(112)	11.1
Acenaphthene	(0.2)	0.2 ± 0.01	(100)	0.05
Fluorene	(15.3)	15.6 ± 1.8	(102)	11.5
Phenanthrene	15.8 ± 1.2	16.1 ± 1.8	102	11.2
Anthracene	(1.3)	1.1 ± 0.2	(88)	18.2
Fluoranthene	23.2 ± 2.0	24.1 ± 2.1	104	8.7
Pyrene	16.7 ± 2.0	17.2 ± 1.9	103	11.0
Benz(a)anthracene	8.7 ± 0.8	8.8 ± 1.0	101	11.4
Chrysene	(9.2)	7.9 ± 0.9	(86)	11.4
Benzo(b)fluoranthene	7.9 ± 0.9	8.5 ± 1.1	108	12.9
Benzo(k)fluoranthene	4.4 ± 0.5	4.1 ± 0.5	91	12.2
Benzo(a)pyrene	5.3 ± 0.7	5.1 ± 0.6	96	11.8
Indeno(1,2,3-cd)pyrene	5.7 ± 0.6	5.2 ± 0.6	91	11.5
Benzo(g,h,i)perylene	4.9 ± 0.7	4.3 ± 0.5	88	11.6
Dibenz(a,h)anthracene	(1.3)	1.1 ± 0.2	(85)	18.2

[a] Relative standard deviations for the SFE values are based on six replicate extractions.

[b] Values in parentheses were obtained from, or compared to, Soxhlet extraction results which were not certified

Data are taken from Reference 10.

TABLE 14

SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SEDIMENT HS-3, USING METHOD 3561 (SFE - SOLID TRAP)

Compound	Certified Value (mg/kg)	SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	9.0 ± 0.7	7.4 ± 0.6	82	8.1
Acenaphthylene	0.3 ± 0.1	0.4 ± 0.1	133	25.0
Acenaphthene	4.5 ± 1.5	3.3 ± 0.3	73	9.0
Fluorene	13.6 ± 3.1	10.4 ± 1.3	77	12.5
Phenanthrene	85.0 ± 20.0	86.2 ± 9.5	101	11.0
Anthracene	13.4 ± 0.5	12.1 ± 1.5	90	12.4
Fluoranthene	60.0 ± 9.0	54.0 ± 6.1	90	11.3
Pyrene	39.0 ± 9.0	32.7 ± 3.7	84	11.3
Benz(a)anthracene	14.6 ± 2.0	12.1 ± 1.3	83	10.7
Chrysene	14.1 ± 2.0	12.0 ± 1.3	85	10.8
Benzo(b)fluoranthene	7.7 ± 1.2	8.4 ± 0.9	109	10.7
Benzo(k)fluoranthene	2.8 ± 2.0	3.2 ± 0.5	114	15.6
Benzo(a)pyrene	7.4 ± 3.6	6.6 ± 0.8	89	12.1
Indeno(1,2,3-cd)pyrene	5.0 ± 2.0	4.5 ± 0.6	90	13.3
Benzo(g,h,i)perylene	5.4 ± 1.3	4.4 ± 0.6	82	13.6
Dibenz(a,h)anthracene	1.3 ± 0.5	1.1 ± 0.3	85	27.3

[a] Relative standard deviations for the SFE values are based on three replicate extractions.

Data are taken from Reference 10.

email a copy of this report to Consol + CEC

Review of
Review of "Sediment Evaluation of Enlow Fork and Tributaries for the First through Fourth Quarters of 2004, Bailey Mine-New Refuse Disposal Facility, Consol Pennsylvania Coal Company, CEC Project 040-148, February 10, 2005"

BACKGROUND/ METHODS

Sampling, testing, and evaluation of the sediments of Enlow Fork and tributaries of Enlow Fork were required by Special Condition 10 of USACE Section 401 Permit No. 200200371, issued on November 26, 2003.

Sampling Sites and Parameters Analyzed

Samples were collected at 7 sites (Table 1). Sampling at five of these sites was initiated prior to 2004 (#14, 11, 10, 12, & 13). During the 2004, samples were also collected at 2 control sites assumed to be representative of background conditions, located upstream of all Consol activity: one on Enlow Fork and a second located on the North Fork of Enlow Fork in Simpson Creek, PA (sampling sites 16 and 15, respectively). Although sampling sites 12 and 13 were located upstream of the Talley run discharge, they cannot be considered representative of background conditions since they are located adjacent to, and could possibly receive drainage from, the Consol site.

Table 1
Sediment Sampling Sites

Site #	Stream	Location
14	Enlow Fork	6500 feet downstream of the Talley Run discharge
11	Enlow Fork	1200 feet downstream of the Talley Run discharge
10	Talley Run	Talley Run discharge
12	Enlow Fork	400 feet upstream of the Talley Run discharge, adjacent to the Consol site
13	Enlow Fork	4000 feet upstream of the Talley Run discharge, adjacent to Consol site
15	North Fork Enlow	upstream of all Consol activity in the town of Simpson Creek, PA
16	Enlow Fork	upstream of all Consol activity

Surface sediment samples were collected at each sampling site (0 to 4 inches) and were analyzed for total Selenium, TCLP selenium, PAHs, Total organic carbon (TOC), grain size, and percent solids. Companion water samples were analyzed for specific conductivity, pH, dissolved oxygen (DO), and water temperature.

Sampling Frequency

On September 4, 2001, pre construction sediment data were collected by the US Fish and Wildlife Service (USFWS) at two of the 7 sites, one located upstream and the other downstream of the Talley Run discharge (sites 12 and 14, respectively). On November 19, 2002, Consol (Moody and Associates Inc.) collected samples from all sites except the two control sites (16 and 15). From the start of construction in 2004, sediment samples were collected quarterly by Moody and Associates Inc: March 24, June 22, September 16, and December 15, 2004.

DATA REVIEW/ RESULTS

Data Quality

Duplicate samples were collected at site 10 on June 22 & at site 14 on Dec 15, 2004. Results of duplicate samples for selenium analyses were acceptable. However, results of

analyses of PAH duplicate samples were questionable. The percent difference between duplicate PAHs ranged between 59 and 273%. This may be an indication of inconsistent sampling techniques, laboratory protocol, or accuracy may have been limited by low detection limits.

PAHs

Total PAH concentrations by stream mile are presented in **Figure 1.** As can be seen in this Figure, there is a definite trend towards increasing concentrations downstream of the control sites (Sites #15 and #16).

PAH results are also presented by sampling site in **Figure 2.** Trend lines for each sampling site over time are also shown in Figure 2. As can be seen in this figure, while there was no change in the trend line at the 2 control sites, there was a decreasing trend was observed at sites 12 and 14, an increasing trend at sites 10 and 11, and a decreasing trend at site 14. However, these data show extreme variation in concentrations observed at all sampling sites throughout the study period (particularly on 6/22/04). As demonstrated in **Figure 3**, because organic compounds bind to fine sediments but not to coarser sands and gravels, analyses of 2004 samples with the higher the % fines also have the highest concentrations of PAHs, no matter where the samples were collected. Therefore, it is likely that erratic PAH concentrations observed over the study period were likely attributable to the % fines and clay in the samples.

Results of the USFW preconstruction survey were orders of magnitude greater than those of Consol's (Moody) 2004 surveys at the same locations. For example 170,353 ug/kg and 1300 ug/kg total PAH were documented at sampling site 12 by the USFWS in 2001 and by Moody in 2004, respectively. Of note, USFWS' TOC concentrations ranged between 14 to 18% while Consol's results from the same sites ranged between 1 and 3%. Differences observed in the data sets could be related to % fines or could also be related to which side of the stream the samples were collected.

Because the goal of Special Condition 10 is to assure compliance with NEPA (no environmental degradation), if data are to be compared to available criteria, it would be more appropriate to use the Lowest Effects Level (**LEL**) guidelines rather than the Severe Effects Level (**SEL**) guidelines. While the SEL guidelines "provide an accurate basis for **predicting the absence sediment toxicity**", the SEL provide an "...accurate basis for **predicting sediment toxicity"** (MacDonald et. al.). LEL = clean to marginally polluted and SEL = heavily polluted.

Sediment data are compared to LEL and SEL guidelines in **Table 2**. While no exceedences of the SEL guidelines were observed in the 2004 data, the total PAH concentrations observed by the USFWS in 2001 at site 12 (400 feet upstream of the Talley Run discharge) did exceed the SEL criteria. In addition, the LEL sediment quality guideline for total PAHs was exceeded at sampling sites located downstream of the 2 control sites, showing a trend towards degradation.

Table 2

Comparison of Total PAH Concentrations (ug/kg) with Sediment Quality Guidelines

Exceeded Lowest Effects Level (LEL) Criteria 4000 ug/kg = Yellow Highlight

Exceeded Consensus based Threshold Effects Concentration TEC (harmful Effects Unlikely) 1610 ug/kg = Green Highlight

Exceeded Severe Effects Level (SEL) Criteria 100000 ug/kg (unadjusted) = Orange Highlight

Exceeded Probable Effect Concentration (PEC) (Harmful Effects Likely) Criteria 22800 ug/kg (unadjusted) = Red Highlight

Total PAH ug/kg

Site #	9/4/01	11/19/02				3/24/04	6/22/04	6/22/04	9/16/04	12/15/04
	T. PAH	T. PAH	TOC	TOC adjusted SEL	TOC adjusted PEC	T. PAH	T. PAH	T. PAH	T. PAH	T. PAH
14	[illegible]	4800	0.46	460	52.44	1190	1545		2693	2918
11		1500	1.28	1280	291.84	5355	926		4029	1634
10		1300	1.22	1220	278.16	4122	268	616	2587	8838
12	[illegible]	1300	0.7	700	159.6	2275	490		606	708
13		1300	0.55	550	125.4	1588	1117		363	1083
15						544	87		272	466
16						73	103		132	84

Selenium

As suggested in Appendix B of Consol's February 3, 2005 letter to the District, results of selenium analyses do not show a clear increase in concentrations in Enlow Fork downstream of existing treatment facility when compared to upstream values **(Figure 4).**

Again, comparison with SQGs is not recommended but some discussion is pertinent. While there are no regulatory guidelines for selenium in sediments, 4.0 mg/kg is frequently cited for the potential for bioaccumulation (http://ks.water.usgs.gov/Kansas/pubs/abstracts/vg.030100.html). In addition, site specific criteria can be even more stringent depending on aquatic life impacts. For example, the selenium SQG recommended for San Francisco Bay is 1.4 mg/kg (http://www.sfei.org/rmp/1997/c0401.htm). As can be seen in **Figure 4**, selenium spikes as high as 3.2 mg/kg were documented downstream of the Talley Run discharge. It is therefore recommended that selenium monitoring be continued to assure documentation of trends over time.

RECOMMENDATIONS/ CONCLUSIONS:

- Continue the PAH and selenium sediment sampling program as agreed, with modifications suggested below. The trigger (a 20% increase) should not be modified based on the results of the first year of study since four sets of data are insufficient for trend analyses.
- Encourage consistency in sampling techniques to assure comparability of results. Samples should be collected from the top few inches rather than the top 4 inches and from the side of the stream that is adjacent to the Consol site (the left descending bank for Enlow Fork, for example) to assure that only new depositional material is collected. Also, as demonstrated in **Table 4** and discussed above, it is easy to bias results simply by collecting coarser material. Recommend that all samples collected have the same % fines (>40%).
- Request a map showing:

1. all streams (Enlow Fork, the North Fork of Enlow Fork, Talley Run, Fletcher Run, Grinnage Run, Owens Run, unnamed tributary to Owens Run, and any other unnamed tributaries mentioned in correspondences)
2. all existing and/or proposed coal slurry dams and sedimentation and/or treatment ponds
3. outfalls from sedimentation and/or treatment ponds
4. seeps draining into Enlow Fork from areas with old or recent fill
5. new and old coal refuse disposal facilities
6. sediment and water sampling sites
7. mitigation wetlands

- Because Consol questioned the ability to identify sources of elevated concentrations of PAHs and selenium (more specifically, activity at their new facility, Feb 2003) with the existing sampling site network, recommend that an additional sampling site on Enlow Fork be added. This site should be located upstream of the North Fork and all Simpson Store, PA municipal outfalls, and downstream of the most upstream edge of the new fill site. It is expected that data from this site would capture impacts from outfalls and runoff from the new fill areas. Once a map showing all streams, activities and outfalls is provided, the location of the new sampling site location can be refined.
- Request a copy of all of Consol's 2004 TOC results of analyses.
- For future reviews, conduct all statistical analyses on raw, not adjusted data.
- Utilize only sampling sites 15 and 16 as representative of background conditions
- Request a description of coal slurry treatment (sedimentation only or chemical treatment?) ponds, including sizes and flow from outfalls.
- Comparison of results with sediment quality guidelines (SQGs) is not recommended since the intent of this Special Condition 10 sediment quality survey is to provide assurance of non-degradation (compliance with NEPA) and effectiveness of treatment. However, since Consol did compare results to SQGs:
    1. Request an explanation /specific reference for adjustment of the **data** rather than the **criteria** by % TOC. I was unable to find reference to data adjustment in MacDonald, Ingersoll, and Berger's paper, "Development and Evaluation of Consensus-based Sediment Quality Guidelines for Freshwater Ecosystems", referenced by Consol. However, adjustment of the SEL **criteria** by % TOC is recommended for the Ontario Sediment Quality standards. These recommended adjustments for TOC will **decrease the criteria value** the lower the % TOC of the sample, rather than **decrease the concentration of contaminants in the sample**.
    2. Encourage comparison with the Low Effects Level (LEL) rather than the Severe Effects Level (SEL) sediment quality guidelines.
- Request from PA copies of Section 401 NPDES permit quarterly data submissions to keep tabs on water quality trends (conductivity, metals, sulfate, and suspended solids), including locations of ground and surface water quality sampling sites.
- Request from the USFWS their 2001 sediment quality data (sample location, units, sample protocol, % fines, etc.).

Figure 1
Total PAHs by Stream Mile
From the Most Downstream Sampling Site (# 14) to the Most Upstream (#16)
2001, 2002, and 2004

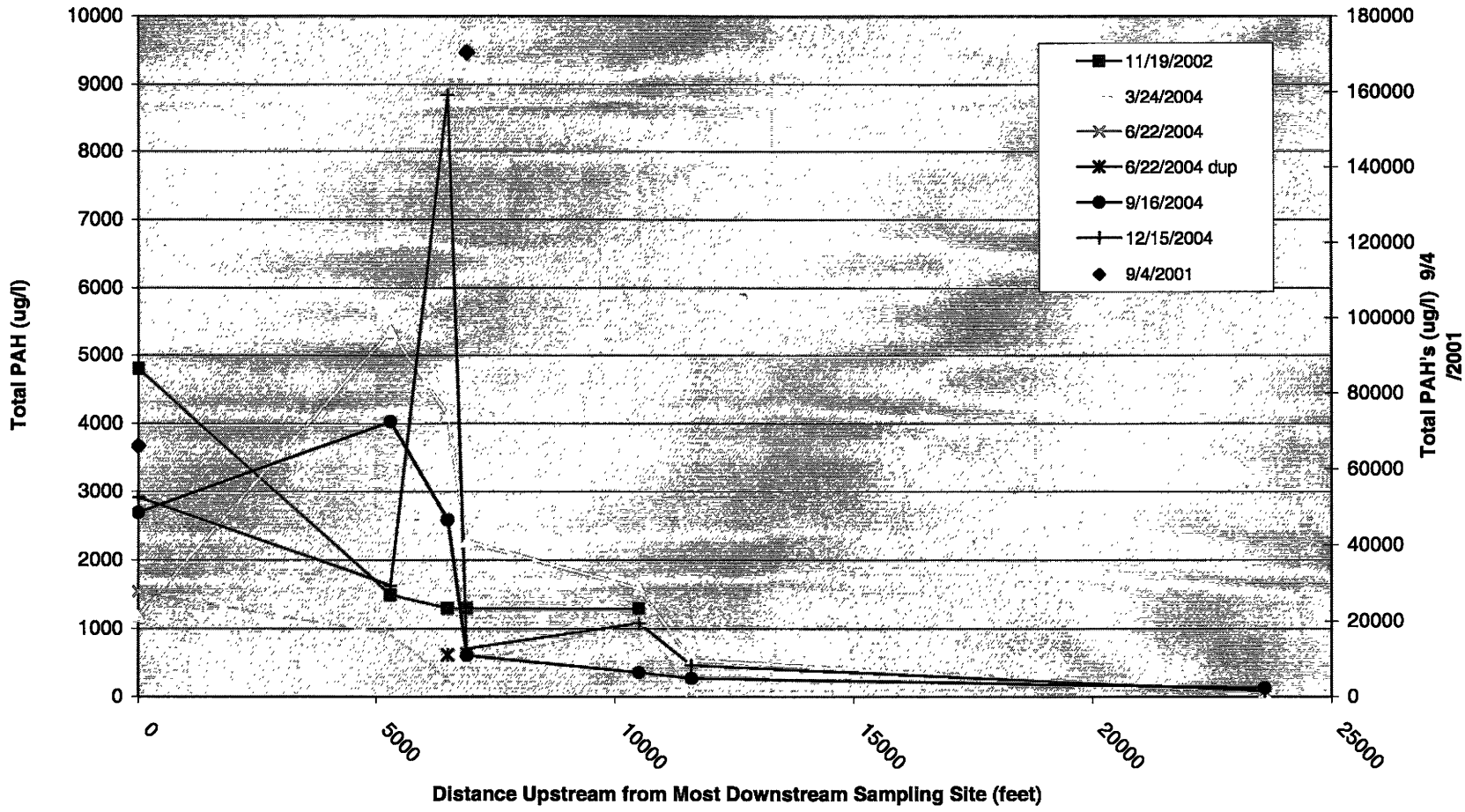


Figure 2
Total PAHs by Site and Date With Trend Lines (dotted lines)
2002 to 2004

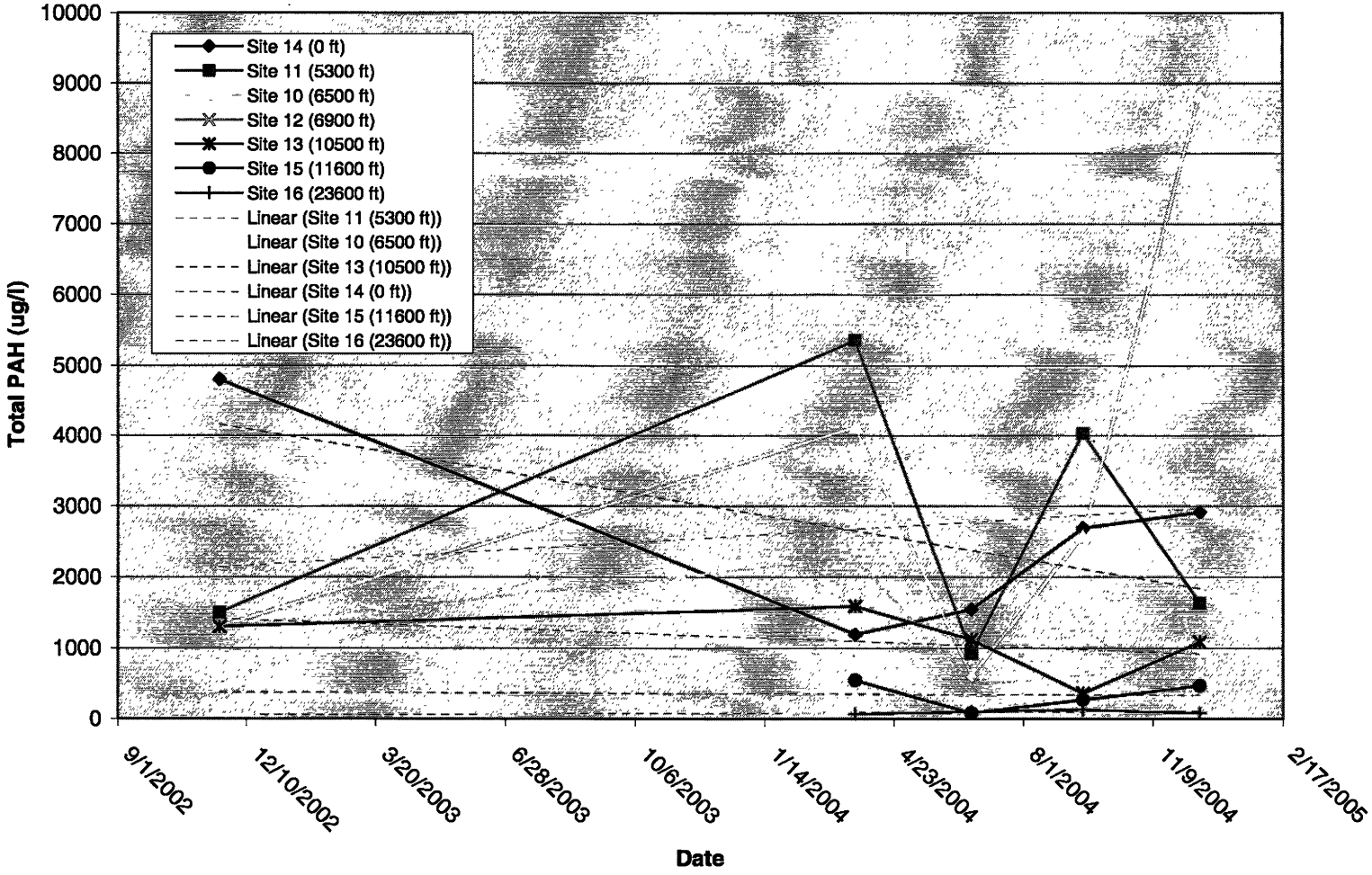


Figure 3
Enlow Fork Consol Coal
% Silt, % clay and Total PAH at Sampling Sites 11 and 12

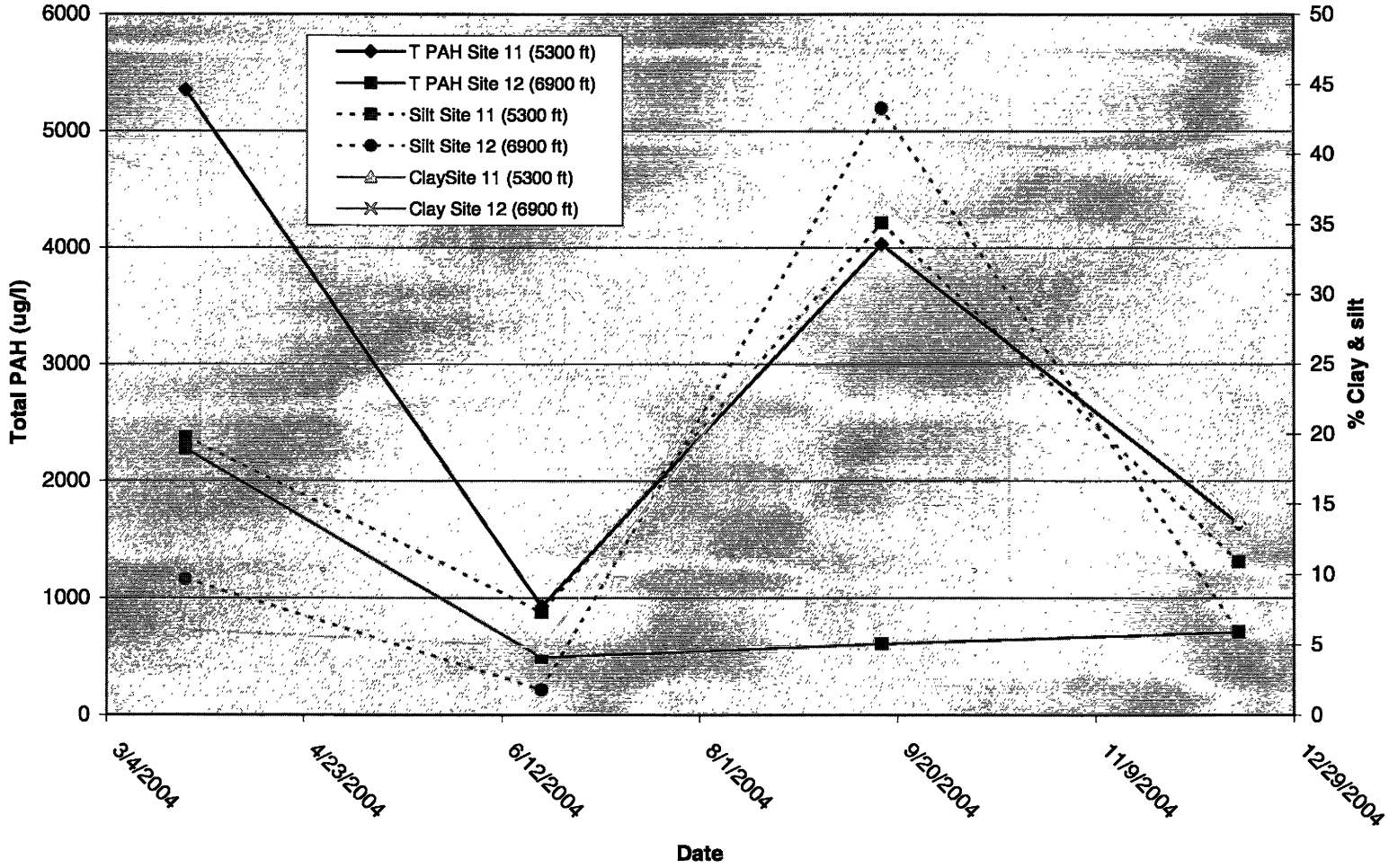
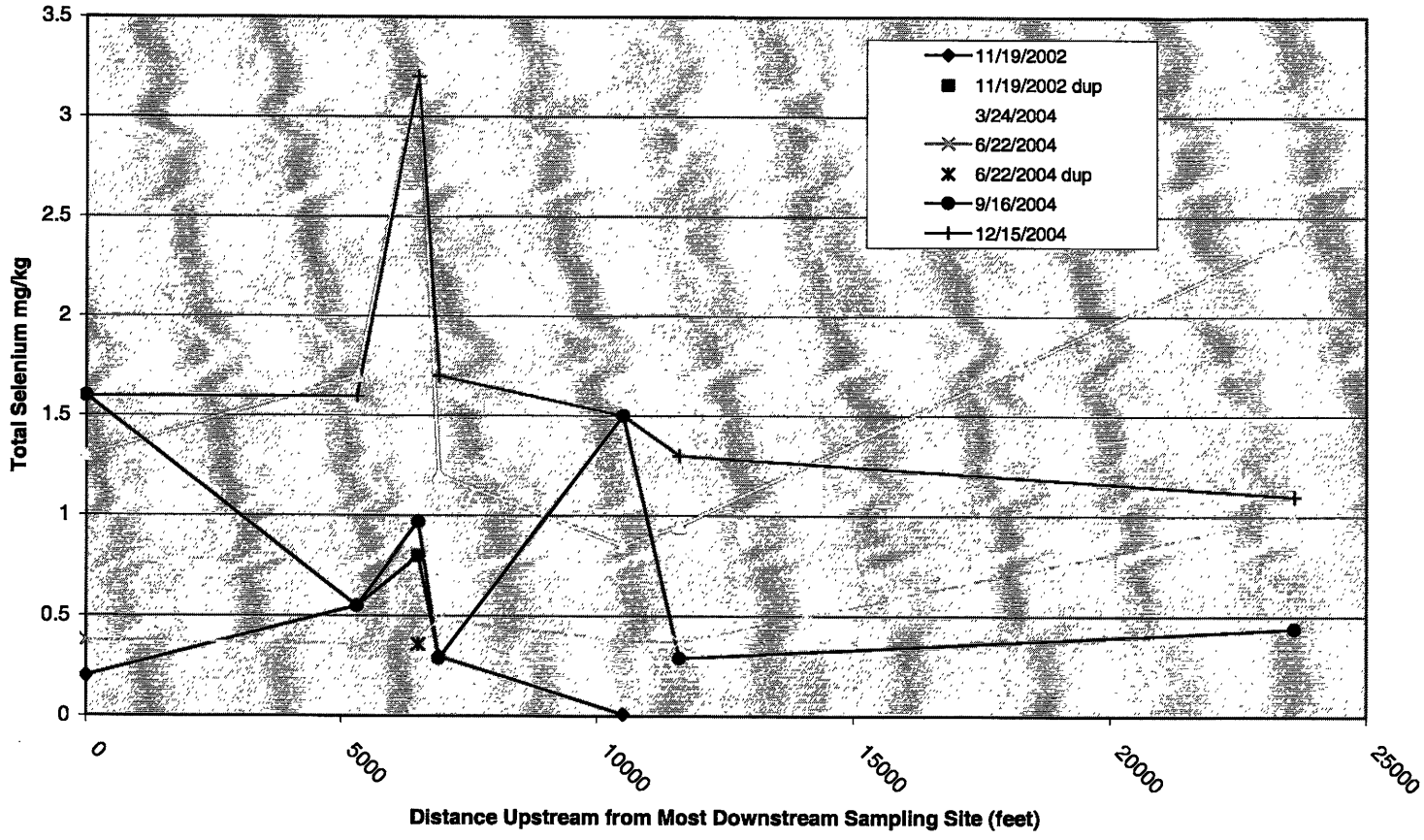
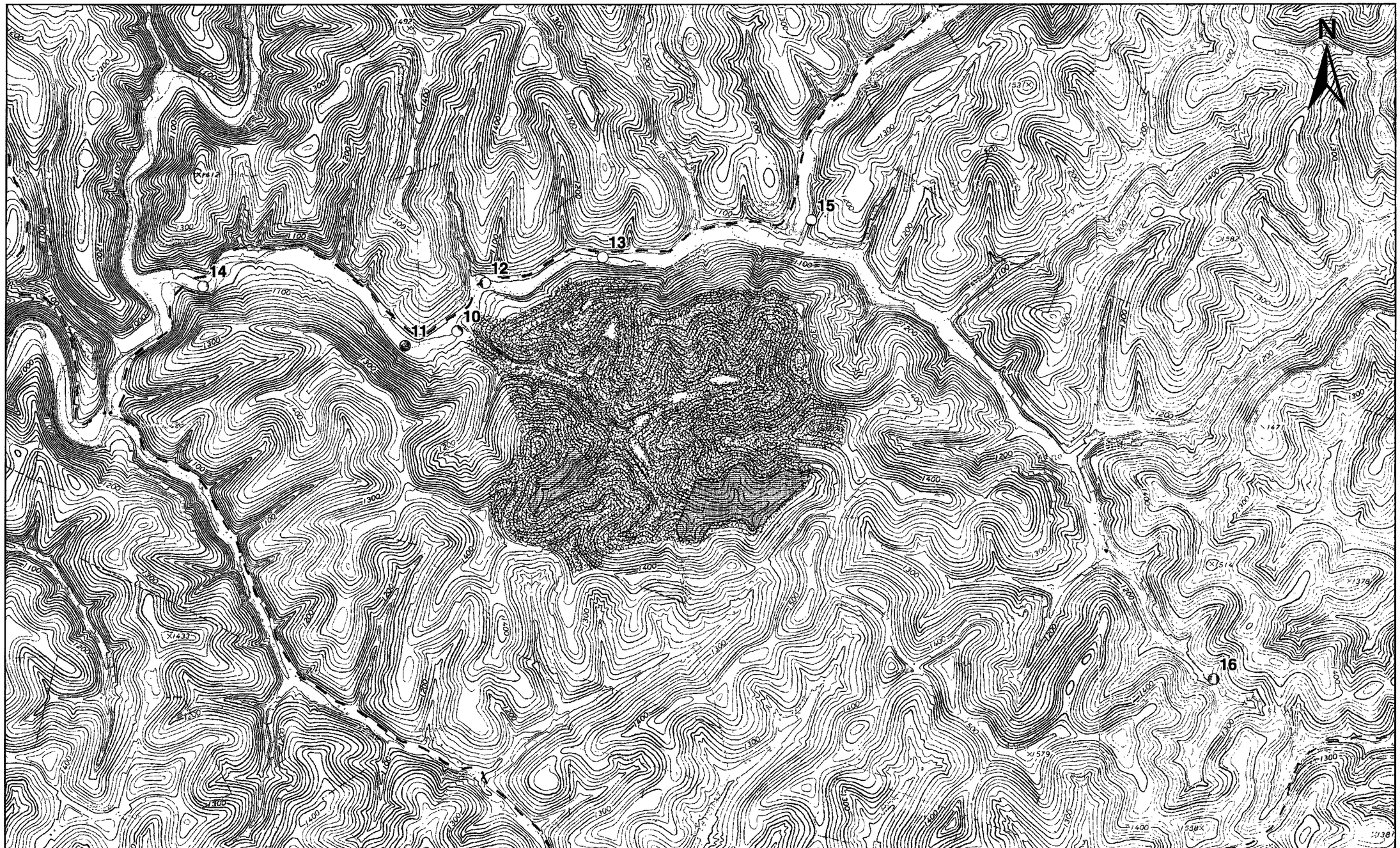


Figure 4
Total Selenium by Stream Mile
From the Most Downstream Sampling Site (#11) to the Most Upstream (#16)
2002 and 2004



REFERENCES

McDonald, D.D. and C. G. Ingersoll, T.A. Berger, 2000. Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Ecosystems. Environmental Contamination and Toxicity, 39, 20-31



USGS Windridge, and Rogersville, PA Quadrangles

0 2,000 4,000 Feet

● Sediment Sampling Stations

DWN. BY: Jeff Mihalik	CHK. BY: Bob Ventorini
SCALE: 1:24000	
DATE: 4/16/04	

ISSUED FOR: CONSOL ENERGY

ISSUED BY:

CIVIL & ENVIRONMENTAL CONSULTANTS, INC.
333 Baldwin Road
Pittsburgh, PA 15205-9702
1-800-365-2324
Columbus, OH * Cincinnati, OH * Indianapolis, IN * Nashville, TN * Chicago, IL * St. Louis, MO * Export, PA

SEDIMENT SAMPLING LOCATIONS
CONSOL PENNSYLVANIA COAL COMPANY
RICHHILL AND GRAY TOWNSHIPS, GREENE COUNTY, PENNSYLVANIA

PROJECT NO.: 040-148 FIGURE 1

J:\Projects\2004\040148\gps.mxd - 9/6/2005 @ 9:07:46 AM

DEPARTMENT OF THE ARMY PERMIT

Jeff, this report is a requirement of special condition No. 10. Please read + call me to discuss. A memo to the record would probably be appropriate. Thanks, Christy x7375

PERMITTEE: Consol Pennsylvania Coal Company

PERMIT NUMBER: 200200371

NOTE: The term you and its derivatives, as used in this permit, means the permittee or any future transferee. The term "this office" refers to the appropriate district or division office of the Corps of Engineers having jurisdiction over the permitted activity under the authority of the commanding officer.

You are authorized to perform work in accordance with the terms and conditions specified below.

PROJECT DESCRIPTION: Consol Pennsylvania Coal Company, 1800 Washington Road; Pittsburgh, PA 15241-1421, IS HEREBY AUTHORIZED BY THE SECRETARY OF THE ARMY TO: PLACE FILL INTO 1.37 ACRES OF WETLAND AND 13,198 LINEAR FEET OF PERENNIAL AND INTERMITTENT STREAM CHANNEL FOR THE CONSTRUCTION OF A NEW COAL REFUSE DISPOSAL FACILITY IN ACCORDANCE WITH THE GENERAL AND SPECIAL CONDITIONS, AND THE PLANS AND DRAWINGS AND ANY ADDITIONAL SPECIAL CONDITIONS ATTACHED HERETO WHICH ARE INCORPORATED IN AND MADE A PART OF THIS PERMIT.

PROJECT LOCATION: THE PROJECT IS LOCATED in unnamed tributaries and wetlands adjacent to unnamed tributaries to Enlow Fork, near West Finley, in Richhill Township and Gray Township, Greene County, Pennsylvania.

PERMIT CONDITIONS

GENERAL CONDITIONS:

1. The time limit for completing the work authorized ends on **November 26, 2013**. If you find that you need more time to complete the authorized activity, submit your request for a time extension to this office for consideration at least one month before the above date is reached.

2. You must maintain the activity authorized by this permit in good condition and in conformance with the terms and conditions of this permit. You are not relieved of this requirement if you abandon the permitted activity, although you must make a good faith transfer to a third party in compliance with General Condition 4 below. Should you wish to cease to maintain the authorized activity, or should you desire to abandon it without a good faith transfer, you may obtain a modification of this permit from this office, which may require restoration of the area.

3. If you discover any previously unknown historic or archaeological remains while accomplishing the activity authorized by this permit, you must immediately notify this office of what you have found. We will initiate the Federal and state coordination required to determine if the remains warrant a recovery effort or if the site is eligible for listing in the National Register of Historic Places.

4. If you sell the property associated with this permit, you must obtain the signature of the new owner in the space provided and forward a copy of the permit to this office to validate the transfer of this authorization.

5. If a conditioned water quality certification has been issued for your project, you must comply with the conditions specified in the certification as special conditions to this permit.

6. You must allow representatives from this office to inspect the authorized activity at any time deemed necessary to ensure that it is being or has been accomplished in accordance with the terms and conditions of your permit.

7. The permittee understands and agrees that, if future operations by the United States require the removal, relocation, or other alteration of the structure or work herein authorized, or if, in the opinion of the Secretary of the Army or his authorized representative, said structure or work shall cause unreasonable obstruction to the free navigation of the navigable waters, the permittee will be required, upon due notice from the Corps of Engineers, to remove, relocate, or alter the structural work or obstructions caused thereby, without expense to the United States. No claim shall be made against the United States on account of any such removal or alteration.

8. A copy of this permit must be kept at the work site at all times and made available to all contractors and subcontractors.

SPECIAL CONDITIONS:

1. In accordance with Pennsylvania Historical and Museum Commission letter dated November 7, 2003, the permittee is required to:

a. Update, analyze, and integrate 1978 survey findings of an adjacent area north of the APE by Pennsylvania State University, Department of Anthropology with this project's data and prepare a final report which is to be provided to the PHMC office by November 7, 2004.

b. Develop a prehistoric settlement model for the Enlow Fork region to be completed no later than November 7, 2004.

c. Create a web page explaining the significance of Native American settlements on the Enlow Fork and have the page completed by November 7, 2004.

d. Submit a written agreement for site no. 36GR273 to the PHMC by November 21, 2003 stating that a Memorandum of Agreement (MOA) will be written and signed by February 7, 2004.

e. Submit an MOA which includes a data recovery plan for site nos. 36GR268, 36GR269, and 36GR272. This MOA must be signed by February 7, 2004. If data recovery on these three sites becomes necessary, all fieldwork, analysis, reporting, and accessioning of collections must be completed no later than November 7, 2005.

f. The Corps must be included as a signatory to the MOAs.

2. The wetland mitigation proposal, submitted by CEC, dated April 28, 2003 which outlines the creation of 1.54 acres of replacement wetlands and the enhancement of 0.30 acre of riparian habitat, must be performed prior to or within one year from the start of the placement of fill for the new refuse disposal facility.

3. The wetland monitoring plan submitted by CEC, dated April 28, 2003, must be implemented with copies of all monitoring reports provided to this office within 60 days of each monitoring event.

4. Surveyed as-built drawings of the wetland mitigation must be provided to this office with the first, third, and final monitoring report.

5. A draft conservation easement for the preservation of 4.86 acres of existing wetland must be provided to this office prior to the start of construction. The Corps will review and approve the terms of the conservation easement prior to recording of the easement at the county courthouse. The easements must be recorded at the county courthouse within 60 days from the date of permit issuance.

6. The stream mitigation proposal, revised March 2003, which included a minimum of 12.5 miles of streambank fencing with controlled crossings, establishment of 100-acres of native grasslands, creation of 20 border-edge cuts, and monitoring, must be implemented as proposed. Copies of the final comprehensive mitigation plan and monitoring reports must be submitted to the Corps for final approval within 60 days of permit issuance or prior to the start of construction. All stream mitigation projects must be completed within one year from the start

of the placement of fill for the new refuse disposal facility.

7. The permittee is required to monitor water quality, riparian plant, fish and macroinvertibrate communities in the restored segments of stream channel.

a. The following chemical parameters will be monitored according to the stream mitigation proposal dated March 2003: ammonia, total nitrogen, potassium, turbidity, pH, dissolved oxygen, temperature, conductivity, phosphates, and fecal coliform. Permanent monitoring stations must be established prior to the start of restoration. A 20% reduction in fecal coliform colonies, turbidity, ammonia, total nitrogen, and phosphates must be evident after the third year of monitoring or additional corrective measures will be required.

b. The established monitoring stations will be monitored for fish and macroinvertibrate communities using a rapid bioassessment protocol before and after restoration efforts have been implemented according to the draft stream mitigation plan dated March 2003, prepared by the Partners for Fish and Wildlife and the California University of Pennsylvania. The fish and macroinvertibrate communities must show a 20% improvement by increasing species diversity in the restored reaches compared to pre-restoration conditions after the third year of monitoring or additional corrective measures will be required.

c. The riparian corridor in restored reaches of stream channel must obtain 90% vegetative cover within one year of restoration efforts. Riparian plant communities must show a 20% improvement in cover and richness after the third year of monitoring or additional corrective measures will be required.

8. Every attempt must be made by the permittee to establish all of the stream mitigation in the Enlow Fork watershed. The permittee is required to establish no less than 50% of the stream mitigation measures within the Enlow Fork watershed.

9. A minimum of five miles of successfully restored reaches of stream channel must be placed under conservation easement by the end of the streambank monitoring period as outlined in the mitigation proposal revised in March 2003. A draft copy of the conservation easements will be submitted to the Corps for review and approval prior to recording at the county courthouse.

10. Sediment sampling and testing for selenium and PAHs must be performed at sampling locations 10 through 14 as identified on the map provided by CEC dated February 25, 2003. An additional sampling location must be established upstream of the new refuse disposal facility. The sediment samples should be taken quarterly from the start of construction and until two years after the existing coal refuse disposal facility is closed and reclaimed. An analysis and summary of the results must be provided to the Corps after each monitoring event. If the levels of selenium and/or PAH values increase by greater than 20% from the samples collected on November 19, 2002, immediate corrective measures will be required.

FURTHER INFORMATION:

1. Congressional Authorities: You have been authorized to undertake the activity described above pursuant to:

Section 404 of the Clean Water Act (33 U.S.C. 1344).

2. Limits of this authorization.

a. This permit does not obviate the need to obtain other Federal, state or local authorizations required by law.

b. This permit does not grant any property rights or exclusive privileges.

c. This permit does not authorize any injury to the property or rights of others.

d. This permit does not authorize interference with any existing or proposed Federal project.

3. Limits of Federal Liability. In issuing this permit, the Federal Government does not assume any liability for the following:

a. Damages to the permitted project or uses thereof as a result of other permitted or unpermitted activities or from natural causes.

b. Damages to the permitted project or uses thereof as a result of current or future activities undertaken by or on behalf of the United States in the public interest.

c. Damages to persons, property, or to other permitted or unpermitted activities or structures caused by the activity authorized by this permit.

d. Design or construction deficiencies associated with the permitted work.

e. Damage claims associated with any future modification, suspension, or revocation of this permit.

4. Reliance on Applicant's Data: The determination of this office that issuance of this permit is not contrary to the public interest was made in reliance on the information you provided.

5. Reevaluation of Permit Decision. This office may reevaluate its decision on this permit at any time the circumstances warrant. Circumstances that could require a reevaluation include, but are not limited to, the following:

a. You fail to comply with the terms and conditions of this permit.

b. The information provided by you in support of your permit application proves to have been false, incomplete, or inaccurate (see 4 above).

c. Significant new information surfaces which this office did not consider in reaching the original public interest decision.

Such a reevaluation may result in a determination that it is appropriate to use the suspension, modification, and revocation procedures contained in 33 CFR 325.7 or enforcement procedures such as those contained in 33 CFR 326.4 and 326.5. The referenced enforcement procedures provide for the issuance of an administrative order requiring you to comply with the terms and conditions of your permit and for the initiation of legal action where appropriate. You will be required to pay for any corrective measures ordered by this office, and if you fail to comply with such directive, this office may in certain situations (such as this specified in 33 CFR 209.170) accomplish the corrective measures by contract or otherwise and bill you for the cost.

6. Extensions. General condition 1 establishes a time limit for the completion of the activity authorized by this permit. Unless there are circumstances requiring either a prompt completion of the authorized activity or a reevaluation of the public interest decision, the Corps will normally give favorable consideration to a request for an extension of this time limit.

Your signature below, as permittee, indicates that you accept and agree to comply with the terms and conditions of this permit.

_____
(PERMITTEE)

_____
(DATE)

This permit becomes effective when the Federal official, designated to act for the Secretary of the Army, has signed below.

_____
(DISTRICT COMMANDER)
RAYMOND K. SCROCCO, COL

_____
(DATE)

When the structures or work authorized by this permit are still in existence at the time the property is transferred, the terms and conditions of this permit will continue to be binding on the new owner(s) of the property. To validate the transfer of this permit and the associated liabilities associated with compliance with its terms and conditions, have the transferee sign and date below.

_____
(TRANSFEREE)

_____
(DATE)

DATE: November 20, 2003

FILE NO: 200200371

NOTIFICATION OF APPLICANT OPTIONS (NAO)
FOR PARTIES ISSUED A DEPARTMENT OF THE ARMY INDIVIDUAL PERMIT

You are hereby advised that the following options are available to you in your evaluation of the enclosed permit:

(1) You may sign the permit and return to the District Engineer for final authorization. Your signature on the permit means that you accept the permit in its entirety, and waive all rights to appeal the permit or its terms and conditions.

(2) You may decline to sign the permit because you object to certain terms and conditions therein, and you may request that the permit be modified accordingly. You must outline your objections to the terms and conditions of the permit in a letter to the District Engineer. Your objections must be received by the District Engineer within 60 days of the date of this NAO, or you will forfeit your right to request changes to the terms and conditions of the permit. Upon receipt of your letter, the District Engineer will evaluate your objections, and may: (a) modify the permit to address all of your concerns, or (b) modify the permit to address some of your objections, or (c) not modify the permit, having determined that the permit should be issued as previously written. In any of these three cases, the District Engineer will send you a final permit for your reconsideration, as well as a Notification of Appeal (NAP) form and a Request for Appeal (RFA) form. Should you decline the final proffered permit, you can appeal the declined permit under the Corps of Engineers Administrative Appeal Process by submitting the completed RFA form to the Division Engineer. The RFA must be received by the Division Engineer within 60 days of the date of the NAP that was transmitted with the second proffered permit.

CONSTRUCTION NOTIFICATION

FILE NO: 200200371

APPLICANT: Consol Pennsylvania Coal Company

PROJECT LOCATION: in an unnamed tributary to Enlow Fork, near West Finley, Greene County, Pennsylvania

Construction will start on _____ and will be completed on _____.
(date) (date)

Signature: _____

Title: _____

NOTE: You must return this form to the following address 10 days prior to commencement of the work.

U. S. Army Corps of Engineers, Pittsburgh District
ATTN: CELRP-OR-F
Room 1834 William S. Moorhead Federal Bldg.
1000 Liberty Avenue
Pittsburgh, PA 15222-4186

CEC

Fax Transmission

Civil & Environmental Consultants, Inc. (CEC)
333 Baldwin Road
Pittsburgh, Pennsylvania 15205-9702
Telephone: 412-429-2324
Toll Free: 800-365-2324
Fax: 412-429-2114

PLEASE DELIVER TO: Christina Schroeder

FROM: Jim Mulge

NUMBER OF PAGES, INCLUDING COVER: 9

SENT BY: JEM DATE: 6/9/05 TIME: 1030 PROJECT NO. 040-148

PLEASE CALL IF ALL PAGES INDICATED ARE NOT RECEIVED. THANK YOU.

MESSAGE:

The letter on the alternative sediment trigger was sound. Thank you for your time. I look forward to talking with you & Rose

FAX NUMBER: 412 644 4711 HARD COPY TO FOLLOW _____

TRANSMITTED _____

CEC

ok 2/23 bs

February 17, 2005

Mr. Todd Shumaker
CONSOL Energy, Inc.
1525 Pleasant Grove Road
P.O. Box J
Claysville, PA 15323

Dear Mr. Shumaker:

Subject: Sediment Evaluation – Alternative Corrective Measure Triggers
New Coal Refuse Disposal Facility, Bailey Mine Complex
Richhill and Gray Townships, Greene County, Pennsylvania
CEC Project 040-148.0005

1.0 INTRODUCTION

Under Task 5 of our December 8, 2004 proposal for professional ecological services, and pursuant to your Department of the Army Permit, Number 200200371 (herein referred to as "Permit"), Civil & Environmental Consultants, Inc. (CEC) presents for CONSOL Energy Inc.'s (CONSOL) consideration this letter report of findings as part of the continuing evaluation of sediments within Enlow Fork and Talley Run adjacent to the Bailey Mine Complex's new coal refuse disposal facility (herein referred to as "Facility").

Pursuant to the requirements of the Permit, the initial tasks of CEC's evaluation of sediments included: (1) the collection of sediment samples from seven sampling stations (Station 10 on Talley Run and Stations 11 through 16 on Enlow Fork); (2) subsequent analysis for concentrations of total selenium [Se] and polycyclic aromatic hydrocarbons [PAHs]; and (3) submittal of reports of findings to CONSOL and the U.S. Army Corps of Engineers. To further this ongoing investigation, CEC is proposing alternative corrective measure triggers in lieu of the criteria currently contained in the Permit (See Section 2.0).

2.0 PURPOSE

Under the requirements of Special Condition 10 of the Permit, CONSOL is to implement immediate corrective measures if [Se] and/or [PAHs] are greater than 20 percent when compared to November 2002 levels (from samples collected by Moody and Associates, Inc.). However, the results from the 2004 sampling quarters (March, June, September, and December) indicate that these levels are not consistently attainable, even at background (upstream) sample locations. The purpose of this investigation is to therefore examine a scientifically credible alternative – an upstream versus downstream comparison using statistical tests. This alternative evaluation method is designed to analyze the data to determine if corrective actions are warranted.

Pittsburgh 333 Baldwin Road
Pittsburgh, Pennsylvania 15205
Phone 412/429-2324
Fax 412/429-2114
Toll Free 800/365-2324
E-mail info@cecinc.com

Chicago 877/863-6026
Cincinnati 800/759-5614
Columbus 888/598-6808
Export 800/899-3610
Indianapolis 877/746-0749
Nashville 800/763-2326
St. Louis 888/250-3879

Corporate Web Site http://www.cecinc.com

3.0 METHODS

Initially, all [Se] and [PAHs] data ([PAHs] were adjusted to 2% total organic carbon; per Ingersoll et al. 2000) collected during the four sampling events (March, June, September, and December of 2004) from Enlow Fork and Talley Run were pooled (i.e., grouped) according to the following general locations for statistical analysis purposes:

- Downstream datasets – Pooled [Se] data and [PAHs] data from Stations 10 on Talley Run and Stations 11 and 14 on Enlow Fork; all located downstream of the Facility.
- Upstream datasets – Pooled [Se] data and [PAHs] data from Stations 12, 13, 15, and 16 on Enlow Fork; all located upstream of the Facility.

For this investigation, it was assumed that the Upstream datasets would serve as appropriate background concentrations for the downstream assessment of the constituents of potential ecological concern.

For this investigation, SYSTAT® Version 10 (SPSS 2000) and the U.S. Environmental Protection Agency's ProUCL Version 3.0 (USEPA 2004) were used to perform all statistical analyses. Probabilities ≤ 0.05 were considered significant.

Employing ProUCL, the Shapiro-Wilk W test was performed on the pooled datasets, $[Se]_{Upstream}$, $[Se]_{Downstream}$, $[PAHs]_{Upstream}$, and $[PAHs]_{Downstream}$, to determine if these data were normally distributed. Next, employing SYSTAT®, descriptive summary statistics, including the sample mean, sample median, standard deviation, standard error, and upper and lower limits of the 95 percent confidence interval were computed from the pooled datasets (Table 1). SYSTAT® was also used to construct normalized density curves of the pooled datasets for graphical comparison of the sample means and sample distributions.

Next, employing SYSTAT®, the (nonparametric/distribution-free) Wilcoxon Signed-Ranks test was performed on the pooled datasets to test for significant differences between the distributions of paired data (e.g., $[Se]_{Upstream}$ and $[Se]_{Downstream}$) in a related-measures design (Table 2).

4.0 RESULTS

The results of the Shapiro-Wilk W tests indicated that most of the datasets were not normally distributed; or the datasets were normally distributed, but the test more than likely did not have enough power (because there was not enough data to demonstrate statistical significance). Therefore, the nonparametric Wilcoxon Signed-Ranks test served as an appropriate test to determine significant differences (i.e., no parametric assumptions were violated).

The following two figures illustrate the normalized density curves of the pooled datasets for graphical comparison of the sample means ($\bar{X}$) and sample distributions of the [Se] datasets (Figure 1) and [PAHs] datasets (Figure 2):

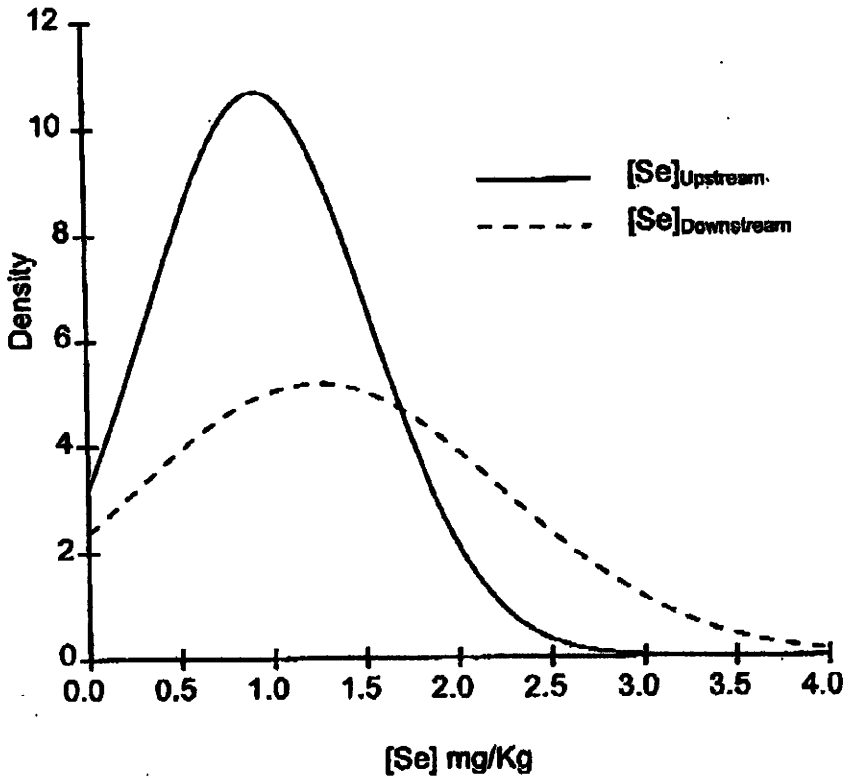


FIGURE 1: Normalized density curves of [Se] datasets;
$\bar{X}_{Upstream}$ = 0.93 mg/Kg and $\bar{X}_{Downstream}$ = 1.25 mg/Kg.

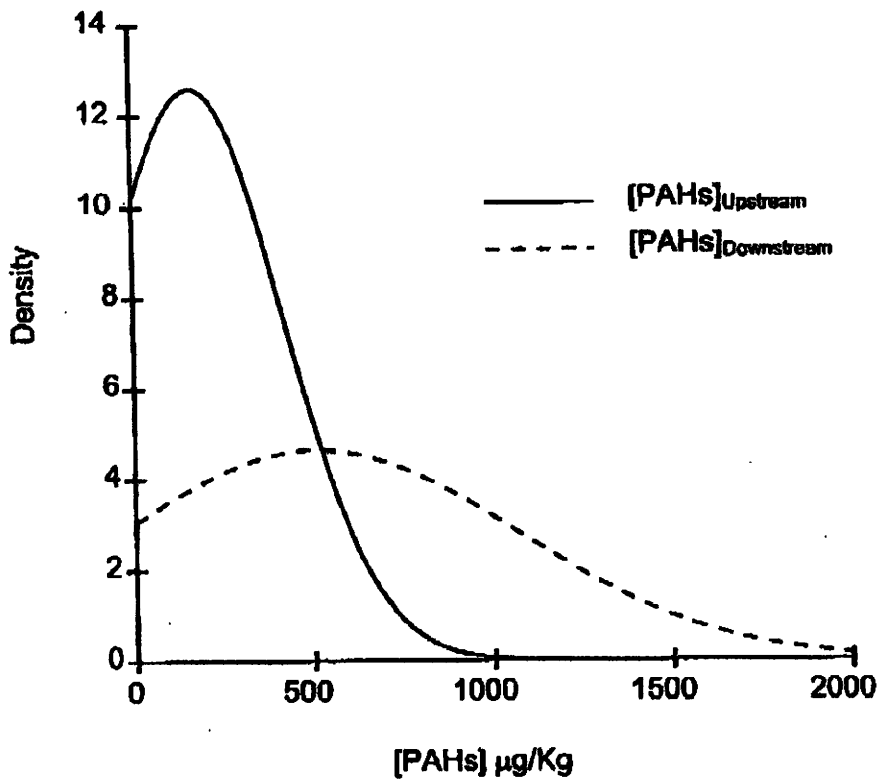


FIGURE 2: Normalized density curves of [PAHs] datasets;

$\bar{X}_{Upstream}$ = 167 µg/Kg and $\bar{X}_{Downstream}$ = 511 µg/Kg.

These two figures illustrate the differences in sample means and sample distributions between the Upstream and Downstream [Se] and [PAHs] datasets. However, these differences are not statistically significant, as described below.

The results of the Wilcoxon-Signed Rank tests demonstrated that the $[Se]_{Upstream}$ and $[Se]_{Downstream}$ datasets did not differ significantly ($P > 0.05$, Table 2). Likewise, the results of the Wilcoxon-Signed Rank tests demonstrated that the $[PAHs]_{Upstream}$ and $[PAHs]_{Downstream}$ datasets also did not differ significantly ($P > 0.05$).

5.0 SUMMARY AND CONCLUSIONS

Under the requirements of the Permit, CONSOL is to implement immediate corrective measures if [Se] and/or [PAHs] are greater than 20 percent when compared to November 2002 levels. However, the results from the 2004 sampling quarters indicate that these levels are not consistently attainable, even at background sample locations. The purpose of this investigation is to therefore examine a scientifically credible alternative that is designed to analyze the data to determine if the required corrective actions are warranted. The alternative evaluation method employed for this investigation consisted of a comparison of upstream and downstream datasets using the Wilcoxon Signed-Ranks test and normalized density curves.1

In conclusion, CEC believes at this time that there is no remarkable difference in [Se] and [PAHs] between sediment samples collected upstream and downstream of the Facility. CEC also believes, based on the data evaluation presented above, that no corrective actions should be imposed on CONSOL at this time. CEC suggests that future corrective actions be based on the statistical approaches employed above. Furthermore, CEC suggests that additional sediment samples be collected, analyzed, and evaluated to provide for a more meaningful and statistically powerful investigation.

6.0 LITERATURE CITED

Department of the Army Permit Number 200200371. 2003. Construction of Coal Refuse Disposal Facility in Richhill Township and Gray Township, Greene County, Pennsylvania. Pittsburgh District Corps of Engineers.

Ingersoll, C.G., D.D. MacDonald, N. Wang, J.L. Crane, L.J. Field, P.S. Haverland, N.E. Kimble, R.A. Lindskoog, C. Severn, and D.E. Smorong. 2000. *Prediction of Sediment Toxicity using Consensus-based Freshwater Sediment Quality Guidelines*. EPA 905/R-00/007. USEPA Great Lakes National Program Office. Chicago, Illinois.

SPSS, Inc. 2000. SYSTAT® Version 10. *Statistics I* and *Statistics II* User Guides. Chicago, Illinois.

United States Environmental Protection Agency (USEPA). 2004. ProUCL Version 3.0. *User Guide*. EPA/600/R04/079. Developed for USEPA by Lockheed Martin Environmental Services. Las Vegas, Nevada.

7.0 CLOSING

This letter report has been prepared in keeping with accepted protocols for the performance of sediment evaluations and using CEC's professional judgment. The results and discussion of this report cannot be considered scientific certainties, but rather our professional opinions based on the data collected during the course of our investigation. It must be recognized that this investigation is based

on field observations, information received from various regulatory officials, and the research of pertinent peer-reviewed literature. No other warranties, either expressed or implied, are made herein.

CEC appreciates the opportunity to continue to provide professional ecological consulting services to CONSOL for this challenging project. Please call us at (412) 429-2324 if you have any questions or require additional information.

Very truly yours,

CIVIL & ENVIRONMENTAL CONSULTANTS, INC.

Robert Ventorini
Assistant Project Manager

James E. Mudge, Ph.D.
Vice President – Ecological Services

R-040-148.0005.FEB17/W

TABLE 1
Pooled Data, Descriptive Summary Statistics, and Sediment Quality Benchmarks
Stream Sediment Evaluation - Alternative Corrective Measure Triggers
New Coal Refuse Disposal Facility, CONSOL Bailey Mine Complex
Richhill and Gray Townships, Greene County, Pennsylvania
CEC Project 040-148

		Total [Se] (mg/Kg)		Total [PAHs] (µg/Kg; Adjusted to 2% TOC)	
		Bailey Mine Upstream	Bailey Mine Downstream	Bailey Mine Upstream	Bailey Mine Downstream
Pooled Data		1.20	3.20	359	261
		0.85	1.70	136	114
		0.95	1.30	87	236
		2.40	0.39	747	68
		0.48	0.36	806	683
		0.72	0.36	55	180
		0.37	0.36	128	150
		1.00	0.97	17	257
		0.29	0.56	31	833
		0.28	0.62	5	149
		0.29	3.20	13	1,966
		0.44	1.60	10	465
		1.70	1.60	114	1,280
		1.60		90	
		1.30		63	
		1.10		17	
Descriptive Summary Statistics	N of Cases	18	13	16	13
	Minimum	0.28	0.36	5	68
	Maximum	2.40	3.20	806	1,966
	Range	2.12	2.84	801	1,898
	Sum	14.87	16.23	2,667	6,642
	Sample Median	0.90	0.97	71	257
	Sample Mean	0.93	1.25	167	511
	95% Confidence Interval Upper Limit (Upper Tolerance Limit)	1.25	1.86	302	850
	95% Confidence Interval Lower Limit	0.61	0.64	32	172
	Standard Error (SE)	0.15	0.28	63	155
	Standard Deviation (SD)	0.60	1.00	253	561
	Variance	0.36	1.01	64,164	314,266
	Coefficient of Variation	0.64	0.80	2	1

hp fax 1240

Log for
-- 6/9/2005 10:02AM

Last Transaction

Date	Time	Type	Identification	Duration	Pages	Result
06/09	09:57a	Received		2:34	9	OK

U.S. Fish and Wildlife Service
Pennsylvania Field Office
315 South Allen Street, Suite 322
State College, PA 16801-4850
Phone (814) 234-4090
Fax (814) 234-0748

Date: 5-19-05

To: Christy Schroeder

From: Cindy Tibbott

No. of pages, including cover sheet: 6

Message: New Consol data

get a map showing outfalls ~~of~~ from new sedimentation ponds and request consol to sample upstream + downstream of outfall

Table 1. Location and description of sediment and surface water samples collected in Enlow Fork and surrounding tributaries, Greene County Pennsylvania, September 4, 2001.

Sample Number	Matrix	Stream Name/Location	Latitude / Longitude	Number of Grabs	Comments	Percent TOC	Percent Moisture	Percent Sand	Percent Clay	Percent Silt
EF001	Water	Hewitt Run	N 39° 51' 11.2" / W 80° 28' 48.9"	1						
EF002	Sediment	Hewitt Run	N 39° 51' 11.2" / W 80° 28' 48.9"	4		0.9	36.4	80.7	3.8	15.5
EF003	Water	Chambers Run	N 39° 51' 26.1" / W 80° 28' 36.6"	1						
EF004	Sediment	Chambers Run	N 39° 51' 26.1" / W 80° 28' 36.6"	4		1.88	47.6	71.5	4.1	24.4
EF005	Water	Blank	NA	NA						
EF006	Sediment	Enlow Fork/Pool C	N 39° 57' 40.9" / W 80° 27' 42.3"	4	Lots of organic matter	1.98	48.5	69.6	3	27.4
EF007	Water	Enlow Fork/Pool C	N 39° 57' 40.9" / W 80° 27' 42.3"	1	Water level low					
EF008	Sediment	Duplicate of EF006	N 39° 57' 40.9" / W 80° 27' 42.3"	4	Lots of organic matter	2.17	48	64.7	6.8	28.5
EF009	Water	Templeton Fork	N 39° 59' 12.8" / W 80° 26' 34.6"	1						
EF010	Sediment	Templeton Fork	N 39° 59' 12.8" / W 80° 26' 34.6"	4	Sandy	1.18	38.3	80.8	2.3	16.9
EF011	Water	Enlow Fork/Downstream	N 39° 58' 18.9" / W 80° 25' 31.6"	1	Precipitate with acid					
EF012	Sediment	Enlow Fork/Downstream	N 39° 58' 18.9" / W 80° 25' 31.6"	7	Petroleum odor	14.9	51	27.6	18.8	53.6
EF013	Water	Duplicate of EF011	N 39° 58' 18.9" / W 80° 25' 31.6"	1	Precipitate with acid					
EF014	Sediment	Duplicate of EF012	N 39° 58' 18.9" / W 80° 25' 31.6"	7	Petroleum odor	18.1	49	35.1	15.4	49.5
EF015	Water	Enlow Fork/Upstream	N 39° 58' 36.7" / W 80° 24' 40.4"	1						
EF016	Sediment	Enlow Fork/Upstream	N 39° 58' 36.7" / W 80° 24' 40.4"	4		1.24	38.3	77	4.3	18.7

Table 2. Contaminants in Enlow Fork and surrounding tributary surface water compared to chronic ambient water quality criteria and wildlife benchmarks, Greene County, Pennsylvania. September 4, 2001.

	EPA 1995	Sample et al. 1996								
	Chronic AWQC	Mink	Belted Kingfisher	EF001	EF003	EF005	EF007	EF009	EF011	EF013	EF015
Aluminum	0.087	0.253	0.38	0.18	0.0888	<.0500	0.0993	0.0747	0.274	0.0955	0.136
Arsenic	0.15	0.216	0.846	<.00500	<.00500	<.00500	<.00500	<.00500	<.00500	<.00500	<.00500
Boron	na	na	na	<.100	<.100	<.100	0.132	0.128	0.205	0.197	0.141
Barium	na	na	na	0.0586	0.0506	<.00500	0.0856	0.0717	0.0777	0.0735	0.0801
Beryllium	0.0053	na	na	<.000500	<.000500	<.000500	<.000500	<.000500	<.000500	<.000500	<.000500
Cadmium	0.0011	0.0044	0.0032	<.000500	<.000500	<.000500	<.000500	<.000500	<.000500	<.000500	<.000500
Chromium	na	19.8	na	<.00300	<.00300	<.00300	<.00300	<.00300	<.00300	<.00300	<.00300
Copper	0.012	0.0387	0.42	<.00500	<.00500	<.00500	<.00500	<.00500	0.00606	<.00500	<.00500
Iron	1	na	na	0.299	0.101	<.100	0.135	0.142	0.614	0.218	0.29
Mercury	0.000012	0.0000045	0.0000065	<.00100	<.00100	<.00100	<.00100	<.00100	<.00100	<.00100	<.00100
Magnesium	na	na	na	6.02	5.4	<.100	10.2	6.59	19.2	18.4	8.72
Manganese	na	na	na	0.0214	0.0105	<.00500	0.0354	0.0361	0.158	0.118	0.0405
Molybdenum	na	na	na	<.0500	<.0500	<.0500	<.0500	<.0500	<.0500	<.0500	<.0500
Nickel	0.16	4.2	2	<.00500	<.00500	<.00500	<.00500	<.00500	0.00519	<.00500	<.00500
Lead	0.0032	9.823	0.493	<.0100	<.0100	<.0100	<.0100	<.0100	<.0100	<.0100	<.0100
Selenium	0.005	0.00071	0.00076	<.00500	<.00500	<.00500	<.00500	<.00500	<.00500	<.00500	<.00500
Strontium	na	na	na	0.157	0.136	0.0014	0.638	0.236	1.78	1.66	0.288
Vanadium	na	na	na	<.00100	<.00100	<.00100	<.00100	<.00100	<.00100	<.00100	<.00100
Zinc	0.11	1.86	0.268	0.0337	0.0386	0.0509	0.0454	0.0272	0.0519	0.0483	0.0313

All values in mg/L.
Light shading indicates value greater than EPA chronic AWQC (EPA 1995).

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Table 3. Contaminants in Enlow Fork and surrounding tributary sediment compared to the consensus-based probable effect concentration (PEC), Greene County, Pennsylvania. September 4, 2001.

		Sediment Station							
	PEC	EF002	EF004	EF006	EF008	EF010	EF012	EF014	EF016
INORGANICS									
Aluminum	na	13248	13171	9645	10047	7209	7837	7334	9498
Arsenic	33	9.84	8.95	8.12	7.61	5.65	10.5	12.2	7.28
Boron	na	<10.0	<10.0	<10.0	<10.0	<10.0	11.3	<10.0	<10.0
Barium	na	188	152	120	136	102	99.1	101	124
Beryllium	na	1.6	1.47	1.21	1.23	0.992	1.1	1.16	1.22
Cadmium	4.98	0.265	0.254	0.218	0.234	<.200	0.34	0.35	<.200
Chromium	na	26.4	23.9	21	21.7	15.1	22.6	22.9	19
Copper	149	22.9	21.7	28.1	18	11.7	19.7	20.1	14.9
Iron	na	34381	30568	26999	26877	22391	19581	19935	25200
Lead	128	22	23.7	15.9	16.3	12.2	15.6	16.7	16.1
Mercury	1.06	<.200	<.200	<.200	<.200	<.200	<.200	<.200	<.200
Magnesium	na	3255	2920	2586	2659	1870	2935	2939	2238
Manganese	na	792	668	601	721	464	753	792	579
Molybdenum	na	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00
Nickel	48.6	27.9	25.5	22.8	23.9	18.4	22.7	25	21.5
Selenium	na	<1.00	<1.00	<1.00	<1.00	<1.00	1.59	1.5	<1.00
Strontium	na	41.7	32	63.2	61.7	21.7	193	188	24.3
Vanadium	na	26.2	26.5	18.8	19.4	15.1	18.8	19.2	19.3
Zinc	459	81.9	86.2	66.7	67.7	50.9	89.6	94.9	65.9
ORGANICS									
Anthracene	0.845	<.00349	0.107	0.129	0.0592	0.0167	1.32	0.497	0.136
Fluorene	0.536	<.00349	0.0254	0.0438	0.0234	0.004	1.2	0.674	0.0228
Naphthalene	0.561	0.0229	0.0215	0.187	0.196	0.0257	43.5	13.6	0.0692
Phenanthrene	1.17	0.0193	0.131	0.206	0.126	0.0337	11.4	4.44	0.155
Benz[a]anthracene	1.05	0.0058	0.217	0.28	0.223	0.0514	1.21	0.593	0.232
Benzo(a)pyrene	1.45	0.0067	0.2	0.0074	0.193	0.0554	0.866	0.472	0.242
Chrysene	1.29	0.0087	0.139	0.194	0.16	0.0385	1.04	0.449	0.17
Fluoranthene	2.23	0.012	0.345	0.505	0.235	0.0742	3.37	1.04	0.429
Pyrene	1.52	0.0113	0.274	0.443	0.217	0.0689	3.28	1.1	0.334
Total PAHs (13 common)	22.8	0.11	1.56	2.31	1.76	0.41	126.67	42.87	1.93
Total PAHs (all)	na	0.3	2.76	5.23	4.44	0.9	340.05	129.88	3.65

All values in ug/g dry weight.
na indicates benchmark not available.
Shading indicates value greater than concensus-based PEC identified by MacDonald et al. 2000. enlowsedcriteria

Table 4. Contaminants in Enlow Fork and surrounding tributary sediment compared to values protective of wildlife species, Greene County, Pennsylvania. September 4, 2001.

	Sample et al. 1996		Sediment Station							
	Woodcock	Shrew	EF002	EF004	EF006	EF008	EF010	EF012	EF014	EF016
Aluminum	59	38	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Arsenic	9.7	2.5	6.25	4.69	4.19	3.96	3.48	5.17	[illegible]	4.49
Boron	132	343	<6.36	<5.24	<5.15	<5.20	<6.17	5.54	<5.10	<6.17
Barium	55	72	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	48.6	51.4	[illegible]
Beryllium	na	na	1.02	0.771	0.623	0.641	0.612	0.538	0.592	0.756
Cadmium	26	35	0.168	0.133	0.112	0.122	<.123	0.167	0.178	<.123
Chromium	6.6	48	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Copper	81	73	14.5	11.4	14.5	9.35	7.21	9.65	10.3	9.19
Iron	na	na	21849	16021	13916	13973	13811	9599	10167	15553
Mercury	0.08	0.57	<.127	<.105	<.103	<.104	<.123	<.0980	<.102	<.123
Magnesium	na	na	2069	1530	1333	1382	1153	1439	1499	1382
Manganese	na	1040	503	350	310	375	286	369	404	358
Molybdenum	46.6	5.2	<3.18	<2.62	<2.58	<2.60	<3.08	<2.45	<2.55	<3.09
Nickel	141	293	17.7	13.4	11.8	12.4	11.4	11.1	12.7	13.3
Lead	15	293	14	12.4	8.19	8.48	7.5	7.64	8.53	9.93
Selenium	1.1	1.2	<.636	<.524	<.515	<.520	<.617	0.78	0.764	<.617
Strontium	na	na	26.5	16.8	32.6	32.1	13.4	94.5	95.8	15
Vanadium	na	7.1	16.7	13.9	9.71	10.1	9.33	9.21	9.78	11.9
Zinc	173	1172	52.1	45.2	34.4	35.2	31.4	43.9	48.4	40.7

All values in ug/g wet weight.
na indicates benchmark unavailable.
Light shading indicates value greater than protective level for shrew.
Dark shading indicates value greater than protective level for woodcock.
Crosshatch indicates value greater than protective level for both shrew and woodcock.

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Appendix A. Polcyclic aromatic hydrocarbon concentrations in sediments of Enlow Fork and surrounding tributaties. All values are ug/g dry weight.

	EF002	EF004	EF006	EF008	EF010	EF012	EF014	EF016
acenaphthylene	<.00349	0.0445	0.0105	0.0078	<.00335	0.25	0.133	<.00353
acenaphthene	<.00349	0.0123	<.00432	<.00418	<.00335	0.0459	0.0231	0.00968
anthracene	<.00349	0.107	0.129	0.0592	0.0167	1.32	0.497	0.136
benzo(a)anthracene	0.00583	0.217	0.28	0.223	0.0514	1.21	0.593	0.232
benzo(a)pyrene	0.00668	0.2	0.0074	0.193	0.0554	0.866	0.377	0.242
benzo(b)fluoranthene	0.00995	0.234	0.302	0.262	0.0656	0.91	0.363	0.3
benzo(e)pyrene	0.00762	0.0869	0.112	0.105	0.028	0.579	0.276	0.106
benzo(g,h,i)perylene	0.00627	0.0777	0.0991	0.0916	0.027	0.464	0.215	0.0983
benzo(k)fluoranthene	<.00349	0.0674	0.0888	0.0736	0.0208	0.231	0.0851	0.0774
biphenyl	0.0062	0.00475	0.0225	0.017	0.0043	0.826	0.451	0.00642
C1-chrysenes	0.00754	0.0842	0.119	0.122	0.0167	2.28	1.34	0.106
C1-dibenzothiophenes	<.00349	0.00792	0.023	0.02	0.0036	2.41	0.905	0.0129
C1-fluoranthenes & pyrenes	0.0129	0.147	0.247	0.154	0.0399	7.43	2.91	0.171
C1-fluorenes	0.00581	0.0169	0.0524	0.0323	0.0069	1.52	0.899	0.02
C1-naphthalenes	0.0429	0.0387	0.482	0.518	0.0617	96.3	32.5	0.166
C1-phenanthrenes & anthracenes	0.0159	0.0792	0.179	0.141	0.03	15.5	5.97	0.111
C2-chrysenes	0.00444	0.0286	0.0567	0.0604	0.0084	2.47	1.34	0.0343
C2-dibenzothiophenes	<.00349	0.00588	0.0219	0.0188	<.00335	1.85	0.726	0.0107
C2-fluorenes	0.00806	0.0196	0.0587	0.0447	0.0137	2.18	1.26	0.028
C2-naphthalenes	0.0277	0.032	0.324	0.348	0.0502	54	19.5	0.117
C2-phenanthrenes & anthracenes	0.0102	0.0503	0.148	0.124	0.0215	15	5.74	0.077
C3-chrysenes	<.00349	<.00416	<.00432	<.00418	<.00335	0.174	0.0899	<.00353
C3-dibenzothiophenes	<.00349	<.00416	0.0151	0.014	<.00335	1.23	0.534	0.00699
C3-fluorenes	0.00402	0.0129	0.0803	0.0802	0.0145	2.3	1.51	0.0181
C3-naphthalenes	0.0199	0.0291	0.247	0.277	<.00335	28.6	14.2	0.0957
C3-phenanthrenes & anthracenes	0.00786	0.0236	0.0958	0.0858	0.0122	11.4	4.32	0.0412
C4-chrysenes	<.00349	0.0138	0.0169	0.0168	0.0042	0.103	0.0533	0.0153
C4-naphthalenes	0.00942	0.0175	0.173	0.18	0.0353	15.9	8.47	<.00353
C4-phenanthrenes & anthracenes	0.00494	0.00697	0.0468	0.0376	0.0056	7.34	2.69	0.0156
chrysene	0.00869	0.139	0.194	0.16	0.0385	1.04	0.449	0.17
dibenz(a,h)anthracene	<.00349	0.0236	0.0272	0.0243	0.0067	0.0865	0.0422	0.0303
dibenzothiophene	<.00349	0.00729	0.0159	0.0118	<.00335	1.15	0.448	0.0102
fluoranthene	0.012	0.345	0.505	0.235	0.0742	3.37	1.04	0.429
fluorene	<.00349	0.0254	0.0438	0.0234	0.004	1.2	0.674	0.0228
indeno(1,2,3-cd)pyrene	0.00493	0.107	0.13	0.11	0.0341	0.292	0.0964	0.133
naphthalene	0.0229	0.0215	0.187	0.196	0.0257	43.5	13.6	0.0692
perylene	<.00349	0.0215	0.0434	0.0293	0.0219	0.0456	0.0211	0.0439
phenanthrene	0.0193	0.131	0.206	0.126	0.0337	11.4	4.44	0.155
pyrene	0.0113	0.274	0.443	0.217	0.0689	3.28	1.1	0.334
INDIVIDUAL ISOMERS								
1,6,7-Trimethyl-naphthalene	0.00718	0.00901	0.0879	0.0638	0.0114	3.82	2.17	0.0221
1-methylnaphthalene	0.019	0.0174	0.201	0.219	0.0309	37.1	12.6	0.0707
1-methylphenanthrene	0.0066	0.0232	0.0615	0.051	0.011	5.43	2.16	0.0373
2,6-dimethylnaphthalene	0.00723	0.00998	0.105	0.0772	0.0112	5.22	2.88	0.0247
2-methylnaphthalene	0.0239	0.0213	0.281	0.3	0.0309	59.1	20	0.0953
Total PAHs	0.30326	2.76101	5.2332	4.4396	0.9013	340.05	129.88	3.65199
Total naphthalenes	0.12282	0.1388	1.413	1.519	0.1729	238.3	88.27	0.4479
Total phenanthrenes & anthracenes	0.06403	0.61507	1.0846	0.7966	0.1711	63.17	24.25	0.7678
Total of 13 common parent PAHs	0.1106	1.5616	2.3139	1.7647	0.4061	126.67	42.968	1.92528

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CONSOL ENERGY

Consol PA Coal Company 1525 Pleasant Grove Road, P.O. Box J, Claysville, PA 15330 (724) 663-3039

CNX Coal – PA Operations

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February 23, 2005

Mr. Scott A. Hans
Department of the Army
Operations and Readiness Division
Regulatory Branch
Pittsburgh District, Corps of Engineers
William S. Moorhead Federal Building
1000 Liberty Avenue
Pittsburgh, Pennsylvania 15222-4186

RE: Bailey Mine Coal Refuse Disposal Areas
CPCC Pennsylvania Coal Company
Richhill Township, Greene County, Pennsylvania

Dear Mr. Hans:

Department of the Army (Department) Permit No. 200200371 (Permit), Special Condition 10 requires the collection and analysis of sediments in the vicinity of the subject facility with a subsequent report to the Department. To fulfill that Permit requirement, find enclosed a report prepared by Civil & Environmental Consultants, Inc. (CEC) entitled **"Sediment Evaluation of Enlow Fork and Tributaries for the First through Fourth Quarters of 2004, Bailey Mine-New Coal Refuse Disposal Facility, CONSOL Pennsylvania Coal Company,"** dated February 10, 2005. Additional copies have been supplied for distribution as you see necessary.

As you may remember from my letter of December 3, 2004, CPCC believes that the Permit requirement which requires immediate corrective measures if the levels of selenium and/or PAHs increase by greater than 20% from the samples collected on November 19, 2002, is not an appropriate or attainable trigger level, even at background sample locations, and to that means CPCC was going to investigate alternatives following the fourth quarter 2004 sampling results. At the request of CPCC, Civil & Environmental Consultants, Inc was to investigate an

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alternative corrective measure trigger by use of an upstream versus downstream data comparison using statistical tests. CEC's evaluation and conclusion is attached for your review.

CPCC would like to, upon your review of the fourth quarter data and CEC's proposed alternative sediment evaluation, meet with you to discuss these matters. At your earliest convenience please call me at (724) 663-3039 so that we may arrange a suitable meeting date for all parties.

Sincerely yours,

Todd M. Shumaker
Compliance Engineer
CNX Coal – PA Operations

Enclosure

cc: w/o enclosures
Jim Goroncy
Mark Stanley
John Owsiany

February 17, 2005

Mr. Todd Shumaker
CONSOL Energy, Inc.
1525 Pleasant Grove Road
P.O. Box J
Claysville, PA 15323

Dear Mr. Shumaker:

Subject: Sediment Evaluation – Alternative Corrective Measure Triggers
New Coal Refuse Disposal Facility, Bailey Mine Complex
Richhill and Gray Townships, Greene County, Pennsylvania
CEC Project 040-148.0005

1.0 INTRODUCTION

Under Task 5 of our December 8, 2004 proposal for professional ecological services, and pursuant to your Department of the Army Permit, Number 200200371 (herein referred to as "Permit"), Civil & Environmental Consultants, Inc. (CEC) presents for CONSOL Energy Inc.'s (CONSOL) consideration this letter report of findings as part of the continuing evaluation of sediments within Enlow Fork and Talley Run adjacent to the Bailey Mine Complex's new coal refuse disposal facility (herein referred to as "Facility").

Pursuant to the requirements of the Permit, the initial tasks of CEC's evaluation of sediments included: (1) the collection of sediment samples from seven sampling stations (Station 10 on Talley Run and Stations 11 through 16 on Enlow Fork); (2) subsequent analysis for concentrations of total selenium [Se] and polycyclic aromatic hydrocarbons [PAHs]; and (3) submittal of reports of findings to CONSOL and the U.S. Army Corps of Engineers. To further this ongoing investigation, CEC is proposing alternative corrective measure triggers in lieu of the criteria currently contained in the Permit (See Section 2.0).

2.0 PURPOSE

Under the requirements of Special Condition 10 of the Permit, CONSOL is to implement immediate corrective measures if [Se] and/or [PAHs] are greater than 20 percent when compared to November 2002 levels (from samples collected by Moody and Associates, Inc.). However, the results from the 2004 sampling quarters (March, June, September, and December) indicate that these levels are not consistently attainable, even at background (upstream) sample locations. The purpose of this investigation is to therefore examine a scientifically credible alternative – an upstream versus downstream comparison using statistical tests. This alternative evaluation method is designed to analyze the data to determine if corrective actions are warranted.

3.0 METHODS

Initially, all [Se] and [PAHs] data ([PAHs] were adjusted to 2% total organic carbon; per Ingersoll et al. 2000) collected during the four sampling events (March, June, September, and December of 2004) from Enlow Fork and Talley Run were pooled (i.e., grouped) according to the following general locations for statistical analysis purposes:

- Downstream datasets – Pooled [Se] data and [PAHs] data from Stations 10 on Talley Run and Stations 11 and 14 on Enlow Fork; all located downstream of the Facility.
- Upstream datasets – Pooled [Se] data and [PAHs] data from Stations 12, 13, 15, and 16 on Enlow Fork; all located upstream of the Facility.

For this investigation, it was assumed that the Upstream datasets would serve as appropriate background concentrations for the downstream assessment of the constituents of potential ecological concern.

For this investigation, SYSTAT® Version 10 (SPSS 2000) and the U.S. Environmental Protection Agency's ProUCL Version 3.0 (USEPA 2004) were used to perform all statistical analyses. Probabilities ≤ 0.05 were considered significant.

Employing ProUCL, the Shapiro-Wilk W test was performed on the pooled datasets, $[Se]_{Upstream}$, $[Se]_{Downstream}$, $[PAHs]_{Upstream}$, and $[PAHs]_{Downstream}$, to determine if these data were normally distributed. Next, employing SYSTAT®, descriptive summary statistics, including the sample mean, sample median, standard deviation, standard error, and upper and lower limits of the 95 percent confidence interval were computed from the pooled datasets (Table 1). SYSTAT® was also used to construct normalized density curves of the pooled datasets for graphical comparison of the sample means and sample distributions.

Next, employing SYSTAT®, the (nonparametric/distribution-free) Wilcoxon Signed-Ranks test was performed on the pooled datasets to test for significant differences between the distributions of paired data (e.g., $[Se]_{Upstream}$ and $[Se]_{Downstream}$) in a related-measures design (Table 2).

4.0 RESULTS

The results of the Shapiro-Wilk W tests indicated that most of the datasets were not normally distributed; or the datasets were normally distributed, but the test more than likely did not have enough power (because there was not enough data to demonstrate statistical significance). Therefore, the nonparametric Wilcoxon Signed-Ranks test served as an appropriate test to determine significant differences (i.e., no parametric assumptions were violated).

The following two figures illustrate the normalized density curves of the pooled datasets for graphical comparison of the sample means ($\bar{X}$) and sample distributions of the [Se] datasets (Figure 1) and [PAHs] datasets (Figure 2):

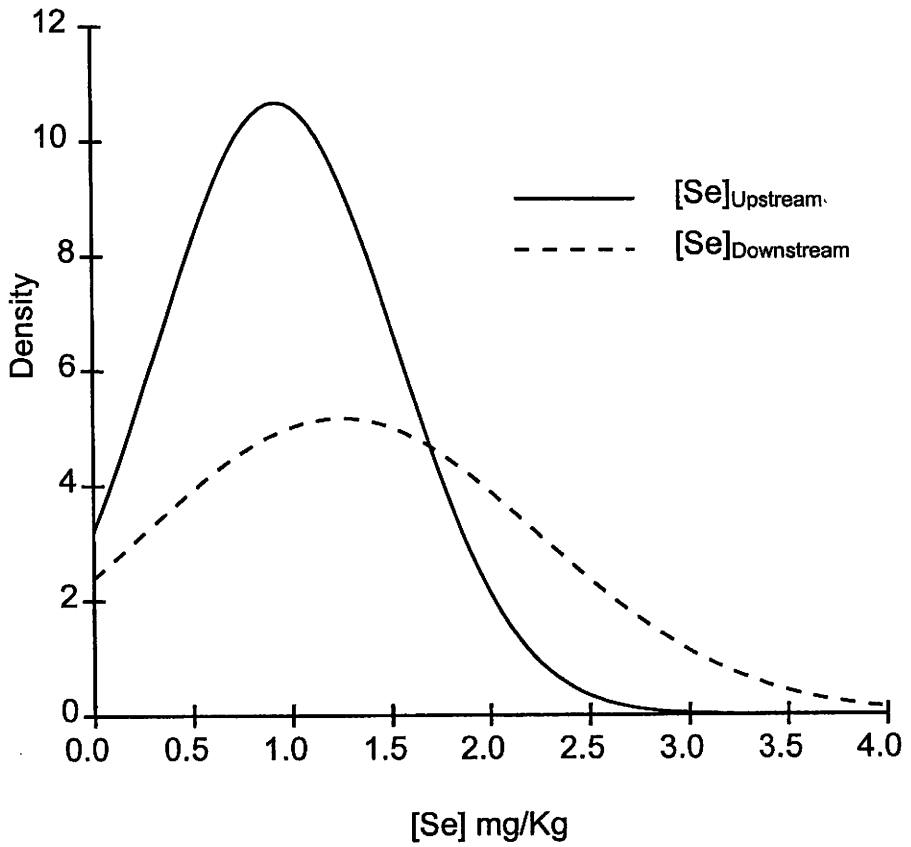


FIGURE 1: Normalized density curves of [Se] datasets;

$\bar{X}_{Upstream}$ = 0.93 mg/Kg and $\bar{X}_{Downstream}$ = 1.25 mg/Kg.

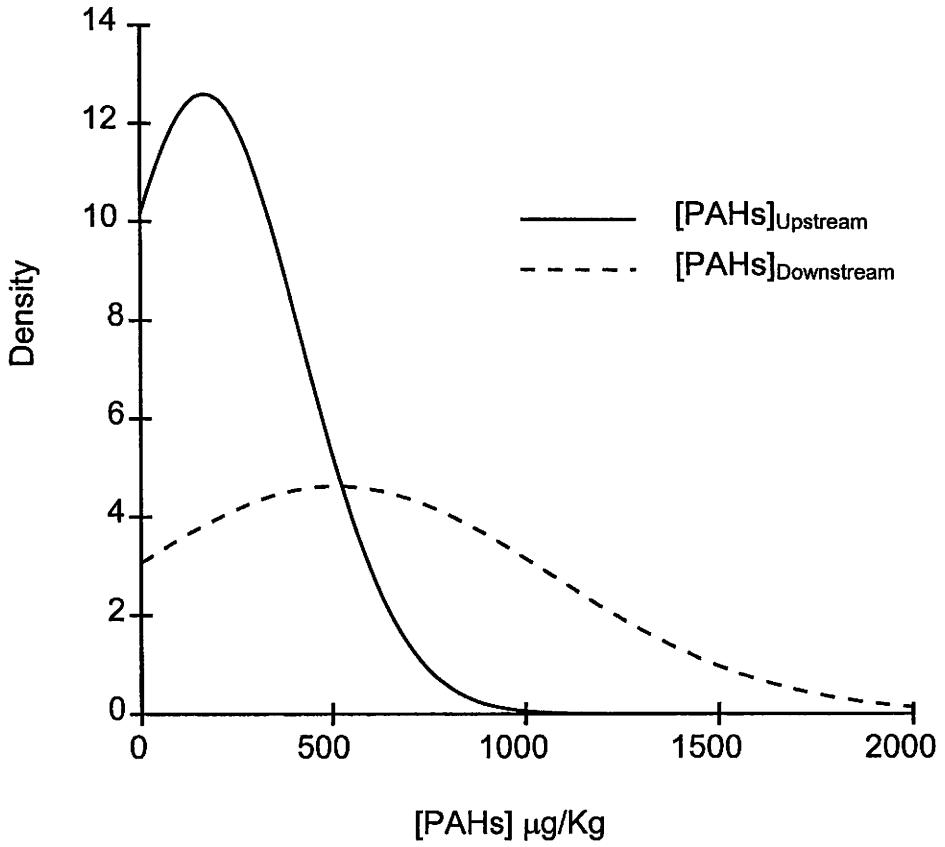


FIGURE 2: Normalized density curves of [PAHs] datasets;

$\bar{X}_{Upstream}$ = 167 µg/Kg and $\bar{X}_{Downstream}$ = 511 µg/Kg.

These two figures illustrate the differences in sample means and sample distributions between the Upstream and Downstream [Se] and [PAHs] datasets. However, these differences are not statistically significant, as described below.

The results of the Wilcoxon-Signed Rank tests demonstrated that the $[Se]_{Upstream}$ and $[Se]_{Downstream}$ datasets did not differ significantly ($P > 0.05$, Table 2). Likewise, the results of the Wilcoxon-Signed Rank tests demonstrated that the $[PAHs]_{Upstream}$ and $[PAHs]_{Downstream}$ datasets also did not differ significantly ($P > 0.05$).

5.0 SUMMARY AND CONCLUSIONS

Under the requirements of the Permit, CONSOL is to implement immediate corrective measures if [Se] and/or [PAHs] are greater than 20 percent when compared to November 2002 levels. However, the results from the 2004 sampling quarters indicate that these levels are not consistently attainable, even at background sample locations. The purpose of this investigation is to therefore examine a scientifically credible alternative that is designed to analyze the data to determine if the required corrective actions are warranted. The alternative evaluation method employed for this investigation consisted of a comparison of upstream and downstream datasets using the Wilcoxon Signed-Ranks test and normalized density curves.1

In conclusion, CEC believes at this time that there is no remarkable difference in [Se] and [PAHs] between sediment samples collected upstream and downstream of the Facility. CEC also believes, based on the data evaluation presented above, that no corrective actions should be imposed on CONSOL at this time. CEC suggests that future corrective actions be based on the statistical approaches employed above. Furthermore, CEC suggests that additional sediment samples be collected, analyzed, and evaluated to provide for a more meaningful and statistically powerful investigation.

6.0 LITERATURE CITED

Department of the Army Permit Number 200200371. 2003. Construction of Coal Refuse Disposal Facility in Richhill Township and Gray Township, Greene County, Pennsylvania. Pittsburgh District Corps of Engineers.

Ingersoll, C.G., D.D. MacDonald, N. Wang, J.L. Crane, L.J. Field, P.S. Haverland, N.E. Kimble, R.A. Lindskoog, C. Severn, and D.E. Smorong. 2000. *Prediction of Sediment Toxicity using Consensus-based Freshwater Sediment Quality Guidelines*. EPA 905/R-00/007. USEPA Great Lakes National Program Office. Chicago, Illinois.

SPSS, Inc. 2000. SYSTAT® Version 10. *Statistics I* and *Statistics II* User Guides. Chicago, Illinois.

United States Environmental Protection Agency (USEPA). 2004. ProUCL Version 3.0. *User Guide*. EPA/600/R04/079. Developed for USEPA by Lockheed Martin Environmental Services. Las Vegas, Nevada.

7.0 CLOSING

This letter report has been prepared in keeping with accepted protocols for the performance of sediment evaluations and using CEC's professional judgment. The results and discussion of this report cannot be considered scientific certainties, but rather our professional opinions based on the data collected during the course of our investigation. It must be recognized that this investigation is based

on field observations, information received from various regulatory officials, and the research of pertinent peer-reviewed literature. No other warranties, either expressed or implied, are made herein.

CEC appreciates the opportunity to continue to provide professional ecological consulting services to CONSOL for this challenging project. Please call us at (412) 429-2324 if you have any questions or require additional information.

Very truly yours,

CIVIL & ENVIRONMENTAL CONSULTANTS, INC.

Robert Ventorini
Assistant Project Manager

James E. Mudge, Ph.D.
Vice President – Ecological Services

R-040-148.0005.FEB17/W

TABLE 1

Pooled Data, Descriptive Summary Statistics, and Sediment Quality Benchmarks
Stream Sediment Evaluation - Alternative Corrective Measure Triggers
New Coal Refuse Disposal Facility, CONSOL Bailey Mine Complex
Richhill and Gray Townships, Greene County, Pennsylvania
CEC Project 040-148

Sampling dates + corresponding activities at new refuse disposal site. w/ correlating events

		Total [Se] (mg/Kg)		Total [PAHs] (µg/Kg; Adjusted to 2% TOC)	
		Bailey Mine Upstream	Bailey Mine Downstream	Bailey Mine Upstream	Bailey Mine Downstream
Pooled Data		1.20	3.20	358	261
		0.85	1.70	136	114
		0.95	1.30	87	236
		2.40	0.39	747	68
		0.48	0.36	806	683
		0.72	0.36	55	180
		0.37	0.38	128	150
		1.00	0.97	17	257
		0.29	0.55	31	833
		0.28	0.62	5	149
		0.29	3.20	13	1,966
		0.44	1.60	10	465
		1.70	1.60	114	1,280
		1.50		90	
		1.30		53	
		1.10		17	
Descriptive Summary Statistics	N of Cases	16	13	16	13
	Minimum	0.28	0.36	5	68
	Maximum	2.40	3.20	806	1,966
	Range	2.12	2.84	801	1,898
	Sum	14.87	16.23	2,667	6,642
	Sample Median	0.90	0.97	71	257
	Sample Mean	0.93	1.25	167	511
	95% Confidence Interval Upper Limit (Upper Tolerance Limit)	1.25	1.86	302	850
	95% Confidence Interval Lower Limit	0.61	0.64	32	172
	Standard Error (SE)	0.15	0.28	63	155
	Standard Deviation (SD)	0.60	1.00	253	561
	Variance	0.36	1.01	64,164	314,266
	Coefficient of Variation	0.64	0.80	2	1

TABLE 2

Nonparametric Statistical Analyses

Stream Sediment Evaluation - Alternative Corrective Measure Triggers

New Coal Refuse Disposal Facility, CONSOL Bailey Mine Complex

Richhill and Gray Townships, Greene County, Pennsylvania

CEC Project 040-148

Shapiro-Wilk W Test Results				
	Bailey Mine Upstream [Se]	Bailey Mine Downstream [Se]	Bailey Mine Upstream [PAHs]	Bailey Mine Downstream [PAHs]
Shapiro-Wilk W Statistic*	0.911	0.816	0.640	0.760
Correlation R	0.956	0.911	0.798	0.868
Critical Value (α=0.05)	0.887	0.866	0.887	0.866
Data Normally Distributed?	Yes	No	No	No

*The closer W is to 1, the more likely the sample data approach a normal distribution.

Wilcoxon Signed-Ranks Test Results		
Z Statistic = (Sum of Signed Ranks)/ $\sqrt{}$(Sum of Squared Ranks)		
	Bailey Mine Upstream [Se]	Bailey Mine Downstream [Se]
Bailey Mine Upstream [Se]	0.000	
Bailey Mine Downstream [Se]	1.153	0.000
Two-Sided Probabilities Using Normal Approximation (α=0.05)		
	Bailey Mine Upstream [Se]	Bailey Mine Downstream [Se]
Bailey Mine Upstream [Se]	1.000	
Bailey Mine Downstream [Se]	0.249**	1.000
Z Statistic = (Sum of Signed Ranks)/ $\sqrt{}$(Sum of Squared Ranks)		
	Bailey Mine Upstream [PAHs]	Bailey Mine Downstream [PAHs]
Bailey Mine Upstream [PAHs]	0.000	
Bailey Mine Downstream [PAHs]	1.887	0.000
Two-Sided Probabilities Using Normal Approximation (α=0.05)		
	Bailey Mine Upstream [PAHs]	Bailey Mine Downstream [PAHs]
Bailey Mine Upstream [PAHs]	1.000	
Bailey Mine Downstream [PAHs]	0.059**	1.000

**Not Considered Significant (P > 0.05).

CONSOL ENERGY

CNX Coal – PA Operations

CNX Coal – PA Operations

Todd M. Shumaker
1525 Pleasant Grove Road
P.O. Box J
Claysville, PA 15323

phone: 724-663-3039
fax: 724-663-3067
email: toddshumaker@consolenergy.com

December 6, 2004

Mr. Scott A. Hans
Department of the Army
Operations and Readiness Division
Regulatory Branch
Pittsburgh District, Corps of Engineers
William S. Moorhead Federal Building
1000 Liberty Avenue
Pittsburgh, Pennsylvania 15222-4186

RE: Bailey Mine Coal Refuse Disposal Areas
CPCC Pennsylvania Coal Company
Richhill Township, Greene County, Pennsylvania

Dear Mr. Hans:

Department of the Army (Department) Permit No. 200200371 (Permit), Special Condition 10 requires the collection and analysis of sediments in the vicinity of the subject facility with a subsequent report to the Department. To fulfill that Permit requirement, find attached a report prepared by Civil & Environmental Consultants, Inc. (CEC) entitled "Sediment Evaluation of Enlow Fork and Tributaries for the First through Third Quarters of 2004, Bailey Mine-New Coal Refuse Disposal Facility, CONSOL Pennsylvania Coal Company," dated October 20, 2004. Additional copies have been supplied for distribution as you see necessary.

Special Condition 10 of the Permit requires immediate corrective measures if the levels of selenium and/or PAHs increase by greater than 20% from the samples collected on November 19, 2002. The CEC report presents data illustrating that on some dates the selenium and PAH levels both upstream and downstream of the subject facility increased by greater than 20%. CPCC believes the "greater than 20% level" is not an appropriate trigger for immediate corrective measures and would like to discuss other alternatives with you after the fourth quarter 2004 samples are collected and you have had an opportunity to review the attached report. CPCC suggests meeting in late January or early February 2005 to discuss these matters. Please call me at (724) 663-3039 to schedule a meeting with you and your staff.

Sincerely yours,

Todd M. Shumaker

Todd Shumaker
Environmental Engineer

Enlcosure

#200200371

Rec'd 12/8/04 gr

Christy

SEVERN TRENT STL

Geotechnical Analysis
Sample Data Summary Package

WET CHEMISTRY

Sample Report Summary

Client Sample No.
#14D

Lab Name: STL BURLINGTON
Contract: C4L160346
SDG No.: 4L160346

Lab Code: STLVT
Case No.: BAILEY
Lab Sample ID: 602376

Matrix: SOLID
Client: STLPAP
Date Received: 12/17/04

% Solids: 72.9

Method	Parameter	Analytical Run Date	Analytical Batch	Units	DF	RL	Conc.	Qual.
IN623	Solids, Percent	12/21/04	N/A	%	1.0		72.9	
IN847	TOC by Lloyd Kahn	12/20/04	BLKLK1220B	mg/Kg	1	686	7640	

Printed on: 12/29/04 02:50 PM

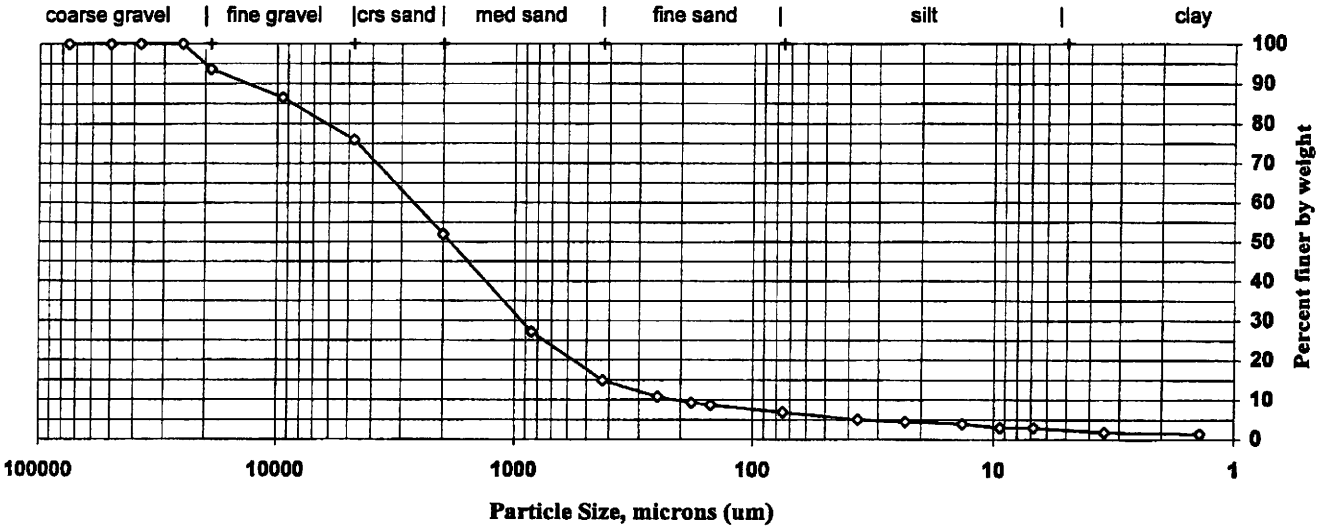
Particle Size of Soils by ASTM D422

Sample preparation method: D2217

Client:	STLPAP	**Project No.:**	24006	**ETR(s) #:**	104428
Client Code:	STLPAP	**Job No.:**	N/A	**SDG(s):**	4L160346
Date Received:	17-Dec-04	**Start Date:**	18-Dec-04	**End Date:**	23-Dec-04

Lab ID: 602378 **Sample ID:** #10

Percent Solids:	75.5%		**Maximum Particle Size:**	25 mm
Specific Gravity:	2.65	(assumed)	**Shape (> #10):**	subrounded
Non-soil mass:	N/A		**Hardness (> #10):**	hard



Sieve size	Particle size, um	Percent finer	Incremental percent
3 inch	75000	100.0	0.0
2 inch	50000	100.0	0.0
1.5 inch	37500	100.0	0.0
1 inch	25000	100.0	0.0
3/4 inch	19000	93.7	6.3
3/8 inch	9500	86.5	7.1
#4	4750	75.9	10.6
#10	2000	51.9	24.0
#20	850	27.1	24.8
#40	425	14.9	12.3
#60	250	10.8	4.1
#80	180	9.3	1.5
#100	150	8.7	0.5
#200	75	6.9	1.9
Hydrometer	36.5	5.1	1.8
|	23.2	4.5	0.5
|	13.5	4.0	0.5
|	9.4	3.0	1.0
|	6.8	3.0	0.0
|	3.5	1.9	1.1
V	1.4	1.5	0.4

Soil Classification	Percent of Total Sample
Gravel	24.1
Sand	69.0
Coarse Sand	24.0
Medium Sand	37.0
Fine Sand	8.0
Silt	3.9
Clay	3.0

Dispersion Device: Mechanical mixer with a metal paddle.
Dispersion Period: 1 minute

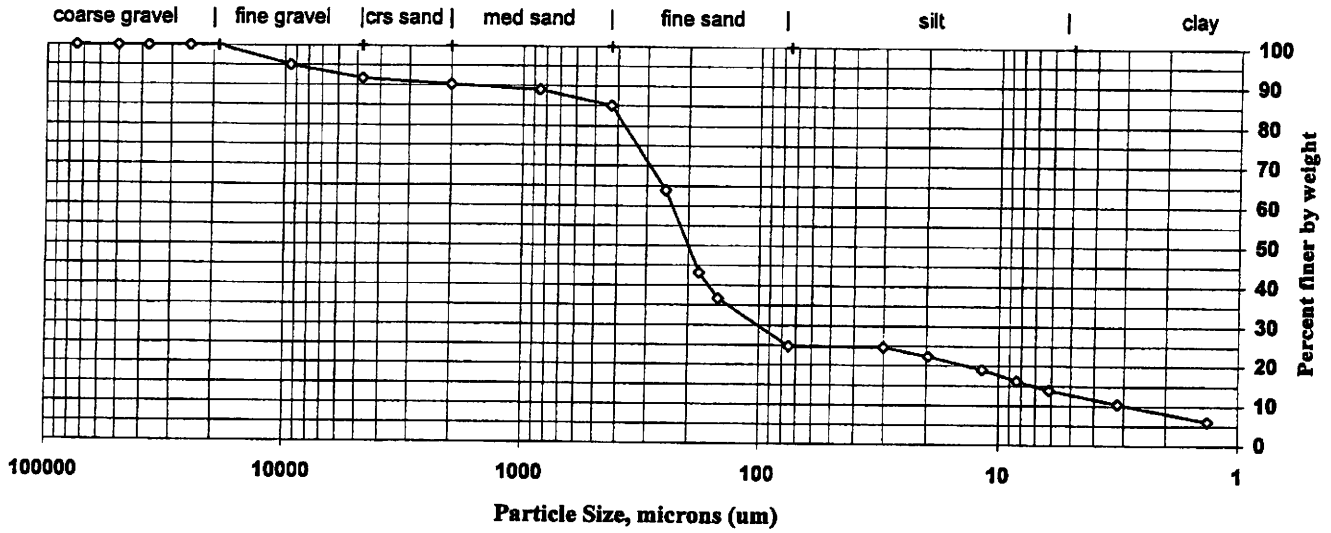
Particle Size of Soils by ASTM D422

Sample preparation method: D2217

Client:	STLPAP	**Project No.:**	24006	**ETR(s) #:**	104428
Client Code:	STLPAP	**Job No.:**	N/A	**SDG(s):**	4L160346
Date Received:	17-Dec-04	**Start Date:**	18-Dec-04	**End Date:**	23-Dec-04

Lab ID: 602377 **Sample ID:** #11

Percent Solids:	66.8%		**Maximum Particle Size:**	19 mm
Specific Gravity:	2.65	(assumed)	**Shape (> #10):**	subrounded
Non-soil mass:	0.0%		**Hardness (> #10):**	hard



Sieve size	Particle size, um	Percent finer	Incremental percent
3 inch	75000	100.0	0.0
2 inch	50000	100.0	0.0
1.5 inch	37500	100.0	0.0
1 inch	25000	100.0	0.0
3/4 inch	19000	100.0	0.0
3/8 inch	9500	95.0	5.0
#4	4750	91.7	3.3
#10	2000	90.2	1.5
#20	850	89.0	1.2
#40	425	85.1	3.9
#60	250	63.9	21.1
#80	180	43.2	20.7
#100	150	36.7	6.5
#200	75	24.8	11.9
Hydrometer	30.1	24.7	0.1
I	19.6	22.4	2.3
I	11.7	19.0	3.4
I	8.4	16.2	2.8
I	6.2	13.9	2.3
I	3.2	10.5	3.4
V	1.3	6.1	4.4

Soil Classification	Percent of Total Sample
Gravel	8.3
Sand	66.9
Coarse Sand	1.5
Medium Sand	5.1
Fine Sand	60.3
Silt	10.9
Clay	13.9

Dispersion Device: Mechanical mixer with a metal paddle.
Dispersion Period: 1 minute

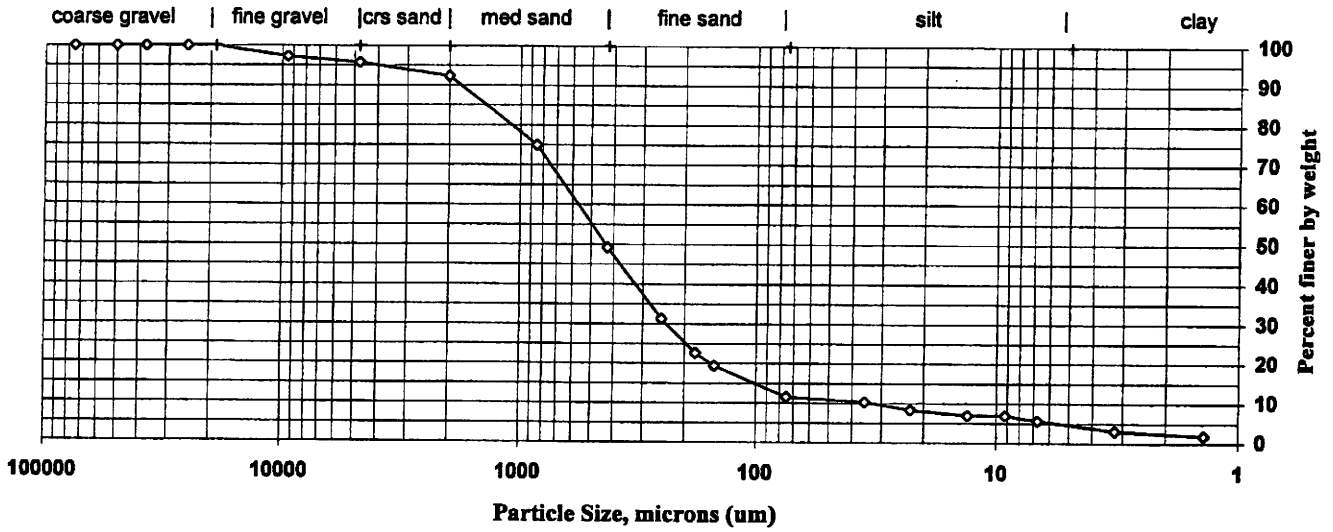
Particle Size of Soils by ASTM D422

Sample preparation method: D2217

Client:	STLPAP	**Project No.:**	24006	**ETR(s) #:**	104428
Client Code:	STLPAP	**Job No.:**	N/A	**SDG(s):**	4L160346
Date Received:	17-Dec-04	**Start Date:**	18-Dec-04	**End Date:**	23-Dec-04

Lab ID: 602379 **Sample ID:** #12

Percent Solids:	67.5%		**Maximum Particle Size:**	19 mm
Specific Gravity:	2.65	(assumed)	**Shape (> #10):**	subrounded
Non-soil mass:	0.0%		**Hardness (> #10):**	hard



Sieve size	Particle size, um	Percent finer	Incremental percent
3 inch	75000	100.0	0.0
2 inch	50000	100.0	0.0
1.5 inch	37500	100.0	0.0
1 inch	25000	100.0	0.0
3/4 inch	19000	100.0	0.0
3/8 inch	9500	97.2	2.8
#4	4750	95.7	1.5
#10	2000	92.3	3.4
#20	850	75.0	17.3
#40	425	49.2	25.8
#60	250	31.3	18.0
#80	180	22.7	8.5
#100	150	19.4	3.3
#200	75	11.5	7.9
Hydrometer	35.3	10.3	1.2
|	22.6	8.3	2.0
|	13.2	7.0	1.3
|	9.2	7.0	0.0
|	6.7	5.7	1.3
|	3.2	3.0	2.6
V	1.4	1.9	1.2

Soil Classification	Percent of Total Sample
Gravel	4.3
Sand	84.2
Coarse Sand	3.4
Medium Sand	43.1
Fine Sand	37.7
Silt	5.9
Clay	5.7

Dispersion Device: Mechanical mixer with a metal paddle.
Dispersion Period: 1 minute

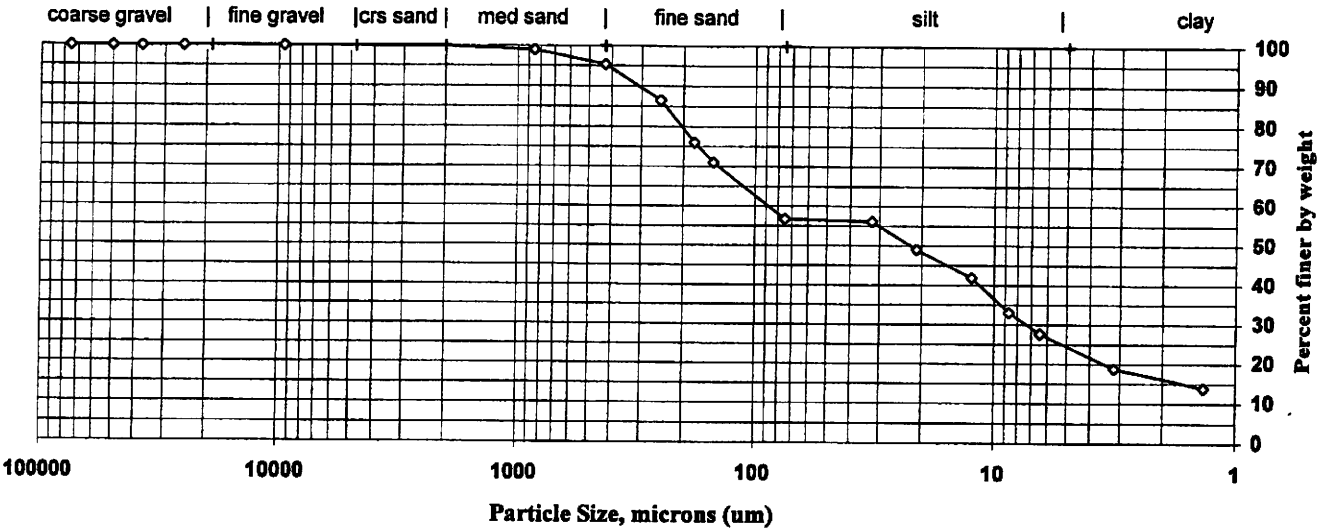
Particle Size of Soils by ASTM D422

Sample preparation method: D2217

Client:	STLPAP	**Project No.:**	24006	**ETR(s) #:**	104428
Client Code:	STLPAP	**Job No.:**	N/A	**SDG(s):**	4L160346
Date Received:	17-Dec-04	**Start Date:**	18-Dec-04	**End Date:**	23-Dec-04

Lab ID: 602380 **Sample ID:** #13

Percent Solids:	47.0%		**Maximum Particle Size:**	Crs sand
Specific Gravity:	2.65	(assumed)	**Shape (> #10):**	subrounded
Non-soil mass:	1.2%		**Hardness (> #10):**	hard



Sieve size	Particle size, um	Percent finer	Incremental percent
3 inch	75000	100.0	0.0
2 inch	50000	100.0	0.0
1.5 inch	37500	100.0	0.0
1 inch	25000	100.0	0.0
3/4 inch	19000	100.0	0.0
3/8 inch	9500	100.0	0.0
#4	4750	100.0	0.0
#10	2000	99.9	0.1
#20	850	99.0	0.9
#40	425	95.3	3.7
#60	250	86.5	8.8
#80	180	76.0	10.5
#100	150	71.0	5.0
#200	75	56.7	14.3
Hydrometer	32.4	56.2	0.5
|	21.0	49.0	7.1
|	12.4	41.9	7.1
|	8.7	33.0	8.9
|	6.4	27.7	5.3
|	3.2	18.8	8.9
V	1.4	13.9	4.9

Soil Classification	Percent of Total Sample
Gravel	0.0
Sand	43.3
Coarse Sand	0.1
Medium Sand	4.6
Fine Sand	38.6
Silt	29.0
Clay	27.7

Dispersion Device: Mechanical mixer with a metal paddle.
Dispersion Period: 1 minute

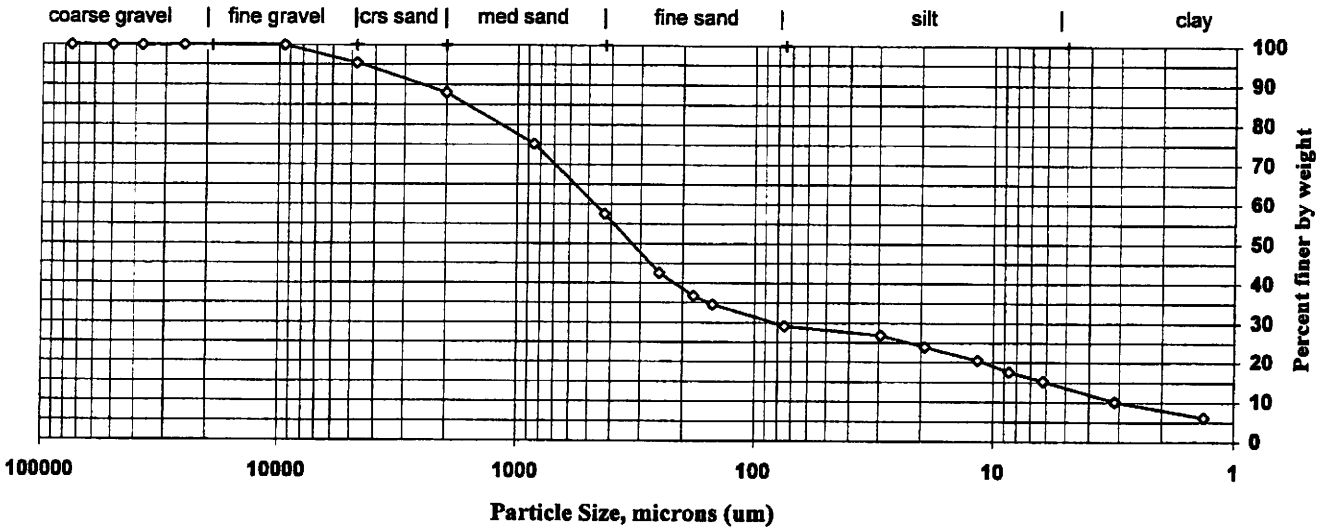
Particle Size of Soils by ASTM D422

Sample preparation method: D2217

Client:	STLPAP	**Project No.:**	24006	**ETR(s) #:**	104428
Client Code:	STLPAP	**Job No.:**	N/A	**SDG(s):**	4L160346
Date Received:	17-Dec-04	**Start Date:**	18-Dec-04	**End Date:**	23-Dec-04

Lab ID: 602375 **Sample ID:** #14

Percent Solids:	71.7%		**Maximum Particle Size:**	9.5 mm
Specific Gravity:	2.65	(assumed)	**Shape (> #10):**	subrounded
Non-soil mass:	N/A		**Hardness (> #10):**	hard



Sieve size	Particle size, um	Percent finer	Incremental percent
3 inch	75000	100.0	0.0
2 inch	50000	100.0	0.0
1.5 inch	37500	100.0	0.0
1 inch	25000	100.0	0.0
3/4 inch	19000	100.0	0.0
3/8 inch	9500	100.0	0.0
#4	4750	95.4	4.6
#10	2000	88.0	7.4
#20	850	75.1	12.9
#40	425	57.5	17.7
#60	250	42.6	14.9
#80	180	36.7	5.9
#100	150	34.6	2.1
#200	75	29.1	5.5
Hydrometer	29.4	26.8	2.3
|	19.3	24.0	2.9
|	11.6	20.5	3.5
|	8.6	17.6	2.9
|	6.2	15.3	2.3
|	3.1	10.1	5.2
V	1.3	6.2	3.9

Soil Classification	Percent of Total Sample
Gravel	4.6
Sand	66.3
Coarse Sand	7.4
Medium Sand	30.5
Fine Sand	28.4
Silt	13.8
Clay	15.3

Dispersion Device: Mechanical mixer with a metal paddle.
Dispersion Period: 1 minute

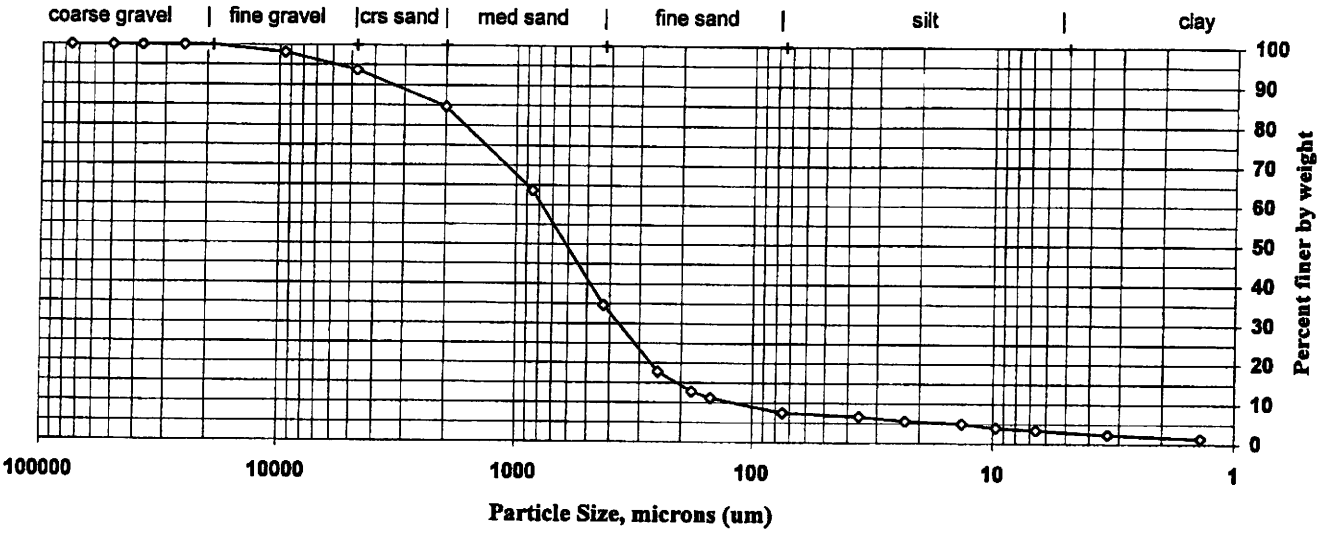
Particle Size of Soils by ASTM D422

Sample preparation method: D2217

Client:	STLPAP	**Project No.:**	24006	**ETR(s) #:**	104428
Client Code:	STLPAP	**Job No.:**	N/A	**SDG(s):**	4L160346
Date Received:	17-Dec-04	**Start Date:**	18-Dec-04	**End Date:**	23-Dec-04

Lab ID: 602376 **Sample ID:** #14D

Percent Solids:	71.7%		**Maximum Particle Size:**	19 mm
Specific Gravity:	2.65	(assumed)	**Shape (> #10):**	subrounded
Non-soil mass:	0.0%		**Hardness (> #10):**	hard



Sieve size	Particle size, um	Percent finer	Incremental percent
3 inch	75000	100.0	0.0
2 inch	50000	100.0	0.0
1.5 inch	37500	100.0	0.0
1 inch	25000	100.0	0.0
3/4 inch	19000	100.0	0.0
3/8 inch	9500	98.1	1.9
#4	4750	93.8	4.4
#10	2000	84.6	9.2
#20	850	63.6	21.0
#40	425	34.7	28.9
#60	250	17.8	16.9
#80	180	12.8	5.0
#100	150	11.1	1.6
#200	75	7.5	3.6
Hydrometer	35.8	6.6	0.9
|	22.9	5.6	1.1
|	13.3	5.0	0.6
|	9.7	4.0	1.1
|	6.6	3.4	0.5
|	3.3	2.4	1.1
V	1.4	1.4	0.9

Soil Classification	Percent of Total Sample
Gravel	6.2
Sand	86.3
Coarse Sand	9.2
Medium Sand	49.9
Fine Sand	27.1
Silt	4.1
Clay	3.4

Dispersion Device: Mechanical mixer with a metal paddle.
Dispersion Period: 1 minute

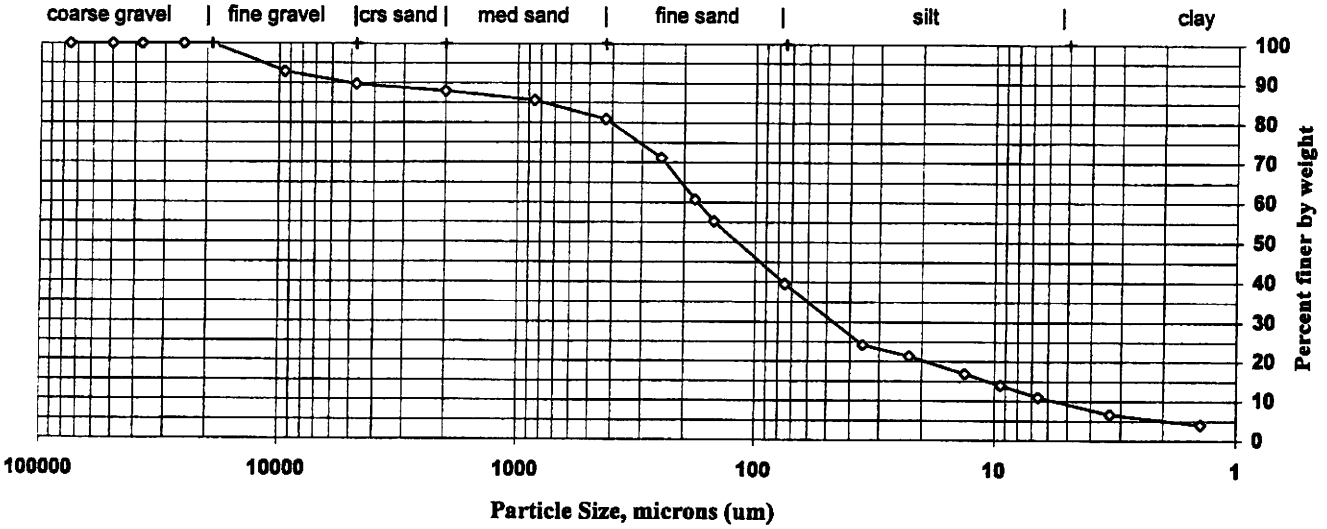
Particle Size of Soils by ASTM D422

Sample preparation method: D2217

Client:	STLPAP	**Project No.:**	24006	**ETR(s) #:**	104428
Client Code:	STLPAP	**Job No.:**	N/A	**SDG(s):**	4L160346
Date Received:	17-Dec-04	**Start Date:**	18-Dec-04	**End Date:**	23-Dec-04

Lab ID: 602381 **Sample ID:** #15

Percent Solids:	60.8%		**Maximum Particle Size:**	19 mm
Specific Gravity:	2.65	(assumed)	**Shape (> #10):**	subrounded
Non-soil mass:	0.2%		**Hardness (> #10):**	hard



Sieve size	Particle size, um	Percent finer	Incremental percent
3 inch	75000	100.0	0.0
2 inch	50000	100.0	0.0
1.5 inch	37500	100.0	0.0
1 inch	25000	100.0	0.0
3/4 inch	19000	100.0	0.0
3/8 inch	9500	92.9	7.1
#4	4750	89.7	3.2
#10	2000	87.9	1.8
#20	850	85.6	2.3
#40	425	80.9	4.7
#60	250	71.2	9.7
#80	180	60.7	10.5
#100	150	55.2	5.5
#200	75	39.6	15.7
Hydrometer	35.3	24.3	15.3
|	22.6	21.3	2.9
|	13.2	16.9	4.4
|	9.4	14.0	2.9
|	6.6	11.0	2.9
|	3.3	6.6	4.4
V	1.4	4.0	2.6

Soil Classification	Percent of Total Sample
Gravel	10.3
Sand	50.1
Coarse Sand	1.8
Medium Sand	7.0
Fine Sand	41.3
Silt	28.5
Clay	11.0

Dispersion Device: Mechanical mixer with a metal paddle.
Dispersion Period: 1 minute

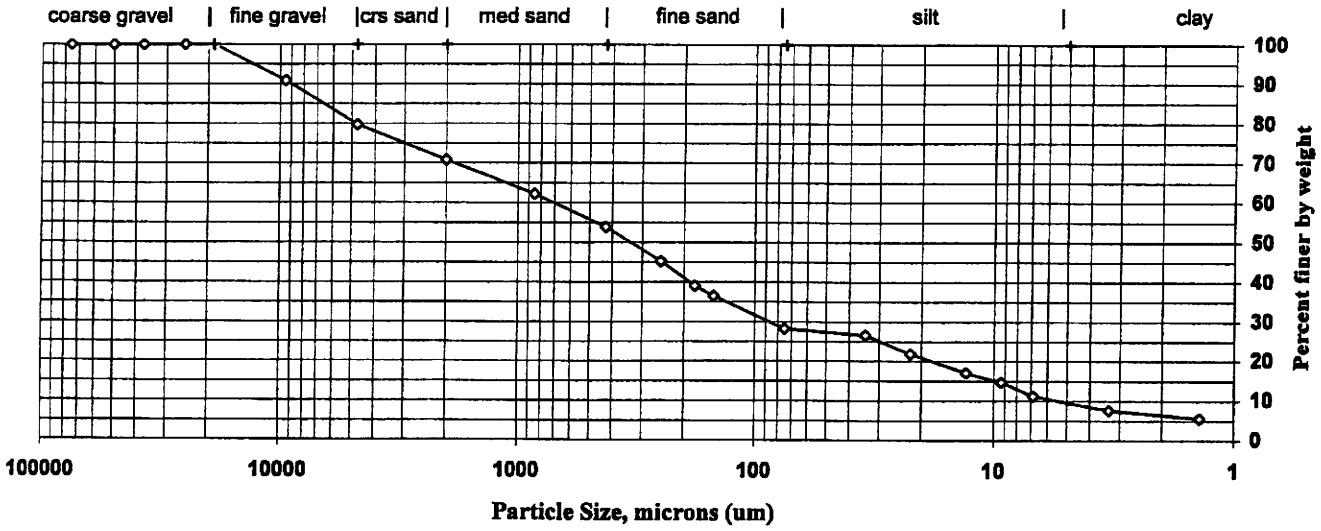
Particle Size of Soils by ASTM D422

Sample preparation method: D2217

Client:	STLPAP	**Project No.:**	24006	**ETR(s) #:**	104428
Client Code:	STLPAP	**Job No.:**	N/A	**SDG(s):**	4L160346
Date Received:	17-Dec-04	**Start Date:**	18-Dec-04	**End Date:**	23-Dec-04

Lab ID: 602382 **Sample ID:** #16

Percent Solids:	52.4%		**Maximum Particle Size:**	19 mm
Specific Gravity:	2.65	(assumed)	**Shape (> #10):**	subrounded
Non-soil mass:	0.8%		**Hardness (> #10):**	hard



Sieve size	Particle size, um	Percent finer	Incremental percent
3 inch	75000	100.0	0.0
2 inch	50000	100.0	0.0
1.5 inch	37500	100.0	0.0
1 inch	25000	100.0	0.0
3/4 inch	19000	100.0	0.0
3/8 inch	9500	90.8	9.2
#4	4750	79.8	11.0
#10	2000	70.8	9.0
#20	850	62.2	8.6
#40	425	53.8	8.4
#60	250	45.2	8.6
#80	180	39.0	6.3
#100	150	36.5	2.5
#200	75	28.2	8.3
Hydrometer	34.3	26.6	1.6
|	22.1	21.9	4.7
|	13.0	17.1	4.7
|	9.3	14.8	2.4
|	6.8	11.2	3.5
|	3.3	7.7	3.5
V	1.4	5.6	2.1

Soil Classification	Percent of Total Sample
Gravel	20.2
Sand	51.6
Coarse Sand	9.0
Medium Sand	17.0
Fine Sand	25.6
Silt	17.0
Clay	11.2

Dispersion Device: Mechanical mixer with a metal paddle.
Dispersion Period: 1 minute

SEVERN TRENT STL

Sample Data Summary Package For Wet Chemistry

WET CHEMISTRY

Sample Report Summary

Client Sample No.

#14

Lab Name: STL BURLINGTON

Contract: C4L160346

SDG No.: 4L160346

Lab Code: STLVT

Case No.: BAILEY

Lab Sample ID: 602375

Matrix: SOLID

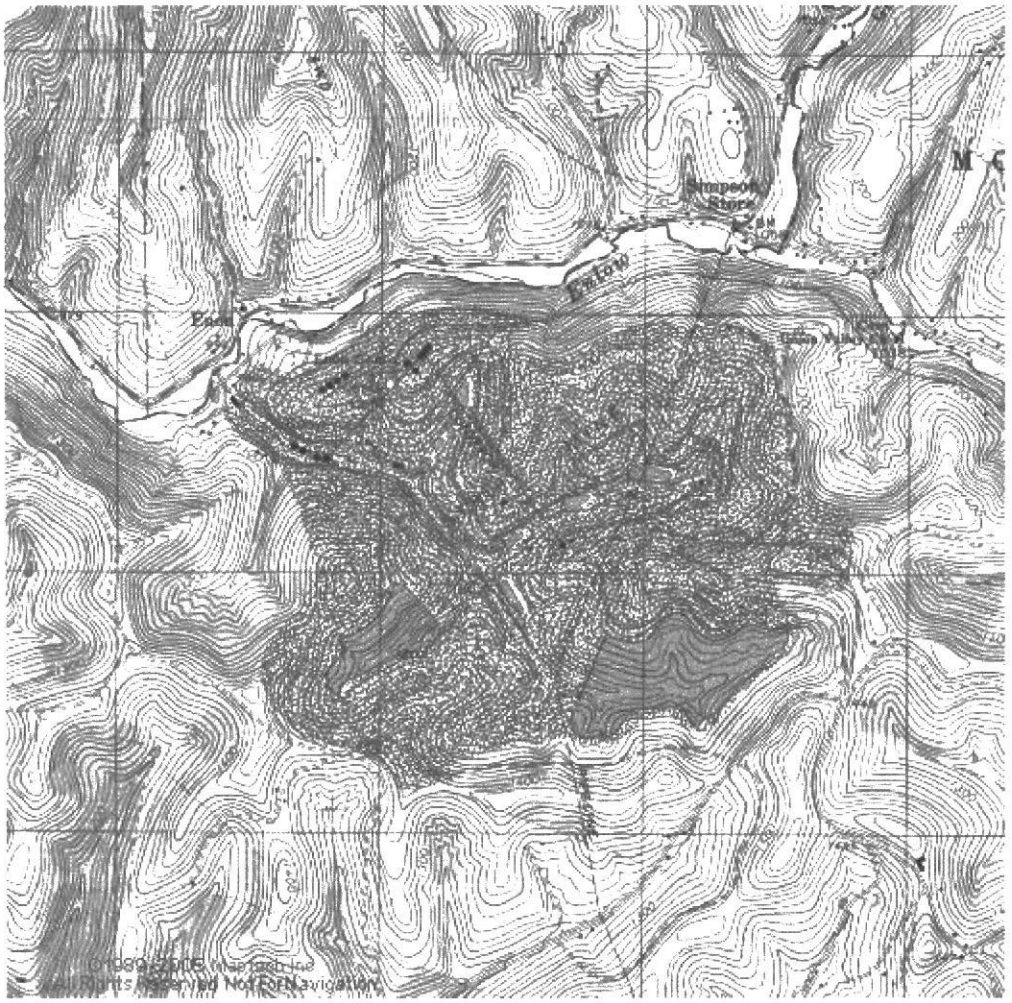
Client: STLPAP

Date Received: 12/17/04

% Solids: 73.2

Method	Parameter	Analytical Run Date	Analytical Batch	Units	DF	RL	Conc.	Qual.
IN623	Solids, Percent	12/21/04	N/A	%	1.0		73.2	
IN847	TOC by Lloyd Kahn	12/27/04	BLKLK1227A	mg/Kg	1	683	4560	

Printed on: 12/29/04 02:50 PM


Snapper Rock
Below
Boat
Copyright © 2000 Maptech, Inc.
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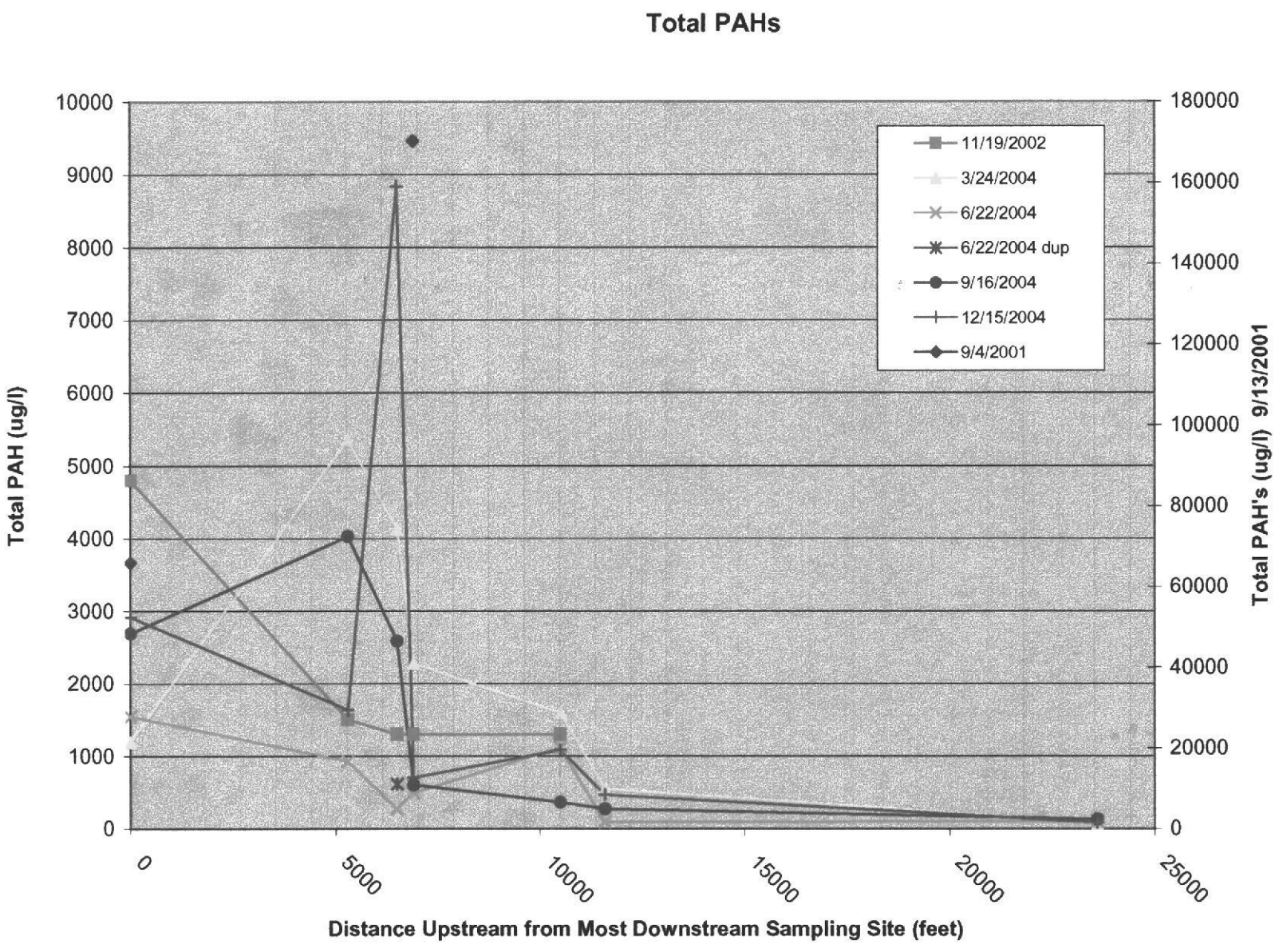
Total PAHs
Total PAH (ug/l)
Total PAH's (ug/l) 9/13/2001
Distance Upstream from Most Downstream Sampling Site (feet)
11/19/2002
3/24/2004
6/22/2004
6/22/2004 dup
9/16/2004
12/15/2004
9/4/2001
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
0
20000
40000
60000
80000
100000
120000
140000
160000
180000
0
5000
10000
15000
20000
25000

Meeting Between CONSOL and Department of the Army (Corps) to Discuss Bailey Mine Refuse Area Permit Special Condition 10

May 11, 2004

Meeting Agenda

1. Introductions
2. Permit No. 2002200371 Special Condition 10 Requirements
3. March 24, 2004 Sediment Results
4. Comparison of 2004 Results to 2002 Results
5. Conclusions
6. Discussion

Permit Special Condition 10 Requirements

- Collection of sediment samples and subsequent testing for polycyclic aromatic hydrocarbons (PAHs) and total selenium (Se)
- Sample at locations 10 through 14 and at an additional sampling location upstream of the new facility. CONSOL added background locations 15 and 16 on the North and South Fork of Enlow Fork, respectively, to meet this requirement.
- Sample quarterly from the start of construction until two years after the facility is closed and reclaimed.
- If PAH or Se levels increase by greater than 20% from the samples collected on November 19, 2002, immediate corrective measures are required.

Sediment Sampling Locations at Bailey Mine Complex
Consol Pennsylvania Coal Company
Richhill and Gray Townships, Greene County, Pennsylvania

Sampling Station	Sampling Station Location
10	Talley Run; essentially all drainage from facilities except NPDES 005.
11	Enlow Fork, about 1,200 feet downstream of Talley Run confluence, just below discharges from sanitary plant and storage yards.
12	Enlow Fork about 1,200 feet above Talley Run confluence.
13	Enlow Fork about 3,800 feet above Talley Run confluence.
14	Enlow Fork about 6,600 feet below Talley Run confluence.
15	Enlow Fork about 8,600 feet above Talley Run confluence.
16	Enlow Fork about 21,400 feet above Talley Run confluence.

Notes:

1. Samples collected by Civil & Environmental Consultants, Inc.

Summary of March 24, 2004 Sediment Results and Comparison to November 19, 2002 Results

- Total concentration for the 13 PAHs commonly used by regulatory agencies to assess aquatic biota effects ranged from 73 to 6,075 µg/kg at stations 16 and 11, respectively, in March 2004.
- Percent change in PAHs (i.e., comparing 2004 results to 2002 results) range from -87% at station 14 to +212% at station 11. Only station 12 results shows a changes less than 20% (i.e., -4%).
- No federal or state sediment quality criteria/guidelines for PAHs or Se

PAH Analysis of Sediment Samples Collected at Bailey Mine Complex

Consol Pennsylvania Coal Company

SAMPLE LOCATION	Total PAHs 030/04	Percent Total Organic Carbon	Total PAH Adjusted 03/04	Total PAHs 11/02	Percent Total Organic Carbon	Total PAH Adjusted 11/02	Percent Change in PAH
10	4122	31.6	261	1300	12.2	213	22
11	6075	17.8	683	1400	12.8	219	212
12	2275	12.7	358	1300	6.99	372	-4
13	1588	4.25	747	1300	5.45	477	57
14	1189.5	9.25	257	4400	4.61	1909	-87
15	544	8.52	128	NS	NS	NS	NS
16	73	27.2	5	NS	NS	NS	NS
PEC	22800		22800	22800		22800	

All values are in units of µg/kg. NS - Not Sampled

Summary and Comparison of Results (Continued)

Sediment sample results for PAHs should be compared to recent United States sponsored Sediment Quality Guidelines (SQGs): "Prediction of sediment toxicity using consensus based freshwater sediment guidelines." Ingersoll et al. (2000). EPA 905/R-00/007

Probable Effects Concentration (PEC)-level above which adverse effects are expected to occur frequently

PEC estimated by Ingersoll et al. (2000) for Total PAH is 22,800 μg/kg

All sample results are well below probable effect concentration of 22,800 μg/kg proposed by Ingersoll et al. (2000)

Summary and Comparison of Results (Continued)

- Total selenium concentrations ranged from 0.85 mg/kg at sampling station 13 to 3.2 mg/kg at station 10 in March 2004. New background station 16 had the second highest concentration of 2.4 mg/kg.
- Percent change in Se (i.e., comparing 2004 results to 2002 results) range from 309% at station 11 to 8,500% at station 13. Station 13 is a background station and discharges from the existing facility occur 3,800 feet downstream from this station.
- Changes may be a reflection of sampling depositional areas/sediments in March 2004 as compared to coarser sediments in November 2002.

Total Selenium in Sediment Samples Collected at Bailey Mine Complex

Consol Pennsylvania Coal Company

Sampling Station	Total Selenium (mg/Kg)	Total Selenium (mg/Kg)	Percent Change
	11/19/02	03/24/04	
10	0.8	3.2	400%
11	0.55	1.7	309%
12	0.3	1.2	400%
13	<0.02	0.85	8500%
14	0.2	1.3	650%
15	NS	0.95	NS
16	NS	2.4	NS

Notes: NS = Not Sampled

Evaluation of Se Results

Sediment sample results for selenium should be compared to potential levels of concern observed in freshwater, see the following references:

1. "Aquatic cycling of selenium: implications for fish and wildlife."1987. Lemly and Smith. U.S. Fish and Wildlife Leaflet 12.
2. " Guidelines for evaluating selenium data from aquatic monitoring and assessment. 1993. Lemly. Enviro. Monit. Assessment 28: 83-100.
3. "Selenium toxicity to aquatic life: an argument for sediment-based water quality criteria."1997. Canton and Van Derveer. ET&C 16(6): 1255-1259.
4. "Guidelines for conducting TMDL consultations on selenium." 2000. Lemly. USFWS Technical Report.

Evaluation of Se Results (Continued)

- Lemly and Smith: $\geq 4\mu g/g$ (mg/kg) Se causes reproductive failure or mortality due to food-chain bioconcentration
- Lemly: Se biological effect thresholds, ppm, dry weight

Plankton & forage fish	30-370
Some freshwater and anadromous fish	4
Some aquatic birds & benthic invertebrates	3-10

- Canton and Van Derveer: "predicted" effect Se level 2.5
  "observed" effect Se level 4.0
- All the 2004 values, except for the 3.2 mg/kg at station 10, are below these sediment concentrations
- Therefore, the results indicate that adverse effects from Se are not likely to be pervasive

Conclusions

- A 20% change in the concentrations of PAHs or Se in sediments does not appear to be an appropriate basis to take immediate corrective measures. For example, percent change in Se at background stations 12 and 13 were 400% and 8,500%, respectively.
- PAH concentrations at all stations do not exceed relevant SQGs and only the Se concentration at station 10 may slightly exceed a threshold aquatic biota effects value identified in the literature cited above.
- CONSOL suggests continuing the quarterly monitoring program and monitor how the concentrations change through time using consistent sampling methodology.

CONSOLENERGY™

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fax: 412/831-4774
e-mail: jonathanpachter@consolenergy.com
web: www.consolenergy.com

JONATHAN M. PACHTER
Manager, Environmental Permitting

Mr. Scott A.Hans
Chief, Regulatory Branch
Operations and Readiness Division
Department of the Army
Pittsburgh District, Corps of Engineers
1000 Liberty Avenue
Pittsburgh, PA 15222-4186

RE: New Bailey Mine Coal Refuse Disposal Areas No.3 and No. 4
Richhill Township, Greene County, PA
Department of the Army Permit No. 200200371
Special Condition No. 6 – Notification of Status of Stream Fencing Work

Dear Mr. Hans:

Please be advised that Consol Pennsylvania Coal Company (CPCC) is contracting with The Foundation for California University of Pennsylvania (CUP) to conduct the stream fencing and monitoring work required by Special Condition Nos. 6 and 7 of the above-referenced permit. A copy of the proposed contract between CPCC and CUP (minus the financial aspects of the contract) is attached for your files. CUP has reached agreement with quite a few property owners to allow the stream fencing work to be done, with much more than 50% to be done in the Enlow Fork watershed. As soon as they are completed by CUP, I will send you a map and table showing the status of property agreements for this fencing, plus a description of the work to be performed during the next two calendar years.

Please call me at (412) 831-4679 with any questions regarding this letter.

Sincerely,

Jonathan M Pachter

Jonathan. M. Pachter
Manager, Environmental Permitting

CC without attachment: Jose' Taracido, CUP

Christy
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2/6/04
pa

CONTRACT
BETWEEN

THE FOUNDATION FOR CALIFORNIA UNIVERSITY OF PENNSYLVANIA
(hereinafter the "Foundation")

AND

CONSOL PENNSYLVANIA COAL COMPANY (hereinafter, "Consol")

WHEREAS, Consol has a need for restoration and baseline biomonitoring work in conjunction with its Bailey Coal Refuse Disposal Site; and

WHEREAS, The Foundation can provide the necessary services to meet the needs of Consol.

NOW, THEREFORE, in consideration of the mutual promises herein contained and with the intent to be legally bound hereby, the parties hereto agree as follows:

1. Foundation agrees to provide Consol the necessary services (including personnel, equipment and supervision to perform the following tasks:

   a. Restoration activities, including border edge cuts, riparian stream bank fencing, alternative drinking water sources, and all necessary permitting needed to complete these activities.
   b. Seasonal baseline monitoring of agriculturally impacted and restored areas, including samples of fish, macro invertebrates, plants, and water during spring, summer and fall.
   c. Periodic status reports on progress and projects implementation.

2. For the aforesaid services, Consol will pay the Foundation the sum of , as follows: commencing March 15, 2004 and continuing on the 15th day of each month thereafter through January 15, 2009, the sum of and the balance of on February 15, 2009.

3. The term of this contract shall be from February 15, 2004 through February 15, 2009.

4. This contract may be modified only by written amendment signed by both parties.

5. A description of the services to be provided by the Foundation is attached hereto as Exhibit "A".

IN WITNESS WHEREOF, the parties hereto have caused this contract to be executed by their duly authorized representatives.

EXHIBIT "A"

Part I – Landowner Contracts

Maintain landowner contracts to participate in this habitat restoration program. Participants will sign an agreement with The Partners for Fish and Wildlife at the Foundation for California University of Pennsylvania to permit restoration (mitigation) activities to occur and to grant access to their property for biomonitoring work as described below.

Part II – Restoration Activity

1. Protect existing streams, wetlands, and spring developments within the watershed with the approximately 12.5 miles of fencing with 2 crossings per mile of stream (This work will commence as soon as a permit has been issued and an aggressive schedule will be maintained to target completion by September, 2004). As per DEP's request selected riparian corridors (2/3 of the fenced areas) will be planted with trees and protected with tree tubes to accelerate revegetation of the streamside area.

2. Establish 20 border-edge cuts on farms throughout the watershed(s) (this work will commence during winter 2003-2004 and will be completed by spring 2004). This is a complimentary wildlife management tool used in conjunction with grass planting and riparian fencing that creates soft edges for wildlife species to transition between established habitats. The number and size are determined by the availability of timber on the property to be restored.

3. Plant 100 acres of native wa4rm-season grasses to increase wildlife habitat in the affected watershed to the extent possible. Determine the seeding mix according to the site needs (e.g., wildlife use only or agricultural and wildlife use). These ratios will establish a pasture-like landscape. Target will be one plant per square yard. Seeding will occur during 2004 and 2005 between April and June of those years.

Part III – Bio-monitoring (to be completed by 2008)

1. Assess the impacts of riparian restoration by monitoring plant, fish, and macro invertebrate communities before and after stream bank restoration, and in both restored and unrestored streams. Initial assessments will occur before stream bank restoration activity has begun to provide a statistical benchmark to document the expected improvements. These assessments will begin, prior to initial restoration activity. During this time 100 m. reaches will be established as permanent reference points at each site (maximum of 12 sites). Sites will be sampled during spring, summer and fall seasons. Monitor restored sites until December 2008. Additionally, a representative number of unrestored and

unprotected stream sections of similar stream order, plant composition, and surrounding land-use will serve as controls. These 100 m. stream sections will serve as the experimental units for all analyses.

2. Water samples will be collected during the spring, summer, and fall season. The Partners for Fish and Wildlife will process samples for NH4, NO3, turbidity, pH, dissolved oxygen, temperature, conductivity, and fecal coliforms. Phosphate samples will be processed by a third party. These parameters were selected because many serve as good barometers for stream health in agriculturally impacted waters. In addition, automated temperature recorders will be placed in the streams to monitor stream temperatures daily to document seasonal shifts as the riparian corridor becomes better established. Fecal coliform colonies will be counted on filtered paper that is incubated using standard water testing procedures. A 20% reduction in fecal coliform colonies, turbidity, NH4, NO3, and phosphates will be used as a benchmark of success.

3. Fish and macro invertebrate populations will be surveyed during the spring, summer, and fall seasons. Fish will be sampled using backpack electro-shocking equipment following the EPA's Rapid Bioassessment Protocol. One pass along a 100 m. section will be made. Each section will be demarcated with fixed reference points to permit repeated seasonal sampling. Each specific section will be chosen at random and marked accordingly. Macro invertebrate populations will be sampled using both kick nets (qualitative) and Hess-samplers (quanitative). Three random samples will be made in each 100 m. section during each sampling season with each apparatus. Samples will be processed by the Partners. Fish and macro invertebrates will be identified to the species and genus level where possible, enumerated, and a reference collection maintained. These sampling techniques will permit abundance estimates to be made for both fish and macro invertebrates. Success among these variables will be determined by examining the shifts in community composition (e.g. Shannon-Weaver diversity index, Coefficient of Community Loss, and species richness) among fish and macro invertebrates and changes in both density and abundance.

4. The plant community within the riparian corridor will be sampled to determine herbaceous and woody plant cover and richness. The plant community will also be sampled at these times to determine herbaceous plant cover and richness (by identifying species and estimating % coverage).

   As per DEP's request selected riparian corridors (2-3 of the fenced areas) will be planted with trees and protected with tree tubes to accelerate revegetation of the streamside area. Planted trees will be monitored for growth and development at diameter breast height for the duration of the biomonitoring.

5. Statistical analyses will include a comparison of before and after treatment effects and a comparison among treatment and reference sites using a nested ANOVA design (standard parametric procedures). In addition, regression analyses may be used to explore the relationships between the various water chemistry parameters and the biological parameters (e.g. macro invertebrates and fish) collected.

Consol Pennsylvania Coal Company

By:_____ Date:_____

The Foundation for California University of Pennsylvania

By: _____ Date:_____
Richard C. Grace, President

CONSOL ENERGY

Consol Pennsylvania Coal Company
1800 Washington Road
Pittsburgh, PA 15241-1421

phone: 412/831-4679
fax: 412/831-4774
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web: www.consolenergy.com

JONATHAN M. PACHTER
Manager, Environmental Permitting

Mr. Scott A.Hans
Chief, Regulatory Branch
Operations and Readiness Division
Department of the Army
Pittsburgh District, Corps of Engineers
1000 Liberty Avenue
Pittsburgh, PA 15222-4186

Post-it® Fax Note 7671	Date 2/4/04	# of pages ▶ 5
To Scott Hans	From Jonathan Pachter	
Co./Dept. Corps of Engineers	Co. Consol Energy	
Phone # 412-395-7104	Phone # 412-831-4679	
Fax # 412-644-4211	Fax # 412-831-4774	

- Hard copy by regular mail -

RE: New Bailey Mine Coal Refuse Disposal Areas No.3 and No. 4
Richhill Township, Greene County, PA
Department of the Army Permit No. 200200371
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Jonathan M. Pachter

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Manager, Environmental Permitting

CC without attachment: Jose' Taracido, CUP

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AND

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Consol Pennsylvania Coal Company

By:_____ **Date:**_____

The Foundation for California University of Pennsylvania

By: _____ **Date:**_____
Richard C. Grace, President

Mitigation Proposal for Bailey Coal Refuse Disposal Site, Greene County, Pennsylvania

Prepared by

The Partners for Fish and Wildlife
California University of Pennsylvania

First Draft: January 2002
Second Draft: October 2002
Third Draft: March 2003

Biological and Environmental Sciences Department and
The Foundation for California University of Pennsylvania
California University of Pennsylvania
California, PA 15419

Executive Summary

CONSOL Energy Inc., (CONSOL) is proposing to fill in 2.5 miles of stream in Greene County, Pennsylvania with coal refuse from its Bailey Central Preparation Plant. As required by law, CONSOL must mitigate for their environmental impact to surrounding streams. CONSOL proposes to fund the enhancement of fish and wildlife habitat in a nearby watershed(s) in Greene County (yet to be determined) and to fund biological monitoring of these habitat improvements to mitigate these losses. Mr. José Taracido, the Partners for Fish and Wildlife Farmland Habitat Program Management Supervisor, will oversee the restoration portion of this project. Restoration will include wetland creation, restoration, and protection, native grassland planting, and border-edge cutting. In addition, streambank fencing will be used to improve streambank stability and to improve water quality. The project will be similar to, but separate from, the Farmland Habitat Restoration Project being directed by California University of Pennsylvania's Partners for Fish and Wildlife Program. Dr. David Argent and Dr. Thad Yorks, Assistant Professors of Biology at California University of Pennsylvania, will direct the biomonitoring portion of this project. Responses to habitat improvements within the watershed will be documented by examining plant, fish, and aquatic invertebrate communities in restored portions of the watershed before and after restoration, and by comparing the same parameters in restored and unrestored portions of the watershed. Water samples will also be collected during the project. The restoration/protection program will be considered successful if measured biological variables improve (by a minimum of 20%) over pre-restoration values. California University of Pennsylvania will conduct the watershed restoration and direct monitoring activities with funding from CONSOL. Funding provided by CONSOL will be administered by the Foundation for California University of Pennsylvania. Preliminary work will begin in September 2002 to enroll potential landowners into the restoration program and restoration will formally begin in September 2003 concurrent with the issued permit. Biomonitoring activities will commence during 2003 and continue until 2007.

Objectives

1. To perform mitigation within affected watershed to the greatest extent possible.
2. To mitigate the loss of fish and wildlife habitat that will occur as result of the new Bailey coal refuse disposal area.
3. To restore, protect, and create fish and wildlife habitat
4. To monitor environmental changes in plants, fish, and macroinvertebrates in response to habitat enhancement
5. To collect water samples before, during and after restoration activities have occurred.

Scope of Activity

Part I – Restoration Activity

1. We will develop and maintain landowner contacts to participate in this habitat restoration program (September 2002-March 2003). Participants will sign an agreement with The Partners for Fish and Wildlife at California University of Pennsylvania to permit restoration (mitigation) activities to occur and to grant us access to their property for biomonitoring work.

2. We will protect existing streams, wetlands, and spring developments within the watershed with the use of streambank fencing on agriculturally (grazed) impacted properties. This will include approximately 12.5 miles of fencing with 2 crossings per mile of stream (This work will commence as soon as a permit has been issued and an aggressive schedule will be maintained to target completion by September 2004).

3. We will establish 20 border-edge cuts on farms throughout the watershed (s) (this work will commence during winter 2003 and will be completed by spring 2004). This is a complimentary wildlife management tool used in conjunction with grass planting and riparian fencing that creates soft edges for wildlife species to transition between established habitats. The number and size are determined by the availability of timber on the property to be restored.

4. We will plant 100-acres of native warm-season grasses to increase wildlife habitat in the affected watershed to the extent possible. The seeding mix will be determined by Jose Taracido according to the site needs (e.g., wildlife use only or agricultural and wildlife use). These ratios will establish a pasture-like landscape. Our target will be one plant per square yard. Seeding will occur during 2004 and 2005 between April and June of those years.

Part II – Bio monitoring (to be completed by 2007):

1. We will assess the impacts of riparian restoration by monitoring plant; fish, wildlife, and macroinvertebrate communities before and after streambank restoration, and in both restored and unrestored streams. Initial assessments will occur before streambank restoration activity has begun to provide a statistical benchmark to document the expected improvements. These assessments will begin in spring 2003, prior to initial restoration activity. During this time 100-m reaches will be established as permanent reference points at each site (maximum of 12 sites). Sites will be sampled during spring, summer, and fall seasons. We will monitor restored sites until December 2007. Additionally, a representative number of unrestored and unprotected stream sections of similar stream order, plant composition, and surrounding land-use will serve as controls. These 100-m stream sections will serve as the experimental units for all analyses.

2. Water samples will be collected by California University of Pennsylvania during the

spring (March - June), summer (July - September) and fall (October – December) seasons. A third party (as yet to be named) and California University of Pennsylvania will process collected samples, which will include: NH_4, NO_3, K, turbidity, pH, dissolved oxygen, temperature, conductivity, and fecal coliforms. California University of Pennsylvania has the equipment and expertise to process samples for NH_4, NO_3, turbidity, pH, dissolved oxygen, temperature, conductivity, and fecal coliforms. Phosphate samples will need to be processed by a third party. These parameters were selected because many serve as a good barometer for stream health in an agriculturally impacted stream. California University of Pennsylvania will use a Hydrolab® to measure NH_4, NO_3, turbidity, pH, dissolved oxygen, temperature, and conductivity. In addition, automated temperature recorders will be placed in the streams to monitor stream temperatures daily to document seasonal shifts as the riparian corridor becomes better established. Fecal coliform colonies will be counted on filtered paper that is incubated using standard water testing procedures. A 20% reduction in fecal coliform colonies, turbidity, NH_4, NO_3, and phosphates will be used as a benchmark of success. Other monitored variables (e.g., conductivity) may change, but are not expected to shift dramatically in response to restoration.

3. Fish and macroinvertebrate populations will be surveyed during the spring (March - June), summer (July - September) and fall (October – December) seasons. Fish will be sampled using backpack electro-shocking equipment following the EPA's Rapid Bioassessment Protocol. One-pass along a 100-m section will be made. Each section will be demarcated with fixed reference points to permit repeated seasonal sampling. Each specific section will be chosen apriori at random (i.e., not during an on-site visit) and marked accordingly. Macro-invertebrate populations will be sampled using both kick nets (qualitative) and Hess-samplers (quantitative). Three random samples will be made in each 100-m section during each sampling season with each apparatus. Samples will be processed at California University of Pennsylvania. Fish and macroinvertebrates will be identified to the species and genus level where possible, respectively, enumerated, and a reference collection maintained at California University of Pennsylvania. These sampling techniques will permit abundance estimates to be made for both fish and macroinvertebrates. Success among these variables will be determined by examining the shifts in community composition (e.g., Shannon-Weaver diversity index, Coefficient of Community Loss, and species richness) among fish and macroinvertebrates and changes in both density and abundance.

5. The <u>plant community</u> within the riparian corridor will be sampled to determine herbaceous and woody plant cover and richness. The plant community will also be sampled at these times to determine herbaceous plant cover and richness (by identifying species and estimating % coverage in 6, 1 m^2 plots/section; 3 plots will be randomly located within the stream bed and 3 on the bank) and shrub stem density and richness (by identifying and counting woody stems<2.54 cm dbh in 6, 1 x 5 m plots/section; 3 plots will be randomly located within the stream bed and 3 on the bank; plots will be oriented with the long axis parallel to the stream channel).

To determine if we have met our one plant per square yard target with warm season grass plantings, we will sample five of the warm season grass plantings during the fall sampling period. Twenty-five, random 0.25-meter square plots will be monitored to assess the cover density of seeded plants.

6. Statistical analyses will include a comparison of before and after treatment effects and a comparison among treatment and reference sites using a nested ANOVA design (standard parametric procedures). In addition, regression analyses may be used to explore the relationships between the various water chemistry parameters and the biological parameters (e.g., macroinvertebrates and fish) collected.

7. We expect to document a minimum of a 20% improvement in the biological and physical parameters monitored. Benchmarks for success will include 20% improvements in water quality parameters like fecal coliforms and nitrogen; other parameters are not expected to change considerably over the life of this project, but will be monitored. We expect to document functional shifts in macroinvertebrate populations from tolerant to intolerant individuals and from autochthonous to allochthonous feeders. With respect to fishes, we anticipate an increase in biomass and abundance because fish will have better spawning habitat and more stable habitat conditions. Lastly, we anticipate a large shift in the plant community because cattle will no longer have grazing access. Over the course of the biomonitoring work we expect to see an increase in diversity, density, and height of herbaceous plants with recruitment of woody plants.

Part III – Schedule*

August 2002 – March 2003

Site surveys and landowner contact and sign-up in designated area(s) – See Attachment for Sub-Contract detailing activities and services to be provided

March 2003 – October 2003

Initiate pre-restoration biomonitoring activities.

September 2003 – November 2003

Streambank fencing restoration
November 2003 – April 2004

Border edge cuts completed

April 2004 – September 2004

Streambank fencing restoration

October 2003 – December 2007

Post-restoration biomonitoring work.

December 2007

We will submit a final report to CONSOL.

* All restoration work will be done with an aggressive schedule to implement restoration as soon as practical. Should inclement weather deter completion of restoration activities by the timeline outlined – work will be completed as soon as possible. The Pennsylvania Department of Environmental Protection will review any deviations from the approved schedule, with justification(s) provided.

* Annual reports will be submitted to CONSOL on 31 December of each year and seasonal reports will be submitted to CONSOL April, July, and October.

Part IV – Project Administration and Responsibility

Dr. David G. Argent, Dr. Thad E. Yorks, and Mr. José Taracido will direct the Project with funding from CONSOL. Mr. Taracido will oversee the fieldwork and management of field crews and Drs. Argent and Yorks will oversee the biomonitoring portion of this project. Administration of project funds will be through the Foundation for California University of Pennsylvania (Mrs. Denise Hines), and the office for this program will be housed at California University of Pennsylvania. CONSOL agrees to complete the outlined project to the best of its ability. Should a landowner leave the program or remove habitat restorations, CONSOL Resources will restore other areas to maintain the amount of restoration discussed in this proposal for the life of the coal refuse disposal site being mitigated.

Part V – Environmental Impacts of Proposed Project and Mitigation

<u>Losses</u>

1. Several thousand feet of stream (including annual and perennial) will be lost through filling in the streams in the proposed coal refuse disposal valley.

<u>Benefits</u>

1. Degraded streams, wetlands, and spring developments in the watershed will be restored and protected improving water quality and fish and wildlife habitat.

2. Native grasslands will be restored throughout the watershed, providing habitat for numerous wildlife species and acting as a bio-filter for agricultural run-off to riparian areas. This restoration technique is used in conjunction with streambank fencing to

provide habitat for the whole watershed, not just the stream because agricultural effects will be seen outside of the corridor and it is important to address them in the restoration plan.

3. Border-edge cuts will provide shrub land habitats for numerous wildlife species, many of which are declining in Pennsylvania.

4. Improved landowner cooperation and satisfaction with conservation efforts and CONSOL.

5. Data on impacts of watershed restoration project.

6. Educational opportunities for students at California University of Pennsylvania who will have access to all data collected in support of this mitigation for thesis work.

WETLAND CHARACTERIZATION FOR

BAILEY MINE SLURRY AND REFUSE HOLLOWS

GREENE COUNTY, PENNSYLVANIA

September 4, 2003

Data and conclusions presented in this document are those developed by B. B. Owen Jr., T. F. Fullerton, & D. E. Pike as presented in their December 22, 2001 report entitled "Wetland Mitigation for Bailey Mine Slurry and Refuse Hollows Greene County, Pennsylvania. The December 22, 2001 report was edited by Michael Baker Jr., Inc. to create this document by deleting references to mitigation.

INTRODUCTION

Consol Pennsylvania Coal Company has proposed the use of two adjacent valleys for the disposal of coarse coal refuse and fine coal refuse from the Bailey Central Preparation Plant, hereafter referred to as the refuse valley and slurry valley (locations shown in Figure 1). These two valleys were surveyed for wetlands in June 2001. A total of 0.102 acres of wetlands were found in the proposed refuse disposal valley and 1.267 acres were found in the proposed slurry disposal valley. Thus a total loss of 1.369 acres would have to be mitigated. The following report details the wetlands that would be lost in the proposed disposal valleys.

METHODS

The wetlands of the proposed slurry and refuse valleys were surveyed in the field in detail according to the Routine Wetland Determination methods of the Army Corps of Engineers Manual (Environmental Laboratory, 1987). Plant identification was primarily according to Strausbaugh and Core (undated) with assistance from other plant guides and nomenclature was updated according to the synonymy in Reed (1997). Plant indicator categories were taken from the Revision of the National List of Plant Species that Occur in Wetlands (ibid). Soils were classified according to the soil survey of Greene and Washington Counties (U.S. Dept. of Agriculture et al., 1983) and their hydric classifications were checked in the list of hydric soils of the United States (U. S. Dept. of Agriculture, 1991). Detailed field data and the plant indicator categories for Jurisdictional Wetlands were summarized on "Standard Data Form 1" from the Army Corps of Engineers Manual (Environmental Laboratory, 1987). Data forms and photographs of each wetland are included in "Biological Resources of the Proposed Bailey Mine Refuse and Slurry Valleys, Greene County, Pennsylvania" by D. E. Pike et.al., dated August 8, 2001 (Attachment 15.1 of the coal refuse disposal permit application).

Wetlands of the proposed slurry and refuse valleys were delineated in July, 2001.

RESULTS

WETLANDS OF THE PROPOSED REFUSE VALLEY

With few exceptions, the wetlands of the refuse valley (Figure 2) were small streamside or seep areas with relatively heavy forest cover. Seven Jurisdictional Wetlands were delineated, totaling 0.102 acres.

Wetland R-1 is a small wetland (0.026 acres) resulting partly from ATV traffic. It had an inundated area about two meters square, while the rest of the wetland varied from saturated soils to dryer areas, resulting in a variety of plants being common. *Bidens frondosa* was dominant around the inundated area, while *Poa trivialis* and *Glyceria striata* dominated the spring flora in surrounding areas.

Wetlands R-2 and R-3 are relatively small somewhat marginal streamside and seep wetlands (0.009 and 0.014 acres, respectively). Wetland R-3 supported a number of *Lindera benzoin*, typical of much of the flood plain in this area.

Wetland R-4 is a somewhat larger streamside wetland (0.033 acres), with shallow soils over gravel. Its spring flora was dominated by *Poa trivialis* while *Impatiens capensis* (as in all future references, could be *I. Pallida* - couldn't be determined in spring collections) was appearing likely to be the late season dominant.

Wetland R-5 is a very small seep wetland (0.004 acres) in heavy forest, and its spring flora was dominated by *Carex prasina*, with *Impatiens capensis* likely to become the late season dominant.

Wetlands R-6 and R-7 are two spring-seep wetlands (0.012 and 0.004 acres, respectively) at the headwaters of the refuse valley. Both are in heavy forest cover, but had different dominant spring herbs. *Carex prasina* dominated Wetland R-6, while *Impatiens capensis* dominated Wetland R-7.

WETLANDS OF THE PROPOSED SLURRY VALLEY

Most of the Jurisdictional Wetlands of the slurry valley (Figure 3) were also streamside or seep areas, but they varied greatly in size, cover and plant composition. This valley was only partially

wooded and most of it was heavily impacted by cattle grazing. Nineteen Jurisdictional Wetlands were delineated, totaling 1.267 acres.

Wetlands S-1 and S-2 are small (0.055 and 0.008 acres, respectively) wetlands recently created by the adjacent railroad embankment. Both are in completely open areas and were heavily dominated by *Typha latifolia* with lesser amounts of other wetland and transitional species.

Wetland S-3 is another small wetland (0.067 acres) in an open area, with early season vegetation dominated by grasses with less abundant sedges and a few other taxa.

Wetland S-4 is a fairly large wetland (0.209 acres) in a mostly open, streamside area. It has areas with almost an inch of water standing between vegetation clumps, but the majority of this wetland is a wet meadow with soil saturation a few inches below the surface. A great variety of herbs grow in this wetland, with some areas dominated in the spring by *Glyceria striata* and others by *Typha latifolia* or *Poa trivialis.* Late season vegetation will find *Aster puniceus, Carex* species and *Polygonum sagittatum* becoming the dominants in most of the areas where spring grasses were dominant.

Wetland S-5 is a small wetland (0.050 acres) that includes a small pooled area and surrounding wet areas dominated by a sparse cover of *Glyceria striata, Bidens frondosa* and a few other taxa. This wetland appears to be the result of an old channel that has been abandoned by the stream, while still maintaining water by virtue of a nearby seep.

Wetland S-6 is a seep area (0.022 acres) in a power line right of way. Having almost no overstory cover, it supported a dense herbaceous layer dominated by *Polygonum hydropiperoides* and *Carex frankii*, with a large spring season representation of *Poa trivialis. Impatiens capensis* and *Bidens frondosa* will likely dominate some of the wetland in late season.

Wetlands S-7 and S-8 are small streamside areas heavily impacted by cattle. Most of the soils were dug up and much of the vegetation either grazed or trampled by cattle. Wetland S-7 (0.090 acres) was dominated in the spring sampling by a mixture of *Leersia virginica, Bidens frondosa* and *Poa trivialis*. Wetland S-8 (0.013 acres) is a seep area near Wetland S-7 that was dominated by *Poa trivialis* and *Pilea pumila* in the spring sampling. Late season vegetation will be dominated by *P. pumila* and possibly *Polygonum hydropiperoides.*

Wetland S-9 (0.020 acres) is an area where the stream spread over a large flat area and created an island of gravely soils that supported some wetland vegetation. *Poa trivialis* and *Pilea pumila* dominated the spring vegetation and again late season vegetation will likely be dominated by *P. pumila* and *Polygonum hydropiperoides.*

Wetland S-10 is the largest wetland of the slurry valley (0.435 acres). It encompassed a large relatively flat, wet meadow with some areas saturated to the surface, grading to transitional areas. Spring vegetation was dominated by a number of grasses and sedges and smooth rush, depending on the specific area.

Wetland S-11 is a small wetland (0.048 acres) in an open area below an abandoned pond. Its spring flora was dominated by *Carex frankii,* with the grasses *Bromus inermis* and *Glyceria striata* also very common. *B. inermis* is a UPL rated grass that dominated the adjacent grazed pasture and despite its rating, it seemed to be thriving in the wetland environment - possibly because it withstands grazing better than its competitors.

Wetland S-12 is a tiny (0.004 acres) wetland at the headwaters of a small tributary. It was heavily impacted by cattle and had spring vegetation dominated by *Poa trivialis* with *Polygonum hydropiperoides* likely to dominate later in the season.

Wetland S-13 is a wet area (0.048 acres) within the abandoned and breached impoundment. A small area of standing water was surrounded by mud flats with sparse vegetation dominated in the spring by *Poa trivialis* and a few wetland plants with *Bromus inermis* again quite common.

Wetland S-14 is a small seep area (0.021 acres) adjacent to the main stream. It was an open area dominated by two sedges and smooth rush, despite the heavy grazing by cattle.

Wetlands S-15 and S-16 are areas (0.080 and 0.031 acres, respectively) very heavily disturbed by cattle, with much of the vegetation destroyed and soils a mass of deep hoof prints. Wetland S-15 was in an area partially shaded by a *Craetagus* thicket. It had scattered vegetation often dominated by *Bidens frondosa.* Wetland S-16 was mostly bare mud with a scattering of plants, *Pilea pumila* being the most abundant.

Wetlands S-17, S-18 and S-19 are headwater wetlands (0.009, 0.045 and 0.012 acres, respectively) that were in mostly open areas. Despite the heavy grazing by cattle, a variety of

vegetation remained, with each area having its own dominant wetland plant, but all areas again having a fair amount of *Bromus inermis* that had invaded from adjacent pasture.

WETLAND FUNCTIONS AND VALUES

Wetlands are multiple value systems and unfortunately the most valuable products of wetlands are public amenities that often have no value to the property owner. Currently popular systems of valuation of wetlands tend to stress the importance of use by fish and game species, physical attributes such as wetland contributions to the hydrologic cycle, control of flooding, water quality, and human uses. There are three wetland assessment methods that are currently accepted by many wetland scientists and regulatory authorities. The first, and probably still the most universally applicable assessment method was the Wetland Evaluation Technique (WET) developed by Adamus et al. (1987). This method of assessment evaluates the following wetland functions:

- Ground water recharge
- Ground water discharge
- Floodflow alteration
- Sediment stabilization
- Sediment and toxicant retention
- Aquatic diversity and abundance
- Nutrient removal or transformation
- Recreation
- Product export
- Uniqueness and heritage
- Wildlife diversity and abundance

These functions are valued in terms of social significance, and the technique can be used to evaluate any wetland. WET allows a rapid assessment of wetland functions and values and assesses the suitability of wetland habitat for waterfowl and other water dependent vertebrates and invertebrates.

A second wetland evaluation technique, EMAP, was developed primarily to evaluate wetland condition, where condition is defined as the state of a set of characteristics which are associated with wetlands and which are valued by society. It evaluates biological diversity, harvestable productivity, flood reduction and shoreline protection, groundwater conservation and water quality improvement.

A third wetland evaluation technique, the hydrogeomorphic or HGM technique was developed by the US Army Corps of Engineers to evaluate wetlands using similar criteria as those of WET to assess the degree to which a wetland functions in comparison to regional reference wetland functions.

WET is the technique best suited to provide an analysis of all wetlands in a region of interest, as opposed to both EMAP and HGM, which only allow comparisons within wetland classes. Thus, for the purposes of the subject analysis WET functions have been considered (Table 1).

The wetlands to be replaced have minimal functions (Table 1) except for groundwater discharge (many were actual seep areas or produced by seeps). The value of this function may be questioned in this area of abundant springs and seeps. Flood flow alteration is not very effective in headwater wetlands as compared to downstream wetlands (Mitch and Gosselink, 1993). None of the wetlands will be particularly effective in sediment stabilization (this is more a function of shoreline wetlands). Sediment and toxicant retention is not expected to be significant. Nutrient removal or transformation will not occur to a significant degree. Although wetlands of the slurry valley do receive elevated nutrient inputs from heavy cattle grazing, these wetlands do not appear to be effective at nutrient removal or transformation. None of the refuse or slurry valley wetlands offer any significant recreation, product export, uniqueness or heritage.

The most significant function in terms of capabilities of wetlands in this region is their ability to offer aquatic habitat and foster wildlife use. The small upland wetlands of the refuse and slurry valleys have virtually no standing water even in the wettest seasons and thus have little to no aquatic diversity and abundance. Similarly, wildlife is not visibly using the small headwater wetlands of the refuse and slurry valleys.

Table 1. Estimates of WET functions for the Slurry Valley Wetlands and Refuse Valley Wetlands.*			
Function	R-1...R-7	S-1....S-19 except S-4	S-4
Ground water recharge	0	0	0
Ground water discharge	2	2	0
Flood flow alteration	1	1	2
Sediment stabilization	0	0	0
Sediment and toxicant retention	1	1	1
Aquatic diversity and abundance	0	0	0
Nutrient removal or transformation	1	1	2
Recreation	0	0	0
Product export	0	0	0
Uniqueness and heritage	0	0	0
Wildlife diversity and abundance	1	1	1

* 0 = no significant function
  1 = minimal function
  2 = moderate function
  3 = high function

CONCLUSIONS

Typical of southwestern Pennsylvania watersheds, both the refuse and slurry valleys had a number of small headwater wetlands associated with the streams in each valley. The refuse valley contained seven discrete Jurisdictional Wetlands totaling only 0.102 acres, while the slurry valley contained 19 Jurisdictional Wetlands totaling 1.267 acres. The wetlands of the refuse valley were mostly very small streamside or seep wetlands under heavy woodland cover. Most were relatively undisturbed natural wetlands of the sort commonly seen associated with stream origins and headwater flood plains in southwestern Pennsylvania and due to their sizes

and headwater placement, they had low levels of wetland functions and values. Wetlands of the slurry valley ranged from wet meadows to headwater seep wetlands. Only wetlands S-1 to S-3 were not impacted by cattle traffic and grazing. Very few of the slurry valley wetlands were in a natural state and most were so highly disturbed that it is difficult to say what the natural vegetation should have been. As discussed above only wetland S-4 was judged to have more than very minimal wetland functions and values.

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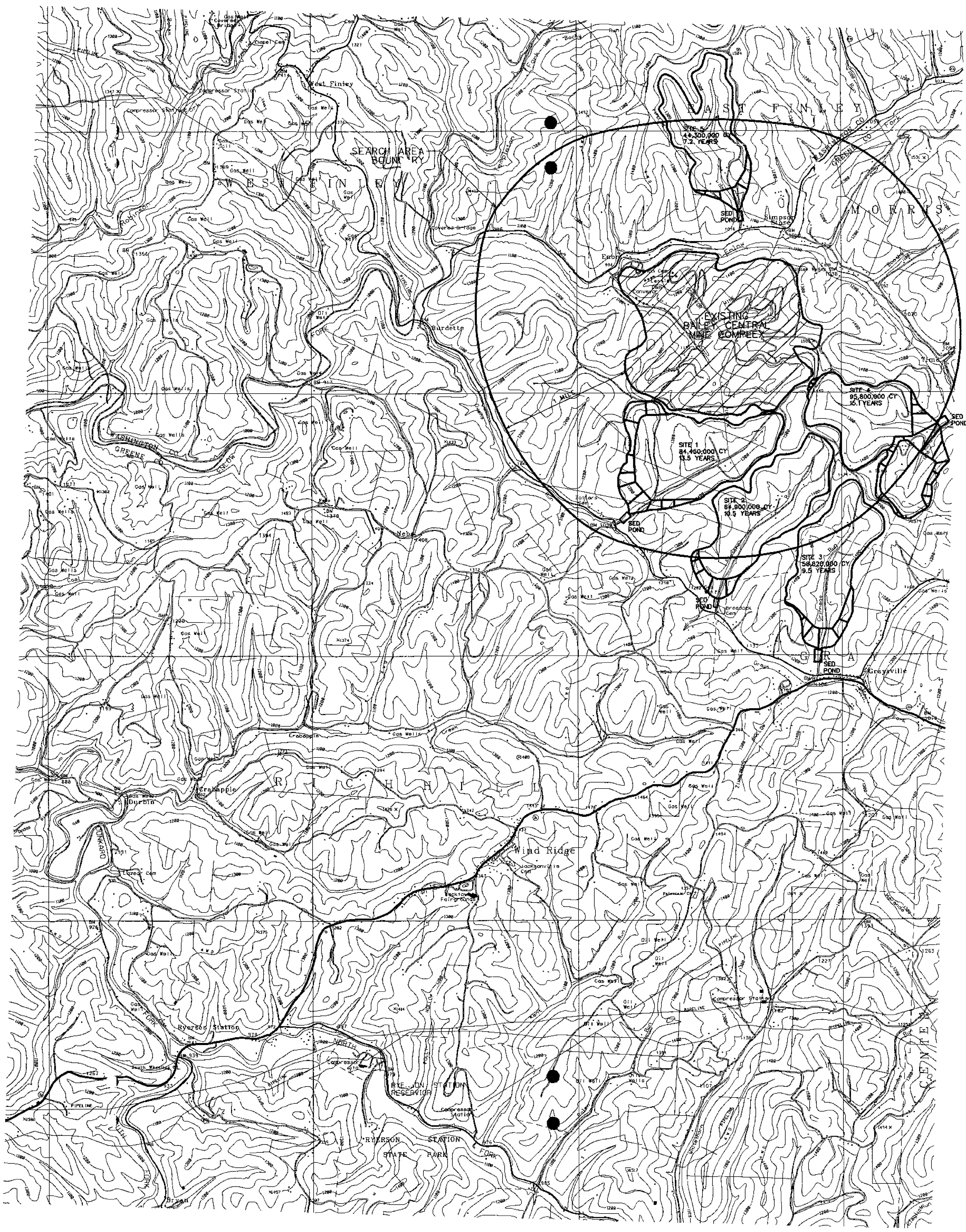


DESIGNED GPH DRAWN DRP CHECKED GPH REVIEWED S.O. 24379-000-0000 CADD FILE SEARCH AREA MAP.DGN	**CONSOL PENNSYLVANIA COAL COMPANY** PITTSBURGH, PENNSYLVANIA **MICHAEL BAKER JR., INC.** CONSULTING ENGINEERS CORAOPOLIS, PENNSYLVANIA	Baker	**EXHIBIT 1 SEARCH AREA MAP** SITE SELECTION STUDY - ALTERNATIVES ANALYSIS BAILEY CENTRAL MINE COMPLEX COAL REFUSE DISPOSAL FACILITY SCALE 1" = 2000' DATE FEB. 15, 2001	SHEET NO. E-1

Bailey Refuse Area - Stream Fencing Information

Close

From: Pachter, Jonathan

To: 'SMTP:Christina.L.Schroeder@LRP02.USACE.ARMY.MIL '

Cc:

Subject: Bailey Refuse Area - Stream Fencing Information

Sent: 2/9/2004 7:47 AM **Importance:** Normal

Christy - attached are a PowerPoint map and a Word Table that contains pertinent stream fencing information for the mitigation required for this project. According to the folks at California University of PA, we have locked up over 15 miles of stream front, requiring 11-14 crossings. Please let me know if you need more information to satisfy Conditions 6 and 6.

Jonathan Pachter

FencingSitesfromCUP2804.ppt Tableoffarms[1].doc

Exemption #6 - Privacy

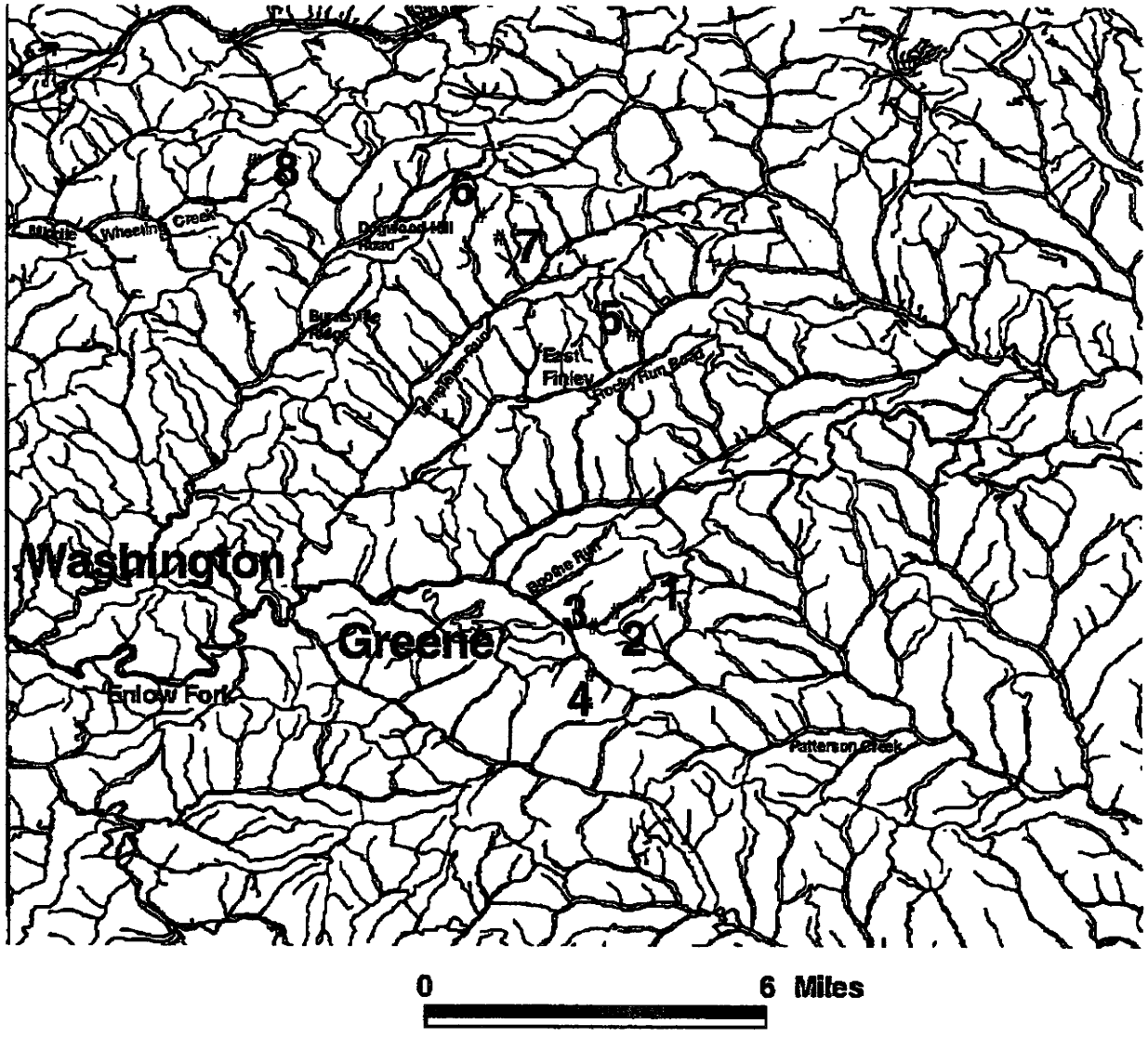
Table – Properties Agreeing to Have Stream Fencing Performed

[redacted]

2. – Consol Coal

[redacted]

Overview of proposed fencing restoration sites



LEGEND

1 - Don Bedillion
2 - Consol Coal
3 - Chuck Williams
4 - Larry Vogel
5 - John Carter
6 - Jim Sloan
7 - Bill Sloan
8 - Jerry Segelstrom

Refer to attached Table for specific site localities

Module 4: Areas Where Mining is Prohibited or Restricted

4.1 Will surface mining activities be conducted within any of the following areas?

Yes	No	
☐	☒	areas which have been designated unsuitable for mining
☐	☒	areas included in a petition, which has been accepted for review by the Department, for designation as unsuitable for mining
☐	☒	Federal Wild and Scenic Rivers System, including study rivers
☐	☒	National System of Trails
☐	☒	300 feet of any public building, school, church, community or institutional building or public park
☐	☒	100 feet of a cemetery or Indian burial ground
☐	☒	National Recreation Areas
☐	☒	National Park

4.2 Identify any of the following which overlie the mine plan or lie within 1,000 feet of a surface mining activity: (show the location on maps in Modules 6.2, 6.3, 9.1, and 18.1)

Yes	No	
☐	☒	Allegheny National Forest
☐	☒	public park
☐	☒	any cultural and historic resources listed on or eligible for inclusion on the National Register of Historic Places
☐	☒	known archaeological sites. Describe the site _____.
☐	☒	State Park
☐	☒	State Forest
☐	☒	State Game Land
☐	☒	Pennsylvania Scenic Rivers System
☐	☒	State Wilderness Area

Attach a completed Cultural Resources Notice for each surface mining activity site to be disturbed under this permit or revision. Include the certified mail return receipt as proof of submission to PA Historical and Museum Commission.

Pennsylvania Historical and Museum Commission has requested that a Phase I archaeological survey of the project area be performed to locate potentially significant archaeological resources. Refer to Attachment 4.2 at the end of this module. The Phase I study will be done during the permit review process and will be included as part of this permit submittal prior to permit approval.

4.3 If any surface mining activities are to be conducted within 300 feet from any occupied dwelling, attach the notarized written waiver of the current owner consenting to surface mining activities closer than 300 feet. Otherwise, show the area as a restricted zone on maps in Module 9.1. (Note that a waiver is not required if the only part of the mining operation within 300 feet is a haul road or access road which connects with an existing public road on the side of the public road opposite the dwelling.)

One occupied dwelling is located within 300 feet of the proposed surface mining activities. CPCC owns the dwelling and a waiver is provided from CPCC.

4.4 Public Roads. If surface mining activities are proposed to be conducted within 100 feet of the outside right of way of a public road or a relocation of a public road is proposed, provide the following information: (Note: if the initial newspaper advertisement does not contain notice of the variance, attach the proof of publication for advertisement of the variance).

ii) surface areas affected by subsidence; and

Refer to the Exhibit 9.1 map.

iii) if site will be used for coal preparation, coal storage, coal refuse disposal or mine drainage treatment, the extent of underground workings and mine pool beneath the site.

Refer to the Exhibit 9.1 map. The maximum mine pool elevation beneath the proposed permit boundary associated with this permit application will be approximately 390 feet above sea level.

20) Proposed coal ash storage areas.

No coal ash storage areas are proposed.

21) Proposed coal storage areas and extent of lined area.

No coal storage areas are proposed.

22) Proposed soil storage areas (identify topsoil, subsoil, and prime farmland soil horizons)

Refer to Sheets 3 and 4 of Exhibit 21.1, Construction Drawings.

23) Proposed water treatment facilities.

The only proposed water treatment facility is a sedimentation pond. Refer to the Exhibit 9.1 map.

24) Proposed air pollution controls.

No air pollution control structures are proposed. Refer to Module 16.

25) Proposed underground and above ground storage tanks.

There is one above ground fuel storage tank proposed at the new refuse site within the proposed refuse garage. No underground storage tanks are proposed with this application.

26) Erosion and sedimentation control facilities.

Refer to Sheet 36 of Exhibit 21.1, Construction Drawings.

27) Explosives storage areas.

No explosive storage areas are proposed with this permit application.

28) Landslide areas.

Refer to the Exhibit 9.1 map.

29) Prime farmland soils.

Refer to the Exhibit 9.1 map. Culleoka soil (CaB) is identified as a prime farmland soil located in small areas at the ridge tops. These soils have not been used for cropland for 5 out of the last 10 years.

30) Prime farmland soils which will be reconstructed.

Since a negative determination can be justified, a Prime Farmland Reconstruction Plan is not required.

31) Prime farmland soils for which a negative determination will be sought.

A negative determination is being sought for the Culleoka soil (CaB) because: 1) the soils to be affected have not been used historically as cropland for any 5 out of the last 10 years, and 2) the affected area is less than 5 acres and will be used to support mining activities for more than 10 years. See Attachment 17.3.b for a copy of a letter from Consol attesting that parcels containing prime farmlands have not been used as cropland for any 5 out of the last 10 years.

32) Wetland mitigation and replacement sites.

Coarse coal refuse will be transported from the preparation plant to the disposal facility by belt conveyor. Refer to Sheet 3 and 4 of the Exhibit 21.1 drawings for the proposed conveyor belt alignment. As indicated on Sheet 3 and 4, coarse coal refuse will be discharged from the belt into a refuse bin. Coarse coal refuse will be hauled from the bin to the disposal area by either a scraper or off-highway truck. It will be spread and compacted using the hauling equipment and/or a self propelled sheepsfoot roller or smooth-wheel vibratory roller.

Runoff from coarse coal refuse embankments as well as leachate will be collected and conveyed to the facility sedimentation pond. Runoff will be collected and conveyed to the pond by perimeter ditches. Both of the coal refuse dams will be provided with an internal drainage system to control seepage, and leachate collected by these systems also will be conveyed to the sedimentation pond. Runoff and leachate discharged into the pond will flow through both chambers of the pond before being discharged off-site. Sedimentation pond discharge will be sampled and tested in accordance with NPDES criteria. The hydrologic monitoring plan outlined under Module 8.6 also will be implemented to monitor facility performance.

Based on the NPDES compliance history at the nearby existing Bailey refuse disposal area, chemical treatment of the coal refuse is not proposed.

ii) If the operation does not involve disposal in abandoned, inactive or active underground mine or in abandoned or unreclaimed surface mines, outline the technical, economic and safety considerations prohibiting such disposal.

No abandoned or unreclaimed surface mines are present in the vicinity of the Bailey Mine Complex. Underground disposal was considered but determined to be not feasible. Refer to the Alternatives Analysis Report on file at PADEP, McMurray District office (approved August 1, 2001) for a detailed evaluation of this disposal option.

4) If the operation will involve the discharge of coal processing wastes, underground mine development wastes, coal ash, mine drainage treatment sludge, flue gas desulfurization sludge, or inert stabilizing materials to underground workings:

Describe the nature of the material to be discharged, the system which will be used to convey the material to the point of discharge, and the means of controlling the material within the underground workings.

Not applicable. The operation will not involve the discharge of coal processing wastes, underground mine development wastes, coal ash, mine drainage treatment sludge, flue gas desulfurization sludge, or inert stabilizing materials to underground workings.

5) If the operation will include the use of fly ash or sewage sludge, describe the purpose for which the material will be used and the site(s) on which it will be used.

Not applicable. The operation will not include the use of fly ash or sewage sludge.

10.2 Existing Structures.

a) List all existing structures which will be used in connection with or to facilitate the mining operation. (Existing structures include roads, bridges, culverts, fills, berms, benches, waste banks, discharge structures, diversions, rail loops, rail sidings, rail spurs, refuse areas, shafts, spoil piles, utility lines, terraces, drains, wells, exploration holes, boreholes, barricades, fences, storage areas, mine buildings, tipples, storage facilities, repair facilities, surge ponds, treatment plants, pipelines, conveyors and other man-made structures or areas disturbed by mining activities).

Discharge from the sedimentation pond will be directed to an existing 8-foot diameter culvert under the railroad embankment.

b) Provide the following information for each existing structure:

5600-PM-MR0324 Rev. 4/2001

NPDES No. PA _____
(for Department Use Only

FORM 12.1A NPDES Information

Identify each point of discharge, the receiving stream and the corresponding latitude and longitude. If none, enter NONE in Column 1.

Discharge Point (001,002, etc.)	Surface Elev.	Source of Discharge (i.e., mine drainage, ring water, surface runoff*, etc.)	Describe Treatment or Other Control Technology Provided	Is Discharge Existing or Proposed?	Description of Discharge		Name of Receiving Stream	Latitude	Longitude
					Average Rate (mgd)	Frequency			
301	1127	Surface runoff (44 Sac) KLK	None	proposed	1.4 mgd	daily	Unnamed tributary to Enlow Fork	39°57'32"	80°22'33"

*If discharge is storm induced runoff indicate site drainage area in acres.

The information on the NPDES form must be certified correct by one of the following, as applicable.

a) In the case of corporations, by a principal executive officer of at least the level of vice president, or his duly authorized representative, if such representative is responsible for the overall operation of the facility from which the discharge described in the NPDES form originates.

b) In the case of a partnership, by a general partner.

c) In the case of a sole proprietorship, by the proprietor.

d) In the case of a municipal, state, or other public facility, by either a principal executive officer, ranking elected official, or other duly authorized employee.

I certify that I am familiar with the information contained in the above table, and that to the best of my knowledge and belief such information is true, complete, and accurate.

Dan R. Baker
Printed Name of Person Signing

March 22, 2002
Date

President
Title

Signature

18 U.S. C. Section 1001 provides that:

Whoever, in any matter within the jurisdiction of any department or agency of the United States knowingly and willfully falsifies, conceals, or covers up by any trick, scheme, or device a material fact, or makes or uses any false, fictitious, or fraudulent statements or representations; or makes or uses any false writing or document knowing same to contain any false, fictitious, or fraudulent statement or entry, shall be fined not more than $10,000 or imprisoned not more than 5 years, or both.

Rev. April, 2002

Module 17: Soils / Prime Farmland

If more than one surface mining activity site is proposed under this application, provide a separate set of maps and responses for each site.

17.1 Soils Map

Provide a USDA soils map which shows the following:

a) the boundaries of the proposed permit area;

b) Prime farmland soils.

Presented as Attachment 17.1 is a USDA soils map showing boundaries of the proposed permit area. CaB soils located within small ridge top areas have been identified by the USDA Natural Resources Conservation Service as prime farmland soils.

17.2 Soils Data

a) List each of the soil series and phases present within the proposed permit area. Provide the results of any borings or test pits made to determine soils depths.

SERIES	*PHASE*	*DESCRIPTION*
Culleoka (Ca)	*CaB* *CaC* *CaD*	*3 to 8 percent slopes* *8 to 15 percent slopes* *15 to 25 percent slopes*
Dormont (Do)	*DoB*	*3 to 8 percent slopes*
	DoC	*8 to 15 percent slopes*
Dormont-Culleoka assoc. (Dt)	*DtD*	*15 to 25 percent slopes*
	DtF	*25 to 50 percent slopes*
Fluvaquents (Fa)	*not applicable*	
Guernsey (Ge)	*GeB*	*3 to 8 percent slopes*
Weikert-Culleoka	*WeB*	*3 to 8 percent slopes*

Records of borings and test pits excavated at the project site are appended to the Module 21 Design Report.

b) Identify the thickness of topsoil present within the proposed permit area.

During subsurface investigations performed in August and September of 2001, test borings revealed topsoil depths ranging from 0.3 foot to a maximum depth of 1.5 feet.

c) If the area has no topsoil or has been previously surface mined, identify the material that will be used as final cover and provide information, including a chemical analysis, demonstrating that the material is capable of supporting the vegetation specified in the reclamation plan. (Borrow areas are required to be mapped at Module 18, section 18.1.e.25.)

Not applicable. Topsoil blankets the project site and will be removed and stockpiled for construction of the one foot thick soil cover component of the final cover. During site preparation, additional soil will be removed from soil borrow areas as needed for use as soil cover. Presented as Attachment 14.2.7a is a plan of the project site presenting proposed borrow areas and estimated average soil thicknesses within those areas. Presented as Attachment 17.2.c is demonstration that sufficient soils are available for cover construction as well as construction of the liner protective cover.

The bottom layer of the two-foot thick final cover will be comprised of soil placed and compacted so as to be equivalent to liner material. This layer will have a thickness of one foot. Liner material for final cover construction will be obtained from the project site. Demonstration that sufficient liner material is available for cover construction is presented in Module 14.

Module 20: Coal Refuse/Coal Ash - Sources and Properties

This module must be completed if coal refuse disposal will take place under the permit. If coal ash will be deposited along with the refuse, appropriate responses must be provided under this module and Module 25.

*State regulations require that certain technical aspects of refuse site design be prepared and certified by a registered professional engineer. See Chapter 90, Sections 90.39, 90.112(b)(1), 90.124.

20.1 Identification of sources

Complete Form 20.1 identifying all sources of the coal refuse which will be disposed of on site, and the types of refuse which will come from each source. If coal ash will be mixed with the refuse also identify the source(s) and type(s) of ash.

Refer to Form 20.1 located at the end of this module.

20.2 Type(s) and amount(s) of incoming coal refuse and coal ash

Complete Form 20.2 identifying the types and amounts of coal refuse and coal ash which will be received on a daily basis.

Refer to Form 20.2 located at the end of this module.

20.3 Chemical properties of coal refuse

a) If leachate characteristics can be determined by analyzing the drainage from an existing site where the material is being deposited, provide an analysis of the drainage for : pH, alkalinity, acidity, total iron, total manganese, total aluminum, sulfates, and specific conductance (in micromho's per liter corrected to 25°C).

The refuse to be deposed of at the newly proposed facility will be the same as currently being disposed of at the existing Bailey Mine Complex Refuse No. 1 facility, resulting in similar discharges. Refer to Section 8.1g of Module 8 of this application for an evaluation of discharges from the existing coal refuse facility.

b) If leachate characteristics cannot be determined by analyzing drainage from an existing site, provide an acid-base account of the refuse produced at the preparation plant or an acid-base account of all strata including coal which will be removed from the mine. Use the method described in Field and Laboratory Methods Applicable to Overburden and Mine Soils, (Sobek, et. al. 1978), published by U.S. E.P.A. (EPA-600/2-78-054).

Since refuse is generally known to be highly variable in sulfur content and potential acidity generated, several samples of each source of coal refuse must be collected and analyzed. Include original laboratory data sheets with the application.

Not applicable. Chemical properties of drainage from the existing Bailey Mine Complex coal refuse disposal site are representative of expected leachate from the proposed site.

20.4 Chemical properties of coal ash

Complete Module 25.

Not applicable. Neither beneficial use of coal ash nor coal ash disposal is proposed as part of this permit application.

20.5 Physical properties of coal refuse (and coal ash)

Include a physical analysis of the coal refuse, including the % moisture, maximum dry density, optimum moisture content, grain size distribution, coefficient of friction, and cohesion.

- If ash will be deposited along with the refuse, include physical analyses on 0:100, 25:75, 50:50, 75:25, and 100:0 mixtures of refuse to ash.

***Coarse Coal Refuse**: Physical and engineering properties of the coarse coal refuse are presented in Section 3.0 and Appendix E of the Design Report attached to Module 21.*

***Fine Coal Refuse**: The only physical property used for design was a density of 40 pcf. This in-situ density value is based on sounding data developed for the existing facility. It was appended to the approved Alternatives Analysis Report. Zero shear strength was assigned to this material for stability calculations.*

***Breaker Rock**: The presence of these materials at the quantities reported will not significantly impact facility performance. They will be disposed in non-structural embankment areas as indicated on the Module 21Construction Drawings.*

FORM 20.1 SOURCES OF COAL REFUSE AND ASH

Source Mine, Preparation Plant, or Ash Generator	Coal Seams From Which Coal Refuse Is Derived	Type of Material Received From Source (Mine Rock, Breaker Rock, Coarse Refuse, Slurry, Filter Cake, Fly Ash, Bottom Ash)
Bailey Central Mine Complex	*Pittsburgh Coal Seam*	*Coarse Coal Refuse, Fine Coal Refuse Slurry, and Breaker Rock.*

FORM 20.2
TYPES AND AMOUNTS OF INCOMING COAL REFUSE AND COAL ASH

Material Type	Amount (TPD or GPD)	Moisture Content (%)
Mine Rock	None	
Breaker Refuse	894 TPD	0%-Amts are reported on dry basis
Coarse Refuse	14,731 TPD	" "
Slurry *(Fine Coal Refuse)*	2992 TPD	" "
Filter Cake	None	

2) Mixing and blending of ash and refuse:

Coal ash and coal refuse will not be mixed and blended as part of this permit application.

3) Application of alkaline materials or bactericides;

Not applicable. Application of alkaline materials or bactericides are not part of this permit application.

4) Spreading at site of deposition;

Refer to Sections 2.2 and 2.3 of the Operation and Maintenance Manual appended to the Module 21 Design Report and to Section 7 of Technical Specifications appended to that same report.

5) Compaction methods (including testing procedures and frequencies);

Refer to Section 7 of Technical Specifications appended to the Module 21 Design Report.

6) Placement of cover.

Soil cover placement will be in accordance with Section 16 of the Technical Specifications appended to the Module 21 Design Report.

21.6 Engineering Certification

a) Indicate critical stages where:

1) Close engineering supervision is required;

Refer to Module 10.3

2) Certification of site development will be provided; and

Certification of the sedimentation pond (both chambers) will be required.

3) Photographic evidence of site development will be provided.

Photographic evidence of site development will be included with the construction certifications.

21.7 Stability Analysis

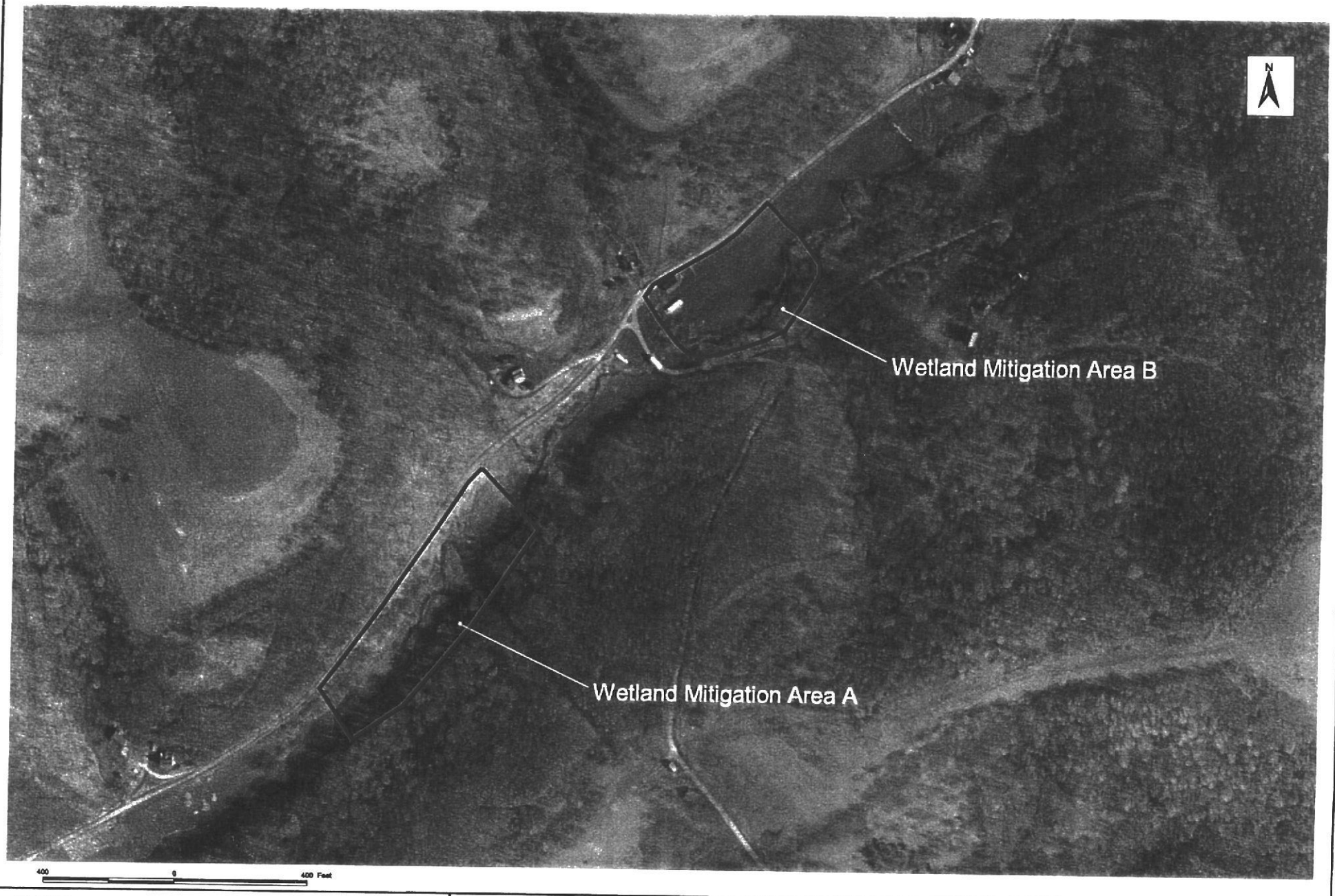
Stability analyses must be completed for all refuse piles greater than 20 feet in height; piles on slopes greater than 36%; and other structures as requested by the Department. If a structure meeting any of these criteria will be constructed or used under this permit, address the following.

a) If there are any clay horizons or known unstable units in the strata beneath the proposed structure explain what measures will be taken to remove or stabilize these units.

Soils underlying the eastern and western coarse coal refuse dams (Main Dam and Saddle Dam A, respectively) consist primarily of clays and silts with varying amounts of rock fragments. Colluvial deposits underlain by residual soils are present at most locations. Results of slope stability analyses indicate that the presence of these soils within the Main Dam foundation will not cause instability. Therefore, no measures will be taken to remove or stabilize the Main Dam foundation soils. Soils beneath Saddle Dam A exhibit signs of movement. Though the location and direction of this movement is such that stability of the structure under final conditions will not be affected, the unstable material will be completely removed and existing springs will be collected and discharged throught the spring drain system in order to enhance stability during initial construction of the upstream toe of the saddle dam. Cutoff trenches will be constructed for seepage control.

Additional unstable areas were located in Coal Refuse Disposal Area No. 4. Again the location and orientation of these unstable areas are such that they will not affect long term stability of the pile.

More detailed discussions of dam foundation conditions and slope stability analyses are presented in the Design Report attached to Module 21.



J:\Projects\220806\bailey_mine.apr\Rocky_run

REFERENCE:

USGS Digital Ortho Quarter Quad
Claysville PA. SE 1995
(download from PASDA website)

LEGEND:

Wetland Mitigation Areas

CEC

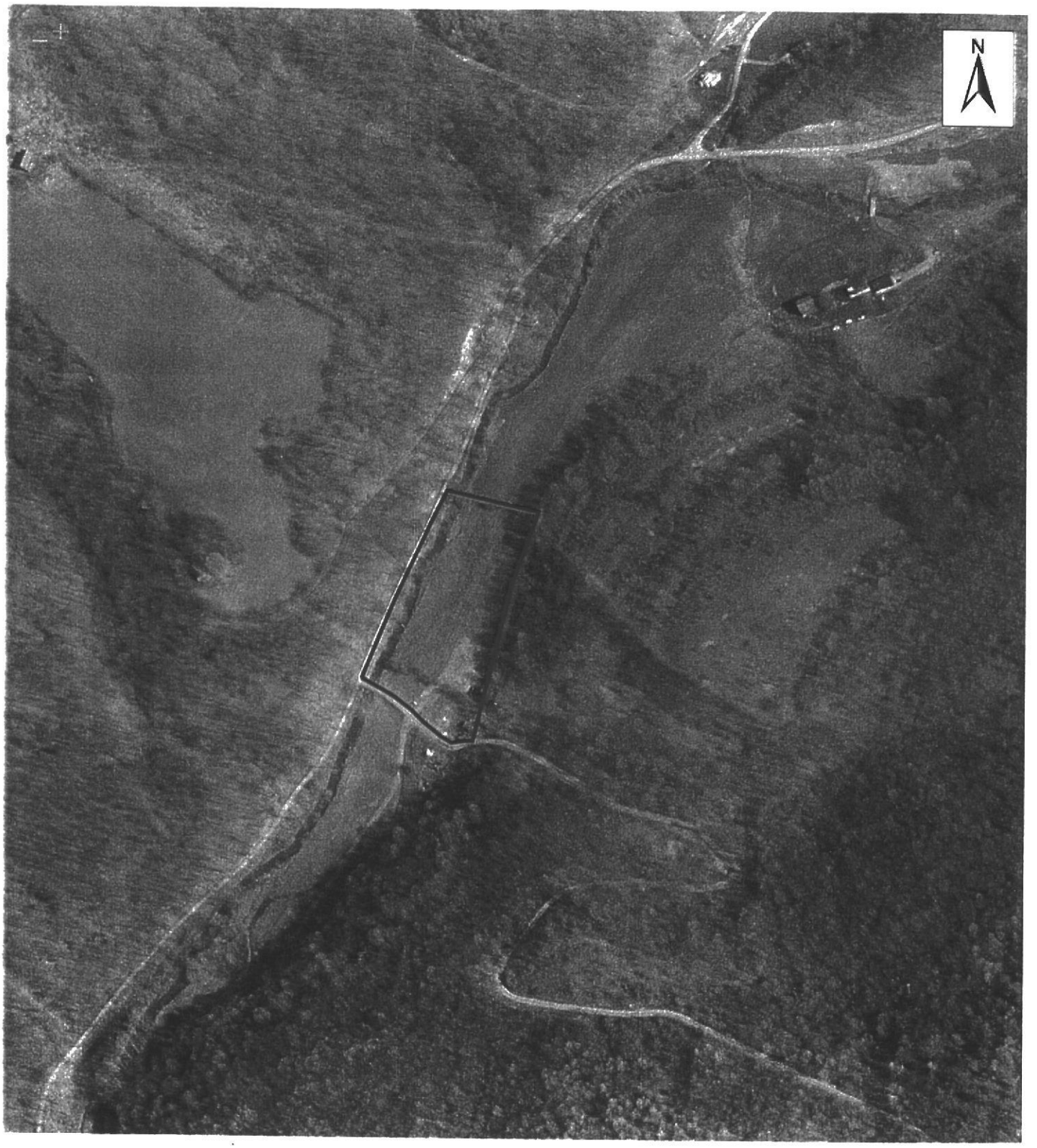
CIVIL & ENVIRONMENTAL CONSULTANTS, INC.
Pittsburgh, PA 15205 - 9702
Columbus, OH. * Cincinnati, OH. * Indianapolis, IN. * Nashville, TN. * St. Louis, MO. * Chicago, ILL. * Export, PA

DWN. BY: JEFF MIHALIK	SCALE:	DATE:
CHK. BY: MRH	1" = 400'	06/25/02

ROCKY RUN WETLAND MITIGATION AREAS A and B
BAILEY MINE REFUSE DISPOSAL AREAS NO. 3 and NO. 4
CONSOL PENNSYLVANIA COAL COMPANY
GREENE COUNTY, PENNSYLVANIA

PROJECT NO.: 220806.0004

FIGURE 2



J:\Projects\220806\bailey_mine\templetonfork_wetland

REFERENCE:

USGS Digital Ortho Quarter Quad
Claysville PA. SE 1995
(download from PASDA website)

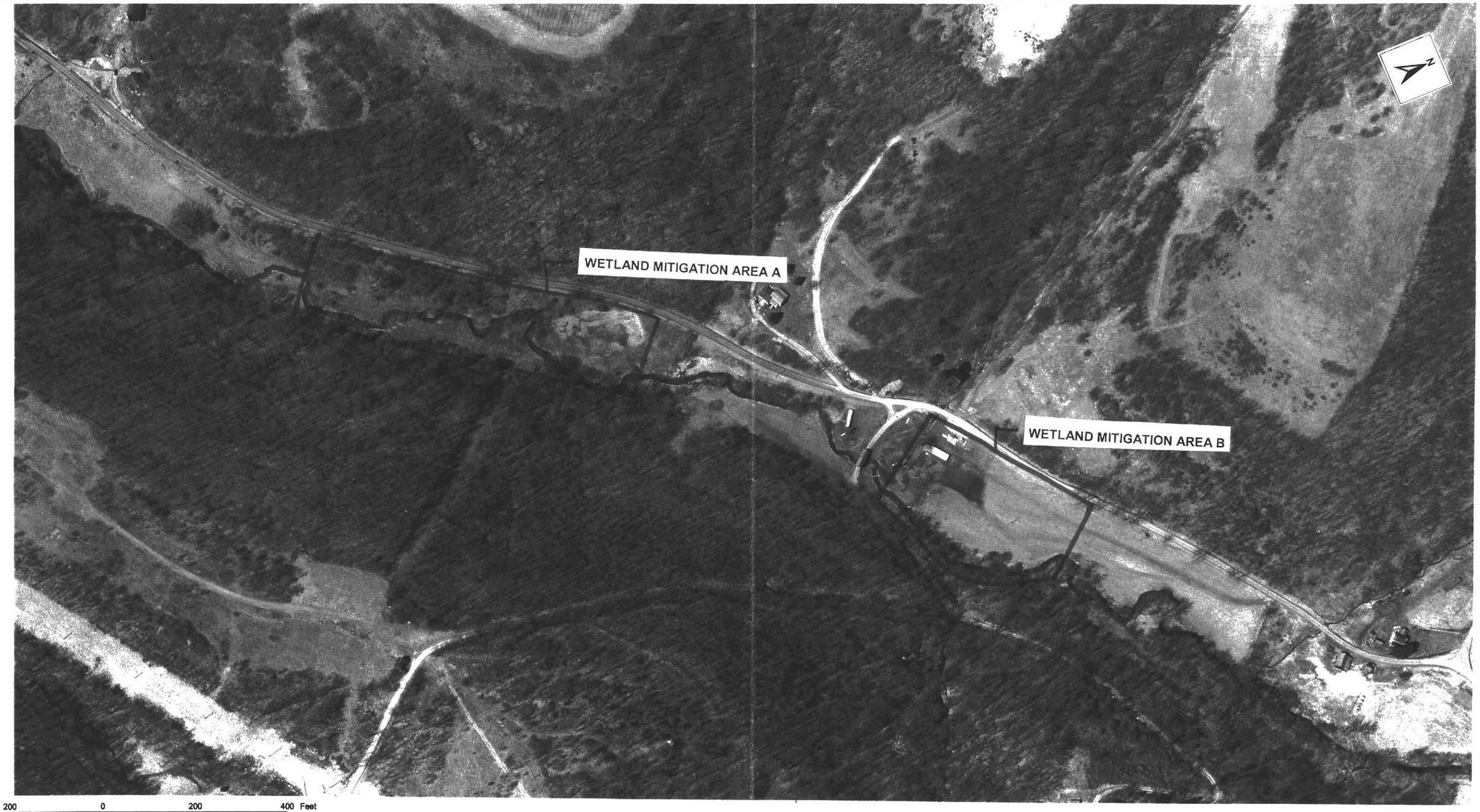
LEGEND:

Wetland Mitigation Area

CIVIL & ENVIRONMENTAL CONSULTANTS, INC.
Pittsburgh, PA 15205 - 9702
Columbus, OH.* Cincinnati, OH. * Indianapolis, IN. * Nashville, TN. * St. Louis, MO. * Chicago, ILL.

TEMPLETON FORK
WETLAND MITIGATION AREA
BAILEY MINE REFUSE DISPOSAL
AREAS NO. 3 and NO. 4
CONSOL PENNSYLVANIA COAL COMPANY
GREENE COUNTY, PENNSYLVANIA

DWN. BY: Jeff Mihalik	SCALE:	DATE:	PROJECT NO.:	
CHK. BY: MRH	1" = 400'	06/25/02	220806.0004	FIGURE 3



REFERENCE:

Source:
Aerial Photograph
by Keddal Aerial Mapping
Pittsburgh, PA (3/21/99)

LEGEND:

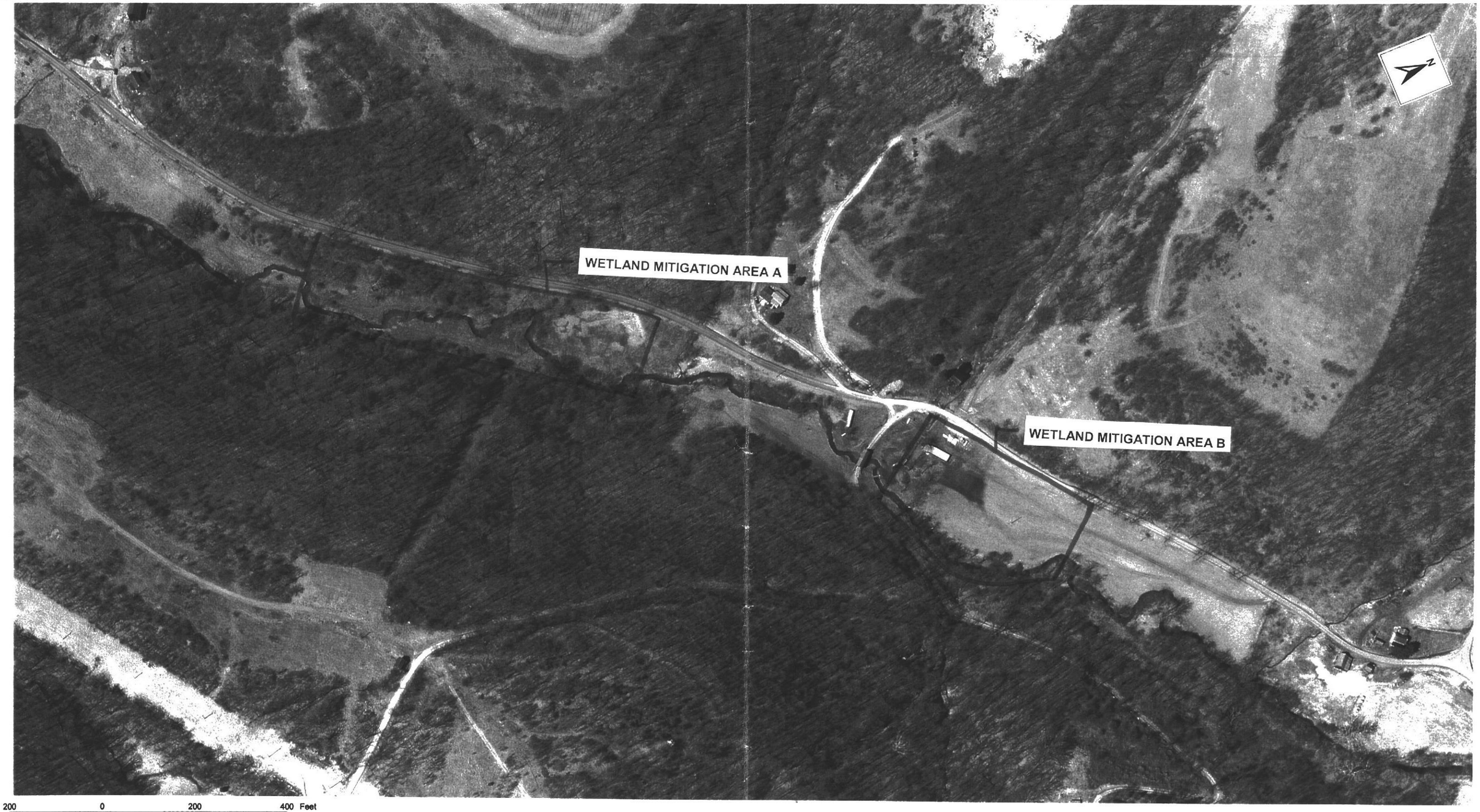
Wetland Mitigation Areas

CEC

CIVIL & ENVIRONMENTAL CONSULTANTS, INC.
Pittsburgh, PA 15205 - 9702
Columbus, OH * Cincinnati, OH * Indianapolis, IN * Nashville, TN * St. Louis, MO * Chicago, Ill

ROCKY RUN WETLAND MITIGATION AREAS A and B
BAILEY MINE REFUSE DISPOSAL AREAS NO. 3 and NO. 4
CONSOL PENNSYLVANIA COAL COMPANY
GREENE COUNTY, PENNSYLVANIA

DWN. BY: JEFF MIHALIK	SCALE: AS SHOWN	DATE: 06/25/02	PROJECT NO.: 220806.0004
CHK. BY: MRH			FIGURE 1



REFERENCE:

Source:
Aerial Photograph
by Keddal Aerial Mapping
Pittsburgh, PA (3/21/99)

LEGEND:

Wetland Mitigation Areas

CEC
CIVIL & ENVIRONMENTAL CONSULTANTS, INC.
Pittsburgh, PA 15205 - 9702
Columbus, OH * Cincinnati, OH * Indianapolis, IN * Nashville, TN * St. Louis, MO * Chicago, Ill

ROCKY RUN WETLAND MITIGATION AREAS A and B
BAILEY MINE REFUSE DISPOSAL AREAS NO. 3 and NO. 4
CONSOL PENNSYLVANIA COAL COMPANY
GREENE COUNTY, PENNSYLVANIA

DWN. BY: JEFF MIHALIK	SCALE:	DATE:	PROJECT NO.:
CHK. BY: MRH	AS SHOWN	06/25/02	220806.0004

FIGURE 1

ALTERNATIVES ANALYSIS FOR THE RELOCATION OF S.R. 4009

Prepared for:

Consol PA Coal Company

Richhill and Gray Townships, Greene County, PA

March 24, 2004

CME
ENGINEERING

Civil Mining Environmental Engineering, Inc.
165 East Union Street, Suite 100
Somerset, Pennsylvania 15501
Phone (814) 443-3344 Fax (814) 444-0365

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Exhibit 2.0: Alternative Analysis Map
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Appendix 2.0: Biological Evaluations of Alignments for the Relocation of S.R. 4009

Appendix 3.0: Emergency Response Plan for the Temporary Closure of S.R. 4009, S.R. 4011 and T-370

Executive Summary

Consol PA Coal Company (Consol) currently operates the Bailey and Enlow Fork Mines, which are located in Washington and Greene Counties, PA. The two mines have operated since April 1984 and April 1990, respectively. Utilizing underground mining techniques, Consol extracts approximately 28 MM raw tons of high quality Pittsburgh coal annually. These mines employ approximately 1050 full-time employees and create and additional 3160 associated jobs. Coal extracted from the mines is processed at the Bailey Preparation Plant. Clean coal is shipped by rail to market. Coal refuse (coarse refuse and slurry) is disposed on-site at an approved coal refuse disposal facility. Consol has recently obtained Coal Refuse Disposal Permit #30020701 for new disposal areas 3 and 4. This permit was issued by the Pennsylvania Department of Environmental Protection (PADEP). The permit includes an approval for permanent stream enclosures and wetland fills and associated mitigation plans.

Construction of refuse areas 3 and 4 will encroach upon public road S.R. 4009. This encroachment will require S.R. 4009 to be relocated. Consol has been working jointly with the Pennsylvania Department of Transportation (PADOT) to design an acceptable relocation alignment for S.R. 4009. A conceptual alignment for the relocated S.R. 4009 was developed with PADOT. This alignment enabled the new roadway to meet current PADOT standards for this class of road. It also served to be the most direct replacement route and therefore, the least disruptive for the users of the portion of S.R. 4009 to be abandoned.

Nine (9) separate alternatives were evaluated. Based on the analysis of all factors, Alternatives 1 and 4 are acceptable replacement roads based upon total costs and nearly balanced cut/fill ratios. Alternative 1 has the lower cost and less environmental impacts. However, Alternative 1 has a longer emergency response time during inclement weather and the proposed route does not connect the same areas as S.R. 4009. Although Alternative 4 has increased environmental impacts when compared to Alternative 1, it more aptly replaces S.R. 4009 and will provide a better quality of highway connection between the Village of Time and the Graysville area. It is Consol's intention to provide a replacement road for S.R. 4009 that best serves the communities' needs with an acceptable environmental impact.

Consol representatives and their consultant CME Engineering met with the local governments affected by the road closure on March 22, 2004. The supervisors from Richhill Township, Gray Township, and Morris Township were in attendance as well as the solicitor for Richhill Township and representatives from PADOT district 12-0. All of the alternatives in the current analysis were explained by Consol and CME at this meeting. The sentiment of the supervisors was that a replacement road was necessary for emergency response and also for the economic needs of the area and for future growth and development. The supervisors were all in agreement that the replacement road should be a direct connection from the Fletcher/Martin Road areas to the village of Time. PADOT stated that Alternative 1 was not an acceptable replacement. Based on the comparison of all the alternatives and the input from those entities directly affected, the preferred route is Alternative 4.

1.0 Introduction

Consol PA Coal Company (Consol) currently operates the Bailey and Enlow Fork Mines, which are located in Washington and Greene Counties, PA. The two mines have operated since April 1984 and April 1990, respectively. Utilizing underground mining techniques, Consol extracts approximately 28 MM raw tons of high quality Pittsburgh coal annually. These mines employ approximately 1050 full-time employees and create and additional 3160 associated jobs. Coal extracted from the mines is processed at the Bailey Preparation Plant. Clean coal is shipped by rail to market. Coal refuse (coarse refuse and slurry) is disposed on-site at an approved coal refuse disposal facility. Consol has recently obtained Coal Refuse Disposal Permit #30020701 for new disposal areas 3 and 4. This permit was issued by the Pennsylvania Department of Environmental Protection (PADEP). The permit includes an approval for permanent stream enclosures and wetland fills and associated mitigation plans. The locations of the refuse areas are delineated on the attached Exhibit 1.0: Site Location Map.

Construction of refuse areas 3 and 4 will encroach upon public road S.R. 4009 as shown on Exhibit 1.0. This encroachment will require S.R. 4009 to be relocated. Consol has been working jointly with the Pennsylvania Department of Transportation (PADOT) to design an acceptable relocation alignment for S.R. 4009. A conceptual alignment for the relocated S.R. 4009 was developed with PADOT. This alignment enabled the new roadway to meet current PADOT standards for this class of highway. It also served to be the most direct replacement route and therefore, the least disruptive for the users of the portion of S.R. 4009 to be abandoned.

1.1 Background

During the permitting review process for refuse areas 3 and 4, it was determined that S.R. 4009 would be affected and that a portion of the road would need to be relocated. However, the conceptual alignment considered at the time was not expected to incur significant environmental impacts. This plan contemplated utilizing an existing railroad grade then quartering across a sloping pasture to a ridge top. The alignment then would follow the higher elevation to its termination at an existing township road. Wetlands were not anticipated on the initial pasture slope or on the ridge top. *The only expected environmental impact was at the departure from the railroad grade where an approximate 100-foot long extension of an existing culvert was anticipated.*

Upon receipt of the refuse disposal permit, Consol retained SP&K Engineering, Inc. (SP&K) to design the road relocation. SP&K subcontracted Earth, Inc. (Earth) to perform a geotechnical evaluation of the conceptual alignment. Earth performed a detailed geotechnical investigation and it was discovered that the conceptual alignment encountered severe slide prone conditions in the pasture area. A copy of the Earth report is attached in Appendix 1.0: Geotechnical Considerations Affecting the Relocation of S.R. 4009. Upon this discovery it was determined that there were only two practical options to construct the roadway on this general alignment. Option 1 entails buttressing the fill to prevent it from

sliding. Option 2 involves total removal of the slide prone material and replacement with suitable structural fill. Option 1 would require building the roadway fill across the pasture bottom where an intermittent stream originates. Option 2 would require excavation of the pasture bottom to attain competent footing. Both methods would result in filling the stream from its origin downstream for approximately 1375 feet.

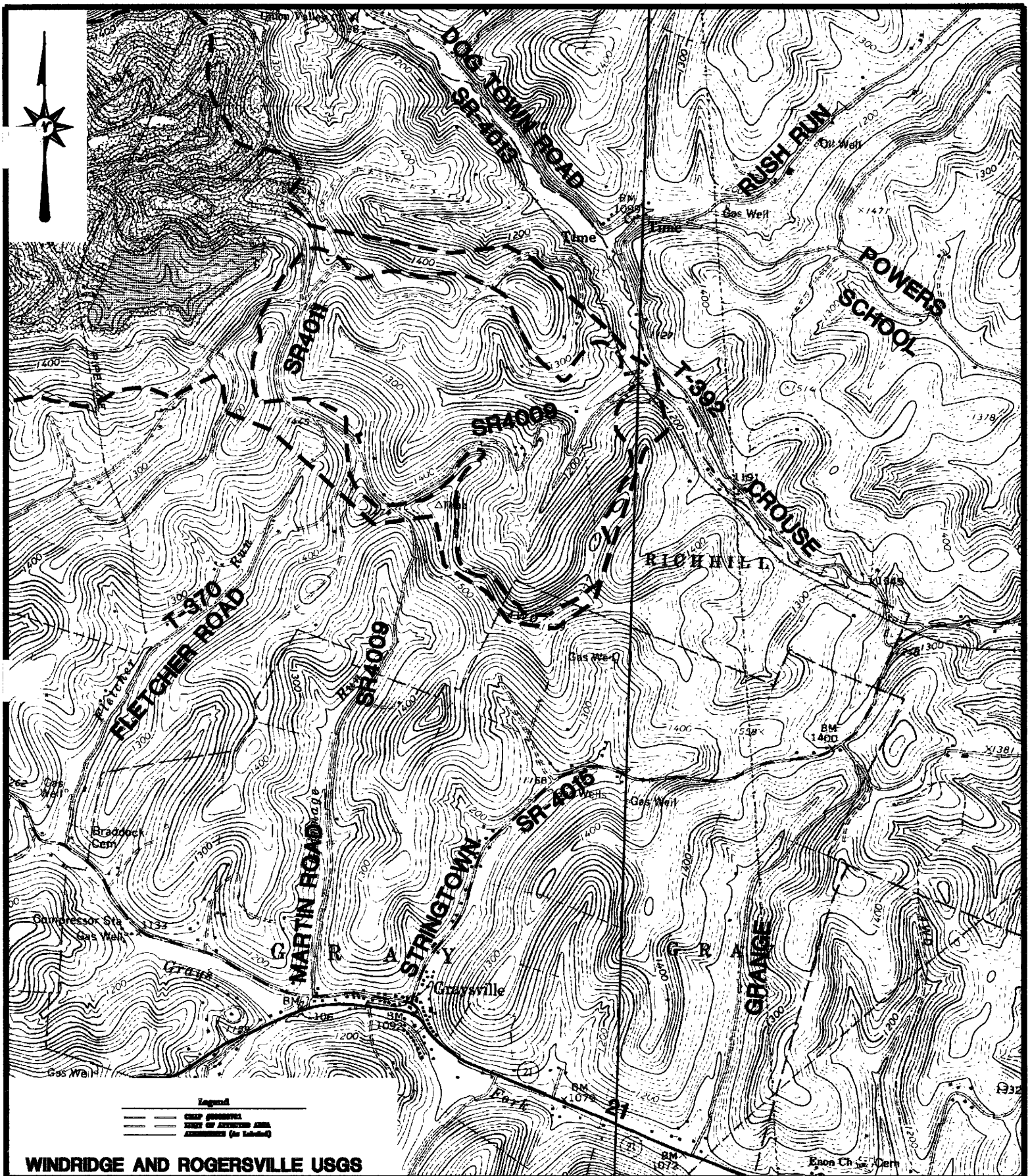
After giving consideration to the potential environmental impacts associated with the options, additional alignments were considered in an effort to minimize environmental impacts. This report describes the S.R. 4009 relocation alternative site process, the existing biological conditions (Refer to Appendix 2: Biological Evaluations of Alignments for the Relocation of S.R. 4009), and the associated environmental effects of each alternative considered.

2.0 Alternatives Evaluation

Consol and its engineering consultants have identified nine (9) alternatives for the relocation of S.R. 4009. Each alternative was designed and evaluated for comparison with the other alternatives. The alternatives considered are delineated on Exhibit 2.0: Alternatives Analysis Map and include:

1. Alternative 1 – Construction of a new road from Stringtown Road (S.R. 4015) to Martin Road (S.R. 4009) paralleling the existing railroad grade.
2. Alternative 2 – Maintain S.R. 4009 in it's existing alignment.
3. Alternative 3 – Construction of a new road from the intersection of S.R. 4009 and the existing railroad to Fletcher Road (T-370) through the Anderson property.
4. Alternative 4 - Similar to Alternative 3 with an adjustment made to avoid impacts on Grinnage Run.
5. Alternative 5 - Similar to Alternatives 3 and 4 only shifted to the north along the top of the ridge.
6. Alternative 6 – No relocation of S.R. 4009, permanent closure of road.
7. Alternative 7 - Upgrade Crouse Road (T-392).
8. Alternative 8 – Similar to Alternatives 3, 4, and 5 only shifted to the south along the top of the ridge.
9. Alternative 9 – Inside the same watershed as the coal refuse disposal facility.

Each alternative is discussed in detail in the following narratives:



WINDRIDGE AND ROGERSVILLE USGS

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EXHIBIT 1.0: SITE LOCATION MAP
for
CONSOL PA COAL CO.
SR 4009 RELOCATION
RICHHILL AND GRAY TOWNSHIP
GREENE COUNTY, PENNSYLVANIA

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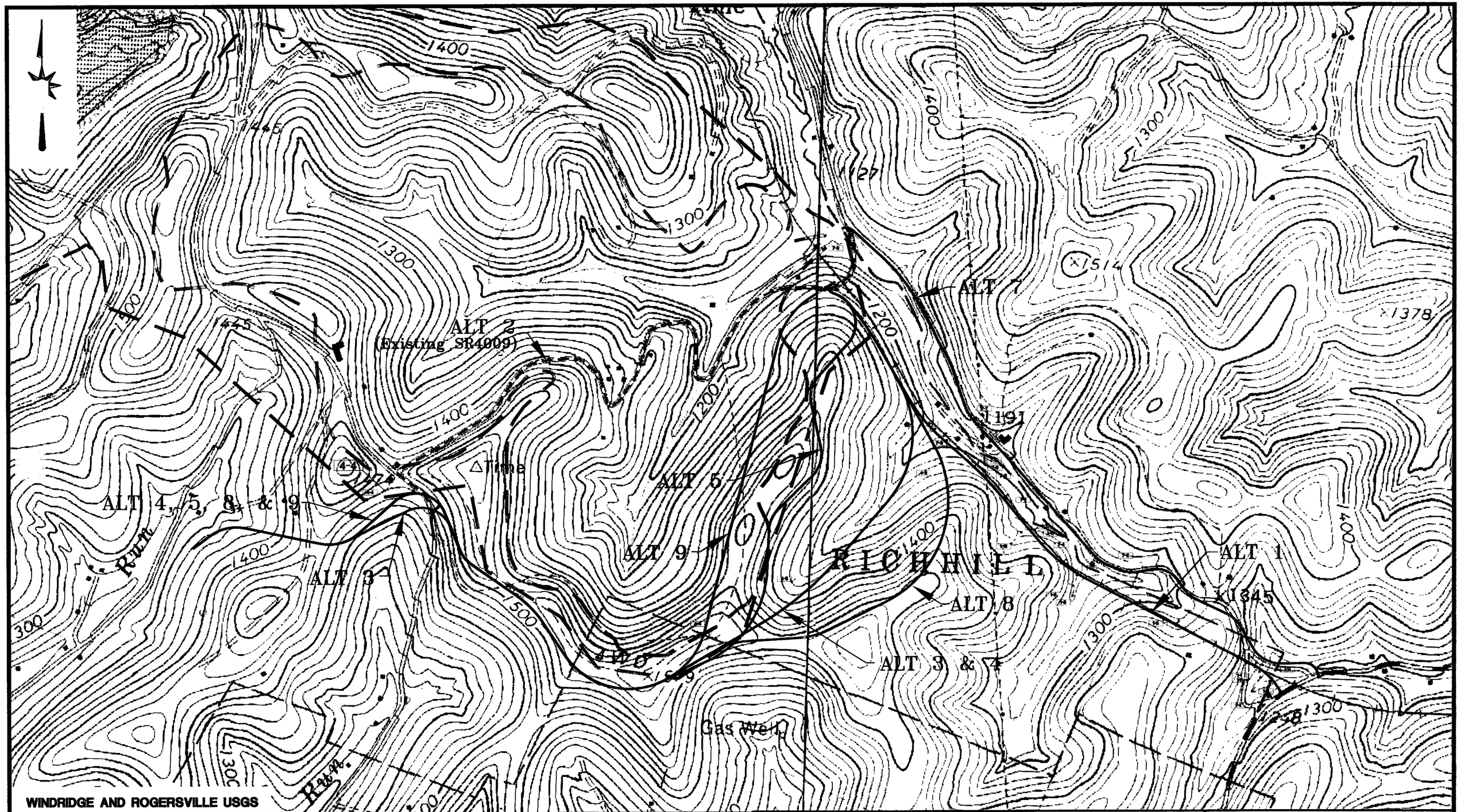
Checked By:	MRT
Date:	01/08/2003
Scale:	1" = 2000'
Project No.:	357-01
File Name:	base.dwg



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- CMAP #30020701
- LIMIT OF AFFECTED AREA
- ALIGNMENTS (As Labeled)

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EXHIBIT 2.0- ALTERNATIVE ANALYSIS MAP for

CONSOL PA COAL CO.

SR 4009 RELOCATION

RICHHILL AND GRAY TOWNSHIP
GREENE COUNTY, PENNSYLVANIA

2.1. Alternative 1

Alternative 1 consists of the construction of 1.08 miles of new road paralleling the railroad tracks from Stringtown Road (S.R. 4015) to S.R. 4009. This alternative is delineated on Exhibit 2.0 and in more detail on Exhibit 2.1: Alternative 1 Site Plan. As shown, this alternative would cross four stream channels and enclose 162 feet of stream channel by extending the culverts that currently exist beneath the railroad. This alternative would also encroach upon approximately 0.01 acres of jurisdictional wetlands located in Tributary "B" and could potentially impact additional jurisdictional wetlands in this same tributary if the construction were to extend beyond the limits of the railroad right of way.

Earthwork quantities taken from "Table 1 – Relocated S.R. 4009 Earthwork Quantities and Geotechnical Impacts on Streams" of Earth's report indicate that construction of this alternative will involve excavation of 333,400 cubic yards of cut and 181,800 cubic yards of embankment fill and 45,000 cubic yards of buttress fill. This results in an excess of 106,600 cubic yards of excavated waste material that will require offsite disposal. The estimated construction cost of this alternative was estimated by SP&K to be $3,681,000.

An emergency response time from Graysville VFD to the Village of Time utilizing this alternative was calculated to be 6 minutes, 42 seconds. The emergency response time for this alternative was calculated using a measured time of 4 minutes, 20 seconds from Graysville VFD to the intersection of the proposed alternative with Stringtown Road (S.R. 4015), an assumed average speed of 40 mph for the newly constructed road and estimated time of 45 seconds from the end of the relocated S.R. 4009 to the Village of Time. The calculated response time for this alternative approximates the response time of the current emergency response route. However, the steeper grade of the existing Stringtown Road will require the fire and rescue crews from the Graysville VFD to utilize the adjacent Grange Road during inclement weather, which will add approximately 2 minutes to the response time to the Village of Time.

Alternative 1 seemingly could be constructed as a cost effective replacement road for S.R. 4009 with minimal environmental impacts, however, it would require excavation into an unstable hillside below an electric power transmission tower. The impacts, including utility involvement have not been quantified. Additionally, this proposed route does not mirror the present course of S.R. 4009. Fletcher and Martin Roads would be connected to create a loop, but this area would no longer have a direct connection to Crouse Road and the Village of Time.

Photographs of this alternative can be found in Figures 1-1 through 1-12 and locations are shown on Exhibit 2.1.

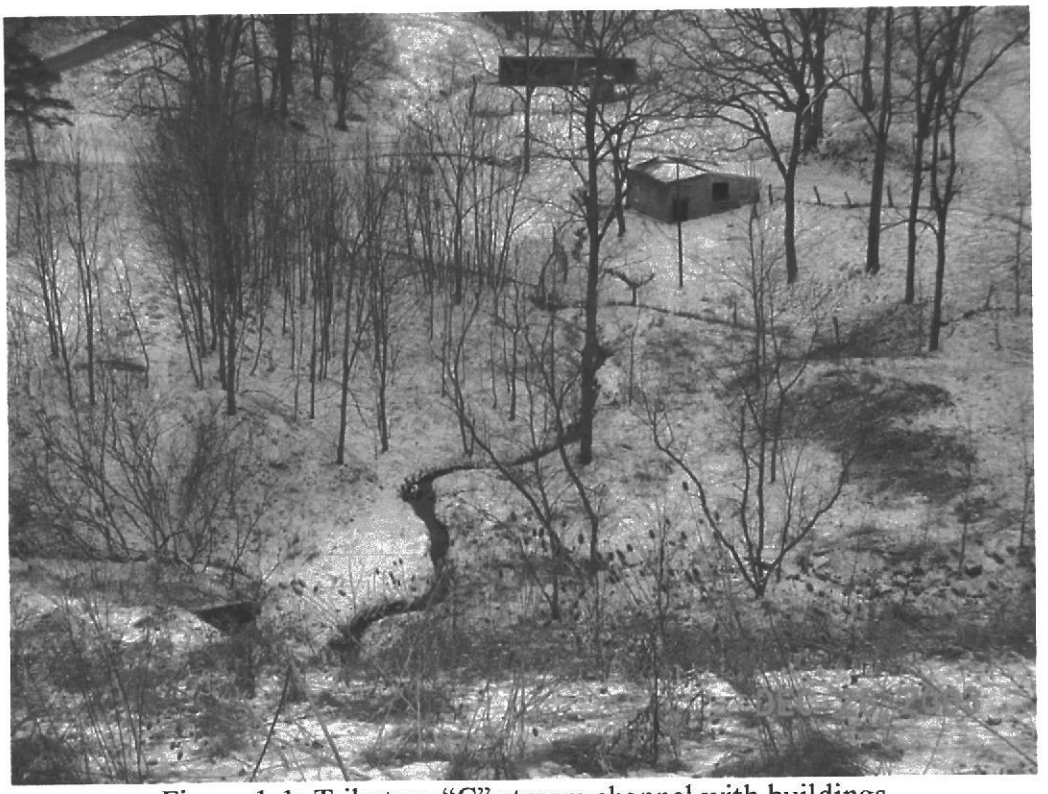

Figure 1-1: Tributary "C" stream channel with buildings

Figure 1-2: Tributary "C" close up at toe with culvert headwall

Figure 1-3: Tributary "C" close up of toe of existing embankment

Figure 1-4: Tributary "C" close up of 82" CMP with headwall

Figure 1-5: Railroad cut looking west

Figure 1-6: Railroad cut looking east

Figure 1-7: Tributary "B" and field with probable wetlands on private property

Figure 1-8: Tributary "B" close up of 60" CMP with headwall and wetland area

Figure 1-9: Seep/Pipe outlet east hillside

Figure 1-10: Estimated 0.4-0.5 acre wetland area on private property

Figure 1-11: Tributary "A" at toe of existing embankment

Figure 1-12: Tributary "A" close up of 42" CMP with headwall

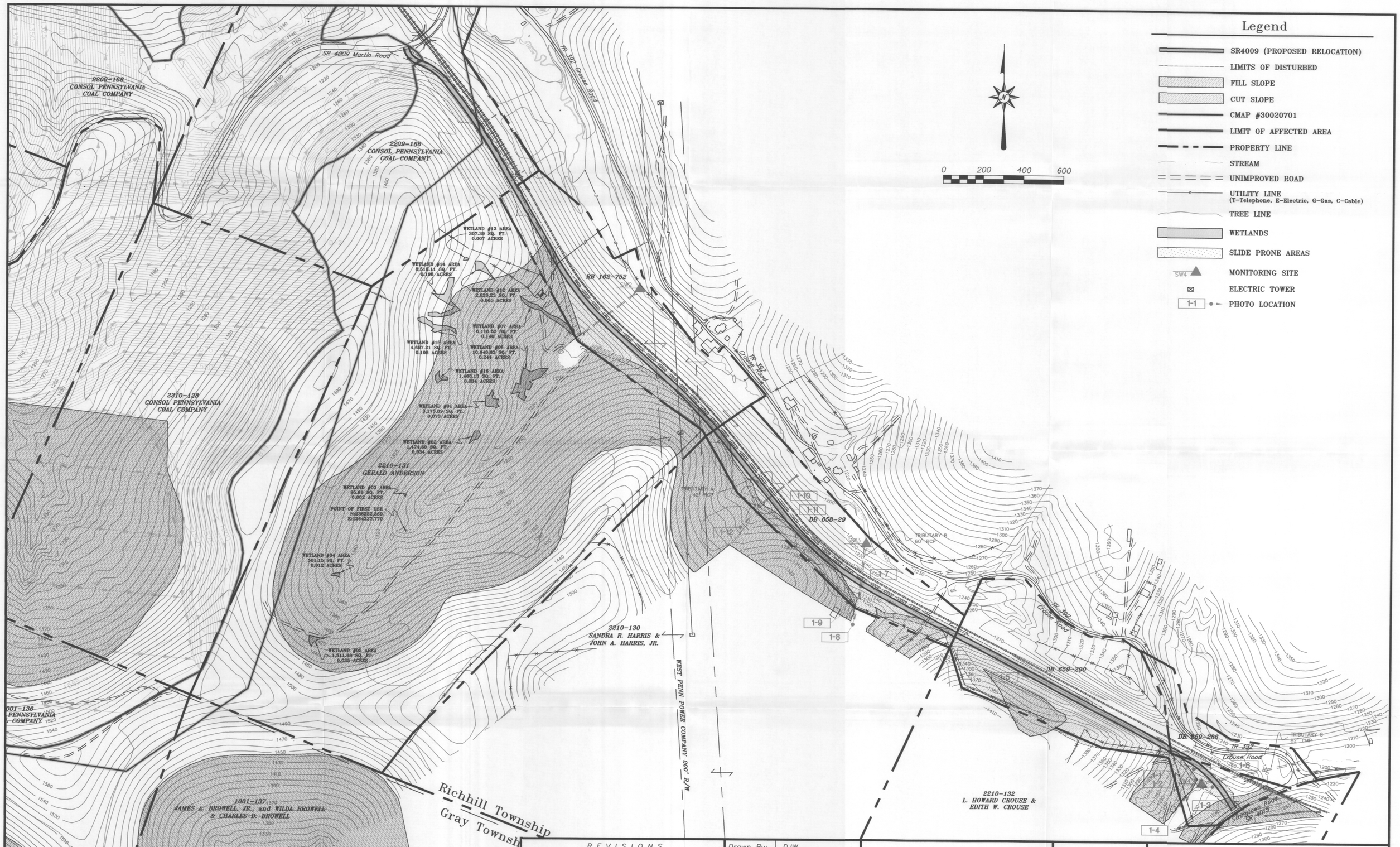

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EXHIBIT 2.1
ALTERNATIVE 1 SITE PLAN
for
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RELOCATION OF SR 4009
RICHHILL AND GRAY TOWNSHIP
GREENE COUNTY, PENNSYLVANIA

2.2. Alternative 2

Alternative 2 involves no relocation of S.R. 4009. Although this alternative would result in no environmental impact, construction of the Coal Refuse Disposal Area would no longer be justifiable due to the significantly decreased life span of the redesigned disposal area. Consol has adequate coal reserves to allow the continuous operation of the Bailey and Enlow Fork Mines for in excess of 20 to 25 years. At the current production rate of 28 MM raw tons of coal per year an estimated 6,000,000 cubic yards of coal refuse will be generated on an annual basis. The currently approved refuse disposal areas provide approximately 12 to 15 years of refuse storage capacity at the current production rates.

Consol previously demonstrated in the CRDP application #30020701 that the approved location of the Coal Refuse Disposal Area is necessary and justifies the proposed environmental impacts created by the facility. This demonstration was detailed in a report prepared by Michael Baker, Inc. that was included in the CRDP application. This refuse disposal area alternative analysis utilized the prescribed site selection process required by the PADEP. The PADEP has issued the permit for the Coal Refuse Disposal Area having been satisfied that the design has adequate longevity to justify the proposed environmental impacts associated with the construction of the Coal Refuse Disposal Area. The storage volume of the Coal Refuse Disposal Area would be significantly decreased if S.R. 4009 is not abandoned and relocated thereby rendering the project unfeasible.

The construction of the new refuse disposal area is necessary for the continued operation of the Bailey Complex and the continued employment of the mining employees and the workers with mining related jobs throughout the area. The permitting of an adjacent area for the refuse disposal requirements of the Bailey Complex in lieu of the relocation of S.R. 4009 is not an option due to the lengthy time requirements of the permitting process. The approved new refuse disposal area is the preferred alternative to minimize environmental impacts and certainly the potential environmental impacts of an alternate refuse disposal area will greatly exceed the impacts of the proposed road relocation.

Additionally, the current cart width and geometry (including hairpin curves) of S.R. 4009 does not meet current highway design and safety standards. A newly constructed road would meet current design standards and will provide improved transportation for the communities throughout the area.

2.3. Alternative 3

Alternative 3 considers a 1.92-mile relocation of S.R. 4009 to the southeast of the existing S.R. 4009 location. This alternative is shown on Exhibit 2.0 and in more detail on Exhibit 2.3: Alternative 3 Site Plan. As shown, this alternative would utilize the existing railroad grade for approximately 1100 feet where it then leaves the railroad and travels along the unnamed tributary to Enlow Fork before it crests a hill, proceeds along a ridge top crossing S.R. 4009 and continuing until its termination at Fletcher Road (T-392). The environmental impacts associated with this alternative include enclosure of 1504 feet of stream channel and the filling of 0.336 acres of jurisdictional wetlands.

Earthwork quantities taken from "Table 1 – Relocated S.R. 4009 Earthwork Quantities and Geotechnical Impacts on Streams" of Earth's report indicate that construction of this alternative will involve excavation of 484,300 cubic yards of cut, 449,800 cubic yards of embankment fill and 120,000 cubic yards of buttress fill resulting in 85,500 cubic yards of borrow material that will require importation to the site. The construction cost of this alternative was estimated by SP&K to be $4,655,000.

An emergency response time from Graysville VFD to the Village of Time utilizing this alternative was calculated to be 6 minutes, 41 seconds. The emergency response time was calculated using a measured time from Graysville VFD to the intersection of the proposed alternative with Martin Road (S.R. 4009), an assumed average speed of 40 mph for the newly constructed road and estimated time of 45 seconds from the end of the relocated S.R. 4009 to the Village of Time.

Alternative 3 can be constructed as a cost effective replacement road for S.R. 4009. However, the environmental impacts of this alternative are greater than Alternative 1, but this proposed route does mirror the present course of S.R. 4009 and would connect Fletcher and Martin Roads to Crouse Road and the Village of Time.

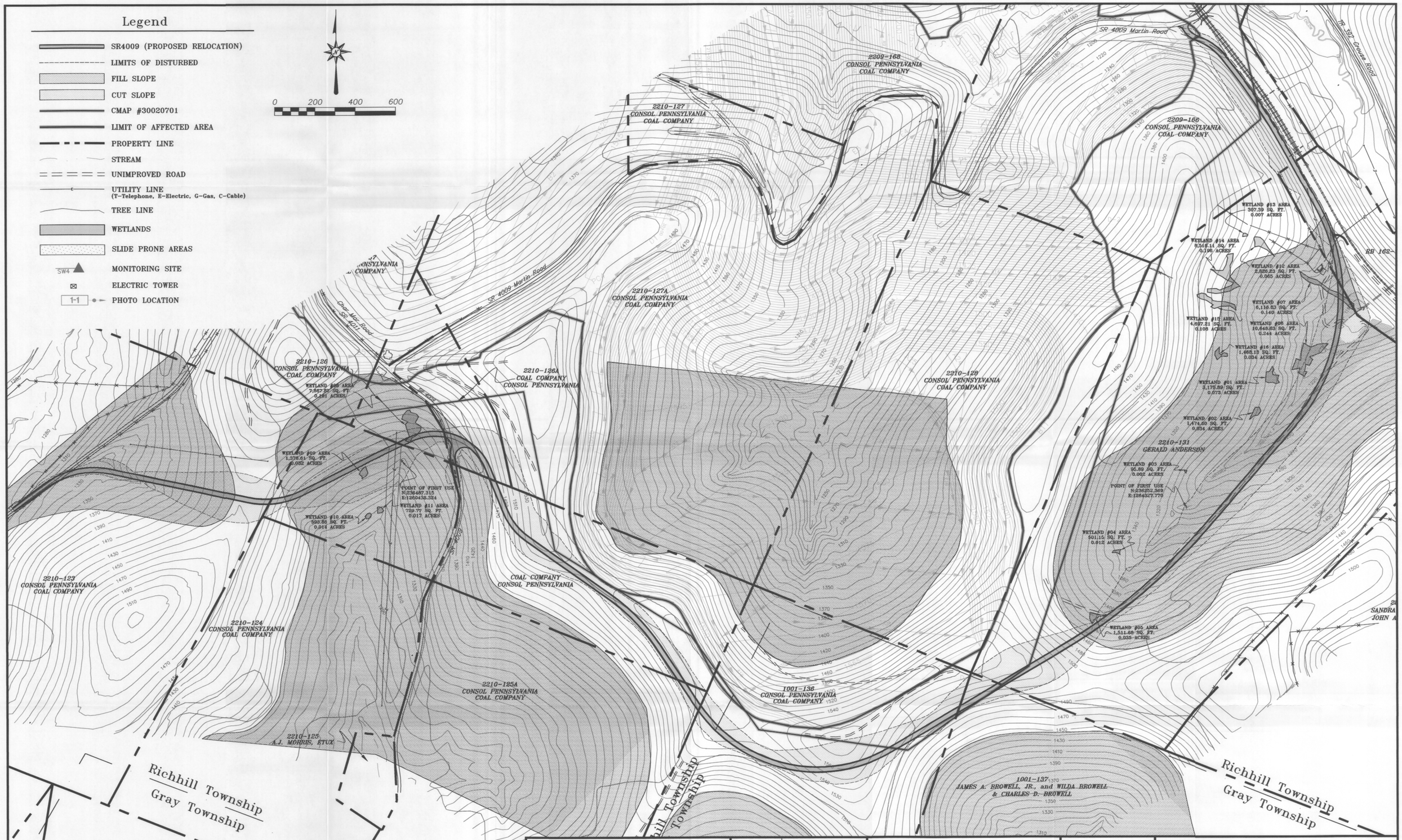

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EXHIBIT 2.3
ALTERNATIVE 3 SITE PLAN
for
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RELOCATION OF SR 4009
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GREENE COUNTY, PENNSYLVANIA

2.4. Alternative 4

Alternative 4 is a variation of Alternative 3 with an alignment adjustment shift to avoid impacts to Grinnage Run and to minimize jurisdictional wetland impacts. This alternative is shown on Exhibit 2.0 and in more detail on Exhibit 2.4: Alternative 4 Site Plan. As shown this alternative would utilize the existing railroad grade for approximately 1100 feet where it then leaves the railroad and travels along the unnamed tributary to Enlow Fork before it crests a hill, proceeds along a ridge top crossing the S.R. 4009 and continuing until its termination at Fletcher Road (T-392). The road has been realigned near the intersection with the existing S.R. 4009 to avoid both 129 feet of stream impact and 0.064 acres of jurisdictional wetlands located in the Grinnage Run watershed. The environmental impacts associated with this alternative include enclosure of 1375 feet of stream channel and the filling of 0.272 acres of jurisdictional wetlands.

Earthwork quantities taken from "Table 1 – Relocated S.R. 4009 Earthwork Quantities and Geotechnical Impacts on Streams" of Earth's report indicate that construction of this alternative will include 548,500 cubic yards of cut, 382,900 cubic yards of embankment fill and 110,000 cubic yards of buttress fill. This results in an excess of 55,600 cubic yards of excavated waste material that will require disposal in a nearby area making this the most balanced alternative considered. The construction cost of this alternative was estimated by SP&K to be $4,794,000.

An emergency response time from Graysville VFD to the Village of Time utilizing this alternative was calculated to be 6 minutes, 41 seconds. The emergency response time for this alternative was calculated using a measured time from Graysville VFD to the intersection of the proposed alternative with Martin Road (S.R. 4009), an assumed average speed of 40 mph for the newly constructed road and estimated time of 45 seconds from the end of the relocated S.R. 4009 to the Village of Time.

Alternative 4 can be constructed as a cost effective replacement road for S.R. 4009. However, the environmental impacts of this alternative are greater than Alternative 1, but this proposed route does mirror the present course of S.R. 4009 and would connect Fletcher and Martin Roads to Crouse Road and the Village of Time. Alternative 4 is preferable to Alternative 3 because of the reduced impacts to Grinnage Run.

Photographs of this alternative can be found in Figures 4-1 through 4-4 and locations are shown on Exhibit 2.4.

Figure 4-1: View along alignment looking southwest

Figure 4-2: View along alignment looking northeast

Figure 4-3: Northeast view of proposed stream enclosure

Figure 4-4: View along alignment looking northeast from top of ridge

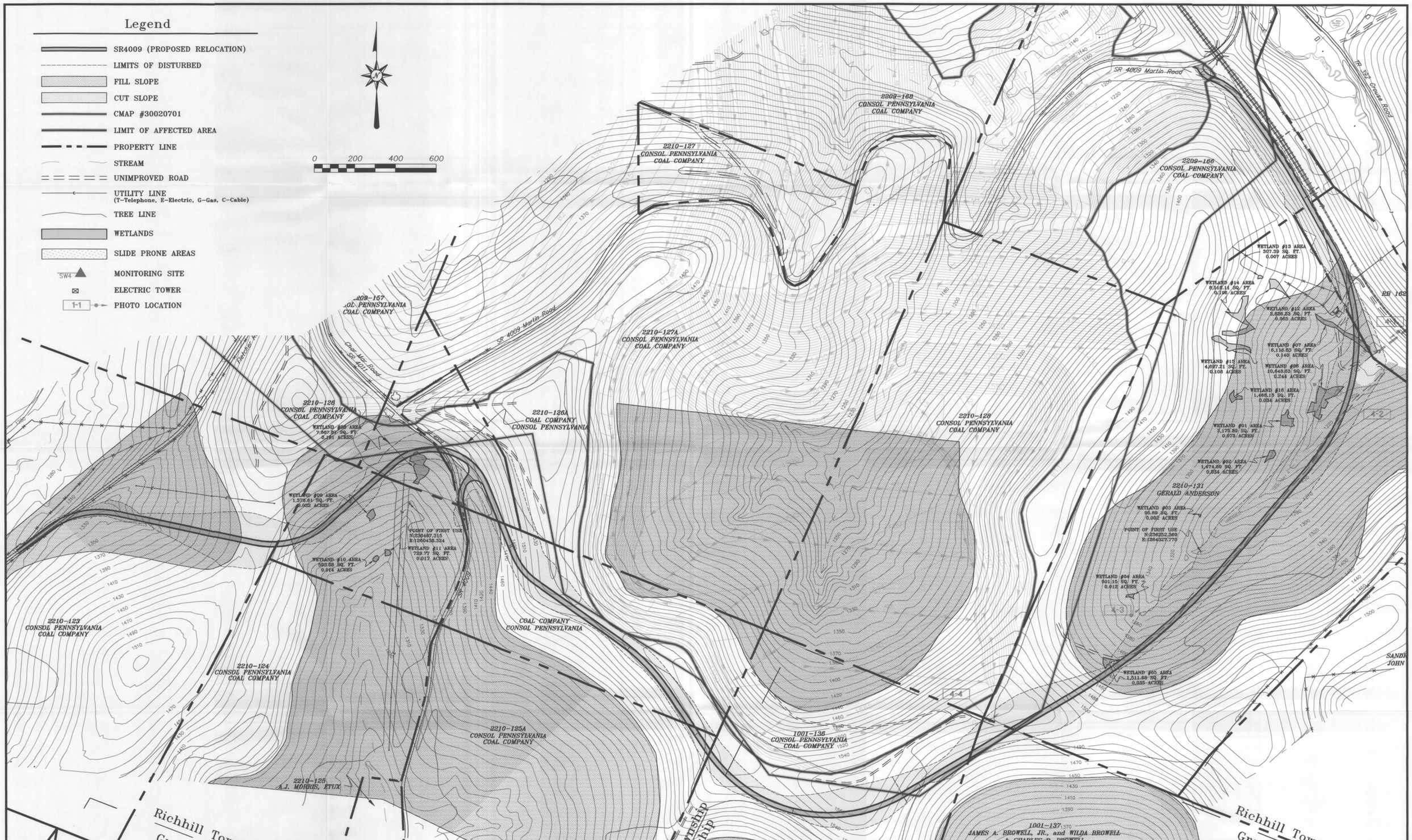

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EXHIBIT 2.4
ALTERNATIVE 4 SITE PLAN
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RELOCATION OF SR 4009
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2.5. Alternative 5

Alternative 5 considered a 1.87-mile relocation of S.R. 4009 to the southeast of the existing S.R. 4009 location along the top of the ridge. This alternative is shown on Exhibit 2.0 and in more detail on Exhibit 2.5: Alternative 5 Site Plan. As shown, this alternative would utilize the existing railroad grade for approximately 1100 feet where it then leaves the railroad and climbs a steep hill to the crest, proceeds along a ridge top through a massive cut, crosses S.R. 4009 and continues with the proposed alignment of alternative 4 until its termination at Fletcher Road (T-392). The direct environmental impacts associated with this alternative involve the filling of 0.028 acres of jurisdictional wetlands. The indirect environmental impacts include the potential dewatering of the uppermost jurisdictional wetlands by the interception of the ground water flowing through strata and fractures toward the stream channel which is further compounded by the interception of water in the recharge area to the stream and the lower wetlands.

Earthwork quantities taken from "Table 1 – Relocated S.R. 4009 Earthwork Quantities and Geotechnical Impacts on Streams" of Earth's report indicate that construction of this alternative will include 1,767,800 cubic yards of cut, 17,300 cubic yards of embankment fill and 30,000 cubic yards of buttress fill resulting in 1,720,500 cubic yards of excavated waste material that will require disposal in a nearby area. The construction cost of this alternative was estimated by SP&K to be $9,485,000.

An emergency response time from Graysville VFD to the Village of Time utilizing this alternative was calculated to be 6 minutes, 37 seconds. The emergency response time for this alternative was calculated using a measured time from Graysville VFD to the intersection of the proposed alternative with Martin Road (S.R. 4009), an assumed average speed of 40 mph for the newly constructed road and estimated time of 45 seconds from the end of the relocated S.R. 4009 to the Village of Time.

Specific concerns related to this alternative include the previously mentioned indirect environmental impacts, enormous construction costs and the additional environmental impacts created by the massive excess waste disposal. The waste materials would be taken to the new refuse disposal area that would reduce the life of this facility by approximately three to four months and would create an added safety concern by introducing additional mobile equipment and human activity within the refuse disposal area.

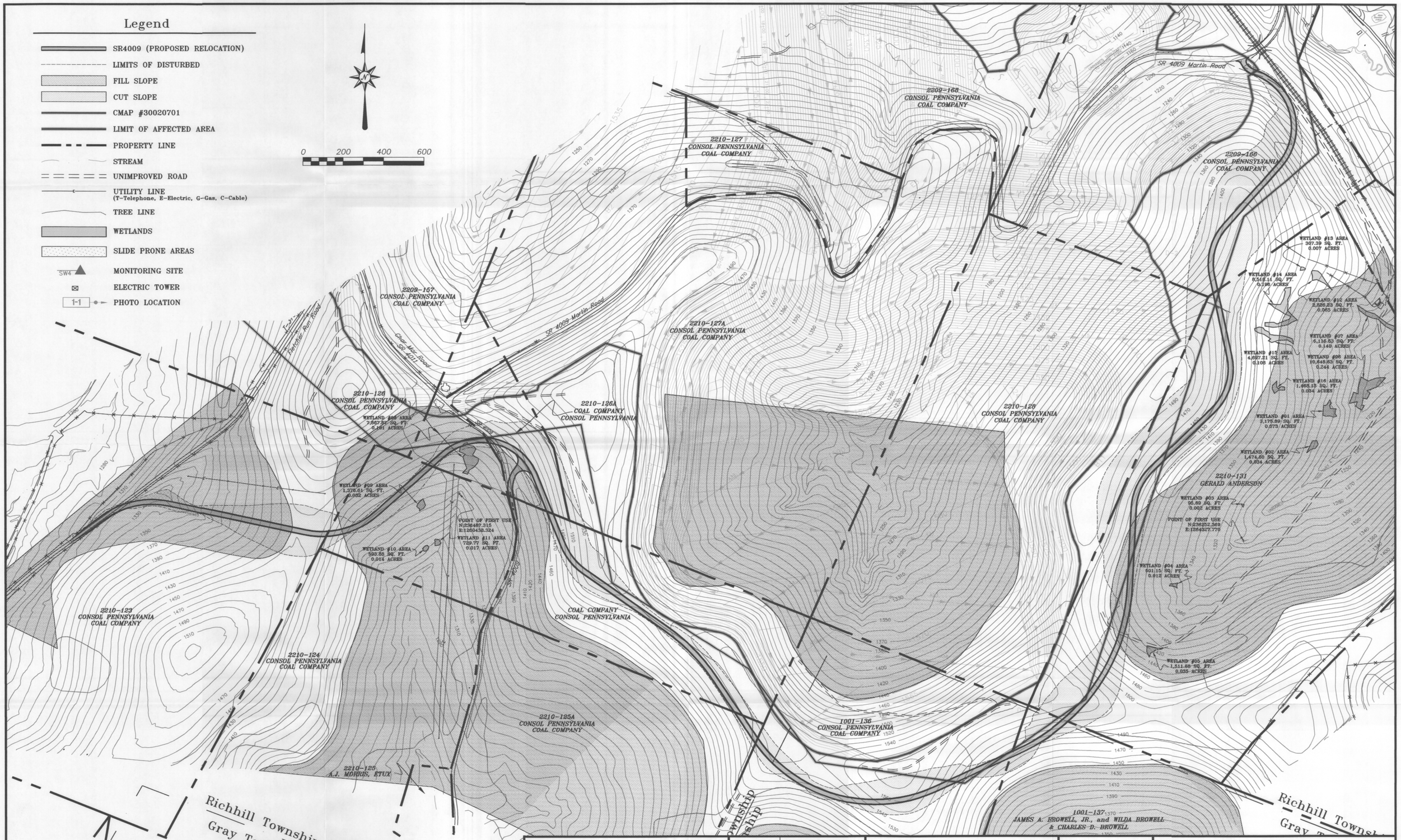

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EXHIBIT 2.5
ALTERNATIVE 5 SITE PLAN
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RELOCATION OF SR 4009
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GREENE COUNTY, PENNSYLVANIA

2.6. Alternative 6

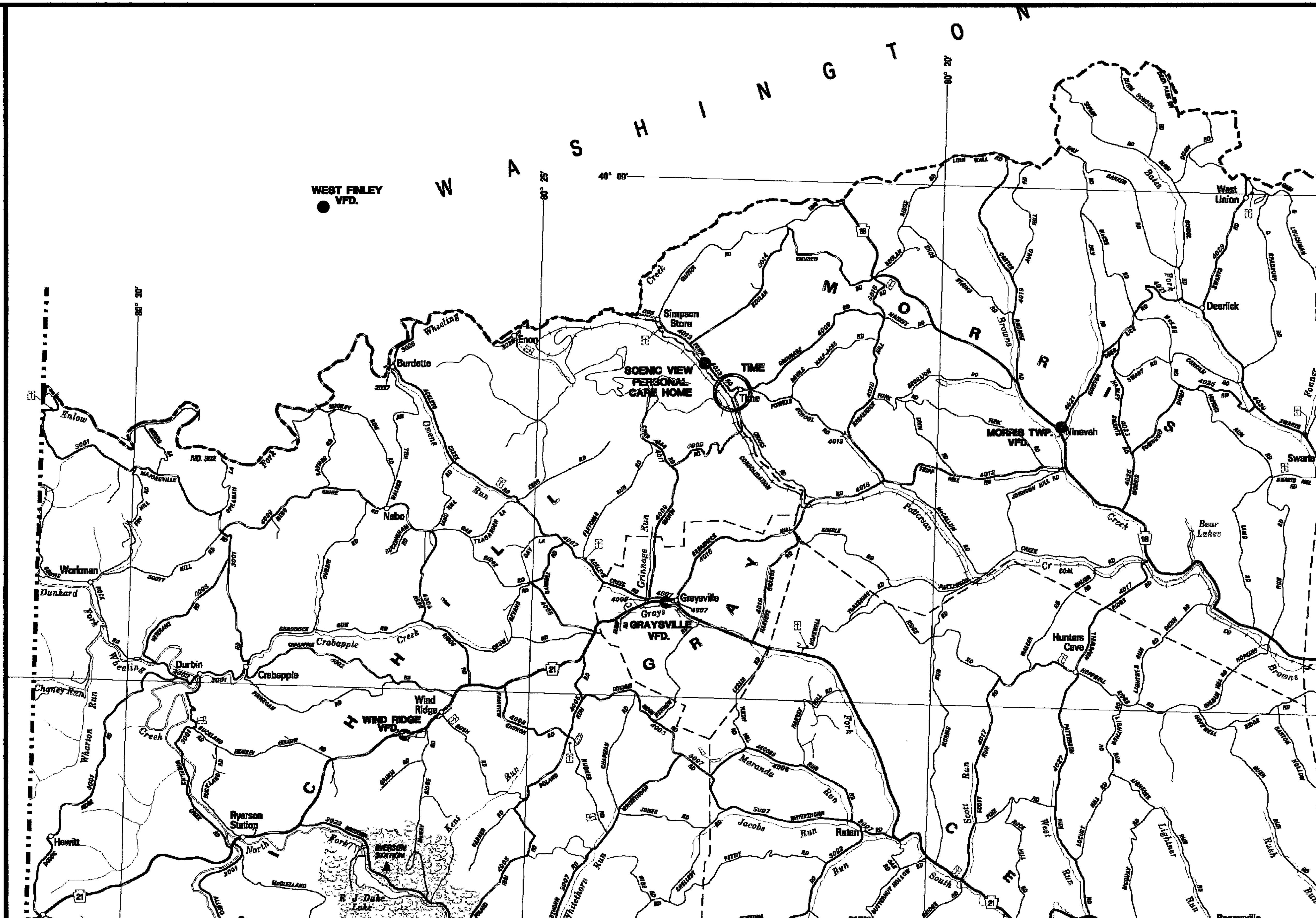
Alternative 6 considered the option of permanently closing S.R. 4009 with no future relocation. Consol and CME personnel met with Ms. Jo Lewis, Greene County Emergency Coordinator, on December 8, 2003, to discuss the Closure of S.R. 4009. At that time, an emergency response plan was requested to be developed (Refer to Appendix 3: Emergency Response Plan for the Temporary Closure of S.R. 4009, S.R. 4011 and T-370) for temporary closing of S.R. 4009. Ms. Lewis indicated that the area in and around the village of Time would be of most concern to provide adequate fire protection. The ambulance (EMS) services are provided by Waynesburg and would not be impacted by this closure. The area adjacent to the Village of Time is covered by four separate Volunteer Fire Departments: Graysville, Morris Township, Wind Ridge and West Finley. The closure would not affect either the West Finley or Morris Township response routes. However, a permanent road closure would affect the route utilized by both Wind Ridge and Graysville. Alternative routes were discussed with Ms. Lewis during the December 8 meeting; however, it was decided that a meeting with all the local Fire Chief's and Township Supervisor's associated with the Closure should be held to discuss alternatives / options.

Consol and CME personnel met with the local Fire Chiefs, Township Supervisors and Ms. Lewis on December 11, 2003 to discuss the permanent closure of S.R. 4009. After lengthy discussions, the Township Supervisors and Fire Department /Emergency Response representatives did not want to pursue the permanent closure of S.R. 4009 due to public safety and emergency response time concerns.

Consol and CME personnel met again with Ms. Jo Lewis on February 23, 2004 to measure actual emergency response times on the various routes that would be affected by the closure of S.R. 4009. The following times were measured from point to point traveling at the approximate speed a fire truck would respond to an emergency call. See Exhibit 2.6: Timed Emergency Response Routes for the location of these routes. The times do not include fire department personnel response time (the time from being dispatched to the time a fire/rescue unit is responding).

- Graysville VFD to the intersection in Time via Martin Road: (6 minutes, 43 seconds, 3.2 miles)
- Graysville VFD to Intersection in Time via Crouse Road: (8 minutes, 34 seconds, 3.7 miles)
- Graysville VFD to the intersection in Time via Route 21, Grange Road and Crouse Road: (9 minutes, 33 seconds, 4.2 miles)
- West Finley VFD to the intersection in Time: (12 minutes, 53 seconds, 7.0 mi)
- West Finley VFD to Scenic View Personal Care Home: (11 minutes, 11 seconds, 6.2 miles)

- Morris Township VFD to Intersection in Time: (8 minutes, 56 seconds, 4.6 miles)
- Graysville VFD via Stringtown Road to Railroad at Stringtown Road: (4 minutes, 20 seconds, 2.0 miles)
- Graysville VFD to Wind Ridge VFD: (4 minutes, 30 seconds, 3.9 miles)



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Emergency Response Routes

● Emergency Facilities

ENE COUNTY HIGHWAY MAP

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EXHIBIT 2.6
Timed Emergency Response Routes
for
CONSOL PA COAL CO.
SR 4009 RELOCATION
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GREENE COUNTY, PENNSYLVANIA

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2.7. Alternative 7

Alternative 7 considered a 1.21-mile upgrade of Crouse Road (T-392). This alternative is shown on Exhibit 2.0 and in more detail on Exhibit 2.7: Alternative 7 Site Plan. As shown, this alternative would require considerable improvements to improve this road from its current condition to meet PADOT and emergency vehicle requirements. The direct environmental impacts associated with this alternative include enclosure of 929 feet of stream channel and the filling of an estimated 0.5 acres of jurisdictional wetlands.

Earthwork quantities from preliminary designs provided by SP&K for this alternative resulted in 282,300 cubic yards of cut and 137,500 cubic yards of fill resulting in 127,300 cubic yards of excavated waste material that will require disposal in a nearby area. The note at the bottom of Table 1 – Relocated S.R. 4009 Earthwork Quantities and Geotechnical Impacts on Streams of Earth report indicates that any improvement to Crouse Road and any uphill reclamation are not geotechnically and practically feasible due to there being in exce4ss of 85% of the roadway length lying within colluvial land forms. More importantly, multiple buildings would have to be razed to accommodate the proposed design. Some of these buildings are old and may have historic value. The construction cost of this alternative was estimated by SP&K to be $3,827,000.

An emergency response time from Graysville VFD to the Village of Time utilizing this alternative was calculated to be 6 minutes, 54 seconds. The emergency response time was calculated using a measured time from Graysville VFD to the Village of Time. However, the steeper grade of the existing Stringtown Road will require the fire and rescue crews from the Graysville VFD to utilize the adjacent Grange Road during inclement weather that will add approximately 2 minutes to the response time to the Village of Time.

Although Alternative 7 appears to be a cost effective replacement road for S.R. 4009, it is not a viable option due to surface acquisition requirements to upgrade the present road to meet PADOT standards and specifications. The cost of the required surface property would be prohibitive if, in fact, the surface property could be purchased at all.

Photographs of this alternative can be found in Figures 7-1 through 7-9 and locations are shown on Exhibit 2.7.

Figure 7-1: Enlow Fork from driveway east of white farm

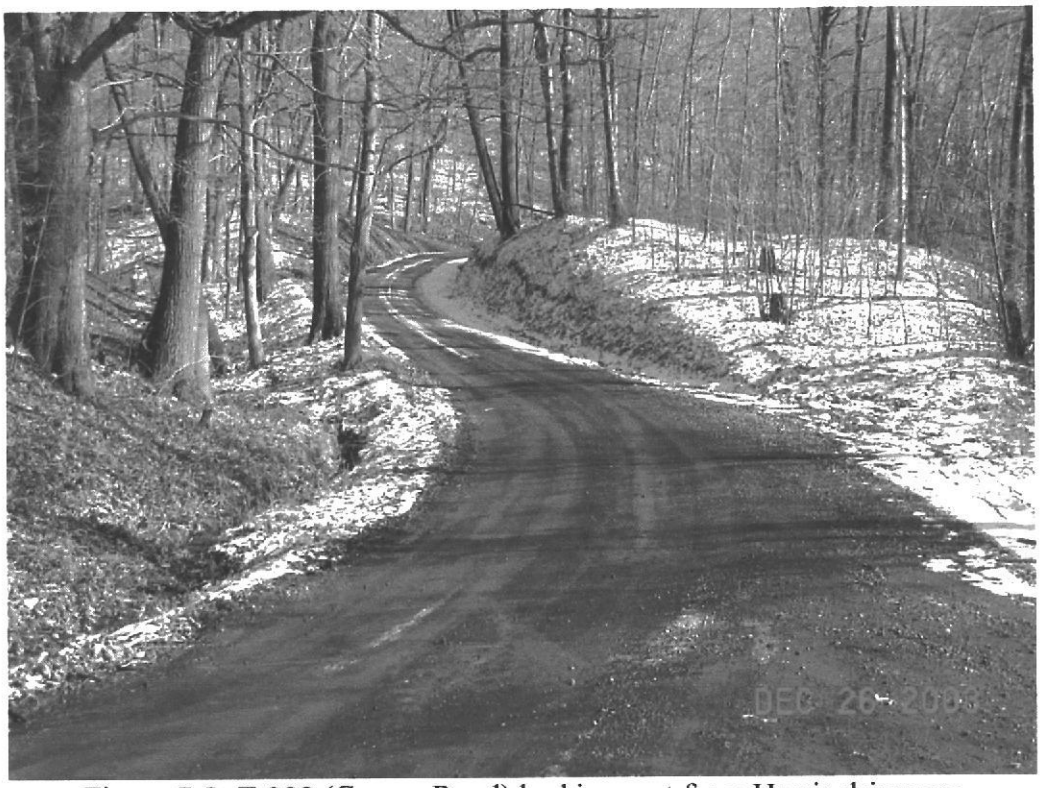

Figure 7-2: T-392 (Crouse Road) looking east from Harris driveway

Figure 7-3: White farm looking west from railroad

Figure 7-4: Enlow Fork from railroad between white and red farm

Figure 7-5: Red farm looking NW down T-392 (Crouse Road)

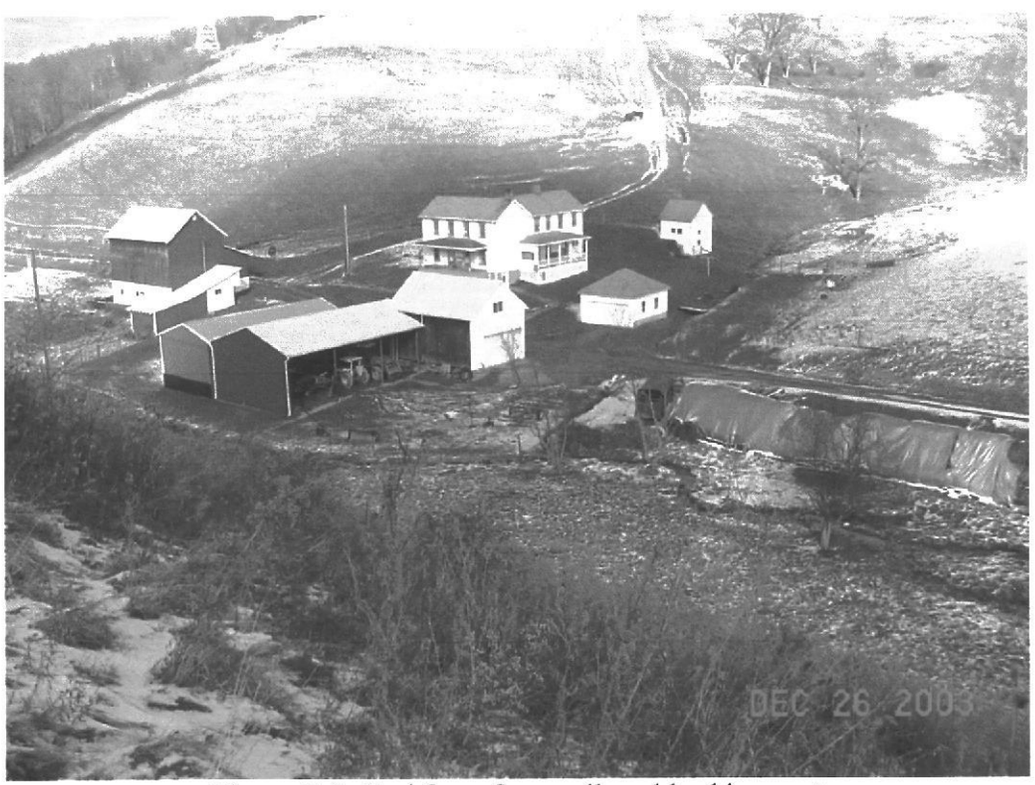

Figure 7-6: Red farm from railroad looking east

Figure 7-9: T-392 (Crouse Road) looking SE from S.R. 4009 up Enlow Fork

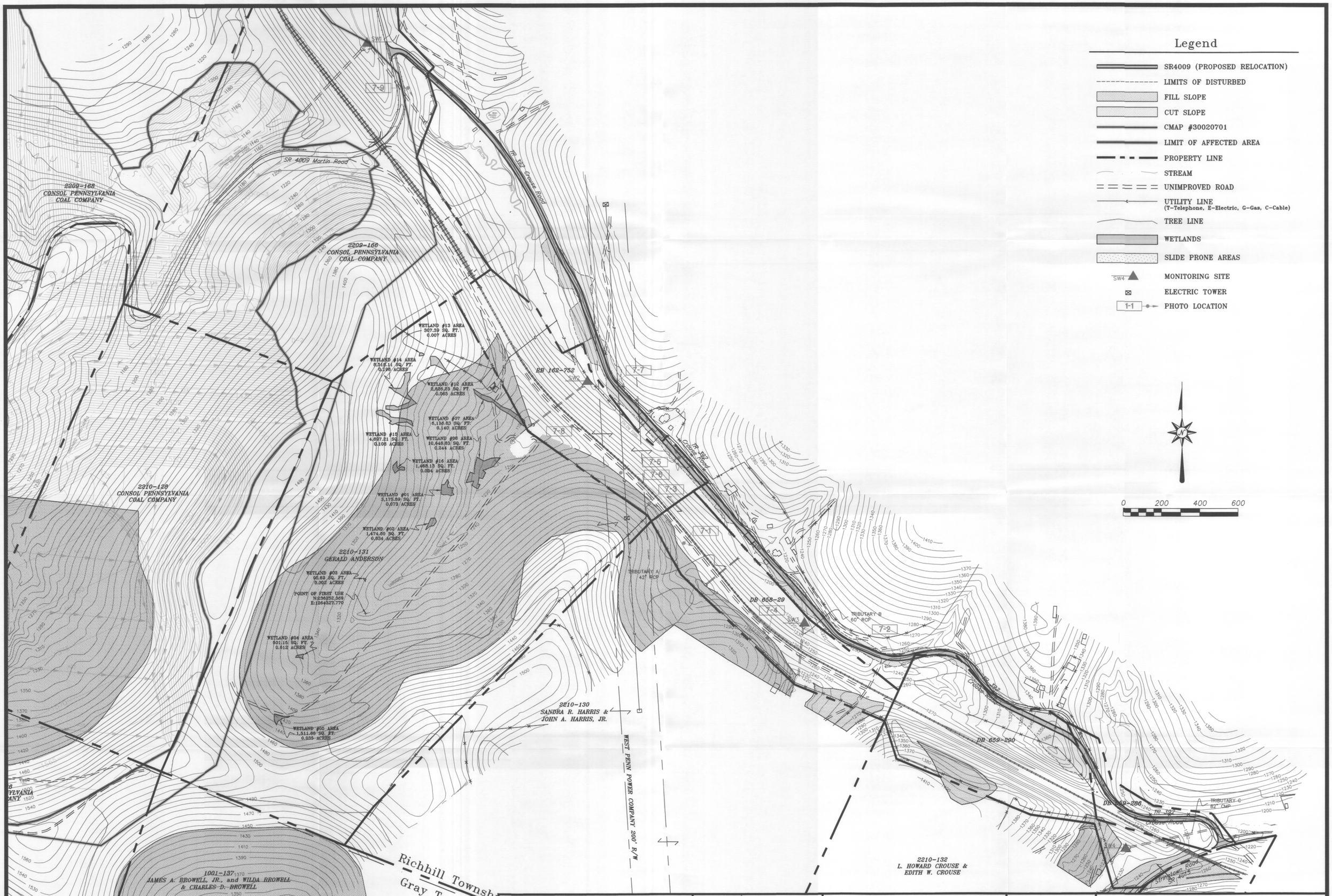

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EXHIBIT 2.7
ALTERNATIVE 7 SITE PLAN
for
CONSOL PA COAL CO.
RELOCATION OF SR 4009
RICHHILL AND GRAY TOWNSHIP
GREENE COUNTY, PENNSYLVANIA

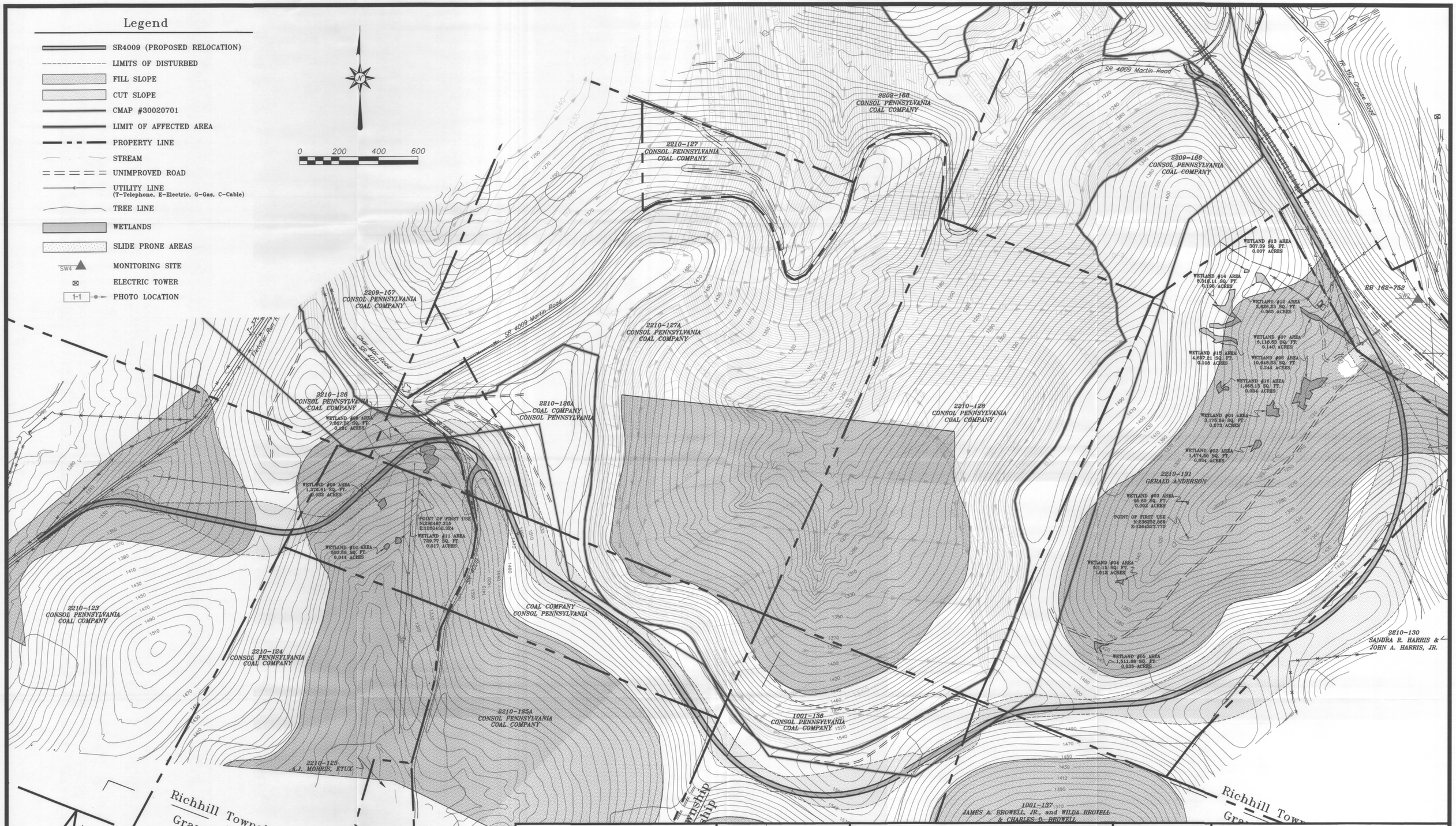
2.8. Alternative 8

Alternative 8 considered a 1.87-mile relocation of S.R. 4009 two ridges to the southeast of the existing location along the top of the ridge. This alternative is shown on Exhibit 2.0 and in more detail on Exhibit 2.8: Alternative 8 Site Plan. As shown, this alternative would utilize the existing railroad grade for approximately 1100 feet where it then leaves the railroad and climbs a steep hill to the crest, proceeds along a ridge top through a massive cut, crosses the S.R. 4009 and continuing with the proposed alignment of Alternative 4 and 5 until its termination at Fletcher Road (T-392). The direct environmental impacts associated with this alternative include enclosure of 400 feet of stream channel and the filling of 0.061 acres of jurisdictional wetlands. The indirect environmental impacts include the dewatering of jurisdictional wetlands by the interception of the ground water flowing through strata and fractures toward the stream channel which is further compounded by the interception of water in the recharge area to the stream and wetlands.

Earthwork quantities taken from "Table 1 – Relocated S.R. 4009 Earthwork Quantities and Geotechnical Impacts on Streams" of Earth's report indicate that construction of this alternative will include 2,393,600 cubic yards of cut, 87,000 cubic yards of embankment fill and 60,000 cubic yards of buttress fill resulting in 2,246,600 cubic yards of excavated waste material that will require disposal in a nearby area. The construction cost of this alternative was estimated by SP&K to be $12,367,000.

An emergency response time from Graysville VFD to the Village of Time utilizing this alternative was calculated to be 6 minutes, 35 seconds. The emergency response time was calculated using a measured time from Graysville VFD to the intersection of the proposed alternative with Martin Road (S.R. 4009), an assumed average speed of 40 mph for the newly constructed road and estimated time of 45 seconds from the end of the relocated S.R. 4009 to the Village of Time.

Specific concerns related to this alternative include the enormous construction costs and the additional environmental impacts created by the massive excess waste disposal. The waste materials would be taken to the new refuse disposal area that would reduce the life of this facility by approximately four to five months and would create an added safety concern by introducing additional mobile equipment and human activity within the refuse disposal area.



REVISIONS			
No.	By	Date	Description
			Revised 3/17/04

Drawn By:	DJW
Checked By:	MRT
Date:	12/12/2003
Scale:	1" = 200'
Project No.:	357-01
File Name:	BASEMAP-3-15-04.DWG
Drawing:	7 of 9

CME
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EXHIBIT 2.8
ALTERNATIVE 8 SITE PLAN
for
CONSOL PA COAL CO.
RELOCATION OF SR 4009
RICHHILL AND GRAY TOWNSHIP
GREENE COUNTY, PENNSYLVANIA

2.9. Alternative 9

Alternative 9 considered a 1.80-mile relocation of S.R. 4009 to the southeast of the existing S.R. 4009 location within the CRDP limits. This alternative adversely affects the proposed refuse pile design capacity by reducing its volume by 2,830,000 cubic yards. This alternative is shown on Exhibit 2.0 and in more detail on Exhibit 2.9: Alternative 9 Site Plan. As shown, this alternative climbs along a steep hill to the crest, proceeds along a ridge top, crosses S.R. 4009 and continues with the proposed alignment of Alternative 4 until its termination at Fletcher Road (T-392). The direct environmental impacts associated with this alternative involve the filling of 0.032 acres of jurisdictional wetlands. The indirect environmental impacts include the potential dewatering of the uppermost jurisdictional wetlands by the interception of the ground water flowing through strata and fractures toward the stream channel which is further compounded by the interception of water in the recharge area to the stream and the lower wetlands.

Earthwork quantities taken from "Table 1 – Relocated S.R. 4009 Earthwork Quantities and Geotechnical Impacts on Streams" of Earth's report indicate that construction of this alternative will include 1,224,300 cubic yards of cut, 14,000 cubic yards of embankment fill and 30,000 cubic yards of buttress fill resulting in 1,180,300 cubic yards of excavated waste material that will require disposal in a nearby area. The construction cost of this alternative was estimated by SP&K to be $7,144,000.

An emergency response time from Graysville VFD to the Village of Time utilizing this alternative was calculated to be 6 minutes, 29 seconds. The emergency response time for this alternative was calculated using a measured time from Graysville VFD to the intersection of the proposed alternative with Martin Road (S.R. 4009), an assumed average speed of 40 mph for the newly constructed road and estimated time of 45 seconds from the end of the relocated S.R. 4009 to the Village of Time.

Specific concerns related to this alternative include the previously mentioned indirect environmental impacts, the enormous construction costs and the additional environmental impacts created by the massive excess waste disposal. The waste materials would be taken to the new refuse disposal area that would reduce the life of this facility by approximately three months and would create an added safety concern by introducing additional mobile equipment and human activity within the refuse disposal area.

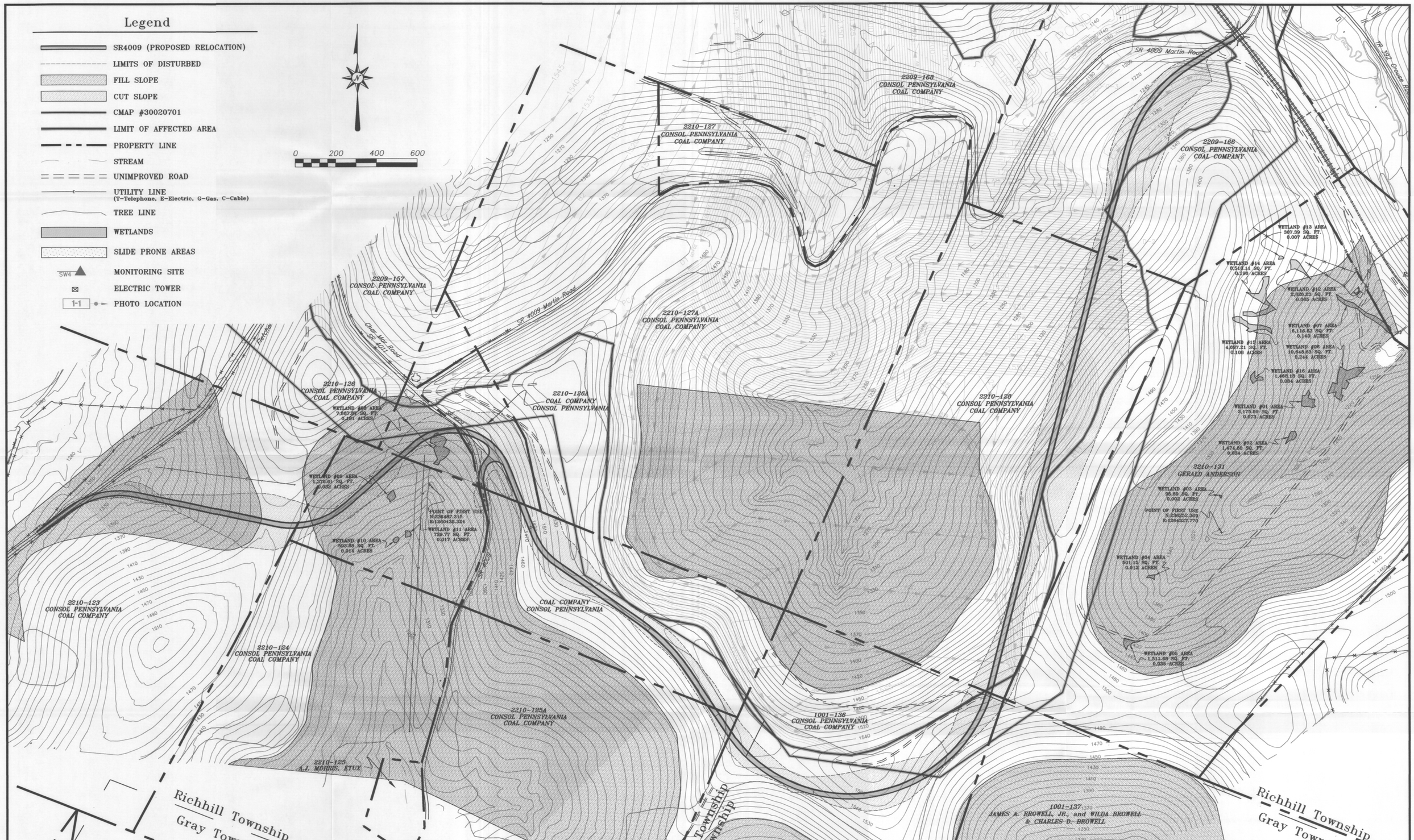

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EXHIBIT 2.9
ALTERNATIVE 9 SITE PLAN
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RELOCATION OF SR 4009
RICHHILL AND GRAY TOWNSHIP
GREENE COUNTY, PENNSYLVANIA

3.0 Conclusion

Construction of Refuse Areas 3 and 4 will encroach upon public road S.R. 4009 which will require S.R. 4009 to be relocated. Consol has been working jointly with PADOT to design an acceptable relocation alignment for S.R. 4009. Nine (9) separate alternatives were evaluated. Table 3.1: Alternative Comparisons summarizes the attributes of each alternative.

Alternatives 1 and 4 are acceptable replacement roads based upon total costs and nearly balanced cut/fill ratios. Alternative 1 has the lower cost and less environmental impacts. However; Alternative 1, in addition to involving excavation into an unstable hillside below an electric tower, has a longer emergency response time during inclement weather and the proposed route does not connect the same areas as S.R. 4009. Although Alternative 4 has increased environmental impacts when compared to Alternative 1, it more aptly replaces S.R. 4009 and will provide a better quality of road connection between the Village of Time and the Graysville area. It is Consol's intention to provide a replacement road for S.R. 4009 that best serves the communities' needs with an acceptable environmental impact.

Consol representatives and their consultant CME Engineering met with the local governments affected by the road closure on March 22, 2004. The supervisors from Richhill Township, Gray Township, and Morris Township were in attendance as well as the solicitor for Richhill Township and representatives from PADOT district 12-0. All of the alternatives in the current analysis were explained by Consol and CME at this meeting. The sentiment of the supervisors was that a replacement road was necessary for emergency response and also for the economic needs of the area and for future growth and development. The supervisors were all in agreement that the replacement road should be a direct connection from the Fletcher/Martin Road areas to the village of Time. PADOT stated that Alternative 1 was not an acceptable replacement. Based on the comparison of all the alternatives and the input from those entities directly affected, the preferred route is Alternative 4.

Alternatives Analysis Table

Alternative	Description	Cut (CY)	Embankment (CY)	Excess Waste (CY)	Emergency Response Time[1]	Construction Costs	Environmental Issues Streams / Wetlands	Mitigation Costs	Other Concerns
1	Parallel Railroad	333,400	226,800	106,600	6 min., 42 sec. 8 min., 30 sec.[2]	$3,681,000	162' Stream 0.010 ac. Wetlands	$13,100	Longer bad weather Emergency response time Different road interconnect than existing conditions Excavation into unstable hillside below electric transmission line
2	Existing S.R. 4009	0	0	0	6 min., 43 sec. 8 min., 30 sec.[2]	$0.00	0' Stream 0.0 ac. Wetlands	$0.00	Unacceptable – Conflicts with approved PADEP Permit Mine closure, loss of jobs Longer bad weather Emergency response time
3	1st Southeast Route Along stream	484,300	569,800	-85,500	6 min., 41 sec.	$4,655,000	1504' Stream 0.336 ac. Wetlands	$80,200	Not preferable to Alternative 4 which has reduced environmental impacts
4	2nd Southeast Route Along Stream Avoids Grinnage Run	548,500	492,900	55,600	6 min., 40 sec.	$4,794,000	1375' Stream 0.272 ac. Wetlands	$73,750	Preferable to Alternative 3 – reduced environmental impacts
5	3rd Southeast Route Top NW Ridge	1,767,800	47,300	1,720,500	6 min., 37 sec.	$9,485,000	0' Stream 0.028 acres Wetlands[3]	$5,000	Excessive Cut with additional required blasting Excessive Construction Cost Excess waste material, decreases Refuse Disposal Volume Possible groundwater interception
6	No Build	0	0	0	8 min., 34 sec.[4]	0	0' Stream 0.0 ac. Wetlands	0	Unacceptable to Communities Increase Emergency Response Time
7	T-392 Improvement Crouse Road	282,300	137,500	144,800	6 min, 54 sec. 8 min., 30 sec.[2]	$3,827,000	929' Stream >0.5 ac. Wetlands	$51,450	Stability Issues Longer bad weather Emergency response time Improbable land acquisition and/or excessive costs
8	4th Southeast Route Top SE Ridge	2,393,600	147,000	2,246,600	6 min., 35 sec.	$12,367,000	400' Stream 0.061 ac. Wetlands	$25,000	Excessive Cut with additional required blasting Excessive Construction Cost Excess waste material, decreases Refuse Disposal Volume
9	Through CRDP Area	1,224,300	44,000	1,180,300	6 min., 29 sec.	$7,144,000	0' Stream 0.032 ac. Wetlands[3]	$5,000	Unacceptable – Conflicts with approved PADEP Permit Premature Mine closure, loss of jobs Excessive Construction Cost Possible groundwater interception

[1] Response time is estimated from Graysville VFD to the intersection of SR-4013 and SR-4009 at the Village of Time.
[2] Bad Weather response time via Grange Road to Stringtown Road.
[3] Does not account for indirect impacts that include the dewatering of wetlands by the interception of the ground water, which is further compounded by the interception of water in the recharge area to the stream and wetlands.
[4] Unimproved Crouse Road

EARTH, INC.
THE GRISTMILL - SUITE 100
101 BELLEVUE ROAD
PITTSBURGH, PA 15229-2107
(412) 931-6393
FAX: (412) 931-2820

March 23, 2004

SP&K Engineering, Inc.
126 Kaider Road
Uniontown, PA 15401

Attention: Mr. Robert C. Ralston, P.E.

Re: Geotechnical Considerations Affecting
The Relocation of S.R. 4009
Associated with the Bailey Coal Refuse Disposal Facility
Richhill, Gray, and Morris Townships
Greene County, Pennsylvania
Earth, Inc. Contract No. 0221

Gentlemen:

Transmitted is one copy of the referenced report addressing geotechnical considerations affecting roadway construction associated with the relocation of S.R. 4009. Of particular concern is the predominant landform found throughout the project area, i.e., colluvium, comprised of both ancient and recent landslides.

Should you have any questions, please give us a call.

Very truly yours,

Earth, Inc.

Michael Sydlik

Michael Sydlik, P.E.
President

cc: Mr. Richard A. Weaver, P.E. – Consol Pennsylvania Coal Company (two copies)
Mr. Sean Isgan, P.E. – CME Engineering (one copy)

GEOTECHNICAL CONSIDERATIONS AFFECTING THE RELOCATION OF S.R. 4009 ASSOCIATED WITH THE BAILEY COAL REFUSE FACILITY RICHHILL, GRAY, AND MORRIS TOWNSHIPS GREENE COUNTY, PENNSYLVANIA

Presented to: SP&K ENGINEERING, INC.
126 KAIDER ROAD
UNIONTOWN, PA 15401

MARCH 23, 2004

Prepared by: EARTH, INC.
THE GRISTMILL - SUITE 100
101 BELLEVUE ROAD
PITTSBURGH, PA 15229-2107

Project Description

This project includes the abandonment of an approximately one mile section of S.R. 4009 associated with the Bailey Coal Refuse Disposal Facility in Richhill and Gray Townships, Greene County, Pennsylvania. A number of relocation alternatives running directly to the south of the proposed facility are under consideration for the replacement of the abandoned roadway.

The majority of these alternatives include an almost 2 mile long relocation on generally higher ground, much of it along ridgetops, except at its western limit where tying into Fletcher Run Road and the eastern limit where tying into existing S. R. 4009 along the west side of a tributary to Enlow Fork. Several alternatives include a partial relocation of S.R. 4009 from Fletcher Run Road to Martin Road with either an upgrade of T-392 (Crouse Road), an uphill relocation of T-392, or widening of the existing railroad shelf on the opposite side of the aforementioned tributary to Enlow Fork. This report generally addresses geotechnical considerations associated with the construction of these new roadways with emphasis in the areas of Martin Road, the Anderson Property, and the railroad. See Figures 1 through 5 which depict Alternatives 1, 3, 4, 5, 8, and 9.

Pertinent Geologic/Geotechnical Background

The project site is located within the Waynesburg Hills section of the Appalachian Plateaus Physiographic Province. This particular portion of the province is described as being very hilly with narrow hilltops and steep sloped, narrow valleys. Local relief is moderate. Bedrock units immediately underlying the site are Permian System in age; more specifically, they belong to the Greene Formation of the Dunkard Group. Please see Figure 6. Rock units of the Greene Formation are sedimentary in origin and include shale, some siltstone and sandstone, and minor amounts of shaly limestone, claystone, carbonaceous shale, and thin coal. Shale is locally interbedded with siltstone and sandstone. Sandstone occurs locally as channel filled deposits. Bedrock dips somewhat in a generally east-southeast direction between the

Washington Anticline to the west and the Nineveh Syncline to the east. Ancient landslides of great areal extent as well as more recent slides are common over much of Greene County.

In fact, landslides are of such a severe problem in southwestern Pennsylvania – and in particular Greene County –that all of the relocation alternatives being considered are affected significantly by their existence. Please see the attached reference from the Pittsburgh Post-Gazette dated January 11, 2004 which indicates that "in one small, movement-prone section of Greene County, a USGS map identifies more than 2,100 landslides."

Even for those alternatives that at first glance do not appear to be directly and/or significantly impacted by landsliding, the unfortunate reality of the matter is that they will be – due to the enormously large quantities of waste excavation generated to avoid or minimize direct impacts on streams.

Discussion

Field reconnaissance along with the results of test borings did indeed result in the verification of immense colluvial landforms (landslides), both ancient and recent in the project area. Please see the attached test boring logs. Some of this colluvium approached 30 feet in depth. Areas of questionable stability shown in gray shading may be seen on Figures 1 through 5. Also noted is the presence of springs. For Alternative 1 along the railroad shelf, excavation will be required into an unstable hillside below an electric power transmission line.

Table 1 presents earthwork quantities associated with the various alternatives and geotechnical impacts on streams. Although on paper it may appear that impacts to streams for several alternatives may be minimal, these alternatives also show vast quantities of excess excavation that must be wasted somewhere. And to be wasted in a manner that allows for stability, it will be necessary to place such material across various other stream valleys. Thus, there will be impacts to streams regardless of which relocation alternative is implemented.

Cut quantities have been increased by 10% to account for an increase in volume (swell) associated with excavation, particularly excavation with significant bedrock quantity when placed as fill of overall lesser density.

For Alternative 1 along the railroad, 15,000 c.y. of buttress fill is required for stability. Although only 162 feet of stream length would be impacted, a total of 4 streams will be affected. For all of the alternatives shown, buttress fill on the order of 30,000 to 40,000 c.y. is required to stabilize the roadway in the Martin Road area. The 30,000 c.y. buttress requirement is associated with alignments passing higher in the watershed, thereby allowing for the avoidance of filling in the headwaters of Grinnage Run. Alternative 3, which shows a 40,000 c.y. buttress requirement, would result in filling in of the headwaters of Grinnage Run for a length of 129 feet.

Alternatives 3, 4, and 8 require filling in the stream on the Anderson property to lengths varying from 400 to 1,375 feet with buttress fill quantities varying from 30,000 to 80,000 c.y. Note, however, that the shorter the length of stream filling, the greater the amount of waste generated for an alternative, reaching an astounding quantity of 2,000,000+ c.y. for Alternate 8 which showed a length of stream filling of only 400 feet. On the other hand, Alternatives 3 (showing 85,500 c.y. of borrow) and 4 (showing 55,600 c.y. of waste) require filling in of the stream channel for a length of 1,375 feet; they would not, however, require wasting in another watershed. Waste generated by Alternative 8 would need to be placed in numerous watersheds. (The aforementioned Alternative 1 bordering the Anderson property would also generate waste of a quantity high enough requiring placement in another watershed.)

Alternatives 5 and 9, showing no direct stream impacts but waste quantifies in excess of 1,000,000 c.y., would require placement in numerous other watersheds for disposal. Additionally, cuts in excess of 100 feet for Alternative 5 and 150 feet for Alternative 9 through east-southeasterly dipping bedrock would undoubtedly intercept significant groundwater flow feeding the stream on the Anderson property.

Alternative 9 would be counterproductive to the very purpose of the project generating its need, i.e., the establishment of the Bailey Coal Refuse Disposal Facility. Significant quantities of coal refuse disposal would be lost.

Alternative 7 (T-392 – Crouse Road – Improvement) and any uphill relocation of Crouse Road are not geotechnically and practically feasible. In excess of 85 percent of the roadway lies within colluvial landforms. Not only would significant quantities of excess excavation be generated by landsliding during construction, the horizontal limits of such construction and its negative impacts both left of right of the roadway would be required, essentially requiring the taking of significant right-of-way from multiple landowners, resulting in the probable razing of most, if not all, of the homes and out structures along the roadway.

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Pittsburgh, Pa. Tuesday, March 23, 2004

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Environment

Region's hills just keep up a slow descent

Sunday, January 11, 2004

By Don Hopey, Pittsburgh Post-Gazette

A little after 4 a.m. Monday, Diane and John McConnell were up and getting an early, soggy start on the work week when they heard a deep rumbling outside their home on Glass Run Road in Baldwin Borough.

A slide waiting to happen: landslide graphic and risk regions in Pa.

John ran outside and found his back yard and part of his garage buried under mud, rock and debris that until moments before had formed part of a seemingly solid hillside on an adjacent property. The force of the landslide toppled some of the garage's 16-inch concrete blocks onto his wife's 2001 Nissan Sentra, ripped off its bumper and pushed it halfway through the closed garage door.

"I was too late to do anything," he said. "There had been smaller landslides before. I probably spent $5,000 since we moved in seven years ago cleaning them up, but they never did any damage. They were just a nuisance. It's a natural thing. The hillsides get wet and then they let go."

After last weekend's saturating rains, it was not surprising that several of the region's hillsides yielded to gravity's pull, falling onto the McConnells' property and blocking Route 28 between the 31st and 40th street bridges and Route 51 in Stowe near the Fleming Park Bridge.

Southwestern Pennsylvania's rolling hills have a long geological reputation of not living up to their elevated topographic names. The region is one of the most landslide-prone areas of North America because of its steep hills and soft and slippery underlying rock layers.

And the widespread regrading and filling of hills and valleys for housing and business development over the past 50 years, plus the use of large

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excavating equipment to slice through hillsides for roads, have made the problem worse by opening up the clay stone layers to inundation from storms.

Add to the mix that the region has more freeze-thaw cycles during the winter than any other in the country and you've got a sure-fire recipe for the hillside rocks to roll.

Although recent subfreezing weather has stabilized the ground, the next slide is only a warming trend away.

"We'll have more problems as the result of the freezing and thaw cycles. That tends to shear off the hillsides like a knife," said Dick Skrinjar, Pennsylvania Department of Transportation spokesman. "This is probably the beginning of a series of episodes over the next several weeks."

That's because the subfreezing weather has caused the water in the saturated slopes to turn to ice and expand, breaking the natural cohesiveness of the hillside soils and rocks, said Charles Shultz, a geology professor recently retired from Slippery Rock University.

"The abundance of landslides is standard operating procedure in the Pittsburgh area," he said. "When the water freezes, it heaves up and puffs out the ground perpendicular to the slope of the road cut. When thaws occur, so do landslides."

Land has been answering to gravity in southwestern Pennsylvania on a regular basis since the last Ice Age. U.S. Geological Survey landslide maps document more than 15,000 ancient and geologically recent major landslides in Allegheny and Washington counties. And in one small, movement-prone section of Greene County, a USGS map identifies more than 2,100 landslides.

American Indian tribes acknowledged the local landscape's unsteady nature. They called the river now known as the Monongahela the "Menaungehilla," which means "river with the sliding banks," or "high banks that break off and fall down."

Such earth movement happened then and happens now because, in many places, the bedrock consists mainly of soft shales and clay stones that weather rapidly when exposed and become slippery when large doses of water from snowmelt or spring rains are added. The so-called "Pittsburgh red beds," a 40- to 60-foot thick layer of mostly reddish, greenish and grayish clay stones and shales are the best known among the highly mobile bedrocks.

According to Shultz, the region is also the site of the oldest known landslide on Earth, the Bakerstown Landslide, near Route 8 in Richland, in northern Allegheny County.

"In all the slopes north of Downtown there are a lot of ancient landslides dating to 25,000 years ago," Shultz said. "When humans go in and start digging around, that tends to reactivate the old slides. When they built Route 28 near Kittanning and Natrona Heights, they made a lot of steep road cuts and opened a lot of red beds."

Skrinjar said that the whole length of Route 28 from the Interstate 279 interchange to Harmarville is a slide-prone area.

"It's just a case," he said, "of the valley soils that have been carved into hills along the rivers wanting to go back to where they were before."

(Don Hopey can be reached at **dhopey@post-gazette.com** *or 412-263-1983.)*

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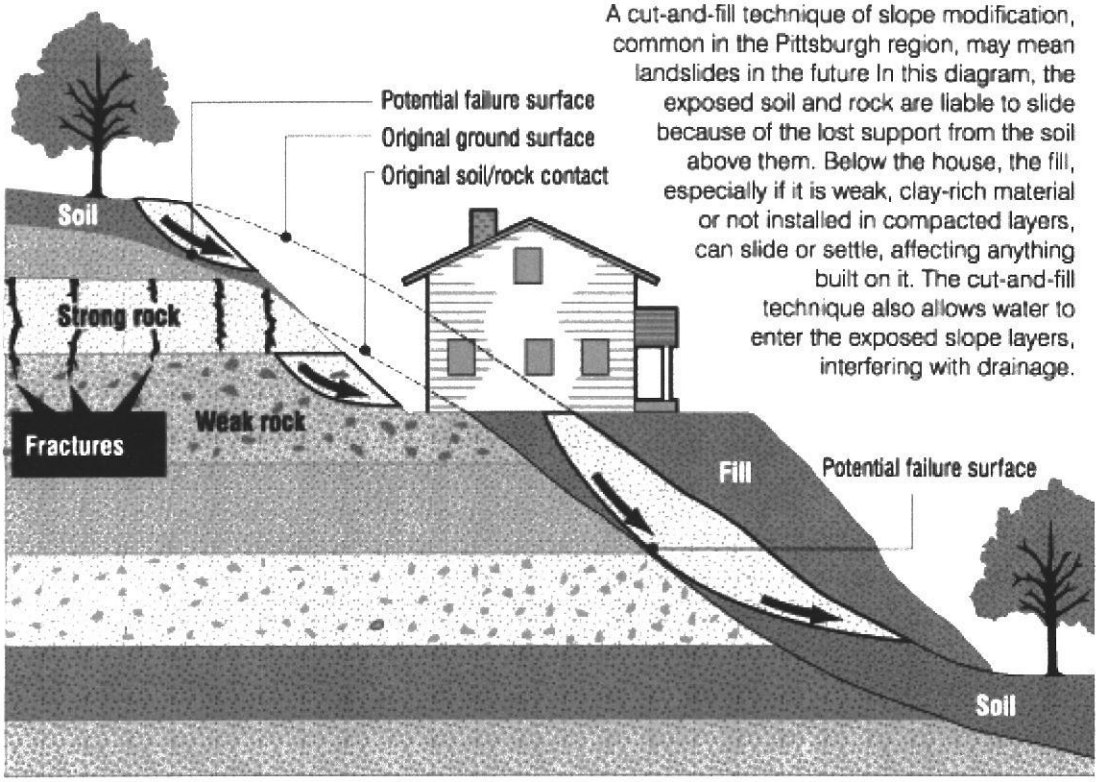
A slide waiting to happen

A cut-and-fill technique of slope modification, common in the Pittsburgh region, may mean landslides in the future In this diagram, the exposed soil and rock are liable to slide because of the lost support from the soil above them. Below the house, the fill, especially if it is weak, clay-rich material or not installed in compacted layers, can slide or settle, affecting anything built on it. The cut-and-fill technique also allows water to enter the exposed slope layers, interfering with drainage.



Types of landslides

Slump
Slump is a rotational sliding of rock or unconsolidated material that moves as a unit along a curved slip surface. Artificially place materials, such as fill and mine waste, typically fail by slumping. Slump often happens in thick, uniform soil, but can also occur in bedrock.

Earth flow
Earth flow is a rapid, mass movement of soil over a defined base surface. The soil is composed mostly of sand and smaller particles. Earth flow often occurs when the soil above an impermeable bedrock or clay layer becomes saturated with water. The pressure of the additional water forces the sand grains apart.

Debris flow
Debris flow is similar to earth flow, but involves soil with a mix of grain sizes — from mud and sand to cobbles and boulders. It moves as a fluid, and depending on the amount of water involved and the steepness of the slope can be very slow or very rapid.

Rock slide
Rock slide is a movement of newly detached segments of bedrock sliding on joint or fault surfaces or any other surface of separation. As with earth flow, one of the main triggering agents is increased water content — as from a heavy rainstorm — which can reduce friction along potential slide surfaces.

Riskiest regions

The shaded areas indicate regions of highest and next-highest landslide risk in Pennsylvania.

- Highest risk
- High to moderate

Source: Landslides in Pennsylvania, Pennsylvania Geological Survey.

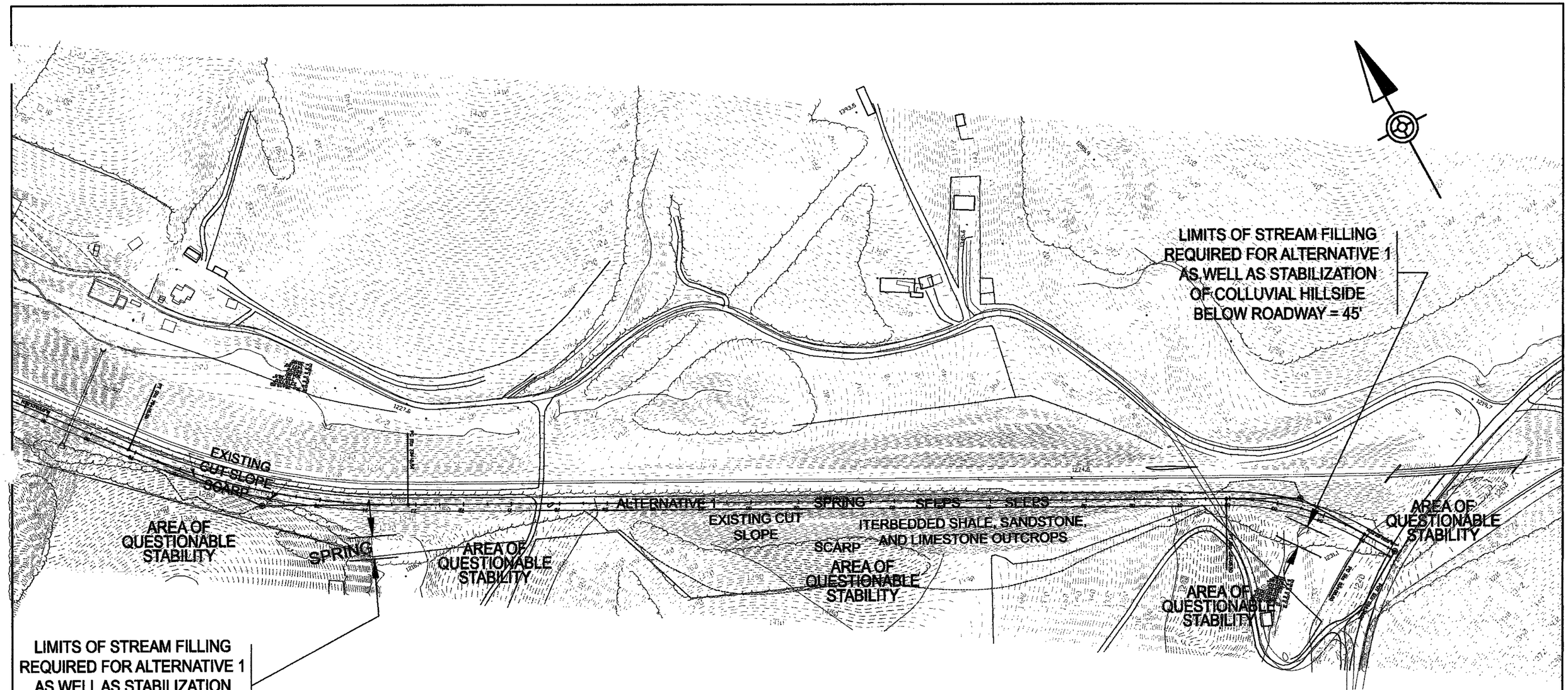
James Hilston/ Post-Gazette

TABLE 1 - RELOCATED S.R. 4009 EARTHWORK QUANTITIES AND GEOTECHNICAL IMPACTS ON STREAMS

ALTERNATIVE	CUT (c.y.)	ADJUSTED CUT [2] (c.y.)	FILL (c.y.)	BUTTRESS FILL [3] (c.y.)			LENGTH OF IMPACTED STREAMS [4]				NUMBER OF STREAMS IMPACTED	WASTE (c.y.)
				ALONG RAILROAD	MARTIN ROAD AREA	ANDERSON PROPERTY	ALONG RAILROAD (ft.)	ALONG MARTIN ROAD (ft.)	ON ANDERSON PROPERTY (ft.)	TOTAL (ft.)		
1 [1]	303,100	333,400	181,800	15,000	30,000	0	162	0	0	162	4	106,600 [5]
3	440,300	484,300	449,800	0	40,000	80,000	0	129	1,375	1,504	2	(85,500) [6]
4	498,600	548,500	382,900	0	30,000	80,000	0	0	1,375	1,375	1	55,600 [7]
5	1,607,100	1,767,800	17,300	0	30,000	0	0	0	0	0	0	1,720,500 [8]
8	2,176,000	2,393,600	87,000	0	30,000	30,000	0	0	400	400	1	2,246,600 [8]
9	1,113,000	1,224,300	14,000	0	30,000	0	0	0	0	0	0	1,180,300 [8,9]

[1] Includes earthwork to construct new roadway from Fletcher Run Road to Martin Road.
[2] Includes 10% swell factor.
[3] Buttress fill required to stabilize colluvial hillside below roadway.
[4] Includes stream filling required for embankment construction across valley as well as stabilization of colluvial hillside below roadway.
[5] A waste quantity of this magnitude would require placement in another watershed, more than likely requiring placement across a stream valley to achieve stability.
[6] This quantity is the amount of borrow required, not waste.
[7] This quantity could be wasted in the existing watershed atop the buttress embankment required for stability.
[8] A waste quantity of this great magnitude would require placement in numerous other watersheds, undoubtedly requiring placement across stream valleys to achieve stability.
[9] This alternative would be counterproductive to the very purpose of the project generating its need, i.e., the establishment of the Bailey Coal Refuse Disposal Facility. Significant quantities of coal refuse disposal would be lost.

NOTE: Alternative 7 (T-390 - Crouse Road - Improvement) and any uphill relocation of Crouse Road are not geotechnically and practically feasible. In excess of 85 percent of the roadway length lies within colluvial landforms. Not only would significant quantities of excess excavation be generated by landsliding during construction, the horizontal limits of such construction and its negative impacts both left and right of the roadway would essentially require the taking of significant right-of-way from multiple landowners, resulting in the probable razing of most, if not all, of the homes and out structures along the road.



RELOCATED S.R. 4009
ALTERNATIVE 1
ALONG RAILROAD

MARCH, 2004

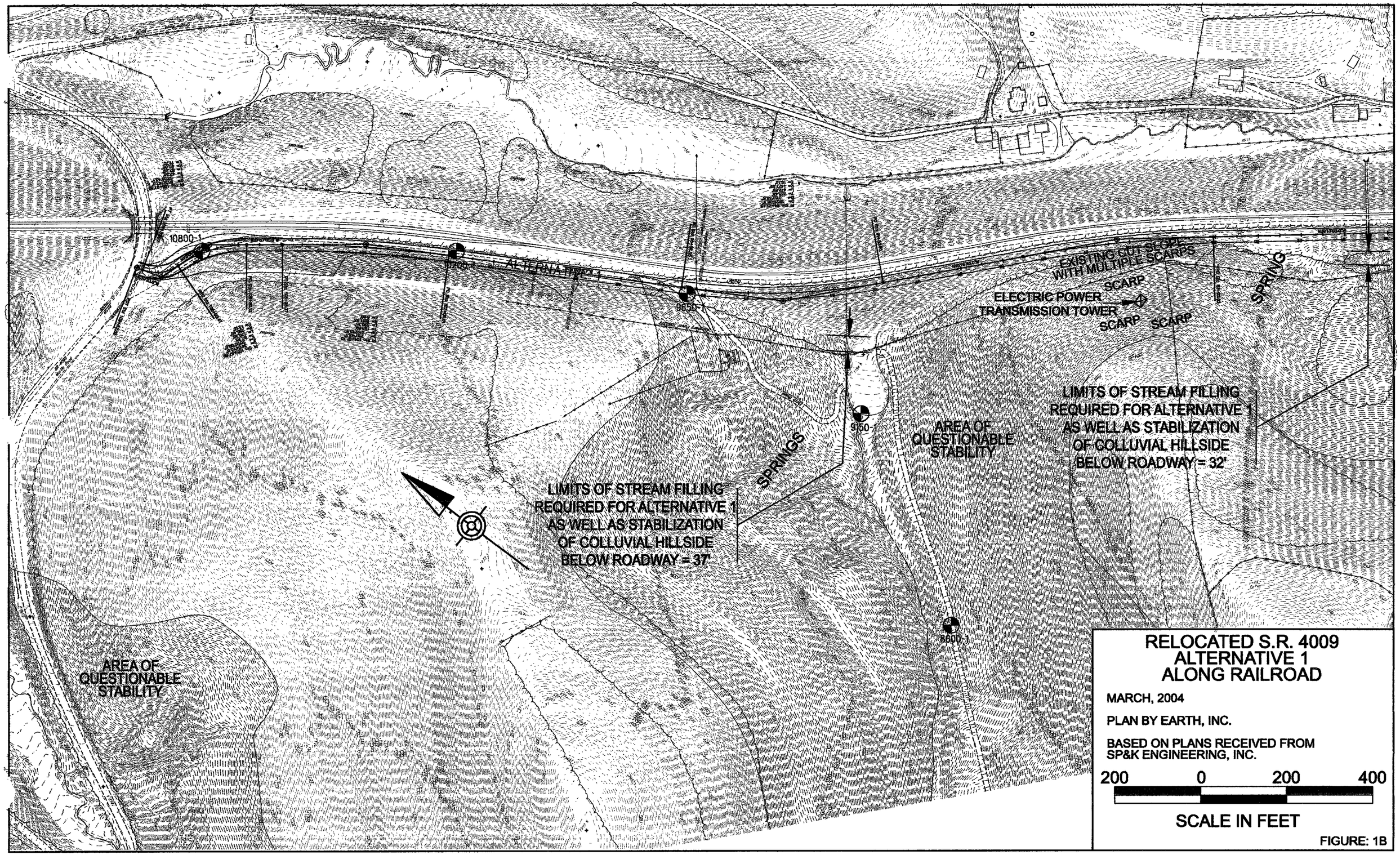
PLAN BY EARTH, INC.

BASED ON PLANS RECEIVED FROM
SP&K ENGINEERING, INC.

200 0 200 400

SCALE IN FEET

FIGURE: 1A



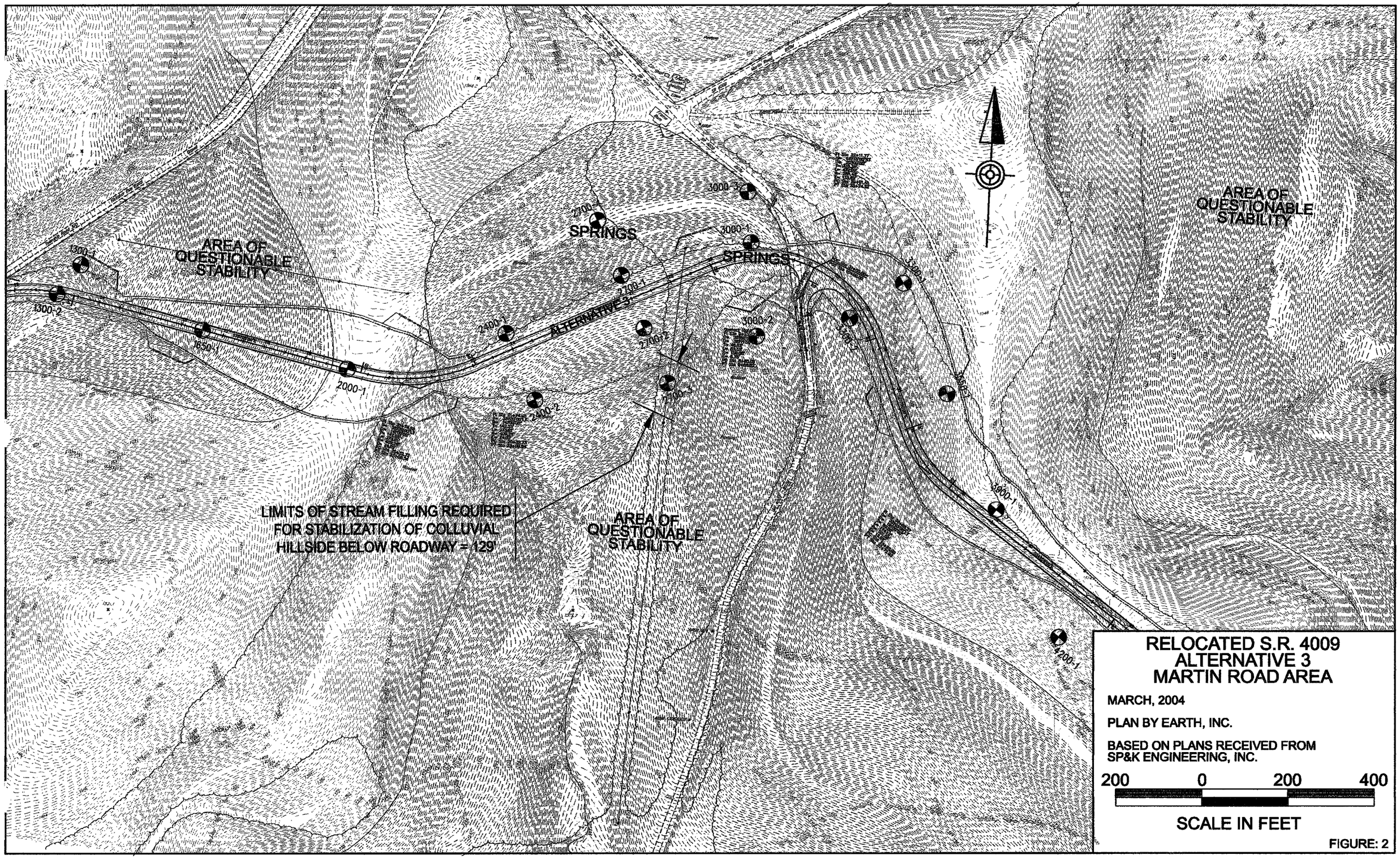
RELOCATED S.R. 4009
ALTERNATIVE 1
ALONG RAILROAD

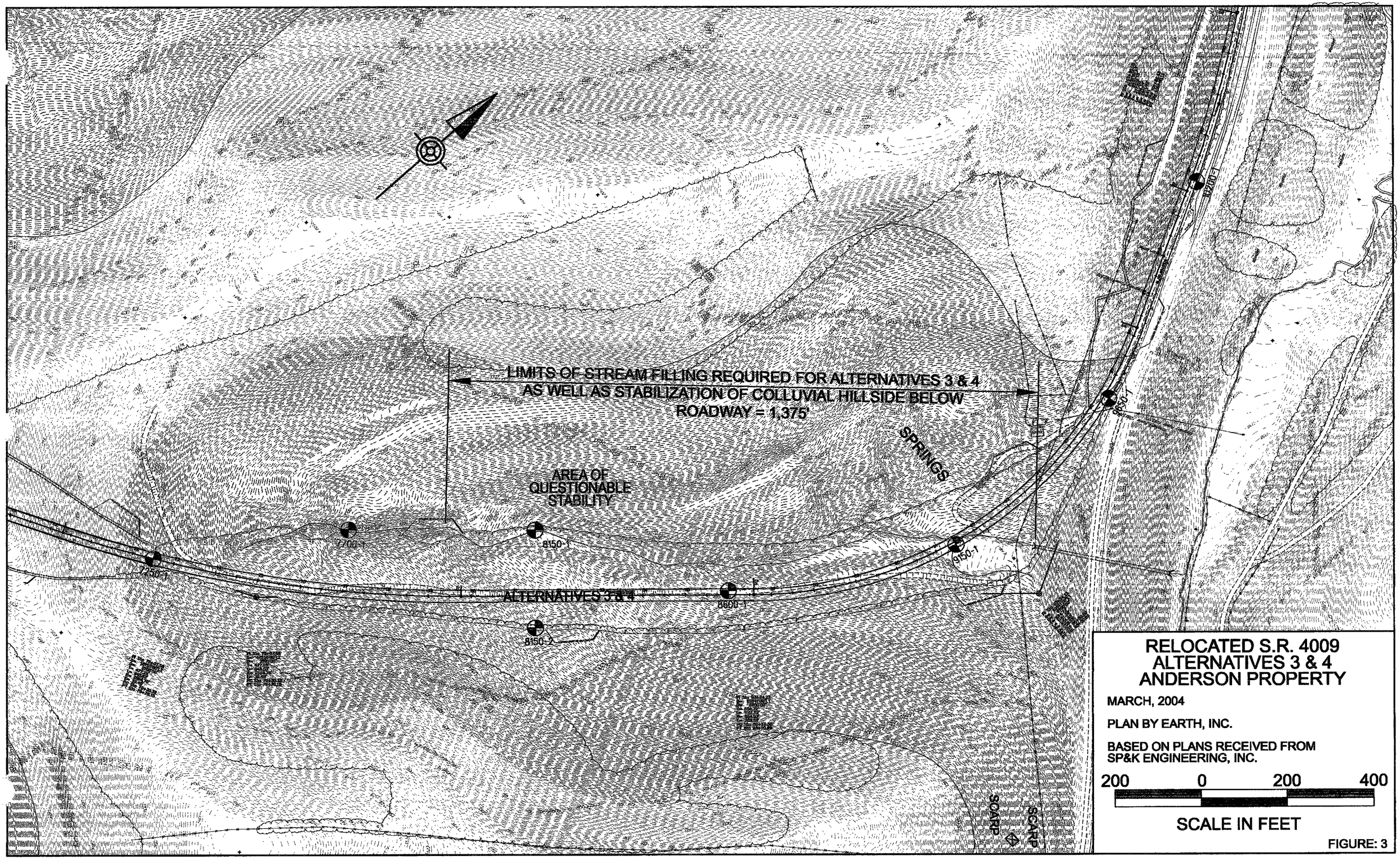
MARCH, 2004

PLAN BY EARTH, INC.

BASED ON PLANS RECEIVED FROM
SP&K ENGINEERING, INC.

FIGURE: 1B


AREA OF QUESTIONABLE STABILITY
1300-1
1300-2
1650-1
2000-1
2400-1
2400-2
2700-1
2700-2
2700-3
2700
SPRINGS
3000-1
3000-2
3000-3
3000
SPRINGS
3300-1
3300-2
3500-1
3800-1
4200-1
ALTERNATIVE 3
LIMITS OF STREAM FILLING REQUIRED FOR STABILIZATION OF COLLUVIAL HILLSIDE BELOW ROADWAY = 129'
AREA OF QUESTIONABLE STABILITY
AREA OF QUESTIONABLE STABILITY
RELOCATED S.R. 4009
ALTERNATIVE 3
MARTIN ROAD AREA
MARCH, 2004
PLAN BY EARTH, INC.
BASED ON PLANS RECEIVED FROM SP&K ENGINEERING, INC.
200 0 200 400
SCALE IN FEET
FIGURE: 2


LIMITS OF STREAM FILLING REQUIRED FOR ALTERNATIVES 3 & 4
AS WELL AS STABILIZATION OF COLLUVIAL HILLSIDE BELOW
ROADWAY = 1,375'
AREA OF
QUESTIONABLE
STABILITY
SPRINGS
7250-1
7700-1
8150-1
8150-2
8600-1
9150-1
9550-1
9700-1
ALTERNATIVES 3 & 4
SCARP
SCARP
RELOCATED S.R. 4009
ALTERNATIVES 3 & 4
ANDERSON PROPERTY
MARCH, 2004
PLAN BY EARTH, INC.
BASED ON PLANS RECEIVED FROM
SP&K ENGINEERING, INC.
200 0 200 400
SCALE IN FEET
FIGURE: 3

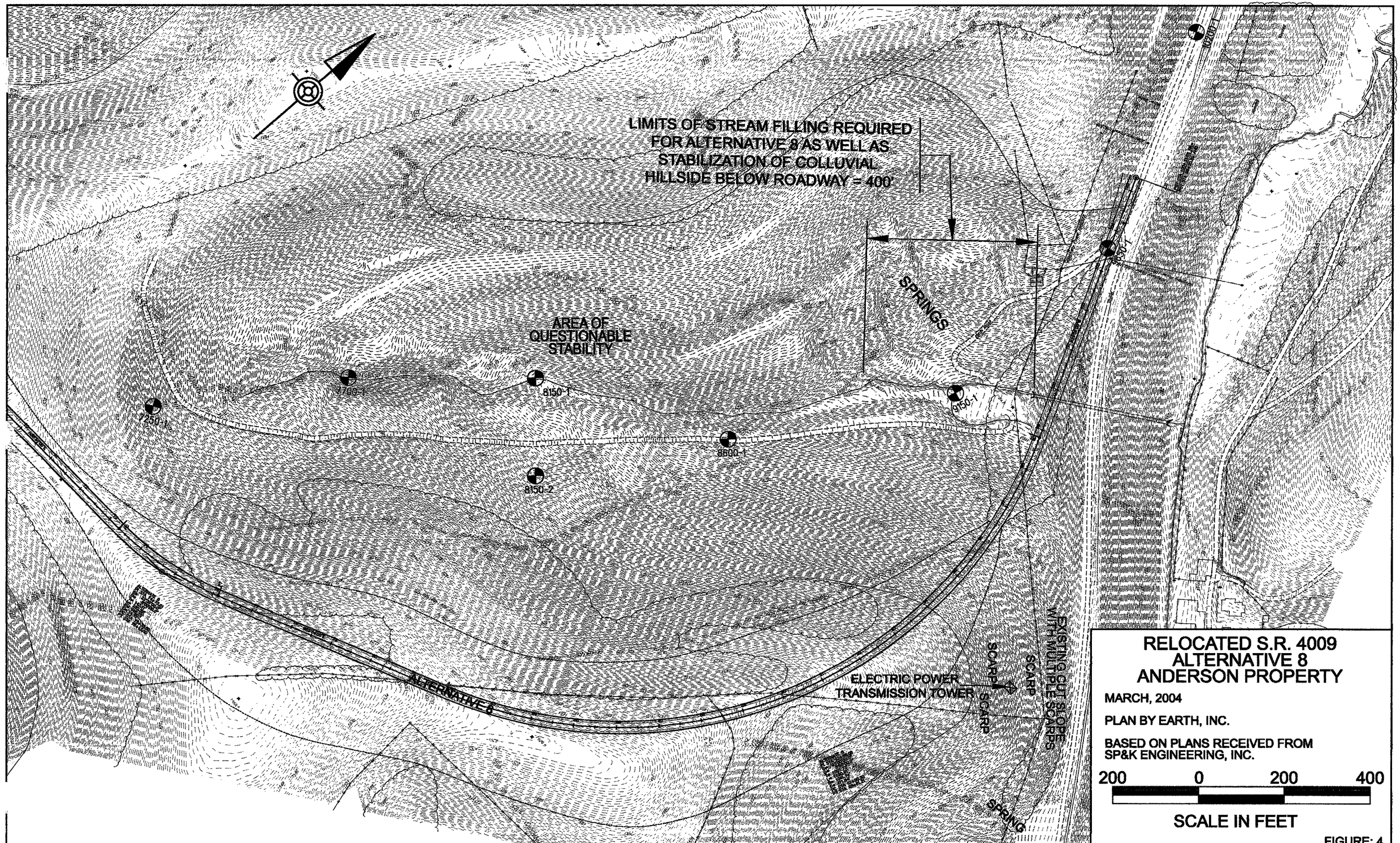

LIMITS OF STREAM FILLING REQUIRED
FOR ALTERNATIVE 8 AS WELL AS
STABILIZATION OF COLLUVIAL
HILLSIDE BELOW ROADWAY = 400'
SPRINGS
AREA OF
QUESTIONABLE
STABILITY
7790-1
8150-1
9150-1
7250-1
8600-1
8150-2
ALTERNATIVE 8
ELECTRIC POWER
TRANSMISSION TOWER
SCARP
SCARP
SCARP
EXISTING CUT SLOPE
WITH MULTIPLE SCARPS
SPRING
RELOCATED S.R. 4009
ALTERNATIVE 8
ANDERSON PROPERTY
MARCH, 2004
PLAN BY EARTH, INC.
BASED ON PLANS RECEIVED FROM
SP&K ENGINEERING, INC.
200 0 200 400
SCALE IN FEET

FIGURE: 4

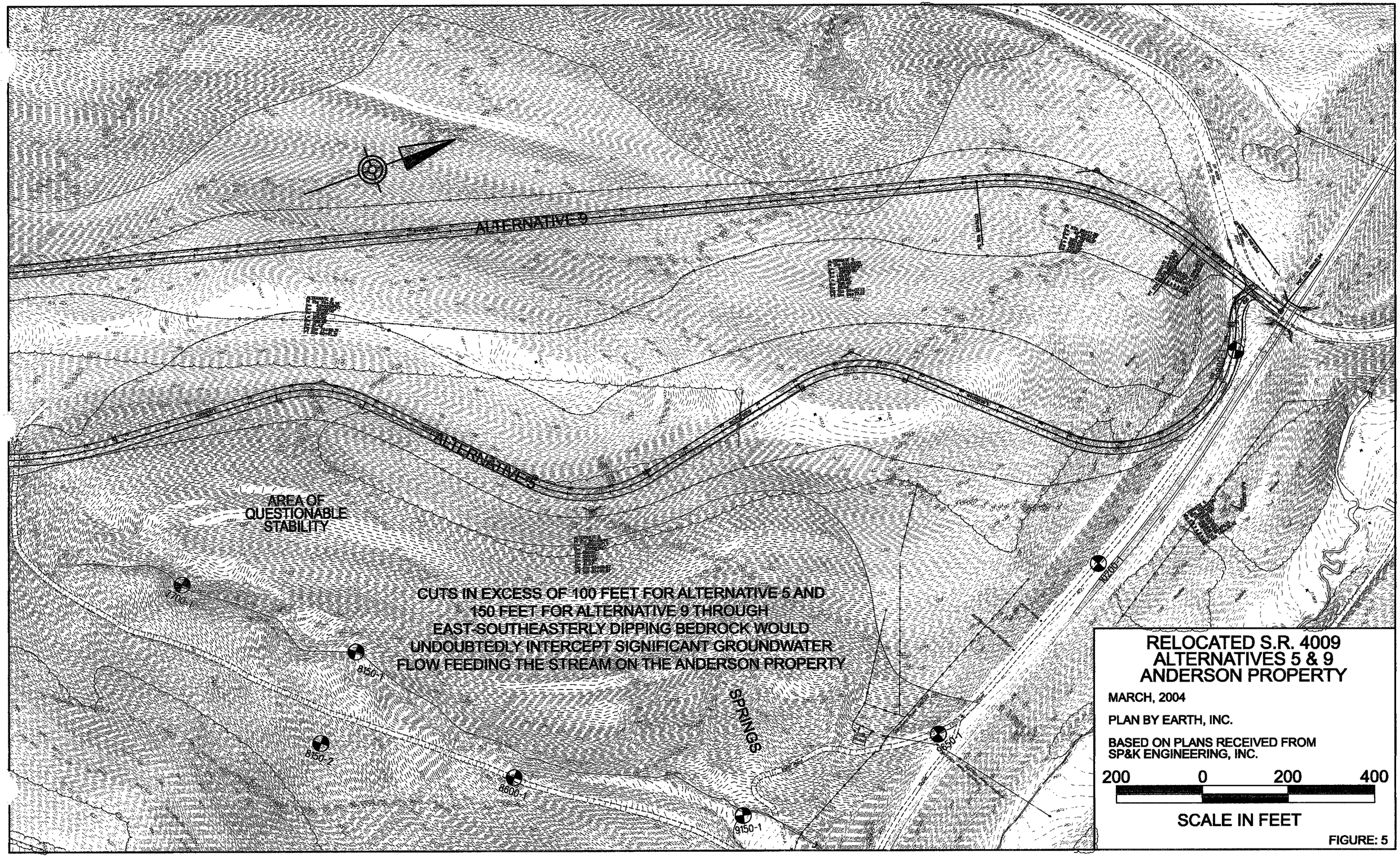
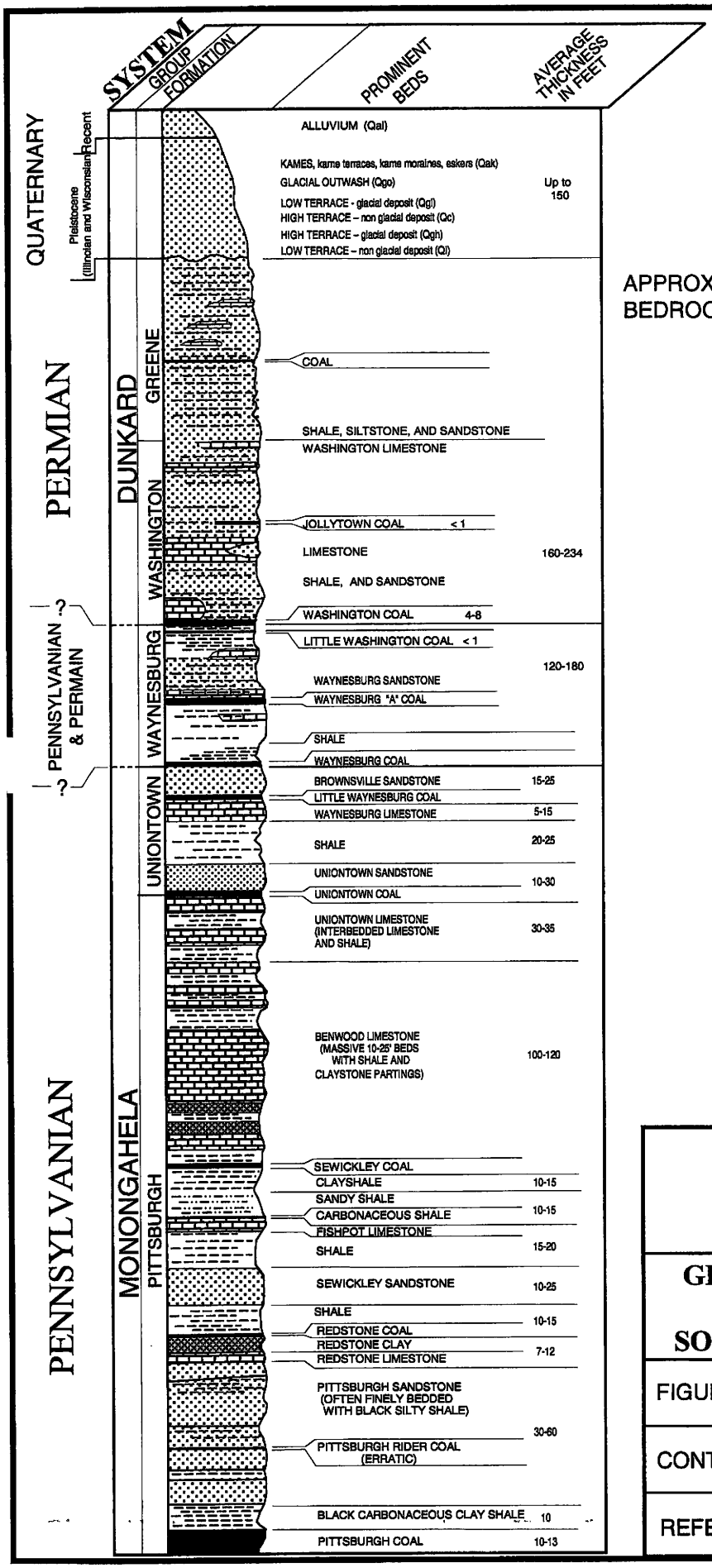

ALTERNATIVE 9
ALTERNATIVE 5
AREA OF QUESTIONABLE STABILITY
CUTS IN EXCESS OF 100 FEET FOR ALTERNATIVE 5 AND 150 FEET FOR ALTERNATIVE 9 THROUGH EAST-SOUTHEASTERLY DIPPING BEDROCK WOULD UNDOUBTEDLY INTERCEPT SIGNIFICANT GROUNDWATER FLOW FEEDING THE STREAM ON THE ANDERSON PROPERTY
SPRINGS
7700-1
8150-1
8150-2
8600-1
9150-1
8650-1
9700-1
RELOCATED S.R. 4009
ALTERNATIVES 5 & 9
ANDERSON PROPERTY
MARCH, 2004
PLAN BY EARTH, INC.
BASED ON PLANS RECEIVED FROM SP&K ENGINEERING, INC.
200 0 200 400
SCALE IN FEET

FIGURE: 5



APPROXIMATE UPPER LIMIT OF BEDROCK BENEATH THE PROJECT SITE

RELOCATION OF S.R. 4009 ASSOCIATED WITH THE BAILEY COAL REFUSE DISPOSAL FACILITY BY THE CONSOL PENNSYLVANIA COAL COMPANY
RICHHILL AND GRAY TOWNSHIPS
GREENE COUNTY, PENNSYLVANIA

GENERALIZED STRATIGRAPHIC COLUMN FOR SOUTHWESTERN PENNSYLVANIA

FIGURE: 6

CONTRACT NO: 0221

EARTH, INC.
PITTSBURGH, PA

REFERENCE: GUIDEBOOK-45th ANNUAL FIELD CONFERENCE OF PENNSYLVANIA GEOLOGISTS

FORM NO: D-481
(6/95)

ENGINEERS FIELD BORING LOG

BORING NO.	1300-1
SHEET	1 OF 2
DATE: START	10/22/03
O.G. END	10/22/03
ELEV.	1318.4

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** **SEGMENT:** **OFFSET:**
STATION: 13+37 **OFFSET FROM CENTERLINE:** 74' Lt.
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Mark Dziak/Test Boring Services, Inc.
EQUIPMENT USED: CME-55 (track mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 25.2 **WATER:** **DEPTH:** 13.5 **TIME:** 2:30 p.m. **DATE:** 10/22/03
CHECKED BY: PWH **DATE:** 10/27/03 **DEPTH:** 14.2 **TIME:** 3:00 p.m. **DATE:** 10/23/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0 – 1.5	S-1	4 6 9	1.5		0.5	ol / a-8; ml / a-4	D	0.0-0.6 ORGANIC SOIL, brown, damp (topsoil) 1317.8	
1.5 – 3.0	S-2	3 5 6	1.5		0.5	cl / a-6	D	0.6-1.5 Clayey SILT with gravel (sandstone fragments), brown, damp, stiff, homogeneous (fill) 1316.9	
3.0 – 4.5	S-3	7 4 7	1.5		1.0	cl / a-6	D	1.5-3.0 Silty CLAY with gravel (sandstone fragments), brown, damp, stiff, homogeneous (fill) 1315.4	
4.5 – 6.0	S-4	5 7 8	1.5		1.0		D	3.0-7.5 Silty CLAY with gravel (sandstone fragments), brown, damp, stiff to very stiff, homogeneous (colluvial soil)	
6.0 – 7.5	S-5	5 4 5	1.5		1.0		D	1310.9	
7.5 – 9.0	S-6	6 5 4	1.5		1.0	cl / a-6	D	7.5-9.0 Sandy silty CLAY with gravel (sandstone fragments), gray and brown, damp, stiff, homogeneous (colluvial soil) 1309.4	
9.0 – 10.5	S-7	4 4 7	1.5		0.5	cl / a-6	D	9.0-12.0 Silty CLAY, brown, damp, stiff to very stiff, homogeneous (colluvial soil)	
10.5 – 12.0	S-8	7 7 9	1.5		0.5		D	1306.4	
12.0 – 13.5	S-9	2 3 4	1.5		0.5		D	12.0-19.5 Sandy silty CLAY with gravel (sandstone fragments), gray to brown, damp, medium to hard, homogeneous (colluvial soil)	
13.5 – 15.0	S-10	8 14 17	1.5		1.0		D		Water level on 10/22/03 @ 13.5; Water level on 10/23/03 @ 14.2
15.0 – 16.5	S-11	5 9 11	1.5		1.0	cl / a-6	D		
16.5 – 17.5	S-12	11 12	1.5		1.5		D		

FORM NO: D-481
(6/95)

ENGINEERS FIELD BORING LOG

BORING NO. 1300-1
SHEET 2 **OF** 2

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
18.0		15							
	S-13	7 9 10	1.5		1.0		D	1298.9	
19.5									
20	S-14	8 9 13	1.5		1.0	ml / a-4	D	19.5-21.0 Sandy clayey SILT with gravel (sandstone fragments), brown, damp, very stiff, homogeneous (colluvial soil) 1297.4	
21.0									
	S-15	6 10 12	1.5		1.0	cl / a-6	D	21.0-22.5 Silty CLAY with gravel (shale fragments), gray, damp, very stiff, homogeneous (colluvial soil) 1295.9	
22.5									
	S-16	9 11 17	1.5			gm / a-4	D	22.5-24.0 Silty GRAVEL (shale fragments), gray, damp, medium dense, homogeneous (residual soil) 1294.4	
24.0									
	S-17	42 30 50/0.2	1.2			gm / a-1-b	D	24.0-25.2 Silty GRAVEL (sandstone fragments) with sand, brown, dry, very dense, homogeneous (weathered bedrock) 1293.2	
25 25.2									
	R-1	core	1.7	85 / 65		T.O.R.		25.2-30.3 CLAYSTONE, gray, very soft to soft, slightly weathered, indistinct bedding, RQD=53% Limestone seam @ 26.8-27.2	
27.2									
27.5	R-2	core	2.8	93 / 47					
30 30.2								1288.1	
	R-3	core	5.0	100 / 78				30.3-35.2 Shaly sandy SILTSTONE, gray, medium, slightly weathered, indistinct bedding, RQD=80%	
32.5									
35 35.2								Clay seam @ 35.0-35.1 1283.2	
								35.2 Bottom of Hole	
37.5									

FORM NO: D-481
(6/95)

ENGINEERS FIELD BORING LOG

BORING NO.	1300-2
SHEET	1 OF 3
DATE: START	10/20/03
O.G. END	10/21/03
ELEV.	1331.9

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** **SEGMENT:** **OFFSET:**
STATION: 13+00 **OFFSET FROM CENTERLINE:** 5' Rt.
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Mark Dziak/Test Boring Services, Inc.
EQUIPMENT USED: CME-55 (track mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 33.8 **WATER:** **DEPTH:** 4.4 **TIME:** 1:00 p.m. **DATE:** 10/21/03
CHECKED BY: PWH **DATE:** 10/22/03 **DEPTH:** 8.3 **TIME:** 2:00 p.m. **DATE:** 10/22/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0								0.0-0.8 ORGANIC SOIL, brown, damp (topsoil) 1331.1	
1.5	S-1	2 2 3	1.0			ol / a-8	D		
2.5 / 3.0	S-2	4 6 5	0.0			ml / a-4		0.8-3.0 Clayey SILT, brown, damp, medium to stiff, homogeneous (colluvial soil) 1328.9	
4.5	S-3	9 8 9	1.5		1.0		D	3.0-9.0 Silty CLAY, orange brown and gray, damp, very stiff, homogeneous (colluvial soil)	
5 / 6.0	S-4	6 9 12	1.5		1.0	cl / a-6	D		Water level on 10/21/03 @ 4.4
7.5	S-5	5 8 12	1.5		1.0		D		
9.0	S-6	7 10 13	1.5		1.0		D	1322.9	Water level on 10/22/03 @ 8.3
10 / 10.5	S-7	3 6 7	1.5		1.0		D	9.0-18.0 Silty CLAY with gravel (shale fragments), orange brown and brown, damp, stiff to very stiff, homogeneous (colluvial soil)	
12.0	S-8	7 9 12	1.5		1.0		D		
12.5 / 13.5	S-9	5 9 11	1.5		1.0	cl / a-6	D		
15.0	S-10	5 9 10	1.2		1.0		D		
15 / 16.5	S-11	8 8 9	1.5		1.0		D		
17.5	S-12	7 7	0.0						

FORM NO: D-481
(6/95)

ENGINEERS FIELD BORING LOG

BORING NO. 1300-2
SHEET 2 **OF** 3

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
18.0		9						1313.9	
19.5	S-13	6 6 6	1.0		1.0	cl / a-6	D	18.0-21.0 Silty CLAY, gray, damp, stiff to very stiff, homogeneous (colluvial soil)	
20 21.0	S-14	5 7 9	1.5		1.0		D	1310.9	
22.5	S-15	8 12 10	1.5		1.0	cl / a-6	D	21.0-27.5 Silty CLAY with gravel (sandstone fragments), brown, damp, very stiff, homogeneous (colluvial soil)	
24.0	S-16	6 7 10	1.5		1.0		D		
25 25.5	S-17	12 11 13	1.5		1.0		D		
27.0	S-18	8 12 15	1.5		1.5		D		
27.5 28.5	S-19	10 14 14	1.5		1.0		D	1304.4	
30.0	S-20	6 8 10	1.5		1.0	cl / a-6	D	27.5-32.0 Sandy silty CLAY with gravel (sandstone fragments), gray, damp, very stiff, homogeneous (colluvial soil)	
31.5	S-21	6 9 12	1.5		1.0		D		
32.5 32.9	S-22	14 45 50/0.4	1.4				D	1299.9	
33.0		auger				gm / a-4		32.0-33.8 Silty GRAVEL (shale fragments), gray, dry, very dense, homogeneous (weathered bedrock)	
33.8	S-23	27 50/0.3	0.8				D	1298.1	
35 36.3	R-1	core	2.4	96 / 64		T.O.R.		33.8-37.8 Silty CLAYSTONE, gray, very soft to soft, slightly weathered, thinly bedded (RD=0°), RQD=40%	
37.5									

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(6/95)

ENGINEERS FIELD BORING LOG

BORING NO. 1300-2
SHEET 3 **OF** 3

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
								1294.1	
	R-2	core	5.0	100 / 40				37.8-39.8 Shaly fine grained SANDSTONE, gray, medium, fresh, thinly bedded (RD=0°), RQD=50% 1292.1	
40								39.8-41.0 CLAYSHALE, gray, very soft to soft, slightly weathered, very thinly bedded (RD=0°), RQD=83% 1290.9	
41.3	R-3	core	0.8	32 / 0				41.0-43.8 Shaly SILTSTONE, gray, medium, slightly weathered, intensely laminated (RD=0°), RQD=0% Clay seam @ 41.6-43.0 1288.1	
42.5									
43.8								43.8 Bottom of Hole	
45									
47.5									
50									
52.5									
55									
57.5									

FORM NO: D-481
(6/95)

ENGINEERS FIELD BORING LOG

BORING NO.	1650-1
SHEET	1 OF 3
DATE: START	10/21/03
O.G. END	10/22/03
ELEV.	1388.3

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** **SEGMENT:** **OFFSET:**
STATION: 16+50 **OFFSET FROM CENTERLINE:** Centerline
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Mark Dzlak/Test Boring Services, Inc.
EQUIPMENT USED: CME-55 (track mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 14.4 **WATER:** **DEPTH:** 30.3 **TIME:** 9:30 a.m. **DATE:** 10/22/03
CHECKED BY: PWH **DATE:** 10/27/03 **DEPTH:** 36.3 **TIME:** 1:00 p.m. **DATE:** 10/31/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0									
1.5	S-1	3 2 3	1.1			ol / a-8	D	0.0-0.7 ORGANIC SOIL, brown, damp (topsoil) 1387.6	
3.0	S-2	4 5 8	1.5		0.5	ml / a-4	D	0.7-3.0 Clayey SILT, brown, damp, medium to stiff, homogeneous (alluvial soil) 1385.3	
4.5	S-3	7 6 11	1.5		0.5	cl / a-6	D	3.0-5.0 Silty CLAY, brown, damp, very stiff, homogeneous (alluvial soil) 1383.3	
6.0	S-4	4 11 16	1.5		1.0	ml / a-4	D	5.0-6.0 Sandy clayey SILT with gravel (sandstone fragments), brown, damp, very stiff, homogeneous (alluvial soil) 1382.3	
7.5	S-5	12 14 15	1.5		1.5	cl / a-6	D	6.0-9.0 Silty CLAY with gravel (shale and sandstone fragments), brown, damp, very stiff, homogeneous (colluvial soil) 1379.3	
9.0	S-6	16 10 13	1.5		1.5		D		
10.5	S-7	10 17 20	1.5		1.0	ml / a-4	D	9.0-10.5 Sandy clayey SILT with gravel (sandstone fragments), brown, damp, hard, homogeneous (residual soil) 1377.8	
12.0	S-8	33 23 22	1.5			gm / a-1-b	D	10.5-14.4 Silty GRAVEL (sandstone fragments), brown, damp, dense to very dense, homogeneous (weathered bedrock)	
13.5	S-9	16 17 18	1.4				D		
14.4	S-10	34 50/0.4	0.9				D	1373.9	
16.4	R-1	core	2.0	100 / 75		T.O.R.		14.4-20.8 Medium to coarse grained SANDSTONE, brown and gray, medium, fresh, indistinct bedding, RQD=48%	
17.5									

FORM NO: D-481
(6/95)

ENGINEERS FIELD BORING LOG

BORING NO. 1650-1
SHEET 2 **OF** 3

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
20	R-2	core	3.9	78 / 32				Calcareous seam @ 20.4-20.8	
21.4								1367.5	
22.5	R-3	core	3.6	72 / 40				20.8-23.5 CLAYSHALE, gray and brown, very soft to soft, slightly weathered, very thinly bedded (RD=0°), RQD=0%	
								1364.8	
25								23.5-26.6 Fine grained SANDSTONE, gray, medium to hard, fresh, indistinct bedding, RQD=65%	
26.4								1361.7	
27.5	R-4	core	3.5	70 / 0				26.6-31.2 Shaly SANDSTONE, brown with gray, soft to medium, slightly weathered, thinly bedded (RD= 0°), RQD=0%	
30									Water level on 10/22/03 @ 30.3
31.4								1357.1	
32.5	R-5	core	5.0	100 / 66				31.2-34.7 Shaly CLAYSTONE, gray and brown, very soft to soft, slightly weathered, thinly bedded (RD= 0°), RQD=60% Limestone seam @ 32.5-32.7	
								1353.6	
35								34.7-38.0 Fine to medium grained SANDSTONE, gray, medium, slightly weathered, indistinct bedding, RQD=82%	
36.4									Water level on 10/31/03 @ 36.3
37.5	R-6	core	1.6	100 / —					

FORM NO: D-481
(6/95)

ENGINEERS FIELD BORING LOG

BORING NO. 1650-1
SHEET 3 OF 3

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
38.0				94				1350.3	
								38.0 Bottom of Hole	
40									
42.5									
45									
47.5									
50									
52.5									
55									
57.5									

FORM NO: D-481
(6/95)

ENGINEERS FIELD BORING LOG

BORING NO.	2000-1
SHEET	1 OF 4
DATE: START	10/16/03
O.G. END	10/20/03
ELEV.	1448.7

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** _____ **SEGMENT:** _____ **OFFSET:** _____
STATION: 20+00 **OFFSET FROM CENTERLINE:** Centerline
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Wayne Ewing/Test Boring Services,
EQUIPMENT USED: CME-45 (track mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 2.8 **WATER:** **DEPTH:** 44.0 **TIME:** 1:00 p.m. **DATE:** 10/20/03
CHECKED BY: PWH **DATE:** 10/28/03 **DEPTH:** 48.8 **TIME:** 5:00 p.m. **DATE:** 10/21/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0	S-1	1 2 2	1.0			ol / a-8	D	0.0-0.6 ORGANIC SOIL, brown, damp (topsoil) 1448.1	
1.5	S-2	27 43 50/0.3	1.3			ml / a-4	D	0.6-2.8 Clayey SILT with gravel (sandstone fragments), brown, damp, medium to hard, homogeneous (weathered bedrock) 1445.9	
2.5 2.8	R-1	core	1.4	70 / 0		T.O.R.		2.8-8.8 Shaly medium grained SANDSTONE, brown, medium, slightly weathered, indistinct bedding, RQD=0%	
4.8 5	R-2	core	2.9	97 / 0					
7.5 7.8	R-3	core	5.0	100 / 0				1439.9 8.8-13.5 CLAYSHALE, brown, very soft to soft, slightly weathered, very thinly bedded (RD=0°), RQD= 0%	
10 12.5 12.8	R-4	core	5.0	100 / 0				1435.2 13.5-18.1 SHALE, gray, soft, slightly weathered, intensely laminated (RD=0°), RQD=0%	
15 17.5									

FORM NO: D-481
(6/95)

ENGINEERS FIELD BORING LOG

BORING NO. 2000-1
SHEET 2 OF 4

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
17.8								1430.6	
								18.1-18.9 Carbonaceous SHALE, black, soft, slightly weathered, thinly bedded (RD=0°), RQD=0% Thin coal seam 1/8" thick @ 18.4 1429.8	T.O.R.? Ask Dave what he meant.
20	R-5	core	5.0	100 / 66				18.9-19.7 LIMESTONE, black, hard, fresh, indistinct bedding, RQD=100% 1429.0	
								19.7-21.4 Calcareous CLAYSTONE, gray, very soft to soft, slightly weathered, indistinct bedding, RQD=82% 1427.3	
22.5 22.8								21.4-23.2 Shaly fine grained SANDSTONE, gray, medium, slightly weathered, indistinct bedding, RQD=61% 1425.5	
25	R-6	core	5.0	100 / 38				23.2-24.9 Sandy SHALE, gray, soft, slightly weathered, very thinly bedded, RQD=0% 1423.8	
								24.9-25.9 CLAYSHALE, gray, very soft, slightly weathered, thinly bedded (RD=0°), RQD=40% 1422.8	
27.5 27.8								25.9-28.1 Shaly fine grained SANDSTONE, gray, medium, fresh, very thinly bedded (RD=0°), RQD=68% 1420.6	
30	R-7	core	5.0	100 / 30				28.1-30.6 CLAYSHALE, gray, very soft, slightly weathered, thinly bedded (RD=0°), RQD=0% 1418.1	
								30.6-32.1 LIMESTONE, gray, hard, fresh, indistinct bedding, RQD=100% 1416.6	
32.5 32.8								32.1-33.1 Interbedded SHALE and CLAYSTONE, gray, soft, fresh, thinly bedded (RD=0°), RQD=0% 1415.6	
35	R-8	core	5.0	100 / 92				33.1-34.5 Shaly fine grained SANDSTONE, gray, soft to medium, fresh, thinly bedded (RD=0°), RQD= 93% Clay seam @ 33.5 1414.2	
								34.5-37.8 Medium grained SANDSTONE, gray, medium, fresh, indistinct bedding, RQD=100%	
37.5									

FORM NO: D-481
(6/95)

ENGINEERS FIELD BORING LOG

BORING NO. 2000-1
SHEET 3 **OF** 4

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
37.8								1410.9	
	R-9	core	1.8	90 / 20				37.8-38.8 Shaly fine grained SANDSTONE, gray, medium, fresh, thinly bedded (RD=0°), RQD=40% 1409.9	
39.8								38.8-40.9 Silty SHALE, gray, soft, fresh, intensely laminated (RD=0°), RQD=0% 1407.8	
40	R-10	core	2.7	90 / 37				40.9-43.1 Sandy calcareous CLAYSTONE, gray, medium, fresh, indistinct bedding, RQD=50%	
42.5 / 42.8								Silty shale seam @ 42.8-43.1 Siltstone seam @ 42.9-48.6 1405.6	
	R-11	core	5.0	100 / 52				43.1-45.7 Fine grained SANDSTONE, gray, medium, fresh, indistinct bedding, RQD=100% 1403.0	Water level on 10/20/03 @ 44.0
45								45.7-50.5 Silty SHALE, gray, soft to medium, fresh, intensely laminated, RQD=15%	
47.5 / 47.8									
50	R-12	core	4.9	98 / 58				1398.2	Water level on 10/21/03 @ 48.8
								50.5-53.7 Shaly SILTSTONE, gray to black, medium, fresh, intensely laminated (RD=0°), RQD=84%	
52.5 / 52.8								1395.0	
55	R-13	core	5.0	100 / 60				53.7-59.9 LIMESTONE, gray, hard, fresh, indistinct bedding, RQD=66%	
								Carbonaceous shale seam @ 56.4-57.3	
57.5									

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ENGINEERS FIELD BORING LOG

BORING NO. 2000-1
SHEET 4 **OF** 4

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
57.8								1388.8	
60	R-14	core	5.0	100 / 48				59.9-61.7 CLAYSHALE, gray, very soft to soft, fresh, thinly bedded (RD=0°), RQD=0% 1387.0	
62.5 / 62.8								61.7-70.8 Shaly SILTSTONE, gray, medium, fresh, intensely laminated (RD=0°), RQD=82%	
65	R-15	core	4.9	98 / 94				Calcareous inclusions below 66.1	
67.5 / 67.8									
70	R-16	core	5.0	100 / 58				1377.9 70.8-72.8 Calcareous CLAYSTONE, gray, very soft to soft, fresh, indistinct bedding, RQD=45% Calcareous shale seam @ 70.8-71.0	
72.5 / 72.8								1375.9 72.8 Bottom of Hole	
75									
77.5									

FORM NO: D-481
(6/95)

ENGINEERS FIELD BORING LOG

BORING NO.	2400-1
SHEET	1 OF 2
DATE: START	10/22/03
O.G. END	10/22/03
ELEV.	1394.2

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** **SEGMENT:** **OFFSET:**
STATION: 24+00 **OFFSET FROM CENTERLINE:** 40' Lt.
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Jim Rice/Test Boring Services, Inc.
EQUIPMENT USED: CME-55 (track mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 9.2 **WATER:** **DEPTH:** 10.7 **TIME:** 11:00 a.m. **DATE:** 10/22/03
CHECKED BY: PWH **DATE:** 10/27/03 **DEPTH:** 9.3 **TIME:** 1:30 p.m. **DATE:** 10/31/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0								0.0-0.5 ORGANIC SOIL, brown, damp (topsoil) 1393.7	
1.5	S-1	4 6 7	1.2		0.5	cl / a-8	D	0.5-6.0 Silty CLAY with gravel (sandstone and shale fragments), brown, damp, stiff to very stiff, homogeneous (colluvial soil)	
2.5 / 3.0	S-2	6 8 9	1.5		1.0		D		
4.5	S-3	4 8 7	1.5		1.0	cl / a-6	D		
5 / 6.0	S-4	7 7 6	1.5		1.0		D	1388.2	
7.5	S-5	5 9 9	1.5		0.5	cl / a-6	D	6.0-8.0 Silty CLAY, brown, damp, very stiff, homogeneous (residual soil) 1386.2	
8.9	S-6	15 50 50/0.4	1.4		1.5	gm / a-4	D	8.0-9.2 Silty GRAVEL (shale fragments), brown, damp, very dense, homogeneous (weathered bedrock) 1385.0	Water level on 10/31/03 @ 9.3
9.0 / 9.2	S-7	auger 50/0.2	0.2			T.O.R.	D		
10 / 11.2	R-1	core	2.0	100 / 50				9.2-11.2 LIMESTONE, gray, hard, fresh, indistinct bedding, RQD=50% 1383.0	Water level on 10/22/03 @ 10.7
12.5 / 14.2	R-2	core	2.2	73 / 0				11.2-12.1 Medium grained SANDSTONE, brown, medium, fresh, indistinct bedding, RQD=0% 1382.1 12.1-14.6 CLAYSHALE, gray, very soft to soft, slightly weathered, very thinly bedded (RD=0°), RQD= 0% 1379.6	
15 / 17.5	R-3	core	5.0	100 / 66				14.6-19.2 Shaly SILTSTONE, gray to black, medium, slightly weathered, intensely laminated (RD=0°), RQD=72% Clay seam @ 16.9-17.9	

FORM NO: D-481
(6/95)

ENGINEERS FIELD BORING LOG

BORING NO. 2400-1
SHEET 2 OF 2

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
19.2								1375.0	
								19.2 Bottom of Hole	
20									
22.5									
25									
27.5									
30									
32.5									
35									
37.5									

FORM NO: D-481
(6/95)

ENGINEERS FIELD BORING LOG

BORING NO.	2400-2
SHEET	1 OF 2
DATE: START	10/14/03
O.G. END	10/14/03
ELEV.	1362.5

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** **SEGMENT:** **OFFSET:**
STATION: 24+00 **OFFSET FROM CENTERLINE:** 130' Rt.
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Wayne Ewing/Test Boring Services,
EQUIPMENT USED: CME-45 (track mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 19.4 **WATER:** **DEPTH:** 8.2 **TIME:** 3:40 p.m. **DATE:** 10/14/03
CHECKED BY: PWH **DATE:** 10/15/03 **DEPTH:** 10.7 **TIME:** 8:30 a.m. **DATE:** 10/16/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0									
1.5	S-1	2 2 2	1.5		0.5	ol / a-8	D	0.0-0.6 ORGANIC SOIL, brown, damp (topsoil) 1361.9	
3.0	S-2	1 2 2	1.2		0.5	cl / a-6	D	0.6-3.0 Silty CLAY, brown, damp, soft, homogeneous (colluvial soil) 1359.5	
4.5	S-3	4 5 7	1.5		1.0		D	3.0-7.5 Silty CLAY with gravel (shale and sandstone fragments), brown, damp, stiff to very stiff, homogeneous (colluvial soil)	
6.0	S-4	9 13 15	1.5		1.5	cl / a-6	D		
7.5	S-5	4 8 11	1.5		1.5		D	1355.0	
9.0	S-6	12 22 17	1.5		1.5		D	7.5-10.5 Sandy clayey SILT with gravel (sandstone and shale fragments), brown, damp, hard, homogeneous (colluvial soil)	Water level on 10/14/03 @ 8.2
10.5	S-7	8 13 18	1.5		1.5	ml / a-4	D	1352.0	
12.0	S-8	13 15 18	1.5		1.5		D	10.5-15.0 Clayey SILT, brown, damp, hard to very stiff, homogeneous (colluvial soil)	Water level on 10/16/03 @ 10.7
13.5	S-9	5 7 10	1.5		1.0	ml / a-4	D		
15.0	S-10	9 12 14	1.5		1.0		D	1347.5	
16.5	S-11	4 6 8	1.5		1.0	cl / a-6	D	15.0-16.5 Silty CLAY, brown, damp, stiff, homogeneous (colluvial soil) 1346.0	
17.5	S-12	16 24	1.5		1.5	ml / —	D	16.5-18.0 Sandy clayey SILT with gravel (shale	

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ENGINEERS FIELD BORING LOG

BORING NO. 2400-2
SHEET 2 **OF** 2

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
18.0		32				a-4		fragments), brown, damp, hard, homogeneous (weathered bedrock) 1344.5	
	S-13	11 27 50/0.4	1.4		4.0	gm / a-4	D	18.0-19.4 Silty GRAVEL (shale fragments) with sand, brown, dry, very dense, homogeneous (weathered bedrock) 1343.1	
19.4						T.O.R.			
20	R-1	core	1.2	60 / 0				19.4-27.7 CLAYSHALE, brown gray, very soft to soft, moderately weathered, intensely laminated (RD= 0°), RQD=6% Sandstone seam @ 20.8-21.1	
21.4									
22.5	R-2	core	1.9	63 / 0					
24.4									
25	R-3	core	5.0	100 / 36				Limestone seam @ 25.2-25.6	
27.5								1334.8 27.7-29.4 Fine grained SANDSTONE, gray, medium, slightly weathered, indistinct bedding, RQD=76%	
29.4								1333.1	
30								29.4 Bottom of Hole	
32.5									
35									
37.5									

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ENGINEERS FIELD BORING LOG

BORING NO.	2700-1
SHEET	1 OF 2
DATE: START	10/14/03
O.G. END	10/14/03
ELEV.	1399.0

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** **SEGMENT:** **OFFSET:**
STATION: 27+00 **OFFSET FROM CENTERLINE:** 60' Lt.
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Mark Dziak/Test Boring Services, Inc.
EQUIPMENT USED: CME-55 (track mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 9.5 **WATER:** **DEPTH:** 2.5 **TIME:** 12:00 p.m. **DATE:** 10/14/03
CHECKED BY: PWH **DATE:** 10/15/03 **DEPTH:** 3.8 **TIME:** 9:15 a.m. **DATE:** 10/16/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0									
1.5	S-1	1 2 4	1.5		0.5	ol / a-8	D	0.0-0.8 ORGANIC SOIL, brown, damp (topsoil) 1398.2	
3.0	S-2	5 7 14	1.5		1.0	cl / a-6	D	0.8-4.5 Silty CLAY with gravel (sandstone and shale fragments), brown, damp, medium to very stiff, homogeneous (colluvial soil)	Water level on 10/14/03 @ 2.5
4.5	S-3	7 8 11	1.5		1.5		D	1394.5	Water level on 10/16/03 @ 3.8
6.0	S-4	11 12 17	1.5		1.5	gc / a-6	D	4.5-7.5 Clayey GRAVEL (shale fragments), brown, damp, medium dense, homogeneous (colluvial soil)	
7.5	S-5	6 5 8	1.5				D	1391.5	
9.0	S-6	11 11 10	1.5		1.5	gc / a-6	D	7.5-9.0 Clayey GRAVEL (shale fragments), brown, damp, medium dense, homogeneous (residual soil)	
9.5	S-7	50	0.5		3.5	gm / a-4	D	1390.0	
12.5	R-1	core	2.7	90 / 43		T.O.R.		9.0-9.5 Silty GRAVEL (shale fragments), brown, dry, very dense, homogeneous (weathered bedrock) 1389.5 9.5-13.5 Medium grained SANDSTONE, gray, medium, slightly weathered, indistinct bedding, RQD=32%	
17.5	R-2	core	4.5	90 / 44				1385.5 13.5-17.2 CLAYSHALE, gray, very soft to soft, slightly weathered, indistinct bedding, RQD=59% 1381.8	

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ENGINEERS FIELD BORING LOG

BORING NO. 2700-1
SHEET 2 OF 2

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
19.5	R-3	core	1.5	75 / 45				17.2-19.5 Shaly SILTSTONE, gray, medium, slightly weathered, intensely laminated (RD=0°), RQD= 39% 1379.5	
20 22.5 25 27.5 30 32.5 35 37.5								19.5 Bottom of Hole	

FORM NO: D-481
(6/95)

ENGINEERS FIELD BORING LOG

BORING NO.	2700-2
SHEET	1 OF 2
DATE: START	10/13/03
O.G. END	10/14/03
ELEV.	1371.6

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** **SEGMENT:** **OFFSET:**
STATION: 27+00 **OFFSET FROM CENTERLINE:** 75' Rt.
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Wayne Ewing/Test Boring Services,
EQUIPMENT USED: CME-45 (track mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 14.9 **WATER:** **DEPTH:** 4.1 **TIME:** 9:00 a.m. **DATE:** 10/14/03
CHECKED BY: PWH **DATE:** 10/15/03 **DEPTH:** 6.3 **TIME:** 9:15 a.m. **DATE:** 10/15/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0 – 1.5	S-1	1 3 5	1.2		0.5	ol / a-8	D	0.0-1.0 ORGANIC SOIL, brown, damp (topsoil) 1370.6	
1.5 – 3.0	S-2	4 5 12	1.5		0.5	cl / a-6	D	1.0-1.5 Silty CLAY, brown, damp, medium, homogeneous (colluvial soil) 1370.1	
3.0 – 4.5	S-3	3 3 6	1.0		0.5	gm / a-2-4	D	1.5-3.0 Silty GRAVEL (sandstone and shale fragments) with sand, brown, damp, medium dense, homogeneous (colluvial soil) 1368.6	Water level on 10/14/03 @ 4.1
4.5 – 6.0	S-4	3 4 5	1.5		0.5	cl / a-6	D	3.0-4.5 Silty CLAY with gravel (shale fragments), brown, damp, stiff, homogeneous (colluvial soil) 1367.1	
6.0 – 7.5	S-5	2 2 4	1.5		0.5	cl / a-6	D	4.5-7.5 Silty CLAY, brown, damp, stiff to medium, homogeneous (colluvial soil) 1364.1	Water level on 10/15/03 @ 6.3
7.5 – 9.0	S-6	4 7 9	1.5		1.0	cl / a-6	D	7.5-10.5 Silty CLAY with gravel (sandstone and shale fragments), brown, damp, very stiff to stiff, homogeneous (colluvial soil)	
9.0 – 10.5	S-7	4 6 7	1.5		1.0		D	1361.1	
10.5 – 12.0	S-8	8 10 13	1.5		1.5	gm / a-4	D	10.5-13.5 Silty GRAVEL (shale fragments), brown, damp, medium dense to dense, homogeneous (residual soil)	
12.0 – 13.5	S-9	8 13 19	1.5		2.5		D	1358.1	
13.5 – 14.9	S-10	28 36 50/0.4	1.4		3.0	gm / a-4	D	13.5-14.9 Silty GRAVEL (shale fragments) with sand, brown, dry, very dense, homogeneous (weathered bedrock) 1356.7	
14.9 – 16.9	R-1	core	2.0	100 / 0		T.O.R.		14.9-21.9 Sandy silty SHALE, brown, soft to medium, moderately weathered, intensely laminated (RD= 0°), RQD=36%	

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ENGINEERS FIELD BORING LOG

BORING NO. 2700-2
SHEET 2 **OF** 2

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
	R-2	core	3.0	100 / 47					
19.9									
20									
								1349.7	
22.5	R-3	core	5.0	100 / 82				21.9-24.9 Fine to medium grained SANDSTONE, gray, medium to hard, fresh, indistinct bedding, RQD= 100%	
24.9								1346.7	
25								24.9 Bottom of Hole	
27.5									
30									
32.5									
35									
37.5									

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(6/95)

ENGINEERS FIELD BORING LOG

BORING NO.	2700-3
SHEET	1 OF 2
DATE: START	10/14/03
O.G. END	10/14/03
ELEV.	1325.6

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** _____ **SEGMENT:** _____ **OFFSET:** _____
STATION: 27+00 **OFFSET FROM CENTERLINE:** 215' Rt.
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Wayne Ewing/Test Boring Services,
EQUIPMENT USED: CME-45 (track mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 14.9 **WATER:** **DEPTH:** 4.3 **TIME:** 3:30 p.m. **DATE:** 10/14/03
CHECKED BY: PWH **DATE:** 10/15/03 **DEPTH:** 1.0 **TIME:** 9:30 a.m **DATE:** 10/16/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0									
1.5	S-1	1 1 3	1.3			ol / a-8	D	0.0-0.6 ORGANIC SOIL, brown, damp (topsoil) 1325.0	Water level on 10/16/03 @ 1.0
2.5 3.0	S-2	1 2 2	0.6		0.5	cl / a-6	M	0.6-4.5 Sandy silty CLAY with gravel (sandstone fragments), brown and red brown, damp to moist, medium to soft, homogeneous (colluvial soil)	
4.5	S-3	2 1 2	0.5		0.5		D	1321.1	Water level on 10/14/03 @ 4.3
5 6.0	S-4	2 10 7	1.5			gm / a-1-b	M	4.5-6.0 Silty GRAVEL (sandstone fragments) with sand, gray, moist, medium dense, homogeneous (colluvial soil) 1319.6	
7.5	S-5	2 4 7	1.5		0.5		D	6.0-12.0 Sandy silty CLAY with gravel (sandstone fragments), gray and brown, damp, stiff to very stiff, homogeneous (colluvial soil)	
9.0	S-6	4 9 11	1.5		1.0	cl / a-6	D		
10 10.5	S-7	3 7 10	1.5		1.0		D		
12.0	S-8	7 12 16	1.5		1.5		D	1313.6	
12.5 13.5	S-9	8 12 20	1.5		2.0	gm / a-4	D	12.0-14.9 Silty GRAVEL (shale fragments), brown and gray, damp to dry, dense to very dense, homogeneous (weathered bedrock)	
14.9	S-10	17 29 50/0.4	1.4		4.0		D	1310.7	
15 15.9	R-1	core	1.0	100 / 70		T.O.R.		14.9-18.6 CLAYSHALE, brown and gray, very soft to soft, moderately weathered, intensely laminated (RD= 0°), RQD=59% Limestone seam @ 16.3-16.7	
17.5	R-2	core	2.0	100 / 75					

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ENGINEERS FIELD BORING LOG

BORING NO. 2700-3
SHEET 2 **OF** 2

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
17.9								1307.0	
	R-3	core	3.0	100 / 17				18.6-19.5 LIMESTONE, gray, hard, slightly weathered, indistinct bedding, RQD=56% 1306.1	
20								19.5-23.4 Calcareous CLAYSTONE, gray, very soft to soft, slightly weathered, indistinct bedding, RQD=38% Clay seam @ 20.1-20.2 Clay seam @ 20.7-20.8 Clay seam @ 21.1-21.3	
20.9									
22.5	R-4	core	3.8	95 / 75				1302.2	
								23.4-24.9 CLAYSHALE, gray, very soft, slightly weathered, indistinct bedding, RQD=100% 1300.7	
24.9									
25								24.9 Bottom of Hole	
27.5									
30									
32.5									
35									
37.5									

FORM NO: D-481
(6/95)

ENGINEERS FIELD BORING LOG

BORING NO.	2700-4
SHEET	1 OF 2
DATE: START	10/14/03
O.G. END	10/14/03
ELEV.	1438.2

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** **SEGMENT:** **OFFSET:**
STATION: 27+00 **OFFSET FROM CENTERLINE:** 200' Lt.
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Mark Dzlak/Test Boring Services, Inc.
EQUIPMENT USED: CME-55 (track mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 9.5 **WATER:** **DEPTH:** 3.4 **TIME:** 5:15 p.m. **DATE:** 10/14/03
CHECKED BY: PWH **DATE:** 10/15/03 **DEPTH:** 3.6 **TIME:** 9:25 a.m. **DATE:** 10/16/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0									
1.5	S-1	2 / 2 / 4	1.0		0.5	ol / a-8	D	0.0-0.6 ORGANIC SOIL, brown, damp (topsoil) 1437.6	
2.5 / 3.0	S-2	3 / 3 / 3	1.5		0.5	cl / a-6	D	0.6-4.5 Silty CLAY, brown, damp, medium, homogeneous (colluvial soil)	
4.5	S-3	1 / 3 / 4	1.5		0.5		D	1433.7	Water level on 10/14/03 @ 3.4 Water level on 10/16/03 @ 3.6
5 / 6.0	S-4	3 / 8 / 13	1.5		1.0		D	4.5-9.0 Clayey SILT, brown, damp to dry, very stiff to hard, homogeneous (colluvial soil)	
7.5	S-5	9 / 15 / 23	1.5		1.0	ml / a-4	D		
9.0	S-6	17 / 13 / 19	1.5		1.0		D	1429.2	
9.5	S-7	50	0.5			ml / a-4	D	9.0-9.5 Gravelly (shale fragments) clayey SILT, gray, dry, hard, homogeneous (weathered bedrock) 1428.7	
10						T.O.R.			
12.5 / 13.0	R-1	core	2.7	77 / 71				9.5-13.2 Calcareous medium grained SANDSTONE, gray, medium to hard, slightly weathered, indistinct bedding, RQD=68% 1425.0	
15	R-2	core	5.0	100 / 30				13.2-16.9 Shaly fine grained SANDSTONE, gray, medium, slightly weathered, thinly bedded (RD=0°), RQD=41% 1421.3	
17.5								16.9-19.5	

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ENGINEERS FIELD BORING LOG

BORING NO. 2700-4
SHEET 2 OF 2

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
18.0								Shaly sandy SILTSTONE, gray, medium, slightly weathered, thinly bedded (RD=0°), RQD=46%	
	R-3	core	1.5	100 / 80					
19.5								1418.7	
								19.5 Bottom of Hole	

20
22.5
25
27.5
30
32.5
35
37.5

FORM NO: D-481
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ENGINEERS FIELD BORING LOG

BORING NO.	3000-1
SHEET	1 OF 2
DATE: START	10/13/03
O.G. END	10/13/03
ELEV.	1422.9

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** **SEGMENT:** **OFFSET:**
STATION: 30+00 **OFFSET FROM CENTERLINE:** 30' Lt.
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Mark Dziak/Test Boring Services, Inc.
EQUIPMENT USED: CME-55 (track mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 13.9 **WATER:** **DEPTH:** 2.6 **TIME:** 1:30 p.m. **DATE:** 10/13/03
CHECKED BY: PWH **DATE:** 10/15/03 **DEPTH:** 4.2 **TIME:** 9:30 a.m. **DATE:** 10/15/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0									
1.5	S-1	2 3 3	1.5		0.5	ol / a-8	D	0.0-0.2 ORGANIC SOIL, brown, damp (topsoil) 1422.7	
3.0	S-2	3 5 8	1.5		0.5	cl / a-6	D	0.2-3.0 Silty CLAY, light brown, damp, medium to stiff, homogeneous (fill) 1419.9	Water level on 10/13/03 @ 2.6
4.5	S-3	4 5 7	1.5		1.0		D	3.0-9.0 Silty CLAY with gravel (sandstone and shale fragments), brown and gray, damp, stiff to very stiff, homogeneous (colluvial soil)	Water level on 10/15/03 @ 4.2
6.0	S-4	8 12 14	1.5		1.5	cl / a-6	D		
7.5	S-5	4 5 9	1.5		1.0		D		
9.0	S-6	9 10 11	1.5		1.5		D	1413.9	
10.5	S-7	5 8 14	1.5			gm / a-4	D	9.0-10.0 Silty GRAVEL (shale fragments) with sand, brown, damp, medium dense, homogeneous (colluvial soil) 1412.9	
12.0	S-8	6 6 9	1.5		1.0	cl / a-6	D	10.0-12.0 Silty CLAY, light brown, damp, very stiff, homogeneous (colluvial soil) 1410.9	
13.5	S-9	3 9 29	1.5			gm / a-4	D	12.0-13.9 Silty GRAVEL (shale fragments), gray, dry, dense to very dense, homogeneous (weathered bedrock) 1409.0	
13.9	S-10	50/0.4	0.4				D		
16.4	R-1	core	2.3	92 / 72		T.O.R.		13.9-15.9 Shaly calcareous CLAYSTONE, gray, soft, moderately weathered, thinly bedded (RD=0°), RQD=65% 1407.0	
17.5								15.9-16.4 Fine grained SANDSTONE, gray, medium, slightly weathered, indistinct bedding, RQD=	

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ENGINEERS FIELD BORING LOG

BORING NO. 3000-1
SHEET 2 OF 2

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
								100% 1406.5	
	R-2	core	5.0	100 / 74				16.4-17.7 LIMESTONE, gray, hard, fresh, indistinct bedding, RQD=0% 1405.2	
20								17.7-22.5 Shaly sandy SILTSTONE, gray, soft to medium, fresh, thinly bedded (RD=0°), RQD=96% Shaly claystone seam @ 19.7-20.0 Shaly claystone seam @ 20.1-20.4	
21.4									
22.5	R-3	core	2.5	100 / 92				1400.4 22.5-23.5 Shaly CLAYSTONE, gray, very soft, fresh, thinly bedded (RD=0°), RQD=100% 1399.4	
23.9								23.5-23.9 LIMESTONE, gray, hard, fresh, indistinct bedding, RQD=100% 1399.0	
25								23.9 Bottom of Hole	
27.5									
30									
32.5									
35									
37.5									

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ENGINEERS FIELD BORING LOG

BORING NO.	3000-2
SHEET	1 OF 2
DATE: START	10/13/03
O.G. END	10/13/03
ELEV.	1398.1

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** _____ **SEGMENT:** _____ **OFFSET:** _____
STATION: 30+00 **OFFSET FROM CENTERLINE:** 190' Rt.
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Mark Dziak/Test Boring Services, Inc.
EQUIPMENT USED: CME-55 (track mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 19.2 **WATER:** **DEPTH:** 16.4 **TIME:** 5:30 p.m. **DATE:** 10/13/03
CHECKED BY: PWH **DATE:** 10/15/03 **DEPTH:** 15.6 **TIME:** 9:00 a.m. **DATE:** 10/15/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0								0.0-0.2 ORGANIC SOIL, brown, damp (topsoil) 1397.9	
1.5	S-1	1 2 3	1.5		0.5	ol / a-8	D		
2.5	S-2	3 3 5	1.5			cl / a-6	D	0.2-3.0 Silty CLAY with gravel (shale fragments), gray brown, damp, medium, homogeneous (colluvial soil) 1395.1	
4.5	S-3	6 9 14	1.5		1.0	gm / a-1-b	D	3.0-4.5 Silty GRAVEL (sandstone fragments), brown, damp, medium dense, homogeneous (colluvial soil) 1393.6	
5	S-4	5 5 7	1.5		1.0		D	4.5-12.0 Silty CLAY with gravel (shale and sandstone fragments), brown and gray, damp, stiff to very stiff, homogeneous (colluvial soil)	
6.0									
7.5	S-5	8 11 14	1.5		1.5		D		
9.0	S-6	4 6 14	1.0		1.5	cl / a-6	D		
10	S-7	4 7 7	1.5		1.0		D		
10.5									
12.0	S-8	6 7 10	1.5		1.0		D	1386.1	
12.5	S-9	11 12 18	1.5			gm / a-1-b	D	12.0-13.5 Silty GRAVEL (sandstone fragments) with sand, brown, damp, medium dense, homogeneous (residual soil) 1384.6	
13.5									
15.0	S-10	10 12 16	1.5		1.5		D	13.5-18.0 Silty GRAVEL (shale fragments) with sand, brown, damp, medium dense to very dense, homogeneous (weathered bedrock)	
15									
16.5	S-11	16 21 31	1.5		2.0	gm / a-4	D		Water level on 10/15/03 @ 15.6
									Water level on 10/13/03 @ 16.4
17.5	S-12	24 34	1.5		2.5		D		

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ENGINEERS FIELD BORING LOG

BORING NO. 3000-2
SHEET 2 **OF** 2

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
18.0		46						1380.1	
19.2	S-13	21 47 50/0.2	1.2			gc / a-6	D	18.0-19.2 Clayey GRAVEL (clayshale fragments), brown and black, damp, very dense, homogeneous (weathered bedrock) 1378.9	
20	S-14	50/0.0				T.O.R.			
21.7	R-1	core	0.5	20 / 0				19.2-29.2 LIMESTONE, gray, hard, fresh, indistinct bedding, RQD=39% Soft clay seam @ 19.5	
22.5								Carbonaceous clayshale seam @ 22.4-22.6	
25	R-2	core	3.2	64 / 56				Carbonaceous clayshale seam @ 25.2-25.9	
26.7									
27.5	R-3	core	1.1	44 / 44				Soft clay seam @ 26.9-27.2	
29.2								1368.9	
30								29.2 Bottom of Hole	
32.5									
35									
37.5									

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ENGINEERS FIELD BORING LOG

BORING NO.	3000-3
SHEET	1 OF 2
DATE: START	10/13/03
O.G. END	10/13/03
ELEV.	1448.4

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** **SEGMENT:** **OFFSET:**
STATION: 30+00 **OFFSET FROM CENTERLINE:** 150' Lt.
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Wayne Ewing/Test Boring Services,
EQUIPMENT USED: CME-45 (track mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 11.3 **WATER:** **DEPTH:** 14.5 **TIME:** 2:00 p.m. **DATE:** 10/13/03
CHECKED BY: PWH **DATE:** 10/15/03 **DEPTH:** 13.2 **TIME:** 9:00 a.m. **DATE:** 10/15/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0 – 1.5	S-1	1 2 3	1.5		0.5	ol / a-8; cl / a-6	D	0.0-0.6 ORGANIC SOIL, brown, damp (topsoil) 1447.8	
1.5 – 3.0	S-2	4 3 3	1.5		1.0	cl / a-6	D	0.6-1.5 Silty CLAY, light brown, damp, medium, homogeneous (colluvial soil) 1446.9	
3.0 – 4.5	S-3	2 3 5	1.3		1.0		D	1.5-4.5 Silty CLAY with gravel (sandstone and shale fragments), brown, damp, medium, homogeneous (colluvial soil) 1443.9	
4.5 – 6.0	S-4	5 10 9	1.5		1.5	gm / a-4	D	4.5-6.0 Silty GRAVEL (shale fragments), brown, damp, medium dense, homogeneous (colluvial soil) 1442.4	
6.0 – 7.5	S-5	7 8 9	1.5		1.0	cl / a-6	D	6.0-10.5 Silty CLAY with gravel (sandstone fragments), red brown and brown, damp, very stiff, homogeneous (colluvial soil)	
7.5 – 9.0	S-6	7 8 12	1.5		1.0		D		
9.0 – 10.5	S-7	4 8 7	1.5		1.0		D	1437.9	
10.5 – 11.3	S-8	35 50/0.3	0.8		3.0	gm / a-4	D	10.5-11.3 Silty GRAVEL (shale fragments) with sand, light brown, dry, very dense, homogeneous (weathered bedrock) 1437.1	
11.3 – 13.3	R-1	core	2.0	100 / 0		T.O.R.		11.3-14.4 Fine grained SANDSTONE, brown, medium, slightly weathered, indistinct bedding, RQD=0% Clay seam @ 12.4-12.6 1434.0	Water level on 10/15/03 @ 13.2
13.3 – 16.3	R-2	core	2.8	93 / 0				14.4-16.3 Carbonaceous SHALE, black, soft to medium, slightly weathered, intensely laminated, RQD= 0% 1432.1	Water level on 10/13/03 @ 14.5
16.3 – 17.5								16.3-21.3 LIMESTONE, gray, hard, fresh, indistinct bedding, RQD=62%	

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ENGINEERS FIELD BORING LOG

BORING NO. 3000-3
SHEET 2 OF 2

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
	R-3	core	5.0	100 / 62					
20								Calcareous clayshale seam @ 19.8-20.2	
21.3								1427.1	
								21.3 Bottom of Hole	
22.5									
25									
27.5									
30									
32.5									
35									
37.5									

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ENGINEERS FIELD BORING LOG

BORING NO.	3300-1
SHEET	1 OF 5
DATE: START	10/22/03
O.G. END	10/23/03
ELEV.	1509.1

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** **SEGMENT:** **OFFSET:**
STATION: 33+00 **OFFSET FROM CENTERLINE:** 115' Lt.
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Wayne Ewing/Test Boring Services,
EQUIPMENT USED: CME-45 (track mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 4.8 **WATER:** **DEPTH:** 49.3 **TIME:** 1:00 p.m. **DATE:** 10/23/03
CHECKED BY: PWH **DATE:** 10/27/03 **DEPTH:** 36.8 **TIME:** 3:30 p.m. **DATE:** 10/30/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0									
1.5	S-1	1 / 1 / 1	1.5			ol / a-8	D	0.0-0.4 ORGANIC SOIL, brown, damp (topsoil) 1508.7	
3.0	S-2	6 / 6 / 8	0.5			ml / a-4	D	0.4-1.5 Clayey SILT, brown, damp, soft, homogeneous (residual soil) 1507.6	
4.5	S-3	6 / 8 / 10	1.5			gm / a-1-b	D	1.5-3.0 Silty GRAVEL (sandstone fragments), brown, damp, medium dense, homogeneous (residual soil) 1506.1	
4.8	S-4	50/0.3	0.3			ml / a-4	D	3.0-4.8 Clayey SILT with gravel (shale fragments), brown, damp, very stiff to hard, homogeneous (residual soil) 1504.3	
6.8	R-1	core	1.0	50 / 0		T.O.R.		4.8-8.6 Shaly fine grained SANDSTONE, brown, medium, moderately weathered, indistinct bedding, RQD=0% 1500.5	
8.8	R-2	core	1.0	50 / 0				8.6-23.2 Sandy shaly SILTSTONE, brown, medium, slightly weathered, thinly bedded (RD=0°), RQD=3%	
12.8	R-3	core	3.5	88 / 12					
14.8	R-4	core	2.0	100 / 0					
17.3	R-5	core	2.5	100 / 0					
17.5									

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ENGINEERS FIELD BORING LOG

BORING NO. 3300-1
SHEET 2 **OF** 5

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
20	R-6	core	4.8	96 / 0					
22.3									
22.5	R-7	core	5.0	100 / 24				1485.9 23.2-29.4 LIMESTONE, gray and brown, hard, slightly weathered, indistinct bedding, RQD=19% Clayshale seam @ 23.6	
25									
27.3								Clayshale seam @ 26.9	
27.5	R-8	core	4.0	80 / 0				1479.7 29.4-35.3 Sandy SILTSTONE, brown, soft to medium, slightly weathered, thinly bedded (RD=0°), RQD=22%	
30									
32.3									
32.5	R-9	core	5.0	100 / 50				1473.8 35.3-38.6 Medium grained SANDSTONE, gray, medium, fresh, indistinct bedding, RQD=67%	
35									
37.3									Water level on 10/30/03 @ 36.8
37.5									

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ENGINEERS FIELD BORING LOG

BORING NO. 3300-1
SHEET 3 **OF** 5

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
40	R-10	core	5.0	100 / 38				1470.5 38.6-40.2 SHALE, brown to black, very soft to soft, fresh, very thinly bedded (RD=0°), RQD=25% 1468.9 40.2-42.8 LIMESTONE, gray, hard, fresh, indistinct bedding, RQD=35% 1466.3	
42.3 42.5 45	R-11	core	5.0	100 / 32				42.8-43.9 CLAYSHALE, gray, very soft, fresh to slightly weathered, very thinly bedded (RD=0°), RQD=0% 1465.2 43.9-50.1 Fine to medium grained SANDSTONE, brown, medium, slightly weathered, indistinct bedding, RQD=44%	Fracture @ 44.2-44.5 (RD=90°)
47.3 47.5 50	R-12	core	5.0	100 / 64				1459.0 50.1-55.7 Shaly sandy SILTSTONE, gray, medium, fresh, intensely laminated to very thinly bedded (RD=0°), RQD=70%	Fracture @ 49.0-49.8 (RD=90°) Water level on 10/23/03 @ 49.3
52.3 52.5 55	R-13	core	5.0	100 / 44				1453.4 55.7-58.6 SHALE, gray, soft, fresh, intensely laminated (RD=0°), RQD=0% Clay seam @ 57.1-57.2	
57.3 57.5									

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ENGINEERS FIELD BORING LOG

BORING NO. 3300-1
SHEET 4 **OF** 5

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
60	R-14	core	5.0	100 / 32				1450.5 58.6-71.1 LIMESTONE, gray, hard, fresh, indistinct bedding, RQD=61%	
62.3									
62.5									
65	R-15	core	5.0	100 / 76					
67.3									
67.5									
70	R-16	core	5.0	100 / 52				1438.0 71.1-75.1 Silty CLAYSTONE, gray, soft to medium, fresh, indistinct bedding, RQD=62%	
72.3									
72.5									
75	R-17	core	5.0	100 / 86				1434.0 75.1-80.3 Sandy SILTSTONE, gray, medium, fresh, indistinct bedding, RQD=88%	
77.3									
77.5									

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ENGINEERS FIELD BORING LOG

BORING NO. 3300-1
SHEET 5 OF 5

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
80	R-18	core	4.7	100 / 87				Clayshale seam @ 80.0-80.3 1428.8	
								80.3-82.0 Fine grained SANDSTONE, gray, medium, fresh, indistinct bedding, RQD=100%	
82.0								1427.1	
82.5								82.0 Bottom of Hole	
85									
87.5									
90									
92.5									
95									
97.5									

FORM NO: D-481
(6/95)

ENGINEERS FIELD BORING LOG

BORING NO.	3300-2
SHEET	1 OF 2
DATE: START	10/15/03
O.G. END	10/15/03
ELEV.	1452.7

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** **SEGMENT:** **OFFSET:**
STATION: 33+00 **OFFSET FROM CENTERLINE:** 35' Rt.
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Mark Dziak/Test Boring Services, Inc.
EQUIPMENT USED: CME-55 (track mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 13.5 **WATER:** **DEPTH:** 16.1 **TIME:** 2:15 p.m. **DATE:** 10/15/03
CHECKED BY: PWH **DATE:** 10/17/03 **DEPTH:** 18.3 **TIME:** 2:30 p.m. **DATE:** 10/16/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0 – 1.5	S-1	1 / 2 / 1	0.8			ol / a-8; cl / a-6	M	0.0-0.3 ORGANIC SOIL, brown, moist (topsoil) 1452.4	
1.5 – 3.0	S-2	2 / 2 / 3	1.5		0.5		D	0.3-1.5 Silty CLAY, brown, moist, soft, homogeneous (colluvial soil) 1451.2	
2.5 – 4.5	S-3	4 / 3 / 6	1.5		0.5		D	1.5-11.0 Silty CLAY with gravel (sandstone and shale fragments), brown, damp, medium to very stiff, homogeneous (colluvial soil)	
4.5 – 6.0	S-4	6 / 7 / 10	1.5		0.5		D		
5 – 7.5	S-5	10 / 13 / 8	1.5		1.0	cl / a-6	D		
7.5 – 9.0	S-6	3 / 6 / 9	1.5		1.0		D		
9.0 – 10.5	S-7	4 / 5 / 20	1.5		1.0		D		
10 – 12.0	S-8	10 / 21 / 31	1.5		1.5		D	1441.7	
12.0 – 13.5	S-9	19 / 28 / 50	1.5		3.5	gm / a-4	D	11.0-13.5 Silty GRAVEL (shale fragments), brown, dry, very dense, homogeneous (weathered bedrock) 1439.2	
13.5 – 15.5	R-1	core	1.1	55 / 0		T.O.R.		13.5-18.8 CLAYSTONE, brown, very soft, highly weathered, indistinct bedding, RQD=0%	
15 – 17.5				42					Water level on 10/15/03 @ 16.1

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ENGINEERS FIELD BORING LOG

BORING NO. 3300-2
SHEET 2 OF 2

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
	R-2	core	1.7	— / 0				1433.9	Water level on 10/16/03 @ 18.3
19.5								18.8-19.6 Calcareous SANDSTONE, gray and brown, medium to hard, moderately weathered, indistinct bedding, RQD=0% 1433.1	
19.6	S-10	50/0.1	0.1				D		
20	R-3	core	1.3	65 / 65				19.6-23.9 Fine grained SANDSTONE, gray, medium, slightly weathered, indistinct bedding, RQD=63%	
21.6									
22.5	R-4	core	3.8	83 / 52				1428.8	
								23.9-25.7 Carbonaceous SHALE, black, soft to medium, slightly weathered, intensely laminated (RD=0°), RQD=33% 1427.0	
25									
26.2								25.7-26.2 LIMESTONE, gray, hard, fresh, indistinct bedding, RQD=80% 1426.5	
27.5								26.2 Bottom of Hole	
30									
32.5									
35									
37.5									

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ENGINEERS FIELD BORING LOG

BORING NO.	3550-1
SHEET	1 OF 5
DATE: START	10/13/03
O.G. END	10/14/03
ELEV.	1527.3

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** **SEGMENT:** **OFFSET:**
STATION: 35+50 **OFFSET FROM CENTERLINE:** 115' Lt.
INSPECTOR (SIGNED): David Walters*/Earth, Inc. **DRILLERS NAME/COMPANY:** Jim Rice/Test Boring Services, Inc.
EQUIPMENT USED: CME-45 (track mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 5.8 **WATER:** **DEPTH:** 37.0 **TIME:** 2:30 p.m. **DATE:** 10/14/03
CHECKED BY: PWH **DATE:** 10/17/03 **DEPTH:** 62.6 **TIME:** 4:00 p.m. **DATE:** 10/15/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0 – 1.5	S-1	1 / 5 / 4	1.0			ol / a-8; ml / a-4	D	0.0-0.4 ORGANIC SOIL, brown, damp (topsoil) 1526.9	
1.5 – 3.0	S-2	6 / 8 / 13	1.5		1.5	cl / a-6	D	0.4-1.5 Sandy clayey SILT with gravel (sandstone fragments), brown, damp, stiff, homogeneous (residual soil) 1525.8	
3.0 – 4.5	S-3	9 / 9 / 11	1.5		1.5		D	1.5-5.0 Silty CLAY with gravel (shale fragments), brown, damp, very stiff, homogeneous (residual soil) 1522.3	
4.5 – 5.8	S-4	8 / 19 / 50/0.3	1.3			ml / a-4	D	5.0-5.8 Gravelly (sandstone fragments) clayey SILT, light brown, dry, hard, homogeneous (weathered bedrock) 1521.5	
5.8 – 7.8	R-1	core	1.2	60 / 25		T.O.R.		5.8-11.7 Calcareous SANDSTONE, brown and gray, medium to hard, moderately weathered, indistinct bedding, RQD=25% Shaly seam @ 5.8-6.1	
7.8 – 10.8	R-2	core	2.0	67 / 20					
10.8 – 13.8	R-3	core	3.0	100 / 13				1515.6 11.7-18.3 Sandy silty SHALE, brown and gray, soft to medium, highly to moderately weathered, laminated 0.1" thick, RQD=0%	
13.8 – 15.8	R-4	core	1.0	50 / 0					
15.8 – 17.5	R-5	core	0.3	15 / 0					

*Inspection completed by Keith Tate/Earth, Inc.

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ENGINEERS FIELD BORING LOG

BORING NO. 3550-1
SHEET 2 **OF** 5

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
17.8									
	S-5	50/0.0						1509.0	
	R-6	core	1.3	65 / 20				18.3-22.8 Shaley SANDSTONE, brown, medium, moderately weathered, medium bedded (RD= 0°), RQD=51%	
19.8									
20	R-7	core	3.0	100 / 63					
22.5								1504.5	
22.8	R-8	core	1.6	80 / 0				22.8-37.8 Silty SHALE, brown, soft, moderately weathered, thinly bedded (RD=0°), RQD=14%	Fracture @ 23.3-23.6 (RD=90°)
24.8									
25	R-9	core	5.0	100 / 0				Lost water @ 25.5	Fracture @ 26.9-27.9 (RD=90°)
27.5									
29.8									
30	R-10	core	2.5	100 / 32					
32.3									
32.5	R-11	core	2.5	100 / 16					
34.8									
35	R-12	core	4.2	100 / 31				Sandy seam @ 35.0-37.8	Water level on 10/14/03 @ 37.0
37.5									

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ENGINEERS FIELD BORING LOG

BORING NO. 3550-1
SHEET 3 OF 5

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
								1489.5	Fracture @ 37.2-37.7 (RD=90°)
								37.8-44.0 Shaly SILTSTONE, gray, medium, moderately weathered, medium bedded (RD=0°), RQD= 44%	
39.0									
40	R-13	core	4.0	100 / 57					
42.5								Calcareous @ 42.4-44.0	
43.0									Fracture @ 43.0-44.0 (RD=90°)
								1483.3	
								44.0-47.1 Calcareous sandy SHALE, brown, soft, highly weathered, very thinly bedded (RD=0°), RQD= 48%	
45	R-14	core	5.0	100 / 48					
								Clay seams @ 46.4-47.1	
								1480.2	
47.5								47.1-59.0 Medium grained SANDSTONE, brown and gray, hard, fresh, thickly bedded (RD=0°), RQD=100%	
48.0									
50	R-15	core	5.0	100 / 100					
52.5									
53.0									
55	R-16	core	5.0	100 / 100					
57.5									

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ENGINEERS FIELD BORING LOG

BORING NO. 3550-1
SHEET 4 OF 5

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
58.0								1468.3	
60	R-17	core	5.0	100 / 68				59.0-60.8 Silty SHALE, gray to black, soft to medium, moderately weathered, intensely laminated (RD=0°), RQD=78% Carbonaceous below 60.0 1466.5	
62.5 63.0								60.8-63.0 LIMESTONE with carbonaceous shale seams, gray, medium to hard, moderately weathered, medium bedded (RD=0°), RQD=45% 1464.3	Water level on 10/15/03 @ 62.6
65	R-18	core	5.0	100 / 60				63.0-64.3 Sandy SHALE, gray, soft, highly weathered, intensely laminated (RD=0°), RQD=46% Very soft @ 63.7-63.9 1463.0	
67.5 68.0								64.3-69.0 Silty SANDSTONE, gray, medium, moderately weathered, thinly bedded (RD=0°), RQD=51% Very broken @ 67.1-68.0 1458.3	Fracture @ 67.1-68.0 (RD=90°)
70	R-19	core	5.0	100 / 12				69.0-73.0 Silty SHALE, brown to gray, soft to medium, highly weathered, thinly bedded (RD=0°), RQD=15%	
72.5 73.0								1454.3	
75	R-20	core	5.0	100 / 68				73.0-78.9 Shaly SILTSTONE, gray, medium, moderately weathered, medium bedded (RD=0°), RQD=73%	Fracture @ 73.0-73.3 (RD=90°)
77.5									

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ENGINEERS FIELD BORING LOG

BORING NO. 3550-1
SHEET 5 **OF** 5

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
78.0								1448.4	
80	R-21	core	5.0	100 / 84				78.9-83.0 LIMESTONE, gray, hard, moderately weathered, thickly bedded (RD=0°), RQD=80%	
82.5									
83.0								1444.3 83.0 Bottom of Hole	
85									
87.5									
90									
92.5									
95									
97.5									

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ENGINEERS FIELD BORING LOG

BORING NO.	3900-1
SHEET	1 OF 4
DATE: START	10/14/03
O.G. END	10/15/03
ELEV.	1532.8

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** **SEGMENT:** **OFFSET:**
STATION: 38+90 **OFFSET FROM CENTERLINE:** 30' Lt.
INSPECTOR (SIGNED): Keith Tate/Earth, Inc. **DRILLERS NAME/COMPANY:** Jim Rice/Test Boring Services, Inc.
EQUIPMENT USED: CME-45 (track mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 11.0 **WATER:** **DEPTH:** 54.0 **TIME:** 2:00 p.m. **DATE:** 10/15/03
CHECKED BY: PWH **DATE:** 10/17/03 **DEPTH:** 55.2 **TIME:** 2:30 p.m. **DATE:** 10/16/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0 – 1.5	S-1	1 3 3	1.0			ol / a-8	M	0.0-0.6 ORGANIC SOIL, brown, moist (topsoil) 1532.2	
1.5 – 3.0	S-2	7 8 5	1.5			sm / a-2-4	M	0.6-3.0 Silty SAND with gravel (shale fragments), brown, moist, loose to medium dense, homogeneous (residual soil) 1529.8	
3.0 – 4.5	S-3	6 7 8	1.5		1.5	cl / a-6	M	3.0-4.5 Silty CLAY, brown, moist, very stiff, homogeneous (residual soil) 1528.3	
4.5 – 6.0	S-4	7 8 12	1.5			ml / a-4	M	4.5-9.0 Sandy clayey SILT with gravel (shale fragments), brown, moist to dry, very stiff to hard, homogeneous (residual soil)	
6.0 – 7.5	S-5	16 19 18	1.5				M		
7.5 – 9.0	S-6	8 14 27	1.5				D	1523.8	
9.0 – 9.9	S-7	21 50/0.4	0.9			ml / a-4	D	9.0-11.0 Gravelly (shale fragments) clayey SILT with sand, brown, dry, hard, homogeneous (weathered bedrock)	
9.9 – 10.5		auger							
10.5 – 11.0	S-8	50 50/0.0	0.5				D	1521.8	
11.0 – 13.0	R-1	core	1.4	70 / 45		T.O.R.		11.0-13.0 SHALE, brown, soft, highly weathered, very thinly bedded (RD=0°), RQD=45% 1519.8	
13.0 – 16.0	R-2	core	3.0	100 / 40				13.0-22.3 Shaly medium grained SANDSTONE, brown, medium, moderately weathered, thinly bedded (RD=0°), RQD=35% Calcite stringers @ 14.9-16.0	Fracture @ 13.3-13.7 (RD=80°)
16.0 – 17.5									

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ENGINEERS FIELD BORING LOG

BORING NO. 3900-1
SHEET 2 OF 4

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
20 21.0	R-3	core	4.9	98 / 42					
22.5 25 26.0	R-4	core	3.9	78 / 18				1510.5 22.3-36.0 Sandy SHALE, brown, soft, highly to moderately weathered, very thinly bedded (RD=0°), RQD= 33% Soft @ 22.5-23.0	Joint @ 22.3-22.5 (RD=60°)
27.5 30 31.0	R-5	core	4.9	98 / 32					
32.5 35 36.0	R-6	core	5.0	100 / 40				1496.8	
37.5								36.0-41.0 Medium grained SANDSTONE, brown, medium, moderately weathered, thinly bedded (RD=0°), RQD=20%	

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ENGINEERS FIELD BORING LOG

BORING NO. 3900-1
SHEET 3 OF 4

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
40 41.0	R-7	core	5.0	100 / 20				1491.8	Fracture @ 37.6-38.7 (RD=90°) Fracture @ 40.5 (RD=90°)
42.5 45 46.0	R-8	core	4.9	98 / 42				41.0-51.9 Sandy SHALE, brown to gray, medium, moderately weathered, very thinly bedded (RD=0°), RQD=37% Sandstone seam @ 44.2-45.0	
47.5 49.0	R-9	core	2.9	97 / 0					
50 51.0	R-10	core	1.5	75 / 65					
52.5 55 56.0	R-11	core	4.7	94 / 72				1480.9 51.9-59.0 Calcareous SANDSTONE, gray, medium, moderately weathered, thinly bedded (RD=0°), RQD=42% Lost water @ 52.0	Fracture @ 52.7-53.2 (RD=90°) Fracture @ 53.8-54.0 (RD=90°) Water level on 10/15/03 @ 54.0 Water level on 10/16/03 @ 55.2
57.5				67				Very broken @ 56.0-59.0	

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ENGINEERS FIELD BORING LOG

BORING NO. 3900-1
SHEET 4 OF 4

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
	R-12	core	2.0	— / 0					
59.0								1473.8	
								59.0 Bottom of Hole	
60									
62.5									
65									
67.5									
70									
72.5									
75									
77.5									

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ENGINEERS FIELD BORING LOG

BORING NO.	4200-1
SHEET	1 OF 2
DATE: START	10/24/03
O.G. END	10/24/03
ELEV.	1478.5

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** **SEGMENT:** **OFFSET:**
STATION: 41+90 **OFFSET FROM CENTERLINE:** 115' Rt.
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Wayne Ewing/Test Boring Services,
EQUIPMENT USED: CME-45 (track mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 13.4 **WATER:** **DEPTH:** 17.1 **TIME:** 12:00 p.m. **DATE:** 10/24/03
CHECKED BY: PWH **DATE:** 10/29/03 **DEPTH:** 22.4 **TIME:** 1:45 p.m. **DATE:** 10/29/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0									
1.5	S-1	1 2 2	1.5			ol / a-8	D	0.0-0.5 ORGANIC SOIL, brown, damp (topsoil) 1478.0	
2.5 3.0	S-2	8 6 7	1.5		1.0	ml / a-4	D	0.5-1.5 Clayey SILT, brown, damp, medium, homogeneous (residual soil) 1477.0	
4.5	S-3	10 11 11	1.5		1.0		D	1.5-9.0 Clayey SILT with gravel (shale fragments), brown, damp, stiff to hard, homogeneous (residual soil)	
5 6.0	S-4	12 17 20	1.2		2.0	ml / a-4	D		
7.5	S-5	20 17 14	1.5		1.5		D		
9.0	S-6	7 7 7	1.5		1.0		D	1469.5	
10 10.5	S-7	11 15 7	1.5			gm / a-2-4	D	9.0-12.0 Silty GRAVEL (sandy shale fragments) with sand, brown, damp, medium dense, homogeneous (weathered bedrock)	
12.0	S-8	4 6 22	1.5				D	1466.5	
12.5 13.4	S-9	46 47 50/0.4	1.4			gm / a-1-b	D	12.0-13.4 Silty GRAVEL (sandstone fragments) with sand, brown, damp, very dense, homogeneous (weathered bedrock) 1465.1	
15 15.4	R-1	core	1.1	55 / 0		T.O.R.		13.4-18.5 Fine to medium grained SANDSTONE, brown, medium, slightly weathered, indistinct bedding, RQD=0%	
17.5	R-2	core	1.6	53 / 0					Water level on

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ENGINEERS FIELD BORING LOG

BORING NO. 4200-1
SHEET 2 **OF** 2

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
									10/24/03 @ 17.1
18.4								Clay seam @ 18.2-18.5 1460.0	
								18.5-19.8 LIMESTONE, gray, hard, slightly weathered, indistinct bedding, RQD=0% 1458.7	
20	R-3	core	4.5	90 / 0				19.8-22.9 CLAYSTONE, gray with brown, very soft to soft, slightly weathered, indistinct bedding, RQD=0%	
22.5								1455.6	Water level on 10/29/03 @ 22.4
23.4								22.9-23.4 Fine grained SANDSTONE, brown, medium, fresh, indistinct bedding, RQD=0% 1455.1	
25								23.4 Bottom of Hole	
27.5									
30									
32.5									
35									
37.5									

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ENGINEERS FIELD BORING LOG

BORING NO.	7250-1
SHEET	1 OF 2
DATE: START	10/27/03
O.G. END	10/27/03
ELEV.	1433.1

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** **SEGMENT:** **OFFSET:**
STATION: 72+50 **OFFSET FROM CENTERLINE:** Centerline
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Wayne Ewing/Test Boring Services,
EQUIPMENT USED: CME-45 (track mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 15.7 **WATER:** **DEPTH:** 3.4 **TIME:** 11:30 a.m. **DATE:** 10/27/03
CHECKED BY: PWH **DATE:** 10/29/03 **DEPTH:** 10.0 **TIME:** 12:45 p.m. **DATE:** 10/29/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0									
1.5	S-1	1 2 2	1.1			ol / a-8	M	0.0-0.9 ORGANIC SOIL, brown, moist, (topsoil) 1432.2	
3.0	S-2	2 1 3	1.2		0.5	cl / a-6	D	0.9-4.5 Silty CLAY, brown, moist to damp, soft to medium, homogeneous (colluvial soil)	
2.5 4.5	S-3	4 3 4	1.4		0.5		D	1428.6	Water level on 10/27/03 @ 3.4
5 6.0	S-4	5 5 4	1.2		1.0	cl / a-6	D	4.5-9.0 Silty CLAY with gravel (sandstone fragments), brown, damp, stiff to very stiff, homogeneous (colluvial soil)	
7.5	S-5	3 4 5	1.5		1.0		D		
9.0	S-6	7 9 9	0.8		1.0		D	1424.1	
10 10.5	S-7	3 4 6	1.5		1.0	cl / a-6	D	9.0-10.5 Silty CLAY, brown and gray, damp, stiff, homogeneous (colluvial soil) 1422.6	Water level on 10/29/03 @ 10.0
12.0	S-8	7 9 10	1.4		1.5	cl / a-6	D	10.5-12.0 Silty CLAY with gravel (shale fragments), brown, damp, very stiff, homogeneous (colluvial soil) 1421.1	
12.5 13.5	S-9	5 6 7	1.5		1.0	cl / a-6	D	12.0-15.5 Silty CLAY, brown, damp, stiff, homogeneous (colluvial soil)	
15.0	S-10	6 5 7	1.5				D	1417.6	
15 15.7	S-11	12 50/0.2	0.7		3.0	ml / a-4	D	15.5-15.7 Sandy clayey SILT with gravel (sandy shale fragments), brown and gray, damp, hard, homogeneous (weathered bedrock)	
17.5	R-1	core	1.8	90 / 70		T.O.R.		1417.4	

FORM NO: D-481
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ENGINEERS FIELD BORING LOG

BORING NO. 7250-1
SHEET 2 **OF** 2

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
17.7								15.7-25.7 Medium grained SANDSTONE, brown and gray, medium, fresh, indistinct bedding, RQD=92% Micaceous below 17.7	
20	R-2	core	3.0	100 / 100					
20.7									
22.5	R-3	core	5.0	100 / 96					
25									
25.7								1407.4	
								25.7 Bottom of Hole	
27.5									
30									
32.5									
35									
37.5									

FORM NO: D-481
(6/95)

ENGINEERS FIELD BORING LOG

BORING NO.	7700-1
SHEET	1 OF 3
DATE: START	10/29/03
O.G. END	10/30/03
ELEV.	1320.6

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** **SEGMENT:** **OFFSET:**
STATION: 77+00 **OFFSET FROM CENTERLINE:** 152' Lt.
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Mark Dziak/Test Boring Services, Inc.
EQUIPMENT USED: CME-55 (track mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 28.2 **WATER:** **DEPTH:** 4.1 **TIME:** 12:30 p.m. **DATE:** 10/30/03
CHECKED BY: PWH **DATE:** 11/3/03 **DEPTH:** 4.1 **TIME:** 1:00 p.m. **DATE:** 10/31/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0 – 1.5	S-1	2 5 7	1.5			ol / a-8	M	0.0-0.5 ORGANIC SOIL, brown, moist, (topsoil) 1320.1	
2.5 – 3.0	S-2	5 6 9	0.7		0.5	cl / a-6	D	0.5-6.0 Silty CLAY with gravel (sandstone fragments), brown, moist to damp, stiff to very stiff, homogeneous (alluvial soil)	
4.5	S-3	4 5 7	1.5		0.5		D		Water level on 10/30/03 @ 4.1 Water level on 10/31/03 @ 4.1
5 – 6.0	S-4	7 10 11	1.5		0.5		D	1314.6	
7.5	S-5	7 7 9	1.5		0.5	ml / a-4	D	6.0-7.5 Clayey SILT with gravel (sandstone fragments), brown, damp, very stiff, homogeneous (colluvial soil) 1313.1	
9.0	S-6	9 9 10	1.5		0.5	ml / a-4	D	7.5-9.0 Clayey SILT, brown, damp, very stiff, homogeneous (colluvial soil) 1311.6	
10 – 10.5	S-7	5 6 10	1.5			cl / a-6	M-W	9.0-12.0 Silty CLAY with gravel (sandstone fragments), brown, moist to wet, very stiff, homogeneous (colluvial soil)	
12.0	S-8	13 12 11	1.5		1.0		W	1308.6	
12.5 – 13.5	S-9	6 13 13	1.5		1.0	ml / a-4	D	12.0-13.5 Clayey SILT with gravel (shale fragments), red brown, damp, very stiff, homogeneous (colluvial soil) 1307.1	
15.0	S-10	7 13 18	1.5		1.0	cl / a-6	M	13.5-18.0 Silty CLAY with gravel (sandstone fragments), brown and gray, moist to damp, hard, homogeneous (colluvial soil)	
15 – 16.5	S-11	1 15 23	1.5		1.0		M		
17.5	S-12	14 18	1.5		1.0		D		

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(6/95)

ENGINEERS FIELD BORING LOG

BORING NO. 7700-1
SHEET 2 **OF** 3

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
18.0		18						1302.6	
19.5	S-13	6 11 20	1.5		1.0	gc / a-2-6	D	18.0-21.0 Clayey GRAVEL (sandstone fragments) with sand, brown, damp, dense, homogeneous (colluvial soil)	
20 21.0	S-14	15 19 21	1.5		1.0		D	1299.6	
22.5	S-15	8 11 18	1.5		1.0	cl / a-6	M	21.0-24.0 Silty CLAY with gravel (sandstone fragments), brown, moist, very stiff to hard, homogeneous (colluvial soil)	
24.0	S-16	29 33 25	1.5		1.0		M	1296.6	
25 25.5	S-17	11 15 19	0.9			ml / a-4	W	24.0-26.5 Sandy clayey SILT with gravel (sandstone fragments), brown, wet, hard to very stiff, homogeneous (residual soil)	
27.0	S-18	10 12 29	1.2				W-D	1294.1	
27.5 28.2	S-19	30 30 50/0.2	1.2		2.5	gm / a-1-b	D	26.5-28.2 Silty GRAVEL (sandstone fragments) with sand, gray, damp, very dense, homogeneous (weathered bedrock)	
						T.O.R.		1292.4	
30 32.2	R-1	core	3.2	80 / 50				28.2-30.0 Carbonaceous SHALE, black, soft, slightly weathered, very thinly bedded (RD=0°), RQD= 0% 1290.6 30.0-36.6 LIMESTONE, gray, hard, fresh, indistinct bedding, RQD=58%	
32.5 35 37.2	R-2	core	3.7	74 / 48				Clayshale seam @ 33.7-34.3 1284.0 36.6-38.2 Fine to medium grained SANDSTONE, gray,	
37.5									

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ENGINEERS FIELD BORING LOG

BORING NO. 7700-1
SHEET 3 **OF** 3

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
38.2	R-3	core	0.9	90 / 40				medium, fresh, indistinct bedding, RQD=62% Sand seam @ 37.9-38.0 1282.4 38.2 Bottom of Hole	
40									
42.5									
45									
47.5									
50									
52.5									
55									
57.5									

FORM NO: D-481
(6/95)

ENGINEERS FIELD BORING LOG

BORING NO.	8150-1
SHEET	1 OF 2
DATE: START	10/29/03
O.G. END	10/29/03
ELEV.	1269.8

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** **SEGMENT:** **OFFSET:**
STATION: 81+50 **OFFSET FROM CENTERLINE:** 161' Lt.
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Mark Dziak/Test Boring Services, Inc.
EQUIPMENT USED: CME-55 (track mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 13.8 **WATER:** **DEPTH:** 3.4 **TIME:** 10:00 a.m. **DATE:** 10/29/03
CHECKED BY: PWH **DATE:** 11/3/03 **DEPTH:** 4.7 **TIME:** 3:00 p.m. **DATE:** 10/30/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0 – 1.5	S-1	3 3 3	0.5			ol / a-8; ml / a-4	D	0.0-0.9 ORGANIC SOIL, brown, damp (topsoil) 1268.9	
1.5 – 3.0	S-2	3 4 8	1.5		0.5	cl / a-6	M-W	0.9-1.5 Clayey SILT, brown, damp, medium, homogeneous (alluvial soil) 1268.3	
3.0 – 4.5	S-3	5 7 9	1.5			ml / a-4	D	1.5-3.0 Silty CLAY with gravel (sandstone fragments), brown, moist to wet, stiff, homogeneous (alluvial soil) 1266.8	Water level on 10/29/03 @ 3.4
4.5 – 6.0	S-4	10 16 27	1.5		1.0	ml / a-4	D	3.0-4.5 Sandy clayey SILT with gravel (sandstone fragments), tan, damp, very stiff, homogeneous (alluvial soil) 1265.3	Water level on 10/30/03 @ 4.7
6.0 – 7.5	S-5	11 11 16	1.5		1.5	cl / a-6	D	4.5-6.0 Clayey SILT, brown, damp, hard, homogeneous (colluvial soil) 1263.8	
7.5 – 9.0	S-6	13 13 13	1.5		1.5		D	6.0-9.0 Silty CLAY with gravel (sandstone fragments), brown, damp, very stiff, homogeneous (colluvial soil) 1260.8	
9.0 – 10.5	S-7	6 6 12	1.5		1.0	ml / a-4	D	9.0-11.0 Clayey SILT with gravel (shale fragments), brown, damp, very stiff, homogeneous (colluvial soil) 1258.8	
10.5 – 12.0	S-8	10 22 34	1.5		3.0	gm / a-4	D	11.0-13.8 Silty GRAVEL (shale fragments), brown, damp, dense to very dense, homogeneous (weathered bedrock) 1256.0	
12.0 – 13.5	S-9	9 13 29	1.5		3.0		D		
13.8	S-10	50/0.3	0.3				D		
13.8 – 16.3	R-1	core	2.5	100 / 36		T.O.R.		13.8-16.1 Calcareous CLAYSTONE, gray, soft to medium, slightly weathered, indistinct bedding, RQD=39% 1253.7	
16.3 – 17.5								16.1-18.2 Medium grained SANDSTONE, gray, medium, fresh, indistinct bedding, RQD=76%	

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ENGINEERS FIELD BORING LOG

BORING NO. 8150-1
SHEET 2 OF 2

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
								1251.6	
	R-2	core	4.7	94 / 78				18.2-18.9 Sandy shaly SILTSTONE, gray, soft to medium, slightly weathered, very thinly bedded (RD=0°), RQD=57% 1250.9	
20								18.9-20.7 Fine grained SANDSTONE, gray, medium, fresh, indistinct bedding, RQD=72% 1249.1	
21.3									
22.5	R-3	core	2.5	100 / 64				20.7-23.8 Silty SHALE, gray, soft to medium, slightly weathered, intensely laminated (RD=0°), RQD= 71% 1246.0	
23.8								23.8 Bottom of Hole	
25									
27.5									
30									
32.5									
35									
37.5									

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ENGINEERS FIELD BORING LOG

BORING NO.	8150-2
SHEET	1 OF 2
DATE: START	10/27/03
O.G. END	10/28/03
ELEV.	1310.3

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** **SEGMENT:** **OFFSET:**
STATION: 81+50 **OFFSET FROM CENTERLINE:** 75' Rt.
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Wayne Ewing/Test Boring Services,
EQUIPMENT USED: CME-45 (track mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 8.8 **WATER:** **DEPTH:** 7.5 **TIME:** 9:30 p.m. **DATE:** 10/28/03
CHECKED BY: PWH **DATE:** 10/29/03 **DEPTH:** 9.4 **TIME:** 12:30 p.m. **DATE:** 10/29/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0								0.0-0.8 ORGANIC SOIL, brown, damp (topsoil) 1309.5	
1.5	S-1	1 2 3	1.1			ol / a-8	D		
								0.8-3.0 Silty CLAY with gravel (sandstone fragments), brown, damp, medium, homogeneous (colluvial soil) 1307.3	
2.5 3.0	S-2	3 3 4	1.2		0.5	cl / a-6	D		
4.5	S-3	7 8 4	1.3		0.5	ml / a-4	D	3.0-4.5 Clayey SILT with sand, brown, damp, stiff, homogeneous (colluvial soil) 1305.8	
5 6.0	S-4	6 8 11	1.3		1.0	cl / a-6	D	4.5-8.0 Silty CLAY with gravel (sandstone fragments), brown, damp, very stiff, homogeneous (colluvial soil) 1302.3	Water level on 10/28/03 @ 7.5
7.5	S-5	4 8 10	1.5		1.0		D		
8.8	S-6	7 11 50/0.3	1.3			ml / a-4	D	8.0-8.8 Clayey SILT, gray, dry, hard, homogeneous (weathered bedrock) 1301.5	
10 10.8	R-1	core	2.0	100 / 20		T.O.R.		8.8-14.4 Fine to medium grained SANDSTONE, brown and gray, medium, fresh, indistinct bedding, RQD=45%	Water level on 10/29/03 @ 9.4
12.5 13.8	R-2	core	3.0	100 / 70					
15	R-3	core	5.0	100 / 30				14.4-16.9 Silty SHALE, brown, soft, slightly weathered, intensely laminated (RD=0°), RQD=0% 1293.4	
17.5								16.9-18.8	

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ENGINEERS FIELD BORING LOG

BORING NO. 8150-2
SHEET 2 OF 2

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
18.8								Medium grained SANDSTONE, gray, medium, fresh, indistinct bedding, RQD=79% 1291.5	
								18.8 Bottom of Hole	
20									
22.5									
25									
27.5									
30									
32.5									
35									
37.5									

FORM NO: D-481
(6/95)

ENGINEERS FIELD BORING LOG

BORING NO.	8600-1
SHEET	1 OF 3
DATE: START	10/28/03
O.G. END	10/28/03
ELEV.	1244.8

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** **SEGMENT:** **OFFSET:**
STATION: 86+00 **OFFSET FROM CENTERLINE:** 10' Lt.
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Wayne Ewing/Test Boring Services,
EQUIPMENT USED: CME-45 (track mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 29.4 **WATER:** **DEPTH:** 10.8 **TIME:** 1:00 p.m. **DATE:** 10/28/03
CHECKED BY: PWH **DATE:** 11/3/03 **DEPTH:** 11.3 **TIME:** 12:15 p.m. **DATE:** 10/29/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0								0.0-0.8 ORGANIC SOIL, brown, damp (topsoil) 1244.0	
1.5	S-1	3 4 4	1.2			ol / a-8	D	0.8-4.5 Clayey SILT, brown, damp, medium, homogeneous (alluvial soil)	
2.5 3.0	S-2	2 2 3	1.3			ml / a-4	D		
4.5	S-3	3 2 3	1.2				D	1240.3	
5 6.0	S-4	4 6 5	1.4		1.0		D	4.5-9.0 Silty CLAY with gravel (sandstone fragments), brown, damp, stiff to very stiff, homogeneous (colluvial soil)	
7.5	S-5	4 7 9	1.5		1.0	cl / a-6	D		
9.0	S-6	6 8 17	1.5		1.0		D	1235.8	
10 10.5	S-7	6 6 7	0.8			gm / a-1-b	D	9.0-10.5 Silty GRAVEL (sandstone fragments) with sand, brown, damp, medium dense, homogeneous (colluvial soil) 1234.3	
12.0	S-8	7 6 7	1.3			ml / a-4	D	10.5-12.0 Clayey SILT, brown, damp, stiff, homogeneous (colluvial soil) 1232.8	Water level on 10/28/03 @ 10.8 Water level on 10/29/03 @ 11.3
12.5 13.5	S-9	3 3 4	1.3		0.5		D	12.0-16.5 Clayey SILT with gravel (sandstone fragments), brown, damp, medium to stiff, homogeneous (colluvial soil)	
15.0	S-10	3 4 7	1.2		0.5	ml / a-4	D		
15 16.5	S-11	3 4 5	0.8		0.5		D	1228.3	
17.5	S-12	4 5	1.5			cl / —	D	16.5-18.0 Silty CLAY, brown, damp, stiff, homogeneous	

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ENGINEERS FIELD BORING LOG

BORING NO. 8600-1
SHEET 2 **OF** 3

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
18.0		7				a-6		(colluvial soil) 1226.8	
19.5	S-13	3 4 5	1.5		0.5	cl / a-6	M	18.0-22.5 Silty CLAY with gravel (sandstone fragments), brown, moist, stiff to hard, homogeneous (colluvial soil)	
20 21.0	S-14	4 4 7	1.5		0.5		M		
22.5	S-15	3 25 9	1.2		1.0		M	1222.3	
24.0	S-16	4 6 6	1.5			ml / a-4	D	22.5-24.0 Clayey SILT with gravel (sandstone fragments), gray, damp, stiff, homogeneous (colluvial soil) 1220.8	
25 25.5	S-17	3 4 4	1.2		0.5	cl / a-6	D-M	24.0-25.5 Silty CLAY with gravel (sandstone fragments), brown, damp to moist, medium, homogeneous (colluvial soil) 1219.3	
27.0	S-18	4 7 9	1.2		0.5	sc / a-2-6	W	25.5-28.5 Clayey SAND with gravel (sandstone fragments), gray, wet to moist, medium dense to dense, homogeneous (residual soil)	
27.5 28.5	S-19	12 16 16	1.5		1.0		M	1216.3	
29.4	S-20	24 50/0.4	0.9		2.5	gm / a-4	M	28.5-29.4 Silty GRAVEL (shale fragments), gray, moist, very dense, homogeneous (weathered bedrock) 1215.4	
30 31.4	R-1	core	2.0	100 / 70		T.O.R.		29.4-34.5 CLAYSTONE, gray, very soft to soft, slightly weathered, indistinct bedding, RQD=51%	
32.5 34.4	R-2	core	3.0	100 / 40				1210.3	
35 37.5	R-3	core	5.0	100 / 88				34.5-39.4 Sandy SILTSTONE, gray, medium, fresh, very thinly bedded (RD=0°), RQD=90%	

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(6/95)

ENGINEERS FIELD BORING LOG

BORING NO. 8600-1
SHEET 3 OF 3

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
39.4								1205.4	
								39.4 Bottom of Hole	
40									
42.5									
45									
47.5									
50									
52.5									
55									
57.5									

FORM NO: D-481
(6/95)

ENGINEERS FIELD BORING LOG

BORING NO.	9150-1
SHEET	1 OF 2
DATE: START	10/28/03
O.G. END	10/28/03
ELEV.	1193.6

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** _____ **SEGMENT:** _____ **OFFSET:** _____
STATION: 91+48 **OFFSET FROM CENTERLINE:** 7' Rt.
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Wayne Ewing/Test Boring Services,
EQUIPMENT USED: CME-45 (track mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 10.6 **WATER:** **DEPTH:** 3.1 **TIME:** 3:00 p.m. **DATE:** 10/28/03
CHECKED BY: PWH **DATE:** 11/3/03 **DEPTH:** 2.9 **TIME:** 12:00 p.m. **DATE:** 10/29/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0 – 1.5	S-1	1 / 1 / 3	1.0			ol / a-8	D	0.0-0.5 ORGANIC SOIL, brown, damp (topsoil) 1193.1	
1.5 – 3.0	S-2	1 / 3 / 2	1.4			ml / a-4	D	0.5-3.0 Clayey SILT, brown, damp, soft to medium, homogeneous (alluvial soil) 1190.6	
3.0 – 4.5	S-3	3 / 6 / 9	1.2		0.5	cl / a-6	D	3.0-4.5 Silty CLAY, brown, damp, very stiff, homogeneous (alluvial soil) 1189.1	Water level on 10/29/03 @ 2.9 Water level on 10/28/03 @ 3.1
4.5 – 6.0	S-4	6 / 9 / 10	1.3		1.0	cl / a-6	M	4.5-10.0 Silty CLAY with gravel (shale and sandstone fragments), brown, moist to wet, very stiff to medium, homogeneous (alluvial soil)	
6.0 – 7.5	S-5	3 / 5 / 8	1.3		0.5		M		
7.5 – 9.0	S-6	4 / 5 / 5	1.2		0.5		M-W		
9.0 – 10.5	S-7	2 / 3 / 32	1.5		1.0		M	1183.6	
10.5 – 10.6	S-8	50/0.1	0.1			cl / a-6	D	10.0-10.6 Silty CLAY with gravel (sandstone fragments), gray, moist to dry, hard, homogeneous (weathered bedrock) 1183.0	
10.6 – 12.6	R-1	core	1.0	50 / 30		T.O.R.		10.6-12.9 Calcareous fine grained SANDSTONE, gray, medium, slightly weathered, indistinct bedding, RQD=26% 1180.7	
12.6 – 15.6	R-2	core	3.0	100 / 70				12.9-14.5 CLAYSTONE, gray, very soft to soft, slightly weathered, indistinct bedding, RQD=63% 1179.1	
15.6 – 17.5								14.5-15.8 Shaly CLAYSTONE, gray, very soft to soft, slightly weathered, thinly bedded (RD=0°), RQD=85% 1177.8	

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ENGINEERS FIELD BORING LOG

BORING NO. 9150-1
SHEET 2 OF 2

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
	R-3	core	5.0	100 / 46				15.8-19.8 Shaly SILTSTONE, gray, soft to medium, fresh, intensely laminated (RD=0°), RQD=45% 1173.8	
20 20.6								19.8-20.6 CLAYSTONE, gray, very soft to soft, fresh, indistinct bedding, RQD=62% 1173.0	
								20.6 Bottom of Hole	
22.5									
25									
27.5									
30									
32.5									
35									
37.5									

FORM NO: D-481
(6/95)

ENGINEERS FIELD BORING LOG

BORING NO.	9650-1
SHEET	1 OF 2
DATE: START	10/16/03
O.G. END	10/16/03
ELEV.	1240.3

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** **SEGMENT:** **OFFSET:**
STATION: 96+43 **OFFSET FROM CENTERLINE:** 12' Rt.
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Todd Zilka/Test Boring Services, Inc.
EQUIPMENT USED: CME-55 (truck mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 13.6 **WATER:** **DEPTH:** 17.2 **TIME:** 12:30 p.m. **DATE:** 10/16/03
CHECKED BY: PWH **DATE:** 10/17/03 **DEPTH:** 18.2 **TIME:** 4:30 p.m. **DATE:** 10/21/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0									
1.5	S-1	3 4 4	0.6			gm / a-2-4	D	0.0-3.0 Silty GRAVEL (slag and limestone fragments) with sand, gray and brown, damp, loose to very dense, homogeneous (fill)	
2.5 2.7	S-2	8 10 50/0.2	1.2				D		
3.0		auger						1237.3	
4.5	S-3	43 12 9	1.5		1.5	cl / a-6	D	3.0-4.5 Silty CLAY with gravel (shale fragments), brown, damp, very stiff, homogeneous (fill) 1235.8	
5 6.0	S-4	6 7 15	1.5		1.0	ml / a-4	D	4.5-9.0 Clayey SILT, brown, damp to dry, very stiff to hard, homogeneous (colluvial soil)	
7.5	S-5	12 8 12	1.5				D		
9.0	S-6	30 26 29	1.5		1.0		D	1231.3	
10 10.5	S-7	7 5 12	1.5		0.5	cl / a-6	D	9.0-10.5 Silty CLAY, brown, damp, very stiff, homogeneous (colluvial soil) 1229.8	
12.0	S-8	5 6 18	1.5			ml / a-4	D	10.5-12.5 Clayey SILT, brown, damp, very stiff, homogeneous (residual soil) 1227.8	
12.5 12.8	S-9	7 50/0.3	0.8		1.5		D		
13.5		auger				gm / a-2-4		12.5-13.6 Silty GRAVEL (sandstone fragments) with sand, brown, dry, very dense, homogeneous (weathered bedrock) 1226.7	
13.6	S-10	50/0.1	0.1			T.O.R.	D		
15 15.6	R-1	core	1.3	65 / 20				13.6-20.1 Fine to medium grained SANDSTONE, brown, medium, slightly weathered, indistinct bedding, RQD=49%	
17.5	R-2	core	2.4	80 / 53					Water level on

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(6/95)

ENGINEERS FIELD BORING LOG

BORING NO. 9650-1
SHEET 2 OF 2

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
									10/16/03 @ 17.2 Water level on 10/21/03 @ 18.2
18.6									
	R-3	core	4.5	90 / 64				Soft @ 19.2-20.1 1220.2 20.1-22.9 CLAYSHALE, brown to gray, soft, slightly weathered, thinly bedded (RD=0°), RQD=54% 1217.4 22.9-23.6 Sandy SILTSTONE, gray, soft to medium, fresh, intensely laminated (RD=0°), RQD=57% 1216.7 23.6 Bottom of Hole	
23.6									

20
22.5
25
27.5
30
32.5
35
37.5

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(6/95)

ENGINEERS FIELD BORING LOG

BORING NO.	10200-1
SHEET	1 OF 1
DATE: START	10/16/03
O.G. END	10/16/03
ELEV.	1234.5

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** **SEGMENT:** **OFFSET:**
STATION: 101+91 **OFFSET FROM CENTERLINE:** 13' Rt.
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Todd Zilka/Test Boring Services, Inc.
EQUIPMENT USED: CME-55 (truck mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 5.5 **WATER: DEPTH:** 3.4 **TIME:** 2:00 p.m. **DATE:** 10/16/03
CHECKED BY: PWH **DATE:** 10/17/03 **DEPTH:** 11.0 **TIME:** 1:30 p.m. **DATE:** 10/24/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0									
1.5	S-1	3 5 5	0.7			gm / a-2-4	D	0.0-2.5 Silty GRAVEL (slag and limestone fragments) with sand, gray, damp, loose to medium dense, homogeneous (fill) 1232.0	
2.5 3.0	S-2	8 6 17	0.5				D		
3.9	S-3	22 50/0.4	0.9			gm / a-4	D	2.5-5.5 Silty GRAVEL (shale fragments), brown, dry, dense to very dense, homogeneous (weathered bedrock)	Water level on 10/16/03 @ 3.4
4.5		auger							
5 5.5	S-4	22 50	1.0				D	1229.0	
7.5	R-1	core	2.0	100 / 55		T.O.R.		5.5-10.5 Silty CLAYSHALE, gray to black, very soft, slightly weathered, thinly bedded (RD=0°), RQD=62% Limestone seam @ 6.9-7.1	
10 10.5	R-2	core	2.4	80 / 70				1224.0	
12.5 15 15.5	R-3	core	5.0	100 / 94				10.5-15.5 Sandy LIMESTONE, gray and brown, hard, slightly weathered, indistinct bedding, RQD=94% Claystone seam @ 12.3-12.7 1219.0	Water level on 10/24/03 @ 11.0 Fracture @ 13.7-14.1 (RD=90°)
17.5								15.5 Bottom of Hole	

FORM NO: D-481
(6/95)

ENGINEERS FIELD BORING LOG

BORING NO.	10800-1
SHEET	1 OF 2
DATE: START	10/16/03
O.G. END	10/16/03
ELEV.	1225.4

PROJECT NAME: S.R. 4009 Relocation on Consol Property **COUNTY** Greene
STATE RT. NO.: 4009 **SECT.:** **SEGMENT:** **OFFSET:**
STATION: 107+86 **OFFSET FROM CENTERLINE:** 5' Rt.
INSPECTOR (SIGNED): David Walters/Earth, Inc. **DRILLERS NAME/COMPANY:** Todd Zilka/Test Boring Services, Inc.
EQUIPMENT USED: CME-55 (truck mount)
DRILLING METHODS: SPT/HSA/NQ2
CASING SIZE: - **DEPTH:** 3.1 **WATER:** **DEPTH:** 7.9 **TIME:** 3:00 p.m. **DATE:** 10/16/03
CHECKED BY: PWH **DATE:** 10/20/03 **DEPTH:** 9.7 **TIME:** 1:45 p.m. **DATE:** 10/24/03
NOT ENCOUNTERED ☐

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
0 – 1.5	S-1	5 6 7	1.5			gm / a-1-b	D	0.0-1.0 Silty GRAVEL (limestone fragments) with sand, gray, damp, medium dense, homogeneous (fill) 1224.4	
1.5 – 2.7	S-2	11 22 50/0.2	1.2		0.5	ml / a-4	D	1.0-2.0 Clayey SILT, brown, damp, stiff to very stiff, homogeneous (fill) 1223.4	
2.7 – 3.0		auger				gm / a-4			
3.0 – 3.1	S-3	50/0.1	0.1			gm / a-4	D	2.0-3.0 Silty GRAVEL (shale fragments), brown, dry, very dense, homogeneous (weathered bedrock) 1222.4	
3.1 – 5.1	R-1	core	2.0	100 / 90		T.O.R.		3.0-3.1 Silty GRAVEL (limestone fragments) with sand, gray, dry, very dense, homogeneous (weathered bedrock) 1222.3	
5.1 – 8.1	R-2	core	3.0	100 / 53				3.1-3.3 LIMESTONE, gray, hard, moderately weathered, indistinct bedding, RQD=0% 1222.1	Water level on 10/16/03 @ 7.9
8.1 – 13.1	R-3	core	5.0	100 / 50				3.3-6.5 CLAYSHALE, brown and gray, soft, slightly weathered, thinly bedded (RD=0°), RQD=69% 1218.9	Water level on 10/24/03 @ 9.7
								6.5-8.4 Fine to medium grained SANDSTONE, brown, medium, fresh, indistinct bedding, RQD=63% 1217.0	
								8.4-10.9 Sandy LIMESTONE, gray and brown, hard, fresh, indistinct bedding, RQD=100% 1214.5	
13.1 – 17.5	R-4	core	3.3	66 / 0				10.9-18.1 CLAYSTONE, brown, very soft to soft, slightly weathered, indistinct bedding, RQD=0% Limestone seam @ 11.7-12.2	

0 2.5 5 7.5 10 12.5 15 17.5

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(6/95)

ENGINEERS FIELD BORING LOG

BORING NO. 10800-1
SHEET 2 OF 2

DEPTH (ft)	SAMPLE NO. AND TYPE/CORE RUN	BLOWS/0.5 ft ON SAMPLER	RECOVERY LGTH. (ft)	RECOVERY (%) / RQD (%)	POCKET PENET (tsf)	USCS / AASHTO	H_2O CONTENT	DESCRIPTION	REMARKS
18.1								1207.3	
								18.1 Bottom of Hole	
20									
22.5									
25									
27.5									
30									
32.5									
35									
37.5									

BIOLOGICAL EVALUATIONS OF ALIGNMENTS FOR THE RELOCATION OF SR4009 BAILEY REFUSE AREA GREENE COUNTY, PENNSYLVANIA

Prepared for

CME Engineering, Inc.
Somerset, Pennsylvania

by

Pike Environmental Consulting
Waynesburg, Pennsylvania

March 2004

INTRODUCTION

The original purpose of this evaluation was to determine if the preferred alignment (designated Alignment 4) for a relocation of State Route 4009, necessitated by development of a new refuse disposal area and slurry impoundment at the Bailey Mine, would impact jurisdictional wetlands. After an onsite meeting, personnel from the Pennsylvania Fish and Boat Commission requested that the evaluation be expanded to include a quantitative and qualitative assessment of the macroinvertebrate populations of an unnamed tributary to Enlow Fork and the headwaters of Grinnage Run that could be impacted by the road relocation. An additional meeting with representatives of several state and federal agencies further expanded the evaluation to include surveys for jurisdictional wetlands along a route designated Alignment 4A. Assessments of macroinvertebrate populations in three unnamed tributaries to Enlow Fork that would be impacted by Alignment 1 and one unnamed tributary to Enlow Fork that would be impacted by Alignment 7 were also added to the evaluation.

METHODS

CME Engineering surveyed and staked the "limits of disturbance" of proposed road Alignment 4, except for a short section where access on private land had been denied. Within this corridor, areas that met the criteria for jurisdictional wetlands, as contained in the US Army Corps of Engineers 1987 Wetlands Delineation Manual, were identified on November 21/22, 2003. Blue Mountain Engineering of Burton, West Virginia surveyed locations of the jurisdictional wetlands for placement on construction plan maps and to determine acreages for the identified wetlands. On February 19, 2004, the additional alignments were surveyed for the presence of jurisdictional wetlands. Routine Wetland Determination Sheets were completed for each identified jurisdictional wetland and are presented in Appendix A of this report.

Neither of the streams that would be impacted by Alignment 4 (for which the Pennsylvania Fish and Boat Commission requested biological information) was large

enough to quantitatively sample using a square-foot Surber sampler. Therefore, semi-quantitative samples were collected by placing a D-frame kicknet in the steam and kicking an area upstream of the net for a period long enough, in the investigator's opinion, to dislodge benthic organisms in approximately one square-foot of substrate. Three such samples were collected in both the Grinnage Run headwaters and the unnamed tributary to Enlow Fork. Qualitative samples were also collected with the D-frame net in areas not sampled quantitatively and by handpicking of specimens from larger rocks, leaf-packs, etc. To be consistent, the additional streams that would be impacted by Alignments 1 and 7 were sampled using the same methods. All samples were preserved with a formaldehyde solution and returned to the lab where specimens were separated from sample debris. The collected specimens were identified to the lowest practicable taxon with the aid of taxonomic keys contained in Merritt and Cummins, 1996; Peckarsky, et al, 1990; Stewart and Stark, 1993 and Pennak, 1989.

The resulting data were used to generate several common population metrics for the aquatic macroinvertebrate communities. The number of taxa present, often referred to as "community richness", is simply a count of the number of taxa present in the sample. Organisms per square-foot is the total number of individuals collected in the square-foot sample. The EPT Index is a count of the number of taxa of organisms from the insect orders Ephemeroptera, Plecoptera and Trichoptera (mayflies, stoneflies and caddisflies respectively) that were in the sample. Members of these orders are often considered indicators of "good" stream conditions.

The Shannon-Weaver Index is one of the most commonly used diversity indices employed when random sampling (in this case Surber sampling) of a community is conducted. The Shannon-Weaver Function (H') taken from Schemnitz (1980) is derived from the formula:

$$H' = -\sum_{i=1}^{S} p_i \log p_i$$

Where S is the number of species, and p_i is the proportion of the number of

individuals consisting of the *i*th species. The logarithmic base is arbitrary.

Redundancy (r) is a measurement of the dominance of one or more taxa in a community, r is inversely proportional to the variety of taxa. It is calculated as:

$$r = \frac{H'\max - H'}{H'\max - H'\min}$$

The theoretical maximum and minimum diversities, H′max and H′min, are calculated as:

$$H'\max = \frac{\log_2 n! - s\log_2 \frac{n}{s}!}{n}$$

$$H'\min = \frac{\log_2 n! - \log_2 (n+s+1)!}{n}$$

The Equitability Index is a measurement of the evenness with which individuals are divided among the taxa present. The Equitability Index (J′) is derived as:

$$J' = \frac{H'}{H'\max}$$

These community metrics were prepared for each Surber replicate sample. In addition, for each station the data from the three Surber replicate samples were pooled to obtain the average number of specimens per square-foot, the EPT taxa present, and to calculate Redundancy, Shannon-Weaver and Equitability Indices.

RESULTS

Wetland surveys conducted November 21 and 22, 2004 identified eleven jurisdictional wetlands within the disturbance area of Alignment 4. There were seven jurisdictional wetlands in the watershed of the unnamed tributary to Enlow Fork. They ranged in size from 0.002 to 0.244 acres and totaled 0.487 acres in the proposed disturbance area of the watershed. In the headwaters of Grinnage Run four jurisdictional wetlands were

identified within the proposed disturbance area. They ranged in size from 0.014 to 0.181 acres with a total of 0.244 acres within the proposed disturbance area. All the identified jurisdictional wetlands were in areas currently used to pasture cattle and most had been impacted from grazing and trampling by cattle. Two days before the site visit a storm with reported local rain falls of nearly 4 inches had occurred. Therefore, the reported hydrologic conditions are probably not what would normally be encountered in late November.

Wetland surveys for Alignments 1, 5, and 7 were conducted on February 19, 2004. Alignment 5 is located nearly on the ridge top to the northwest of the unnamed tributary where Alignment 4 would be located. Five wetlands were identified in the Alignment 5 corridor upslope of Alignment 4. They ranged in size from 0.007 to 0.196 acres totaling approximately 0.41 acres. Nearly all the springs and seeps supplying these wetlands originated at about the same elevation on the hillside. In the Grinnage Run headwaters Alignment 4A is moved slightly upslope to avoid the wetlands that would be impacted by Alignment 4.

Alignment 1 would connect SR4009 and Stringtown Road by paralleling to the southwest the existing railroad right-of-way. In addition to the unnamed tributary considered above, this alignment would impact three other unnamed tributaries to Enlow Fork, designated Tributaries "A", "B" and "C" located between the Alignment 4/4A unnamed tributary and Stringtown Road. Wetland and macroinvertebrate surveys on this alignment where limited to property within the railroad right-of-way. Because there was essentially no undisturbed land between the toe of the embankment supporting the rail bed and adjacent private property, no mapping of wetlands was prepared for Tributaries "A", "B" and "C". Tributary "B" upstream of the railroad right-of-way contains a suspected jurisdictional wetland that could be impacted if Alignment 1 were built.

Alignment 7 is an upgrade of Crouse Road between SR4009 and Stringtown Road. A portion of this alignment would encroach on the unnamed tributary to Enlow Fork that flows adjacent to Crouse Road. There appear to be riparian wetlands scattered along the

unnamed tributary. Since the stream was on private property, no formal wetland delineations were made at this time, but it could be assumed construction of this alignment would impact jurisdictional wetlands.

Results of the aquatic macroinvertebrate surveys conducted for Alignment 4 are contained in Tables 1 and 2. As stated above, there had been heavy rains prior to sample collection. The stream channel of the unnamed tributary had been greatly impacted by this storm, with even larger size substrate materials having been redistributed within the channel. Because of this the number of taxa (34) and individuals collected was a bit surprising (Table 1). In the headwater area of Grinnage Run there were few taxa represented with numbers of individuals also quite low (Table 2). It appeared that the upper section of the watershed would normally have been dry, or at least had very low flows, during the late fall. The stream channel in the location where samples were collected did not show as much disturbance of substrate materials as had been seen in the unnamed tributary to Enlow Fork. This was probably because the site was so high in the watershed that water volumes were not sufficient, even with the high rainfall, to greatly disturb the substrates.

Macroinvertebrates collected from Unnamed Tributaries "A", "B" and "C" on Alignment 1 are contained in Tables 3, 4 and 5 respectively. Tributary A, which does not appear on USGS topographic maps, drains a very small watershed. Flow at the culvert conducting this tributary under the railroad right-of-way was very low on February 19 and it appears this tributary is probably dry a large portion of the year. Even under these conditions, 22 aquatic macroinvertebrate taxa were collected in the quantitative and qualitative samples (Table 3). Tributaries "B" and "C" appear on USGS topographic maps as intermittent streams. On February 19 these streams had relatively high flows, but probably do go dry during many years. Quantitative and qualitative sampling produced 37 taxa from Tributary "B" and 38 taxa from Tributary "C" (Tables 4 and 5, respectively).

The unnamed tributary that flows adjacent to Crouse Road, which would be upgraded by Alignment 7, is mostly on private property. The upper section of this tributary near

where a driveway from Crouse Road crosses the railroad to a private residence was sampled. Thirty-one taxa were collected in the quantitative and qualitative samples. Again, it appears this stream probably goes dry during many years.

The population metrics derived from the macroinvertebrate data are contained in Tables 7 through 12. The metrics for the Alignment 4 unnamed tributary macroinvertebrate community (Table 7) are within the range of those typically found in small streams in the late fall. Because of the low numbers of organisms found in the headwater sample from Grinnage Run, the population metrics generated from those samples (Table 8) are rather meaningless.

Population metrics for the three unnamed tributaries (in addition to the unnamed Alignment 4 tributary) that would be impacted by construction of Alignment 1 are presented in Tables 9 through 11. Tributary "A", which probably contains water for only short periods during most years, had relatively low diversity metrics (Table 9). The other two unnamed tributaries (Tributaries "B" and "C") had Shannon-Weaver indices slightly higher (Tables 10 and 11, respectively) than those reported for the unnamed tributary that would be impacted by construction of Alignment 4 (Table 7). The unnamed tributary that parallels Crouse Road (Alignment 7) had a moderately diverse macroinvertebrate population (Table 12).

Fish were not expected in any of the streams investigated and specific sampling for fish was therefore not conducted. However, two blacknose dace (*Rhinichthys atratulus)* were caught incidentally in one macroinvertebrate sample from unnamed tributary "C", the stream that flows parallel to Stringtown Road. Pennsylvania Fish and Boat Commission representatives during their initial site visit did want to know if fish migration from Enlow Fork was impeded in any way by a culvert that carried the unnamed tributary on Alignment 4 under the railroad grade in the lower portion of the watershed. The culvert appeared to be placed such that fish would not be prevented from entering the culvert, but there was a rather steep gradient in the stream channel section between the culvert and Enlow Fork.

Appendix B contains photographs of the identified jurisdictional wetlands, the stream sampling sites and the downstream end of the culvert carrying the unnamed tributary to Enlow Fork on Alignment 4 under the railroad grade.

CONCLUSIONS

The jurisdictional wetlands identified within the disturbance areas of the various road alignments were typical of wetlands in the southwestern Pennsylvania. Several of these wetlands were below hillside seeps. Others were riparian wetlands, especially in the watershed of the unnamed tributary to Enlow Fork on Alignment 4. All the wetlands have been impacted from cattle grazing.

Aquatic macroinvertebrate populations were diverse and relatively numerous in all but the headwater area of Grinnage Run and unnamed tributary "A" on Alignment 1. Both of these collecting points were in stream sections that would be expected to go dry during most years.

Road Alignment 4, the preferred alignment for replacement of SR 4009, would impact approximately 0.487 acres of jurisdictional wetlands in the watershed of the unnamed tributary and approximately 0.244 acres in the headwaters of Grinnage Run. Construction of this alignment would impact the macroinvertebrate community of the unnamed tributary by removal of habitat. Of the aquatic communities investigated in this survey, the macroinvertebrate community of this unnamed tributary was about average in diversity. According to the owner of the property containing this unnamed tributary, the stream goes dry nearly every year. Weather during 2003 was exceptionally wet and probably allowed a macroinvertebrate community not seen in most years to become established. Indeed, sampling of this stream produced mostly early instars of insects, suggesting that the population had not been established on a long term basis.

Road Alignment 5 would impact approximately 0.376 acres of jurisdictional wetlands in the unnamed tributary watershed directly. However, this road alignment would probably intercept, and possibly eliminate, the water sources supplying all the wetlands identified in the watershed (approximately 0.863 acres). In addition, this alignment could eliminate a significant amount of the ground water supplying flow in the unnamed tributary.

Alignment 1 would require enclosing portions of four unnamed tributaries to Enlow Fork. Two of these tributaries (Tributaries "B" and "C") had more diverse macroinvertebrate populations than the unnamed tributary that would be impacted by Alignment 4. Unnamed tributary "C" did have fish present. Although not delineated because of there locations on private property, at least one, and possibly two, jurisdictional wetlands would be encroached upon by construction of this alignment.

The upgrade of Crouse Road (Alignment 7) would impact a much larger unnamed tributary to Enlow Fork. Sampling in the headwaters of this tributary showed macroinvertebrate populations with higher diversities than those in the unnamed tributary on Alignment 4, and would be expected to increase in diversity further downstream. It would also be expected that fish are present in this stream. Construction of this alignment would require encroachment on the riparian area of the unnamed tributary and would most likely impact wetlands.

REFERENCES

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Table 1. Macroinvertebrates Collected From An Unnamed Tributary to Enlow Fork On The Bailey Refuse Road Relocation Alignment 4, Greene County, Pennsylvania December 8, 2003

Taxa	REP 1	REP 2	REP 3	Combined	Qualitative
Turbellaria					
Hymanella		2	1	3	
Phagocata	7	1	1	9	X
Oligochaeta					
Enchytraeidae	2			2	X
Lumbriculidae		1		1	
Naididae	9	1	8	18	
Gastropoda					
Physella					X
Bivalvia					
Pisidium	1			1	
Sphaerium					X
Ephemeroptera					
Acerpenna		2		2	
Leptophlebia	3		3	6	X
Procloeon	2		4	6	X
Plecoptera					
Allocapnia		1		1	
Nemoura	3		1	4	
Trichoptera					
Ironoquia	2	9	2	13	X
Madeophylax	2	1	3	6	
Neophylax					X
Potamyia	9		6	15	X
Ptilostomis	1			1	X
Wormaldia		1		1	X
Coleoptera					
Agabus					X
Helophorus		1		1	
Hydroporus					X
Laccobius		1		1	X
Laccophilus					X
Tropisternus			1	1	

Table 1. Macroinvertebrates Collected From An Unnamed Tributary to Enlow Fork On The Bailey Refuse Road Relocation Alignment 4, Greene County, Pennsylvania December 8, 2003 (continued)

Taxa	REP 1	REP 2	REP 3	Combined	Qualitative
Diptera					
Bezzia			4	4	
Chironomidae	57	17	38	112	X
Chrysops			1	1	
Culicoides			1	1	
Pedicia	1	1	3	5	
Pseudoloimnophila	3		11	14	
Tipula	3	4	1	8	X
Isopoda					
Caecidotea			1	1	
Amphipoda					
Crangonyx					X
Total Taxa	15	14	18	27	18
Total Specimens	105	43	90	238	NA

Table 2. Macroinvertebrates Collected From The Headwaters Of Grinnage Run On The Bailey Refuse Road Relocation Alignment 4, Greene County, Pennsylvania December 8, 2003

Taxa	REP 1	REP 2	REP 3	Combined	Qualitative
Oligochaeta					
Enchytraeidae	1			1	
Lumbriculidae	2		1	3	
Trichoptera					
Pycnopsyche		1		1	
Coleoptera					
Tropisternus					X
Diptera					
Chironomidae	2	3	2	7	
Dixa			1	1	
Pseudolimnophila		1		1	
Simuliidae		1		1	
Tipula					X
Total Taxa	3	4	3	7	2
Total Specimens	5	6	4	15	NA

Table 3. Macroinvertebrates Collected From Unnamed Tributary "A" to Enlow Fork On The Bailey Refuse Road Relocation Alignment 1, Greene County, Pennsylvania February 19, 2004

Taxa	REP 1	REP 2	REP 3	Combined	Qualitative
Turbellaria					
Phagocata		2	1	7	X
Oligochaeta					
Enchytraeidae		1		1	
Lumbriculidae	1	1	1	3	
Tubificidae			1	1	
Ephemeroptera					
Leptophlebia	4	3		7	X
Plecoptera					
Soyedina	2		5	7	X
Trichoptera					
Cheumatopsyche		1		1	
Ironoquia			1	1	X
Neophylax	2	1	11	12	X
Pycnopsyche		1		1	X
Rhyacophila			1	1	
Coleoptera					
Laccobius					X
Diptera					
Chironomidae	10	8	45	63	X
Ceratopogon					X
Dasyhelea	1			1	
Dicranota		1		1	
Hexatoma			1	1	
Pedicia	1	2		3	
Pseudolimnophila		1	1	2	
Serromyia			1	1	
Simuliidae	1	2	1	4	X
Tipula		1		1	
Total Taxa	8	13	12	20	10
Total Specimens	22	25	70	119	NA

Table 4. Macroinvertebrates Collected From Unnamed Tributary "B" to Enlow Fork On The Bailey Refuse Road Relocation Alignment 1, Greene County, Pennsylvania February 19, 2004

Taxa	REP 1	REP 2	REP 3	Combined	Qualitative
Turbellaria					
Phagocata	3	1		4	
Oligochaeta					
Enchytraeidae	2			2	
Gastropoda					
Fossaria					X
Physella	1			1	
Bivalvia					
Pisidium	13		4	17	X
Ephemeroptera					
Acerpenna	1			1	
Leptophlebia					X
Paraleptophlebia		1		1	
Stenacron		2		2	
Stenonema					X
Odonata					
Cordulegaster					X
Plecoptera					
Amphinemura	2			2	
Diploperla	1	1	1	3	X
Isoperla	31	4	5	40	X
Paraleuctra	1	2	2	5	
Soyedina					X
Trichoptera					
Cheumatopsyche	34	8	15	57	X
Chimarra	1		8	9	X
Ironoquia	1		1	2	
Neophylax	8	4	4	16	X
Ptilostomis	1			1	X
Pycnopsyche	2			2	X
Rhyacophila	1	3	2	6	X

Table 4. Macroinvertebrates Collected From Unnamed Tributary "B" to Enlow Fork On The Bailey Refuse Road Relocation Alignment 1, Greene County, Pennsylvania February 19, 2004 (continued)

Taxa	REP 1	REP 2	REP 3	Combined	Qualitative
Lepidoptera					
Crambus	1			1	
Coleoptera					
Anchytarsus	23		3	26	X
Dubiraphia	1	1	1	3	
Optioservus	6			6	X
Stenelmis	6	2		8	
Diptera					
Chironomidae	111	15	19	145	X
Chrysops	1			1	
Dixella		1		1	
Hexatoma			1	1	
Pseudolimnophila	24	4		28	X
Simuliidae	4		9	13	X
Tipula	2	2	2	6	X
Isopoda					
Caecidotea		1		1	
ecapoda					
Cambarus juvenile		3	1	4	
Total Taxa	26	17	16	32	20
Total Specimens	282	55	78	415	NA

Table 5. Macroinvertebrates Collected From Unnamed Tributary "C" to Enlow Fork On The Bailey Refuse Road Relocation Alignment 1, Greene County, Pennsylvania February 19, 2004

Taxa	REP 1	REP 2	REP 3	Combined	Qualitative
Turbellaria					
Phagocata	1	3	2	6	
Oligochaeta					
Lumbriculidae			3	3	
Gastopoda					
Gyraulus		1		1	
Ephemeroptera					
Ameletus		1		1	
Eurylophella	2		6	8	X
Leptophlebia					X
Paraleptophlebia	3		1	4	X
Stenacron					X
Stenonema					X
Odonata					
Cordulegaster					X
Plecoptera					
Amphinemura		1		1	X
Clioperla	3	4	3	10	X
Diploperla	3	5	2	10	X
Isoperla	9	1	3	13	
Leuctra	2	3	1	6	
Paraleuctra	7	3	3	13	X
Peltoperla		4	1	5	
Soyedina	4		2	6	
Hemiptera					
Aquarius					X
Microvelia					X
Trichoptera					
Cheumatopsyche	38	49	26	113	X
Chimarra	2			2	
Neophylax	2	4	4	10	X
Pycnopsyche			1	1	X
Wormaldia		3		3	

Table 5. Macroinvertebrates Collected From Unnamed Tributary "C" to Enlow Fork On The Bailey Refuse Road Relocation Alignment 1, Greene County, Pennsylvania February 19, 2004 (continued)

Taxa	REP 1	REP 2	REP 3	Combined	Qualitative
Coleoptera					
Helichus	1			1	
Laccobius			1	1	
Optioservus			1	1	
Stenelmis			4	4	
Tropistrenus	1			1	
Diptera					
Chironomidae	17	40	56	113	X
Chrysops			1	1	
Dicranota	1			1	
Pseudolimnophila	5		2	7	
Simuliidae	3	7	3	13	X
Tipula		2	1	3	X
Amphipoda					
Crangonyx	1		1	2	X
Decapoda					
Cambarus juvenile	1		1	2	
Total Taxa	20	16	24	32	19
Total Specimens	106	131	129	366	NA

Table 6. Macroinvertebrates Collected From An Unnamed Tributary to Enlow Fork On The Bailey Refuse Road Relocation Alignment 7, Greene County, Pennsylvania February 19, 2004

Taxa	REP 1	REP 2	REP 3	Combined	Qualitative
Turbellaria					
Phagocata	13	9	34	56	X
Oligochaeta					
Enchytraeidae			1	1	
Lumbriculidae	3	3		6	X
Gastropoda					
Physella		1			
Stagnicola			1	1	
Bivalvia					
Pisidium	1			1	
Ephemeroptera					
Ameletus	3	3	3	9	X
Leptophlebia	1	7	2	10	X
Paraleptophlebia	15	13	1	29	X
Plecoptera					
Diploperla	2			2	X
Isoperla			2	2	X
Leuctra					X
Soyedina	1		2	3	X
Sweltsa	1			1	
Trichoptera					
Cheumatopsyche	4	7	21	32	X
Ironoquia		1		1	
Mystacides		2		2	
Neophylax		1	3	4	X
Pycnopsyche	3	6	1	10	
Rhyacophila	1	1	3	5	X

Table 6. Macroinvertebrates Collected From An Unnamed Tributary to Enlow Fork On The Bailey Refuse Road Relocation Alignment 7, Greene County, Pennsylvania February 19, 2004 (continued)

Taxa	REP 1	REP 2	REP 3	Combined	Qualitative
Coleoptera					
Dubiraphia	1			1	
Hydrobius					X
Hydroporus	3			3	
Tropisternus		1		1	
Diptera					
Bezzia			1	1	
Chironomidae	2	4	3	9	X
Dicranota	2	2	10	14	X
Pseudolomnophila	1			1	
Simuliidae	1	1		2	
Tipula	1			1	X
Amphipoda					
Crangonyx	2	5		7	X
Total Taxa	20	17	15	28	17
Total Specimens	61	67	88	215	NA

Table 7. Population Metrics For Macroinvertebrates Collected From An Unnamed Tributary To Enlow Fork On The Bailey Refuse Road Relocation Alignment 4, Greene County, Pennsylvania December 8, 2003

Metric	REP 1	REP 2	REP 3	Combined
Total Taxa	15	14	18	27
Organisms/square-foot	105	43	90	79.3
EPT Index	7	5	6	10
Shannon-Weaver Index	2.560	2.868	3.056	3.135
Redundancy	0.2723	0.1624	0.2000	0.2846
Equitability	0.6552	0.7533	0.7328	0.6593

Table 8. Population Metrics For Macroinvertebrates Collected From The Headwaters Of Grinnage Run On The Bailey Refuse Road Relocation Alignment 4, Greene County, Pennsylvania December 8, 2003

Metric	REP 1	REP 2	REP 3	Combined
Total Taxa	3	4	3	7
Organisms/square-foot	5	6	4	5
EPT Index	0	1	0	1
Shannon-Weaver Index	1.522	1.792	1.500	2.280
Redundancy	0.0162	0.0449	0.0199	0.1037
Equitability	0.9602	0.8960	0.9464	0.8122

Table 9. Population Metrics For Macroinvertebrates Collected From Unnamed Tributary "A" To Enlow Fork On The Bailey Refuse Road Relocation Alignment 1, Greene County, Pennsylvania February 19, 2004

Metric	REP 1	REP 2	REP 3	Combined
Total Taxa	8	13	12	20
Organisms/square-foot	22	25	70	39.7
EPT Index	3	4	4	7
Shannon-Weaver Index	2.404	3.254	1.889	2.710
Redundancy	0.1206	0.0687	0.3571	0.2900
Equitability	0.8013	0.8794	0.5269	0.6270

Table 10. Population Metrics For Macroinvertebrates Collected From Unnamed Tributary "B" To Enlow Fork On The Bailey Refuse Road Relocation Alignment 1, Greene County, Pennsylvania February 19, 2004

Metric	REP 1	REP 2	REP 3	Combined
Total Taxa	26	17	19	32
Organisms/square-foot	282	55	78	138.3
EPT Index	12	8	8	14
Shannon-Weaver Index	3.109	3.525	3.334	3.466
Redundancy	0.2901	0.0930	0.1232	0.2694
Equitability	0.6615	0.8625	0.8335	0.6932

Table 11. Population Metrics For Macroinvertebrates Collected From Unnamed Tributary "C" To Enlow Fork On The Bailey Refuse Road Relocation Alignment 1, Greene County, Pennsylvania February 19, 2004

Metric	REP 1	REP 2	REP 3	Combined
Total Taxa	20	16	24	32
Organisms/square-foot	106	131	129	122
EPT Index	11	11	12	16
Shannon-Weaver Index	3.297	2.726	3.052	3.248
Redundancy	0.1804	0.2587	0.2567	0.3034
Equitability	0.7628	0.6815	0.6656	0.6496

Table 12. Population Metrics For Macroinvertebrates Collected From An Unnamed Tributary To Enlow Fork On The Bailey Refuse Road Relocation Alignment 7, Greene County, Pennsylvania February 19, 2004

Metric	REP 1	REP 2	REP 3	Combined
Total Taxa	20	17	15	28
Organisms/square-foot	61	67	88	71.7
EPT Index	9	9	9	13
Shannon-Weaver Index	3.607	3.610	2.784	3.678
Redundancy	0.1109	0.0828	0.2200	0.1926
Equitability	0.8346	0.8833	0.7126	0.7651

APPENDIX A

ROUTINE WETLAND DETERMINATION FORMS FOR JURISDICTIONAL WETLANDS IDENTIFIED WITHIN THE ALIGNMENTS FOR THE RELOCATION OF SR 4009 BAILEY REFUSE AREA

DATA FORM
ROUTINE WETLAND DETERMINATION
(1987 COE Wetland Delineation Manual)

Project/Site:	Bailey Road Relocation	**Date:**	11/21/03
Applicant/Owner:	Consol Pennsylvania Coal Company	**County:**	Greene
Investigator(s):	D E Pike	**State:**	PA

Do normal circumstances exist on the site?	Yes X	No	**Community ID:**
Is the site significantly disturbed (Atypical?)	Yes	No X	Wetland 1
Is the area a potential problem area?	Yes	No X	**Plot ID:**
(if needed, explain on reverse.)			

VEGETATION

	Dominant Plant Species:	Stratum:	Indicator:		Dominant Plant Species:	Stratum:	Indicator:
1.	*Carex frankii*	Herb	OBL	11.			
2.	*Cyperus strigosus*	Herb	FACW	12.			
3.	*Juncus effusus*	Herb	FACW+	13.			
4.	*Epilobium coloratum*	Herb	OBL	14.			
5.	*Eupatorium perfoliatum*	Herb	FACW+	15.			
6.	*Dipsacus sylvestris*	Herb	N	16.			
7.	*Agrimonia parviflora*	Herb	FAC	17.			
8.				18.			
9.				19.			
10.				20.			

Percent of Dominant Species that are OBL, FACW or FAC (excluding FAC-)	86%

Remarks:

The area delineated was within the "limits of disturbance" of the proposed project. The wetland extended upslope.

HYDROLOGY

____ Recorded Data (Describe in Remarks)	**Wetland Hydrology Indicators:**
____ Stream, Lake, or Tide Gauge	Primary Indicators:
____ Aerial Photographs	X Inundated
X No Recorded Data Available	X Saturated in upper 12 inches
	____ Water Marks
Field Observations:	____ Drift Lines
	____ Sediment Deposits
Depth of Surface Water: 0-2 (inches)	X Drainage Patterns in Wetlands
Depth to Free Water in Pit: 0-6 (inches)	Secondary Indicators:
Depth to Saturated Soil: 2 (inches)	____ Oxidized Root Channels in Upper 12 Inches
	____ Water Stained Leaves
	____ Local Soil Survey Data
	____ FAC-Neutral Test
	____ Others (Explain in Remarks)

Remarks:

A very heavy rain occurred 2 days prior to site visit. The wetland was below a hillside seep.

Project/Site: Bailey Road Relocation
Site/Area ID: Wetland 1

SOILS

Map Unit Name:
(Series and Phase): Dormont-Culleoka
(Taxonomy Subgroup) _____

Drainage Class: Moderately well to well drained
Field Observations Confirm Mapped Type?
Yes _____ No X

Profile Description:

Depth (inches):	Horizon:	Matrix Color (Munsell Moist):	Mottle Colors (Munsell Moist):	Mottle (Abundance/Size):	Texture, Concretions, Structure:
0-9	A	10YR5/1	10YR5/6	20%/Medium	

Hydric Soil Indicators:

	Histosol		Concretions
	Histic Epipedon		High Organic Content in Surface Layer in Sandy Soils
	Sulfidic Odor		Organic Streaking in Sandy Soil
	Aquic Moisture Regimes		Listed on Local Hydric Soils List
	Reducing Conditions		Listed on National Hydric Soils List
X	Gleyed or Low Chroma Colors		Other (Explain in Remarks)

Remarks:

WETLAND DETERMINATION

Hydrophytic Vegetation Present?	Yes X	No		Is this Sampling Point Within a Wetland?
Wetland Hydrology Present?	Yes X	No		Yes X
Hydric Soils Present?	Yes X	No		No

Remarks:

All three wetland indicator criteria were met.

DATA FORM
ROUTINE WETLAND DETERMINATION
(1987 COE Wetland Delineation Manual)

Project/Site: Bailey Road Relocation **Applicant/Owner:** Consol Pennsylvania Coal Company **Investigator(s):** D E Pike		**Date:** 11/21/03 **County:** Greene **State:** PA
Do normal circumstances exist on the site?	Yes X	No ____
Is the site significantly disturbed (Atypical?)	Yes ____	No X
Is the area a potential problem area? (if needed, explain on reverse.)	Yes ____	No X
		Community ID: Wetland 2 **Plot ID:**

VEGETATION

	Dominant Plant Species:	Stratum:	Indicator:		Dominant Plant Species:	Stratum:	Indicator:
1.	*Cyperus strigosus*	Herb	FACW	11.			
2.	*Carex frankii*	Herb	OBL	12.			
3.	*Agrimonia parviflora*	Herb	FACW	13.			
4.	*Eupatorium perfoliatum*	Herb	FACW+	14.			
5.	*Epilobium coloratum*	Herb	OBL	15.			
6.	*Juncus effusus*	Herb	FACW+	16.			
7.	*Dipsacus sylvestris*	Herb	N	17.			
8.				18.			
9.				19.			
10.				20.			

Percent of Dominant Species that are OBL, FACW or FAC (excluding FAC-) 86%

Remarks:

HYDROLOGY

____ Recorded Data (Describe in Remarks) ____ Stream, Lake, or Tide Gauge ____ Aerial Photographs X No Recorded Data Available	**Wetland Hydrology Indicators:** Primary Indicators: X Inundated X Saturated in upper 12 inches ____ Water Marks ____ Drift Lines ____ Sediment Deposits X Drainage Patterns in Wetlands
Field Observations: Depth of Surface Water: 0-2 (inches) Depth to Free Water in Pit: 4 (inches) Depth to Saturated Soil: 2 (inches)	Secondary Indicators: ____ Oxidized Root Channels in Upper 12 Inches ____ Water Stained Leaves ____ Local Soil Survey Data ____ FAC-Neutral Test ____ Others (Explain in Remarks)

Remarks:

The wetland was below a hillside seep.

Project/Site: Bailey Road Relocation
Site/Area ID: Wetland 2

SOILS

Map Unit Name:
(Series and Phase): Dormont-Culleoka
(Taxonomy Subgroup) _____

Drainage Class: Moderately well to well drained
Field Observations Confirm Mapped Type?
Yes _____ No X

Profile Description:

Depth (inches):	Horizon:	Matrix Color (Munsell Moist):	Mottle Colors (Munsell Moist):	Mottle (Abundance/Size):	Texture, Concretions, Structure:
0-9	A	3N/	None		

Hydric Soil Indicators:

	Histosol		Concretions
	Histic Epipedon		High Organic Content in Surface Layer in Sandy Soils
	Sulfidic Odor		Organic Streaking in Sandy Soil
	Aquic Moisture Regimes		Listed on Local Hydric Soils List
	Reducing Conditions		Listed on National Hydric Soils List
X	Gleyed or Low Chroma Colors		Other (Explain in Remarks)

Remarks:

WETLAND DETERMINATION

Hydrophytic Vegetation Present?	Yes	X	No		Is this Sampling Point Within a Wetland?
Wetland Hydrology Present?	Yes	X	No		Yes X
Hydric Soils Present?	Yes	X	No		No

Remarks:

All three wetland indicator criteria were met.

DATA FORM
ROUTINE WETLAND DETERMINATION
(1987 COE Wetland Delineation Manual)

Project/Site: Bailey Road Relocation **Applicant/Owner:** Consol Pennsylvania Coal Company **Investigator(s):** D E Pike			**Date:** 11/21/03 **County:** Greene **State:** PA
Do normal circumstances exist on the site? Is the site significantly disturbed (Atypical?) Is the area a potential problem area? (if needed, explain on reverse.)	Yes X Yes ____ Yes ____	No ____ No X No X	**Community ID:** Wetland 3 **Plot ID:**

VEGETATION

	Dominant Plant Species:	Stratum:	Indicator:		Dominant Plant Species:	Stratum:	Indicator:
1.	*Cyperus strigosus*	Herb	FACW	11.			
2.	*Juncus effusus*	Herb	FACW+	12.			
3.	*Eleocharis acicularis*	Herb	OBL	13.			
4.				14.			
5.				15.			
6.				16.			
7.				17.			
8.				18.			
9.				19.			
10.				20.			

Percent of Dominant Species that are OBL, FACW or FAC (excluding FAC-)	100%

Remarks:

HYDROLOGY

____ Recorded Data (Describe in Remarks) ____ Stream, Lake, or Tide Gauge ____ Aerial Photographs X No Recorded Data Available	**Wetland Hydrology Indicators:** Primary Indicators: ____ Inundated X Saturated in upper 12 inches ____ Water Marks ____ Drift Lines ____ Sediment Deposits X Drainage Patterns in Wetlands
Field Observations: Depth of Surface Water: 0 (inches) Depth to Free Water in Pit: 4 (inches) Depth to Saturated Soil: 2 (inches)	Secondary Indicators: X Oxidized Root Channels in Upper 12 Inches ____ Water Stained Leaves ____ Local Soil Survey Data ____ FAC-Neutral Test ____ Others (Explain in Remarks)

Remarks:

Project/Site: Bailey Road Relocation
Site/Area ID: Wetland 3

SOILS

Map Unit Name:
(Series and Phase): Dormont-Culleoka
(Taxonomy Subgroup)

Drainage Class: Moderately well to well drained
Field Observations Confirm Mapped Type?
Yes ____ No X

Profile Description:

Depth (inches):	Horizon:	Matrix Color (Munsell Moist):	Mottle Colors (Munsell Moist):	Mottle (Abundance/Size):	Texture, Concretions, Structure:
0-6	A	10YR5/1	None		

Hydric Soil Indicators:

	Histosol		Concretions
	Histic Epipedon		High Organic Content in Surface Layer in Sandy Soils
	Sulfidic Odor		Organic Streaking in Sandy Soil
	Aquic Moisture Regimes		Listed on Local Hydric Soils List
	Reducing Conditions		Listed on National Hydric Soils List
X	Gleyed or Low Chroma Colors		Other (Explain in Remarks)

Remarks:

The soil was shallow and rocky.

WETLAND DETERMINATION

Hydrophytic Vegetation Present?	Yes X	No		Is this Sampling Point Within a Wetland?
Wetland Hydrology Present?	Yes X	No		Yes X
Hydric Soils Present?.	Yes X	No		No

Remarks:

Although the soils were shallow, it was felt all three wetland indicator criteria were met.

DATA FORM
ROUTINE WETLAND DETERMINATION
(1987 COE Wetland Delineation Manual)

Project/Site: Bailey Road Relocation **Applicant/Owner:** Consol Pennsylvania Coal Company **Investigator(s):** D E Pike		**Date:** 11/21/03 **County:** Greene **State:** PA
Do normal circumstances exist on the site?	Yes X	No ____
Is the site significantly disturbed (Atypical?)	Yes ____	No X
Is the area a potential problem area? (if needed, explain on reverse.)	Yes ____	No X
		Community ID: Wetland 4 **Plot ID:**

VEGETATION

	Dominant Plant Species:	Stratum:	Indicator:		Dominant Plant Species:	Stratum:	Indicator:
1.	*Cyperus strigosus*	Herb	FACW	11.			
2.	*Juncus effusus*	Herb	FACW+	12.			
3.				13.			
4.				14.			
5.				15.			
6.				16.			
7.				17.			
8.				18.			
9.				19.			
10.				20.			

Percent of Dominant Species that are OBL, FACW or FAC (excluding FAC-)	100%

Remarks:

The vegetation had all been mowed or grazed.

HYDROLOGY

____ Recorded Data (Describe in Remarks) ____ Stream, Lake, or Tide Gauge ____ Aerial Photographs X No Recorded Data Available	**Wetland Hydrology Indicators:** Primary Indicators: X Inundated X Saturated in upper 12 inches ____ Water Marks ____ Drift Lines ____ Sediment Deposits X Drainage Patterns in Wetlands
Field Observations: Depth of Surface Water: 0-3 (inches) Depth to Free Water in Pit: 4 (inches) Depth to Saturated Soil: 4 (inches)	Secondary Indicators: X Oxidized Root Channels in Upper 12 Inches ____ Water Stained Leaves ____ Local Soil Survey Data ____ FAC-Neutral Test ____ Others (Explain in Remarks)

Remarks:

There was flowing water through the area due to recent heavy rains.

Project/Site: Bailey Road Relocation
Site/Area ID: Wetland 4

SOILS

Map Unit Name:
(Series and Phase): Dormont-Culleoka
(Taxonomy Subgroup) _____

Drainage Class: Well to moderately well drained
Field Observations Confirm Mapped Type?
Yes _____ No X

Profile Description:

Depth (inches):	Horizon:	Matrix Color (Munsell Moist):	Mottle Colors (Munsell Moist):	Mottle (Abundance/Size):	Texture, Concretions, Structure:
0-9	A	10YR5/2	None		

Hydric Soil Indicators:

	Histosol		Concretions
	Histic Epipedon		High Organic Content in Surface Layer in Sandy Soils
	Sulfidic Odor		Organic Streaking in Sandy Soil
	Aquic Moisture Regimes		Listed on Local Hydric Soils List
	Reducing Conditions		Listed on National Hydric Soils List
X	Gleyed or Low Chroma Colors		Other (Explain in Remarks)

Remarks:

WETLAND DETERMINATION

Hydrophytic Vegetation Present?	Yes	X	No		Is this Sampling Point Within a Wetland?
Wetland Hydrology Present?	Yes	X	No		Yes X
Hydric Soils Present?	Yes	X	No		No

Remarks:

All three wetland indicator criteria were met.

DATA FORM
ROUTINE WETLAND DETERMINATION
(1987 COE Wetland Delineation Manual)

Project/Site: Bailey Road Relocation **Applicant/Owner:** Consol Pennsylvania Coal Company **Investigator(s):** D E Pike			**Date:** 11/221/03 **County:** Greene **State:** PA
Do normal circumstances exist on the site? Is the site significantly disturbed (Atypical?) Is the area a potential problem area? (if needed, explain on reverse.)	Yes X Yes ____ Yes ____	No ____ No X No X	**Community ID:** Wetland 5 **Plot ID:**

VEGETATION

	Dominant Plant Species:	Stratum:	Indicator:		Dominant Plant Species:	Stratum:	Indicator:
1.	*Juncus effusus*	Herb	FACW+	11.			
2.	*Cyperus strigosus*	Herb	FACW	12.			
3.				13.			
4.				14.			
5.				15.			
6.				16.			
7.				17.			
8.				18.			
9.				19.			
10.				20.			

Percent of Dominant Species that are OBL, FACW or FAC (excluding FAC-)	100%

Remarks:

Most of the vegetation in this wetland had been mowed or grazed.

HYDROLOGY

____ Recorded Data (Describe in Remarks) ____ Stream, Lake, or Tide Gauge ____ Aerial Photographs X No Recorded Data Available	**Wetland Hydrology Indicators:** Primary Indicators: X Inundated X Saturated in upper 12 inches ____ Water Marks ____ Drift Lines ____ Sediment Deposits X Drainage Patterns in Wetlands
Field Observations: Depth of Surface Water: 0-2 (inches) Depth to Free Water in Pit: 4 (inches) Depth to Saturated Soil: 2 (inches)	Secondary Indicators: X Oxidized Root Channels in Upper 12 Inches ____ Water Stained Leaves ____ Local Soil Survey Data ____ FAC-Neutral Test ____ Others (Explain in Remarks)

Remarks:

The wetland was below a hillside seep. Due to recent heavy rains water was flowing through the wetland area.

Project/Site: Bailey Road Relocation
Site/Area ID: Wetland 5

SOILS

Map Unit Name:
(Series and Phase): Dormont-Culleoka
(Taxonomy Subgroup) _____

Drainage Class: Well to moderately well drained
Field Observations Confirm Mapped Type?
Yes _____ No X

Profile Description:

Depth (inches):	Horizon:	Matrix Color (Munsell Moist):	Mottle Colors (Munsell Moist):	Mottle (Abundance/Size):	Texture, Concretions, Structure:
0-9	A	10YR5/1	None		

Hydric Soil Indicators:

	Histosol		Concretions
	Histic Epipedon		High Organic Content in Surface Layer in Sandy Soils
	Sulfidic Odor		Organic Streaking in Sandy Soil
	Aquic Moisture Regimes		Listed on Local Hydric Soils List
	Reducing Conditions		Listed on National Hydric Soils List
X	Gleyed or Low Chroma Colors		Other (Explain in Remarks)

Remarks:

WETLAND DETERMINATION

Hydrophytic Vegetation Present?	Yes X	No		Is this Sampling Point Within a Wetland?	
Wetland Hydrology Present?	Yes X	No		Yes X	
Hydric Soils Present?	Yes X	No		No	

Remarks:

All three wetland indicator criteria were met.

DATA FORM
ROUTINE WETLAND DETERMINATION
(1987 COE Wetland Delineation Manual)

Project/Site: Bailey Road Relocation **Applicant/Owner:** Consol Pennsylvania Coal Company **Investigator(s):** D E Pike			**Date:** 11/21/03 **County:** Greene **State:** PA
Do normal circumstances exist on the site? Is the site significantly disturbed (Atypical?) Is the area a potential problem area? (if needed, explain on reverse.)	Yes X Yes ____ Yes ____	No ____ No X No X	**Community ID:** Wetland 6 **Plot ID:**

VEGETATION

	Dominant Plant Species:	Stratum:	Indicator:		Dominant Plant Species:	Stratum:	Indicator:
1.	*Cyperus strigosus*	Herb	FACW	11.			
2.	*Carex frankii*	Herb	OBL	12.			
3.	*Juncus effusus*	Herb	FACW+	13.			
4.	*Eplobium coloratum*	Herb	OBL	14.			
5.	*Eupatorium perfoliatum*	Herb	FACW+	15.			
6.	*Agrimoia parviflora*	Herb	FAC	16.			
7.	*Phalaris arundinacea*	Herb	FACW+	17.			
8.	*Rosa multiflora*	Shrub	FACU	18.			
9.	*Dipsacus sylvestris*	Herb	N	19.			
10.				20.			

Percent of Dominant Species that are OBL, FACW or FAC (excluding FAC-) 78%

Remarks:

HYDROLOGY

____ Recorded Data (Describe in Remarks) ____ Stream, Lake, or Tide Gauge ____ Aerial Photographs X No Recorded Data Available	**Wetland Hydrology Indicators:** Primary Indicators: X Inundated X Saturated in upper 12 inches ____ Water Marks
Field Observations: Depth of Surface Water: 0-2 (inches) Depth to Free Water in Pit: 6 (inches) Depth to Saturated Soil: 8 (inches)	____ Drift Lines ____ Sediment Deposits X Drainage Patterns in Wetlands Secondary Indicators: ____ Oxidized Root Channels in Upper 12 Inches ____ Water Stained Leaves ____ Local Soil Survey Data ____ FAC-Neutral Test ____ Others (Explain in Remarks)

Remarks:

Project/Site: Bailey Road Relocation
Site/Area ID: Wetland 6

SOILS

Map Unit Name:
(Series and Phase): Dormont-Culleoka
(Taxonomy Subgroup) _____

Drainage Class: Well to moderately well drained
Field Observations Confirm Mapped Type?
Yes _____ No X

Profile Description:

Depth (inches):	Horizon:	Matrix Color (Munsell Moist):	Mottle Colors (Munsell Moist):	Mottle (Abundance/Size):	Texture, Concretions, Structure:
0-9	A	10YR5/1	None		

Hydric Soil Indicators:

	Histosol		Concretions
	Histic Epipedon		High Organic Content in Surface Layer in Sandy Soils
	Sulfidic Odor		Organic Streaking in Sandy Soil
	Aquic Moisture Regimes		Listed on Local Hydric Soils List
	Reducing Conditions		Listed on National Hydric Soils List
X	Gleyed or Low Chroma Colors		Other (Explain in Remarks)

Remarks:

WETLAND DETERMINATION

Hydrophytic Vegetation Present?	Yes X	No		Is this Sampling Point Within a Wetland?
Wetland Hydrology Present?	Yes X	No		Yes X
Hydric Soils Present?	Yes X	No		No

Remarks:

All three wetland indicator criteria were met.

DATA FORM
ROUTINE WETLAND DETERMINATION
(1987 COE Wetland Delineation Manual)

Project/Site: Bailey Road Relocation **Applicant/Owner:** Consol Pennsylvania Coal Company **Investigator(s):** D E Pike			**Date:** 11/21/03 **County:** Greene **State:** PA
Do normal circumstances exist on the site? Is the site significantly disturbed (Atypical?) Is the area a potential problem area? (if needed, explain on reverse.)	Yes X Yes ____ Yes ____	No ____ No X No X	**Community ID:** Wetland 7 **Plot ID:**

VEGETATION

	Dominant Plant Species:	Stratum:	Indicator:		Dominant Plant Species:	Stratum:	Indicator:
1.	*Cyperus strigosus*	Herb	FACW	11.			
2.	*Carex frankii*	Herb	OBL	12.			
3.	*Epilobium coloratum*	Herb	OBL	13.			
4.	*Eupatorium perfoliatum*	Herb	FACW+	14.			
5.	*Juncus effusus*	Herb	FACW+	15.			
6.	*Agrimoia parviflora*	Herb	FAC	16.			
7.				17.			
8.				18.			
9.				19.			
10.				20.			

Percent of Dominant Species that are OBL, FACW or FAC (excluding FAC-) 100%

Remarks:

HYDROLOGY

____ Recorded Data (Describe in Remarks) ____ Stream, Lake, or Tide Gauge ____ Aerial Photographs X No Recorded Data Available	**Wetland Hydrology Indicators:** Primary Indicators: X Inundated X Saturated in upper 12 inches ____ Water Marks
Field Observations: Depth of Surface Water: 0-2 (inches) Depth to Free Water in Pit: 3 (inches) Depth to Saturated Soil: 2 (inches)	____ Drift Lines ____ Sediment Deposits X Drainage Patterns in Wetlands Secondary Indicators: ____ Oxidized Root Channels in Upper 12 Inches ____ Water Stained Leaves ____ Local Soil Survey Data ____ FAC-Neutral Test ____ Others (Explain in Remarks)

Remarks:

The wetland was in a drainage channel and its riparian area.

Project/Site: Bailey Road Relocation
Site/Area ID: Wetland 7

SOILS

Map Unit Name:
(Series and Phase): Dormont-Culleoka
(Taxonomy Subgroup)

Drainage Class: Well to moderately well drained
Field Observations Confirm Mapped Type?
Yes ____ No X

Profile Description:

Depth (inches):	Horizon:	Matrix Color (Munsell Moist):	Mottle Colors (Munsell Moist):	Mottle (Abundance/Size):	Texture, Concretions, Structure:
0-9	A	10YR5/2	7.5YR5/6	Few/small	

Hydric Soil Indicators:

	Histosol		Concretions
	Histic Epipedon		High Organic Content in Surface Layer in Sandy Soils
	Sulfidic Odor		Organic Streaking in Sandy Soil
	Aquic Moisture Regimes		Listed on Local Hydric Soils List
	Reducing Conditions		Listed on National Hydric Soils List
X	Gleyed or Low Chroma Colors		Other (Explain in Remarks)

Remarks:

WETLAND DETERMINATION

Hydrophytic Vegetation Present?	Yes X	No		Is this Sampling Point Within a Wetland?
Wetland Hydrology Present?	Yes X	No		Yes X
Hydric Soils Present?	Yes X	No		No

Remarks:

All three wetland indicator criteria were met.

DATA FORM
ROUTINE WETLAND DETERMINATION
(1987 COE Wetland Delineation Manual)

Project/Site: Bailey Road Relocation **Applicant/Owner:** Consol Pennsylvania Coal Company **Investigator(s):** D E Pike			**Date:** 11/21/03 **County:** Greene **State:** PA
Do normal circumstances exist on the site? Is the site significantly disturbed (Atypical?) Is the area a potential problem area? (if needed, explain on reverse.)	Yes X Yes ____ Yes ____	No ____ No X No X	**Community ID:** Wetland 8 **Plot ID:**

VEGETATION

	Dominant Plant Species:	Stratum:	Indicator:		Dominant Plant Species:	Stratum:	Indicator:
1.	*Cyperus strigosus*	Herb	FACW	11.			
2.	*Juncus effusus*	Herb	FACW+	12.			
3.	*Dipsacus sylvestris*	Herb	N	13.			
4.				14.			
5.				15.			
6.				16.			
7.				17.			
8.				18.			
9.				19.			
10.				20.			

Percent of Dominant Species that are OBL, FACW or FAC (excluding FAC-) 67%

Remarks:

Most of the vegetation had been grazed.

HYDROLOGY

____ Recorded Data (Describe in Remarks) ____ Stream, Lake, or Tide Gauge ____ Aerial Photographs X No Recorded Data Available	**Wetland Hydrology Indicators:** Primary Indicators: X Inundated X Saturated in upper 12 inches ____ Water Marks
Field Observations: Depth of Surface Water: 0-1 (inches) Depth to Free Water in Pit: 6 (inches) Depth to Saturated Soil: 4 (inches)	____ Drift Lines ____ Sediment Deposits X Drainage Patterns in Wetlands Secondary Indicators: ____ Oxidized Root Channels in Upper 12 Inches ____ Water Stained Leaves ____ Local Soil Survey Data ____ FAC-Neutral Test ____ Others (Explain in Remarks)

Remarks:

The area looked like it may have been a shallow dug watering hole that has filled in.

Project/Site: Bailey Road Relocation
Site/Area ID: Wetland 8

SOILS

Map Unit Name:
(Series and Phase): Dormont-Culleoka
(Taxonomy Subgroup)

Drainage Class: Moderately well to well drained
Field Observations Confirm Mapped Type?
Yes ____ No X

Profile Description:

Depth (inches):	Horizon:	Matrix Color (Munsell Moist):	Mottle Colors (Munsell Moist):	Mottle (Abundance/Size):	Texture, Concretions, Structure:
0-9	A	10YR5/1	None		

Hydric Soil Indicators:

	Histosol		Concretions
	Histic Epipedon		High Organic Content in Surface Layer in Sandy Soils
	Sulfidic Odor		Organic Streaking in Sandy Soil
	Aquic Moisture Regimes		Listed on Local Hydric Soils List
	Reducing Conditions		Listed on National Hydric Soils List
X	Gleyed or Low Chroma Colors		Other (Explain in Remarks)

Remarks:

WETLAND DETERMINATION

Hydrophytic Vegetation Present?	Yes X	No		Is this Sampling Point Within a Wetland?
Wetland Hydrology Present?	Yes X	No		Yes X
Hydric Soils Present?	Yes X	No		No

Remarks:

All three wetland indicator criteria were met.

DATA FORM
ROUTINE WETLAND DETERMINATION
(1987 COE Wetland Delineation Manual)

Project/Site: Bailey Road Relocation **Applicant/Owner:** Consol Pennsylvania Coal Company **Investigator(s):** D E Pike			**Date:** 11/21/03 **County:** Greene **State:** PA
Do normal circumstances exist on the site? Is the site significantly disturbed (Atypical?) Is the area a potential problem area? (if needed, explain on reverse.)	Yes X Yes ____ Yes ____	No ____ No X No X	**Community ID:** Wetland 9 **Plot ID:**

VEGETATION

	Dominant Plant Species:	Stratum:	Indicator:		Dominant Plant Species:	Stratum:	Indicator:
1.	*Cyperus strigosus*	Herb	FACW	11.			
2.	*Juncus effusus*	Herb	FACW+	12.			
3.	*Dipsacus sylvestris*	Herb	N	13.			
4.				14.			
5.				15.			
6.				16.			
7.				17.			
8.				18.			
9.				19.			
10.				20.			

Percent of Dominant Species that are OBL, FACW or FAC (excluding FAC-)	67%

Remarks:

Most of the vegetation had been grazed.

HYDROLOGY

____ Recorded Data (Describe in Remarks) ____ Stream, Lake, or Tide Gauge ____ Aerial Photographs X No Recorded Data Available	**Wetland Hydrology Indicators:** Primary Indicators: X Inundated X Saturated in upper 12 inches ____ Water Marks
Field Observations: Depth of Surface Water: 0-2 (inches) Depth to Free Water in Pit: 3 (inches) Depth to Saturated Soil: 2 (inches)	____ Drift Lines ____ Sediment Deposits X Drainage Patterns in Wetlands Secondary Indicators: ____ Oxidized Root Channels in Upper 12 Inches ____ Water Stained Leaves ____ Local Soil Survey Data ____ FAC-Neutral Test ____ Others (Explain in Remarks)

Remarks:

Project/Site: Bailey Road Relocation
Site/Area ID: Wetland 9

SOILS

Map Unit Name:
(Series and Phase): Dormont-Culleoka
(Taxonomy Subgroup) _____

Drainage Class: Moderately well to well drained
Field Observations Confirm Mapped Type?
Yes _____ No X

Profile Description:

Depth (inches):	Horizon:	Matrix Color (Munsell Moist):	Mottle Colors (Munsell Moist):	Mottle (Abundance/Size):	Texture, Concretions, Structure:
0-9	A	10YR4/1	None		

Hydric Soil Indicators:

	Histosol		Concretions
	Histic Epipedon		High Organic Content in Surface Layer in Sandy Soils
	Sulfidic Odor		Organic Streaking in Sandy Soil
	Aquic Moisture Regimes		Listed on Local Hydric Soils List
	Reducing Conditions		Listed on National Hydric Soils List
X	Gleyed or Low Chroma Colors		Other (Explain in Remarks)

Remarks:

WETLAND DETERMINATION

Hydrophytic Vegetation Present?	Yes X	No		Is this Sampling Point Within a Wetland?
Wetland Hydrology Present?	Yes X	No		Yes X
Hydric Soils Present?	Yes X	No		No

Remarks:

All three wetland indicator criteria were met.

DATA FORM
ROUTINE WETLAND DETERMINATION
(1987 COE Wetland Delineation Manual)

Project/Site: Bailey Road Relocation **Applicant/Owner:** Consol Pennsylvania Coal Company **Investigator(s):** D E Pike			**Date:** 11/22/03 **County:** Greene **State:** PA
Do normal circumstances exist on the site? Is the site significantly disturbed (Atypical?) Is the area a potential problem area? (if needed, explain on reverse.)	Yes X Yes ___ Yes ___	No ___ No X No X	**Community ID:** Wetland 10 **Plot ID:**

VEGETATION

	Dominant Plant Species:	Stratum:	Indicator:		Dominant Plant Species:	Stratum:	Indicator:
1.	*Cyperus strigosus*	Herb	FACW	11.			
2.	*Epilobium coloratum*	Herb	OBL	12.			
3.	*Amaranthus retroflexus*	Herb	FACU	13.			
4.	*Polygonum* sp.	Herb	?	14.			
5.				15.			
6.				16.			
7.				17.			
8.				18.			
9.				19.			
10.				20.			

Percent of Dominant Species that are OBL, FACW or FAC (excluding FAC-) 50%

Remarks:

There smartweed (*Polygonum*) could not be identified from the material present.

HYDROLOGY

___ Recorded Data (Describe in Remarks) ___ Stream, Lake, or Tide Gauge ___ Aerial Photographs X No Recorded Data Available	**Wetland Hydrology Indicators:** Primary Indicators: X Inundated X Saturated in upper 12 inches ___ Water Marks
Field Observations: Depth of Surface Water: 0-3 (inches) Depth to Free Water in Pit: 1 (inches) Depth to Saturated Soil: 1 (inches)	___ Drift Lines ___ Sediment Deposits X Drainage Patterns in Wetlands Secondary Indicators: ___ Oxidized Root Channels in Upper 12 Inches ___ Water Stained Leaves ___ Local Soil Survey Data ___ FAC-Neutral Test ___ Others (Explain in Remarks)

Remarks:

The wetland appeared to be a shallow dug watering hole that has partially filled in.

Project/Site: Bailey Road Relocation
Site/Area ID: Wetland 10

SOILS

Map Unit Name:
(Series and Phase): Dormont-Culleoka
(Taxonomy Subgroup)

Drainage Class: Moderately well to well drained
Field Observations Confirm Mapped Type?
Yes ____ No X

Profile Description:

Depth (inches):	Horizon:	Matrix Color (Munsell Moist):	Mottle Colors (Munsell Moist):	Mottle (Abundance/Size):	Texture, Concretions, Structure:
0-9	A	5PB2.5/1	None		

Hydric Soil Indicators:

	Histosol		Concretions
	Histic Epipedon		High Organic Content in Surface Layer in Sandy Soils
	Sulfidic Odor		Organic Streaking in Sandy Soil
	Aquic Moisture Regimes		Listed on Local Hydric Soils List
	Reducing Conditions		Listed on National Hydric Soils List
X	Gleyed or Low Chroma Colors		Other (Explain in Remarks)

Remarks:

WETLAND DETERMINATION

Hydrophytic Vegetation Present?	Yes X	No		Is this Sampling Point Within a Wetland?
Wetland Hydrology Present?	Yes X	No		Yes X
Hydric Soils Present?	Yes X	No		No

Remarks:

All three wetland indicator criteria were met.

DATA FORM
ROUTINE WETLAND DETERMINATION
(1987 COE Wetland Delineation Manual)

Project/Site: Bailey Road Relocation **Applicant/Owner:** Consol Pennsylvania Coal Company **Investigator(s):** D E Pike			**Date:** 11/22/03 **County:** Greene **State:** PA
Do normal circumstances exist on the site? Is the site significantly disturbed (Atypical?) Is the area a potential problem area? (if needed, explain on reverse.)	Yes X Yes ____ Yes ____	No ____ No X No X	**Community ID:** Wetlan 11 **Plot ID:**

VEGETATION

	Dominant Plant Species:	Stratum:	Indicator:		Dominant Plant Species:	Stratum:	Indicator:
1.	*Cyperus strigosus*	Herb	FACW	11.			
2.	*Carex frankii*	Herb	OBL	12.			
3.	*Epilobium coloratum*	Herb	OBL	13.			
4.	*Agrimonia parviflora*	Herb	FAC	14.			
5.	*Juncus effusus*	Herb	FACW+	15.			
6.				16.			
7.				17.			
8.				18.			
9.				19.			
10.				20.			

Percent of Dominant Species that are OBL, FACW or FAC (excluding FAC-)	100%

Remarks:

HYDROLOGY

____ Recorded Data (Describe in Remarks) ____ Stream, Lake, or Tide Gauge ____ Aerial Photographs X No Recorded Data Available	**Wetland Hydrology Indicators:** Primary Indicators: X Inundated X Saturated in upper 12 inches ____ Water Marks
Field Observations: Depth of Surface Water: 0-2 (inches) Depth to Free Water in Pit: 4 (inches) Depth to Saturated Soil: 1 (inches)	____ Drift Lines ____ Sediment Deposits X Drainage Patterns in Wetlands Secondary Indicators: X Oxidized Root Channels in Upper 12 Inches ____ Water Stained Leaves ____ Local Soil Survey Data ____ FAC-Neutral Test ____ Others (Explain in Remarks)

Remarks:

Project/Site: Bailey Road Relocation
Site/Area ID: Wetland 11

SOILS

Map Unit Name:
(Series and Phase): Dormont-Culleoka
(Taxonomy Subgroup) _____

Drainage Class: Moderately well to well drained
Field Observations Confirm Mapped Type?
Yes _____ No X

Profile Description:

Depth (inches):	Horizon:	Matrix Color (Munsell Moist):	Mottle Colors (Munsell Moist):	Mottle (Abundance/Size):	Texture, Concretions, Structure:
0-9	A	5PB2.5/1	None		

Hydric Soil Indicators:

	Histosol		Concretions
	Histic Epipedon		High Organic Content in Surface Layer in Sandy Soils
	Sulfidic Odor		Organic Streaking in Sandy Soil
	Aquic Moisture Regimes		Listed on Local Hydric Soils List
	Reducing Conditions		Listed on National Hydric Soils List
X	Gleyed or Low Chroma Colors		Other (Explain in Remarks)

Remarks:

WETLAND DETERMINATION

Hydrophytic Vegetation Present?	Yes X	No		Is this Sampling Point Within a Wetland?
Wetland Hydrology Present?	Yes X	No		Yes X
Hydric Soils Present?	Yes X	No		No

Remarks:

All three wetland indicator criteria were met.

DATA FORM
ROUTINE WETLAND DETERMINATION
(1987 COE Wetland Delineation Manual)

Project/Site: Bailey Road Relocation **Applicant/Owner:** Consol Pennsylvania Coal Company **Investigator(s):** D E Pike		**Date:** 2/19/04 **County:** Greene **State:** PA
Do normal circumstances exist on the site? Yes X No ____ Is the site significantly disturbed (Atypical?) Yes ____ No X Is the area a potential problem area? Yes ____ No X (if needed, explain on reverse.)		**Community ID:** Wetland 12 **Plot ID:**

VEGETATION

	Dominant Plant Species:	Stratum:	Indicator:		Dominant Plant Species:	Stratum:	Indicator:
1.	*Juncus effusus*	Herb	FACW+	11.			
2.	*Carex* sp.	Herb		12.			
3.				13.			
4.				14.			
5.				15.			
6.				16.			
7.				17.			
8.				18.			
9.				19.			
10.				20.			

Percent of Dominant Species that are OBL, FACW or FAC (excluding FAC-)	100%

Remarks:

Little identifiable vegetation was present, but it appeared that the area was dominated by hydrophytic species.

HYDROLOGY

____ Recorded Data (Describe in Remarks) ____ Stream, Lake, or Tide Gauge ____ Aerial Photographs X No Recorded Data Available	**Wetland Hydrology Indicators:** Primary Indicators: X Inundated ____ Saturated in upper 12 inches ____ Water Marks ____ Drift Lines ____ Sediment Deposits X Drainage Patterns in Wetlands
Field Observations: Depth of Surface Water: 0-2 (inches) Depth to Free Water in Pit: ____ (inches) Depth to Saturated Soil: ____ (inches)	Secondary Indicators: X Oxidized Root Channels in Upper 12 Inches ____ Water Stained Leaves ____ Local Soil Survey Data ____ FAC-Neutral Test ____ Others (Explain in Remarks)

Remarks:

A spring is the water source for this wetland. There was a heavy flow on the day visited.

DATA FORM
ROUTINE WETLAND DETERMINATION
(1987 COE Wetland Delineation Manual)

Project/Site: Bailey Road Relocation **Applicant/Owner:** Consol Pennsylvania Coal Company **Investigator(s):** D E Pike		**Date:** 2/19/04 **County:** Greene **State:** PA
Do normal circumstances exist on the site?	Yes X / No ___	**Community ID:** Wetland 14
Is the site significantly disturbed (Atypical?)	Yes ___ / No X	**Plot ID:**
Is the area a potential problem area? (if needed, explain on reverse.)	Yes ___ / No X	

VEGETATION

	Dominant Plant Species:	Stratum:	Indicator:		Dominant Plant Species:	Stratum:	Indicator:
1.	*Juncus effusus*	Herb	FACW+	11.			
2.	*Carex* sp.	Herb		12.			
3.				13.			
4.				14.			
				15.			
6.				16.			
7.				17.			
8.				18.			
9.				19.			
10.				20.			

Percent of Dominant Species that are OBL, FACW or FAC (excluding FAC-)	100%

Remarks:

Little identifiable vegetation was present, but it appeared that the area was dominated by hydrophytic species.

HYDROLOGY

___ Recorded Data (Describe in Remarks) ___ Stream, Lake, or Tide Gauge ___ Aerial Photographs X No Recorded Data Available	**Wetland Hydrology Indicators:** Primary Indicators: X Inundated ___ Saturated in upper 12 inches ___ Water Marks
Field Observations: Depth of Surface Water: 0-2 (inches) Depth to Free Water in Pit: ___ (inches) Depth to Saturated Soil: ___ (inches)	___ Drift Lines ___ Sediment Deposits X Drainage Patterns in Wetlands Secondary Indicators: X Oxidized Root Channels in Upper 12 Inches ___ Water Stained Leaves ___ Local Soil Survey Data ___ FAC-Neutral Test ___ Others (Explain in Remarks)

Remarks:

There were 2 springs and numerous seeps supplying water to this wetland.

Project/Site: Bailey Road Relocation
Site/Area ID: Wetland 14

SOILS

Map Unit Name:
(Series and Phase): Dormont-Culleoka
(Taxonomy Subgroup): _____

Drainage Class: Moderately well to well drained
Field Observations Confirm Mapped Type?
Yes _____ No X

Profile Description:

Depth (inches):	Horizon:	Matrix Color (Munsell Moist):	Mottle Colors (Munsell Moist):	Mottle (Abundance/Size):	Texture, Concretions, Structure:
0-9	A	10YR4/1	None		

Hydric Soil Indicators:

	Histosol		Concretions
	Histic Epipedon		High Organic Content in Surface Layer in Sandy Soils
	Sulfidic Odor		Organic Streaking in Sandy Soil
	Aquic Moisture Regimes		Listed on Local Hydric Soils List
	Reducing Conditions		Listed on National Hydric Soils List
X	Gleyed or Low Chroma Colors		Other (Explain in Remarks)

Remarks:

WETLAND DETERMINATION

Hydrophytic Vegetation Present?	Yes X	No		Is this Sampling Point Within a Wetland?
Wetland Hydrology Present?	Yes X	No		Yes X
Hydric Soils Present?	Yes X	No		No

Remarks:

All three wetland indicator criteria were met.

DATA FORM
ROUTINE WETLAND DETERMINATION
(1987 COE Wetland Delineation Manual)

Project/Site: Bailey Road Relocation **Applicant/Owner:** Consol Pennsylvania Coal Company **Investigator(s):** D E Pike		**Date:** 2/19/04 **County:** Greene **State:** PA
Do normal circumstances exist on the site?	Yes X	No _____
Is the site significantly disturbed (Atypical?)	Yes _____	No X
Is the area a potential problem area? (if needed, explain on reverse.)	Yes _____	No X
		Community ID: Wetland 15 **Plot ID:**

VEGETATION

	Dominant Plant Species:	Stratum:	Indicator:		Dominant Plant Species:	Stratum:	Indicator:
1.	*Carex* spp.	Herb		11.			
2.	*Dipsacus sylvestris*	Herb	NI	12.			
3.				13.			
4.				14.			
5.				15.			
6.				16.			
7.				17.			
8.				18.			
9.				19.			
10.				20.			

Percent of Dominant Species that are OBL, FACW or FAC (excluding FAC-)

Remarks:

Little identifiable vegetation was present, but it appeared that the area would be dominated by hydrophytic species during the growing season.

HYDROLOGY

_____ Recorded Data (Describe in Remarks) _____ Stream, Lake, or Tide Gauge _____ Aerial Photographs X No Recorded Data Available	**Wetland Hydrology Indicators:** Primary Indicators: X Inundated _____ Saturated in upper 12 inches _____ Water Marks
Field Observations: Depth of Surface Water: 0-2 (inches) Depth to Free Water in Pit: _____ (inches) Depth to Saturated Soil: _____ (inches)	_____ Drift Lines _____ Sediment Deposits X Drainage Patterns in Wetlands Secondary Indicators: _____ Oxidized Root Channels in Upper 12 Inches _____ Water Stained Leaves _____ Local Soil Survey Data _____ FAC-Neutral Test Others (Explain in Remarks)

Remarks:

Project/Site: Bailey Road Relocation
Site/Area ID: Wetland 15

SOILS

Map Unit Name:
(Series and Phase): Dormont-Culleoka
(Taxonomy Subgroup): _____

Drainage Class: Moderately well to well drained
Field Observations Confirm Mapped Type?
Yes _____ No X

Profile Description:

Depth (inches):	Horizon:	Matrix Color (Munsell Moist):	Mottle Colors (Munsell Moist):	Mottle (Abundance/Size):	Texture, Concretions, Structure:
0-9	A	2.5YR4/1	None		

Hydric Soil Indicators:

	Histosol		Concretions
	Histic Epipedon		High Organic Content in Surface Layer in Sandy Soils
	Sulfidic Odor		Organic Streaking in Sandy Soil
	Aquic Moisture Regimes		Listed on Local Hydric Soils List
	Reducing Conditions		Listed on National Hydric Soils List
X	Gleyed or Low Chroma Colors		Other (Explain in Remarks)

Remarks:

WETLAND DETERMINATION

Hydrophytic Vegetation Present?	Yes X	No		Is this Sampling Point Within a Wetland?
Wetland Hydrology Present?	Yes X	No		Yes X
Hydric Soils Present?	Yes X	No		No

Remarks:

All three wetland indicator criteria were met.

DATA FORM
ROUTINE WETLAND DETERMINATION
(1987 COE Wetland Delineation Manual)

Project/Site: Bailey Road Relocation **Applicant/Owner:** Consol Pennsylvania Coal Company **Investigator(s):** D E Pike		**Date:** 2/19/04 **County:** Greene **State:** PA
Do normal circumstances exist on the site? Yes X No ____ Is the site significantly disturbed (Atypical?) Yes ____ No X Is the area a potential problem area? Yes ____ No X (if needed, explain on reverse.)		**Community ID:** Wetland 16 **Plot ID:**

VEGETATION

	Dominant Plant Species:	Stratum:	Indicator:		Dominant Plant Species:	Stratum:	Indicator:
1.	*Juncus effusus*	Herb	FACW+	11.			
2.	*Eupatorium perfoliatum*	Herb	FACW+	12.			
3.	*Carex* sp.	Herb		13.			
4.				14.			
5.				15.			
6.				16.			
7.				17.			
8.				18.			
9.				19.			
10.				20.			

Percent of Dominant Species that are OBL, FACW or FAC (excluding FAC-)	100%

Remarks:

Little identifiable vegetation was present, but it appeared that the area would be dominated by hydrophytic species during the growing season.

HYDROLOGY

____ Recorded Data (Describe in Remarks) ____ Stream, Lake, or Tide Gauge ____ Aerial Photographs X No Recorded Data Available	**Wetland Hydrology Indicators:** Primary Indicators: X Inundated ____ Saturated in upper 12 inches ____ Water Marks
Field Observations: Depth of Surface Water: 0-2 (inches) Depth to Free Water in Pit: ____ (inches) Depth to Saturated Soil: ____ (inches)	____ Drift Lines ____ Sediment Deposits X Drainage Patterns in Wetlands Secondary Indicators: ____ Oxidized Root Channels in Upper 12 Inches ____ Water Stained Leaves ____ Local Soil Survey Data ____ FAC-Neutral Test Others (Explain in Remarks)

Remarks:

Project/Site: Bailey Road Relocation
Site/Area ID: Wetland 16

SOILS

Map Unit Name:
(Series and Phase): Dormont-Culleoka
(Taxonomy Subgroup): _____

Drainage Class: Moderately well to well drained
Field Observations Confirm Mapped Type?
Yes _____ No X

Profile Description:

Depth (inches):	Horizon:	Matrix Color (Munsell Moist):	Mottle Colors (Munsell Moist):	Mottle (Abundance/Size):	Texture, Concretions, Structure:
0-9	A	10YR5/1	7.5YR5/8	common/very small	

Hydric Soil Indicators:

	Histosol		Concretions
	Histic Epipedon		High Organic Content in Surface Layer in Sandy Soils
	Sulfidic Odor		Organic Streaking in Sandy Soil
	Aquic Moisture Regimes		Listed on Local Hydric Soils List
	Reducing Conditions		Listed on National Hydric Soils List
X	Gleyed or Low Chroma Colors		Other (Explain in Remarks)

Remarks:

WETLAND DETERMINATION

Hydrophytic Vegetation Present?	Yes X	No		Is this Sampling Point Within a Wetland?
Wetland Hydrology Present?	Yes X	No		Yes X
Hydric Soils Present?	Yes X	No		No

Remarks:

All three wetland indicator criteria were met.

APPENDIX B

PHOTOGRAPHS FOR THE BIOLOGICAL EVALUATIONS OF ALIGNMENTS FOR THE RELOCATION OF SR4009 BAILEY REFUSE AREA

Figure 1. Bailey road Alignment 4 wetland 1 November 21, 2003.

Figure 2. Bailey road Alignment 4 wetland 1 November 21, 2003.

Figure 3. Bailey road Alignment 4 wetland 2 November 21, 2003.

Figure 4. Bailey road Alignment 4 wetland 2 November 21, 2003.

Figure 5. Bailey road Alignment 4 wetland 3 November 21, 2003.

Figure 6. Bailey road Alignment 4 wetland 3 November 21, 2003.

Figure 7. Bailey road Alignment 4 wetland 4 November 21, 2003.

Figure 8. Bailey road Alignment 4 wetland 4 November 21, 2003.

Figure 9. Bailey road Alignment 4 wetland 5 November 21, 2003.

Figure 10. Bailey road Alignment 4 wetland 5 November 21, 2003.

Figure 11. Bailey road Alignment 4 wetland 6 November 21, 2003.

Figure 12. Bailey road Alignment 4 wetland 6 November 21, 2003.

Figure 13. Bailey road Alignment 4 wetland 6 November 21, 2003.

Figure 14. Bailey road Alignment 4 wetland 6 November 21, 2003.

Figure 15. Bailey road Alignment 4 wetland 7 November 21, 2003.

Figure 16. Bailey road Alignment 4 wetland 7 November 21, 2003.

Figure 17. Bailey road Alignment 4 wetland 8 November 21, 2003.

Figure 18. Bailey road Alignment 4 wetland 8 November 21, 2003.

Figure 19. Bailey road Alignment 4 wetland 9 November 21, 2003.

Figure 20. Bailey road Alignment 4 wetland 9 November 21, 2003

Figure 21. Bailey road Alignment 4 wetland 10 November 22, 2003.

Figure 22. Bailey road Alignment 4 wetland 10 November 22, 2003.

Figure 23. Bailey road Alignment 4 wetland 11 November 22, 2003.

Figure 24. Bailey road Alignment 4 wetland 11 November 22, 2003.

Figure 25. Bailey road Alignment 4A wetland 12 February 19, 2004.

Figure 26. Bailey road Alignment 4A wetland 12 February 19, 2004.

Figure 27. Bailey road Alignment 4A wetland 13 February 19, 2004.

Figure 28. Bailey road Alignment 4A wetland 13 February 19, 2004.

Figure 29. Bailey road Alignment 4A wetland 14 February 19, 2004.

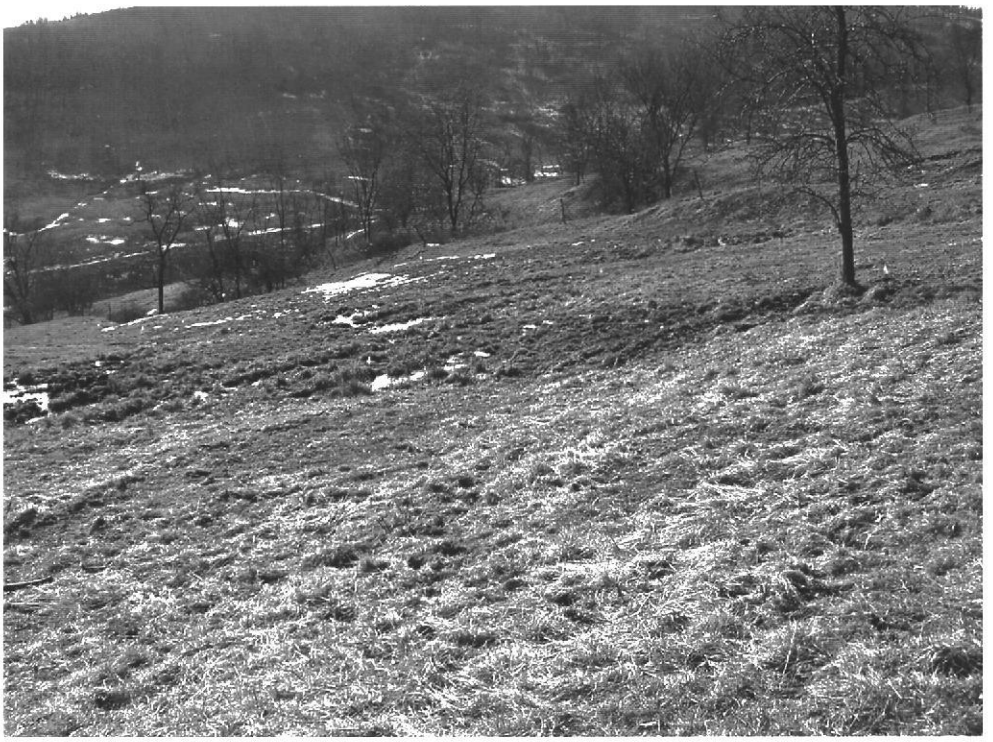

Figure 30. Bailey road Alignment 4A wetland 14 February 19, 2004.

Figure 31. Bailey road Alignment 4A wetland 14 February 19, 2004.

Figure 32. Bailey road Alignment 4A wetland 14 February 19, 2004.

Figure 33. Bailey road Alignment 4A wetland 15 February 19, 2004.

Figure 34. Bailey road Alignment 4A wetland 15 February 19, 2004.

Figure 35. Bailey road Alignment 4A wetland 15 February 19, 2004.

Figure 36. Bailey road Alignment 4A wetland 15 February 19, 2004.

Figure 37. Bailey road Alignment 4A wetland 16 February 19, 2004.

Figure 38. Bailey road Alignment 4A wetland 16 February 19, 2004.

Figure 39. Bailey road Alignment 4 Grinnage Run headwaters sampling station looking downstream December 8, 2003.

Figure 40. Bailey road Alignment 4 Grinnage Run headwaters sampling station looking upstream December 8, 2003.

Figure 41. Bailey road Alignment 4 unnamed tributary to Enlow Fork sampling station looking downstream December 8, 2003.

Figure 42. Bailey road Alignment 4 unnamed tributary to Enlow Fork sampling station looking upstream December 8, 2003.

Figure 43. Downstream end of culvert carrying the Bailey road Alignment 4 unnamed tributary to another unnamed tributary to Enlow Fork under railroad grade December 8, 2003.

Figure 44. Another view of the culvert on the Bailey road Alignment 4 unnamed tributary to another unnamed tributary to Enlow Fork December 8, 2003.

Figure 45. Bailey road Alignment 1 unnamed tributary "A" sampling station looking upstream February 19, 2004.

Figure 46. Bailey road Alignment 1 unnamed tributary "A" sampling station looking downstream February 19, 2004.

Figure 47. Bailey road Alignment 1 unnamed tributary "B" sampling station looking upstream February 19, 2004.

Figure 48. Bailey road Alignment 1 unnamed tributary "B" sampling station looking downstream February 19, 2004.

Figure 49. Bailey road Alignment 1 unnamed tributary "C" sampling station looking upstream February 19, 2004.

Figure 50. Bailey road Alignment 1 unnamed tributary "C" sampling station looking downstream February 19, 2004.

Figure 51. Bailey road Alignment 7 unnamed tributary sampling station looking upstream February 19, 2004.

Figure 52. Bailey road Alignment 7 unnamed tributary sampling station looking downstream February 19, 2004.

ADDENDUM TO

BIOLOGICAL EVALUATIONS OF ALIGNMENTS FOR THE RELOCATION OF SR4009 BAILEY REFUSE AREA GREENE COUNTY, PENNSYLVANIA

Prepared for

CME Engineering, Inc.
Somerset, Pennsylvania

by

Pike Environmental Consulting
Waynesburg, Pennsylvania

March 2004

INTRODUCTION

Road Alignment 1 would require the extension of culverts carrying four unnamed tributaries under an existing railroad line to a larger unnamed tributary to Enlow Fork. A report describing the macroinvertebrate populations of the four tributaries and the wetlands of the tributary that would be impacted by this alignment and Alignment 4 was previously submitted to CME Engineering, Inc. Because of the small size of three of the tributaries (referred to as Tributaries "A", "B" and "C" in that report), uncertainty of property ownership and the low probability that construction of Alignment 1 would be feasible, wetland delineations for those tributaries were not conducted at that time.

Because of objections to several of the proposed alignments for the Bailey road relocation, a reassessment of the possible alternatives showed construction of Alignment 1 might be more feasible than originally thought. Therefore, on March 8, 2004 Tributaries "A", "B" and "C" were examined for the presence of jurisdictional wetlands.

METHODS

The same procedures described in the original assessment of the proposed road alignments were used to determine the presence of jurisdictional wetlands in the three tributaries. Since road construction activities are currently not expected to impact areas on private properties, only areas on railroad property were delineated.

RESULTS

Tributary "A" is a channel that drains a very small watershed. A portion of the watershed is a small natural stream, with a poorly defined channel that appears to be intermittent. Diversion channels that carry drainage from along the railroad grade are stabilized with boulder size rock. There was no hydrophytic vegetation evident during the March survey of the tributary. "Soils" were small gravel material with some fine sediments trapped

within interstitial spaces. Hydrology appeared to be storm runoff. This area did not meet Corps criteria for jurisdictional wetlands.

Tributary "B" drains a larger watershed and probably goes dry only during sever drought periods. Soils within the wetland on railroad property were shallow (rocky material stopped the soil probe at about 10") with 5PB4/1 coloration. Heavy root staining was present. During the growing season it appears this riparian wetland would be dominated by sensitive fern (*Onoclea sensibilis*), along with a species of *Carex*. There were a few willows (*Salix*) present, but they that could not be identified from the material available. The stream supplied water to the small depression that defined the wetland. This site met all three Corps criteria for a jurisdictional wetland. The wetland, on the railroad right-of-way only consisted of an area approximately 30' X 15' in size.

Tributary "C" was the largest stream of the four that would be impacted by construction of alignment 1. A relatively broad riparian zone has formed just upstream of the culvert carrying the stream under the railroad grade. Soils in the upper 9 inches of the riparian zone had 10YR3/2 coloration, but there were no mottles or staining present, and therefore did not meet the Corps definition of hydric soils. Because of rocky materials, the soil probe could not be driven below the "A" horizon. At the time of this survey there were remains of sedges (*Carex* sp.), soft rush (*Juncus effuses*) and unidentifiable grasses immediately next to the stream channel. Further from the stream, there were some specimens of small-flower groovebur (*Agrimonia parviflora*), teasel (*Dipsacus sylvestris*), blackberry (*Rubus* sp.), burdock (*Arctium minus*), willows (*Salix* sp.) and a few clumps cattails (*Typha latifolia*) along with numerous unidentifiable plant remains. It did not appear that during the growing season this site would be dominated by hydrophytic species. The riparian area was rather high above the base of the stream channel and probably is only wet during high flows. The area where cattails were seen was in a small channel that drains from the railroad grade. It was determined this site did not meet the Corps criteria for a jurisdictional wetland.

Alignment 1 would parallel the railroad through a large cut in a hillside. Within the cut, the railroad grade has drainage channels on both sides of the rail bed. There were a few scattered clumps of sedges seen in the drainage channel, but it did not appear that jurisdictional wetlands would be found anywhere within the cut area.

ADDENDUM TO

APPENDIX A

ROUTINE WETLAND DETERMINATION FORMS FOR JURISDICTIONAL WETLANDS IDENTIFIED WITHIN THE ALIGNMENTS FOR THE RELOCATION OF SR 4009 BAILEY REFUSE AREA

DATA FORM
ROUTINE WETLAND DETERMINATION
(1987 COE Wetland Delineation Manual)

Project/Site: Bailey Road Relocation **Applicant/Owner:** Consol Pennsylvania Coal Company **Investigator(s):** D. Pike			**Date:** 3/8/04 **County:** Greene **State:** PA
Do normal circumstances exist on the site? Is the site significantly disturbed (Atypical?) Is the area a potential problem area? (if needed, explain on reverse.)	Yes ____ Yes X Yes X	No X No ____ No ____	**Community ID:** Alignment 1 **Plot ID:** Tributary "A"

VEGETATION

Dominant Plant Species:	Stratum:	Indicator:	Dominant Plant Species:	Stratum:	Indicator:
1.			11.		
2.			12.		
3.			13.		
4.			14.		
5.			15.		
6.			16.		
7.			17.		
8.			18.		
9.			19.		
10.			20.		

Percent of Dominant Species that are OBL, FACW or FAC (excluding FAC-)	0%

Remarks:

No identifiable plant remains were present, however it did not appear that any hydrophytic vegetation would be present during the growing season.

HYDROLOGY

____ Recorded Data (Describe in Remarks) ____ Stream, Lake, or Tide Gauge ____ Aerial Photographs X No Recorded Data Available	**Wetland Hydrology Indicators:** Primary Indicators: ____ Inundated ____ Saturated in upper 12 inches ____ Water Marks
Field Observations: Depth of Surface Water: 0 (inches) Depth to Free Water in Pit: NA (inches) Depth to Saturated Soil: NA (inches)	____ Drift Lines ____ Sediment Deposits ____ Drainage Patterns in Wetlands Secondary Indicators: ____ Oxidized Root Channels in Upper 12 Inches ____ Water Stained Leaves ____ Local Soil Survey Data ____ FAC-Neutral Test ____ Others (Explain in Remarks)

Remarks:

Heavy rains had occurred the two days prior to sampling so there was some flow, but it appears the stream only has flow following storm events. A soil probe could not be inserted at this site.

Project/Site: Bailey Road Relocation
Site/Area ID: Alignment 1/Tributary " A"

SOILS

Map Unit Name:
(Series and Phase): Site is disturbed, but would have
(Taxonomy Subgroup): been Dormont-Culleoka

Drainage Class: Well to moderately well
Field Observations Confirm Mapped Type?
Yes _____ No X

Profile Description:

Depth (inches):	Horizon:	Matrix Color (Munsell Moist):	Mottle Colors (Munsell Moist):	Mottle (Abundance/Size):	Texture, Concretions, Structure:

Hydric Soil Indicators:

_____	Histosol	_____	Concretions
_____	Histic Epipedon	_____	High Organic Content in Surface Layer in Sandy Soils
_____	Sulfidic Odor	_____	Organic Streaking in Sandy Soil
_____	Aquic Moisture Regimes	_____	Listed on Local Hydric Soils List
_____	Reducing Conditions	_____	Listed on National Hydric Soils List
_____	Gleyed or Low Chroma Colors	_____	Other (Explain in Remarks)

Remarks:

No real soils existed at this site.

WETLAND DETERMINATION

Hydrophytic Vegetation Present?	Yes _____	No	X	Is this Sampling Point Within a Wetland?
Wetland Hydrology Present?	Yes _____	No	X	Yes _____
Hydric Soils Present?	Yes _____	No	X	No X

Remarks:

The site is not a jurisdictional wetland.

DATA FORM
ROUTINE WETLAND DETERMINATION
(1987 COE Wetland Delineation Manual)

Project/Site: Bailey Road Relocation **Applicant/Owner:** Consol Pennsylvania Coal Company **Investigator(s):** D. Pike			**Date:** 3/8/04 **County:** Greene **State:** PA
Do normal circumstances exist on the site?	Yes X	No	**Community ID:**
Is the site significantly disturbed (Atypical?)	Yes	No X	Alignment 1
Is the area a potential problem area?	Yes	No X	**Plot ID:**
(if needed, explain on reverse.)			Tributary "B"

VEGETATION

	Dominant Plant Species:	Stratum:	Indicator:		Dominant Plant Species:	Stratum:	Indicator:
1.	*Onoclea sensibilus*	Herb	FACW	11.			
2.	*Carex* sp.	Herb	?	12.			
3.	*Salix* sp.	Shrub	?	13.			
4.				14.			
5.				15.			
6.				16.			
7.				17.			
8.				18.			
9.				19.			
10.				20.			

Percent of Dominant Species that are OBL, FACW or FAC (excluding FAC-)	33%

Remarks:

Little identifiable plant material was present. Less than 50% of the identifiable plant species were FAC or wetter, but it appeared the area would be dominated by hydrophytic species during the growing season.

HYDROLOGY

____ Recorded Data (Describe in Remarks) ____ Stream, Lake, or Tide Gauge ____ Aerial Photographs X No Recorded Data Available	**Wetland Hydrology Indicators:** Primary Indicators: X Inundated X Saturated in upper 12 inches ____ Water Marks ____ Drift Lines ____ Sediment Deposits X Drainage Patterns in Wetlands
Field Observations: Depth of Surface Water: 0-4 (inches) Depth to Free Water in Pit: NA (inches) Depth to Saturated Soil: 0-2 (inches)	Secondary Indicators: X Oxidized Root Channels in Upper 12 Inches ____ Water Stained Leaves ____ Local Soil Survey Data ____ FAC-Neutral Test ____ Others (Explain in Remarks)

Remarks:

Heavy rains had occurred the two days prior to sampling. The wetland appears to be in a low, riparian area that receives water primarily from runoff.

Project/Site: Bailey Road Relocation
Site/Area ID: Alignment 1/Tributary " B"

SOILS

Map Unit Name:
(Series and Phase): Fluvaquents
(Taxonomy Subgroup): _____

Drainage Class: Poorly to somewhat poorly
Field Observations Confirm Mapped Type?
Yes _____ No X

Profile Description:

Depth (inches):	Horizon:	Matrix Color (Munsell Moist):	Mottle Colors (Munsell Moist):	Mottle (Abundance/Size):	Texture, Concretions, Structure:
0-9	A	5PB4/1	none		

Hydric Soil Indicators:

	Histosol		Concretions
	Histic Epipedon		High Organic Content in Surface Layer in Sandy Soils
	Sulfidic Odor		Organic Streaking in Sandy Soil
	Aquic Moisture Regimes		Listed on Local Hydric Soils List
	Reducing Conditions		Listed on National Hydric Soils List
X	Gleyed or Low Chroma Colors		Other (Explain in Remarks)

Remarks:

Because of gleyed coloration, hydric soils are present.

WETLAND DETERMINATION

Hydrophytic Vegetation Present?	Yes X	No		Is this Sampling Point Within a Wetland?
Wetland Hydrology Present?	Yes X	No		Yes X
Hydric Soils Present?	Yes X	No		No

Remarks:

All three wetland criteria were met.

DATA FORM
ROUTINE WETLAND DETERMINATION
(1987 COE Wetland Delineation Manual)

Project/Site:	Bailey Road Relocation		**Date:** 3/8/04
Applicant/Owner:	Consol Pennsylvania Coal Company		**County:** Greene
Investigator(s):	D. Pike		**State:** PA
Do normal circumstances exist on the site?	Yes X	No	**Community ID:** Alignment 1
Is the site significantly disturbed (Atypical?)	Yes	No X	**Plot ID:** Tributary "C"
Is the area a potential problem area? (if needed, explain on reverse.)	Yes	No X	

VEGETATION

	Dominant Plant Species:	Stratum:	Indicator:		Dominant Plant Species:	Stratum:	Indicator:
1.	*Carex* sp.	Herb	?	11.			
2.	*Juncus effusus*	Herb	FACW+	12.			
3.	*Salix* sp.	Shrub	?	13.			
4.	*Agrimonia parviflora*	Herb	FAC	14.			
5.	*Typha latifolia*	Herb	OBL	15.			
6.	*Arctium minus*	Herb	NI	16.			
7.	*Dipsacus sylvestris*	Herb	NI	17.			
8.	*Rubus* sp.	Shrub	?	18.			
9.				19.			
10.				20.			

Percent of Dominant Species that are OBL, FACW or FAC (excluding FAC-) 38%

Remarks:

Of the identifiable plant material, less than 50% of the species were FAC or wetter. During the growing season the area could have a higher percentage of hydrophytic vegetation.

HYDROLOGY

____ Recorded Data (Describe in Remarks) ____ Stream, Lake, or Tide Gauge ____ Aerial Photographs X No Recorded Data Available	**Wetland Hydrology Indicators:** Primary Indicators: ____ Inundated ____ Saturated in upper 12 inches ____ Water Marks
Field Observations: Depth of Surface Water: 0 (inches) Depth to Free Water in Pit: NA (inches) Depth to Saturated Soil: >12 (inches)	____ Drift Lines ____ Sediment Deposits X Drainage Patterns in Wetlands Secondary Indicators: ____ Oxidized Root Channels in Upper 12 Inches ____ Water Stained Leaves ____ Local Soil Survey Data ____ FAC-Neutral Test ____ Others (Explain in Remarks)

Remarks:

The area in question is in low drainage channels on both sides of the main stream.

Project/Site: Bailey Road Relocation
Site/Area ID: Alignment 1/Tributary "C"

SOILS

Map Unit Name:
(Series and Phase): Fluvaquents
(Taxonomy Subgroup): _____

Drainage Class: Poorly to somewhat poorly
Field Observations Confirm Mapped Type?
Yes _____ No X

Profile Description:

Depth (inches):	Horizon:	Matrix Color (Munsell Moist):	Mottle Colors (Munsell Moist):	Mottle (Abundance/Size):	Texture, Concretions, Structure:
0-9	A	10YR3/2	none		

Hydric Soil Indicators:

_____	Histosol	_____	Concretions
_____	Histic Epipedon	_____	High Organic Content in Surface Layer in Sandy Soils
_____	Sulfidic Odor	_____	Organic Streaking in Sandy Soil
_____	Aquic Moisture Regimes	_____	Listed on Local Hydric Soils List
_____	Reducing Conditions	_____	Listed on National Hydric Soils List
_____	Gleyed or Low Chroma Colors	_____	Other (Explain in Remarks)

Remarks:

Rocks prevented collection of soils below 9". Without secondary hydric soil indicators, soils with a chroma of 2 do not meet the hydric soils criteria.

WETLAND DETERMINATION

Hydrophytic Vegetation Present?	Yes _____	No	X	Is this Sampling Point Within a Wetland?
Wetland Hydrology Present?	Yes _____	No	?	Yes _____
Hydric Soils Present?	Yes _____	No	X	No X

Remarks:

The area in question does not meet the required wetland criteria.

ADDENDUM TO

APPENDIX B

PHOTOGRAPHS FOR THE BIOLGICAL EVALUATIONS OF
ALIGNMENTS FOR THE RELOCATION OF SR4009
BAILEY REFUSE AREA

Figure 1. Alignment 1/Tributary "A" non-wetland site February 19, 2004.

Figure 2. Alignment 1/Tributary "A" non-wetland site February 19, 2004.

Figure 3. Alignment 1/Tributary "B" wetland March 8, 2004.

Figure 4. Alignment 1/Tributary "B" wetland March 8, 2004.

Figure 5. Alignment 1/Tributary "B" wetland March 8, 2004.

Figure 6. Alignment 1/Tributary "B" wetland March 8, 2004.

Figure 7. Alignment 1/Tributary "C" non-wetland March 8, 2004.

Figure 8. Alignment 1/Tributary "C" non-wetland March 8, 2004.

Figure 9. Alignment 1/Tributary "C" non-wetland March 8, 2004.

Figure 10. Alignment 1/Tributary "C" non-wetland March 8, 2004.

Emergency Response Plan For the Temporary Closure of S.R. 4009, S.R. 4011 and T-370

Prepared for:

Consol PA Coal Company

December 16, 2003

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December 16, 2003

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P.O. Box 355
Eighty Four, PA 15330

RE: Consol PA Coal Company
Emergency Response Plan
For the closing of S.R. 4009, S.R. 4011 and T-370

Dear Mr. Goroncy,

As discussed with Ron Lehman today, enclosed are twelve (12) copies of the Emergency Response Plan for the temporary closure of S.R. 4009, S.R. 4011 and T-370. Please refer to the attachment for distribution of these copies.

If you should have any questions or require any additional information, please feel free to contact this office at your convenience.

Sincerely,

Mark R. Tercek, PE
Vice-President

0357.02.01ks

Enclosures

cc: CME Engineering, Inc. – 0357-02 (Somerset Office)

Attachment to Emergency Response Plan

Distribution List:

Mr. Jim Inman
Graysville Volunteer Fire Department
181 Stringtown Road
Graysville, PA 15337

Mr. Jeff Lash, Chief
Morris Township Volunteer Fire Department
P.O. Box 98
Ninevah, PA 15353

Ms. Joe Lewis
1195 West Roy Furman Highway
Graysville, PA 15337
(Note: Ms. Lewis will receive 2 copies – 1 copy for the 911 Emergency Coordination Program and 1 copy for Richhill Township VFD)

Mr. Steve Emery
West Finley Volunteer Fire Department
481 West Finley Road
West Finley, PA 15377

One (1) copy for Morris Township Supervisors and Richhill Township Supervisors.

One (1) copy for PADOT.

Three (3) copies plus one additional for Consol.

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Exhibit 3.0: Proposed Emergency Response Routes

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Executive Summary

Consol PA Coal Company (Consol) intends to temporarily close a segment of S.R. 4009, all of S.R. 4011 and a segment of Township Road T-370 (collectively referred to as the Closure). Prior to the Closure, PADOT requested that Consol prepare an Emergency Response Plan to determine any significant impacts the closure may cause. Consol contracted CME Engineering, Inc. (CME) to assist in preparing the Plan.

Consol and CME personnel met with Fire Chiefs from Graysville, Richhill, West Finley VFD, a representative from Morris Township VFD and Supervisors from Richhill and Morris Townships, and Jo Lewis, Greene County 911 Coordinator, on December 11, 2003 to discuss the Closure plans.

The Closure will not affect ambulance (EMS) services. The closure will have no effect on the response routes from either the Morris Township VFD or the West Finley VFD to an emergency in or around the village of Time. Based on discussions with representatives from the Wind Ridge VFD, Graysville VFD, and local township supervisors, a plan was developed to address the Closure. Consol has agreed to assist with the following plan. By Consol implementing the following, the closure will have little to no impact on an emergency response from either Wind Ridge or Graysville VFD as well.

- Have a contractor assist in snow removal on Crouse Road during the winter months.
- Assist in widening Crouse road where feasible and agree to reimburse Richhill Township for material to improve Crouse Road.
- Top-coat Powers School Road in the next paving season.
- Conduct a public open house to answer questions with the area residents prior to the Closing.

By implementing this plan, the Closure of S.R. 4009, S.R. 4011 and T-370 can be implemented with essentially no effect to any emergency response situations. This Plan was discussed and developed with the aforementioned Fire Chiefs, Township Supervisors and EMA personnel.

1.0 Introduction

Consol PA Coal Company (Consol) intends to temporarily close a segment of SR. 4009, all of S.R. 4011 and a segment of Township Road T-370 (collectively referred to as the Closure). These roads are primarily located in Richhill Township; Greene County, PA. Exhibit 1.0: Site Location Map delineates the roads that will be closed. Prior to the closure, PADOT requested that Consol prepare an Emergency Response Plan to determine any significant impacts the closure may cause. Consol contracted CME Engineering, Inc. (CME) to assist in preparing the Plan.

2.0 Existing Emergency Response

Initially, Consol and CME personnel met with Ms. Jo Lewis, Greene County Emergency Coordinator, on December 8, 2003, to discuss the Closure. Ms. Lewis indicated that the area in and around the village of Time would be of most concern for fire protection. The ambulance (EMS) services are provided by Waynesburg and would not be impacted by this closure. Accordingly, the remainder of this Plan addresses fire protection type emergencies. The area of most concern is covered by four separate Volunteer Fire Departments: Graysville, Morris Township; Wind Ridge and West Finley. Exhibit 2.0: Existing Emergency Response Routes delineates the location of each fire department and the emergency route that is utilized. As shown, the Closure would not affect either West Finley or Morris Township response routes. The Closure would affect the route utilized by both Wind Ridge and Graysville. Alternative routes were discussed with Ms. Lewis during the December 8 meeting; however, it was decided that a meeting with all the local Fire Chief's and Township Supervisor's associated with the Closure should be held to discuss alternatives / options.

3.0 Alternatives Meeting

Consol and CME personnel met with the local Fire Chiefs, Township Supervisors and Ms. Lewis on December 11, 2003 to discuss the Closure Plan. Appendix A provides a list of those attending the meeting.

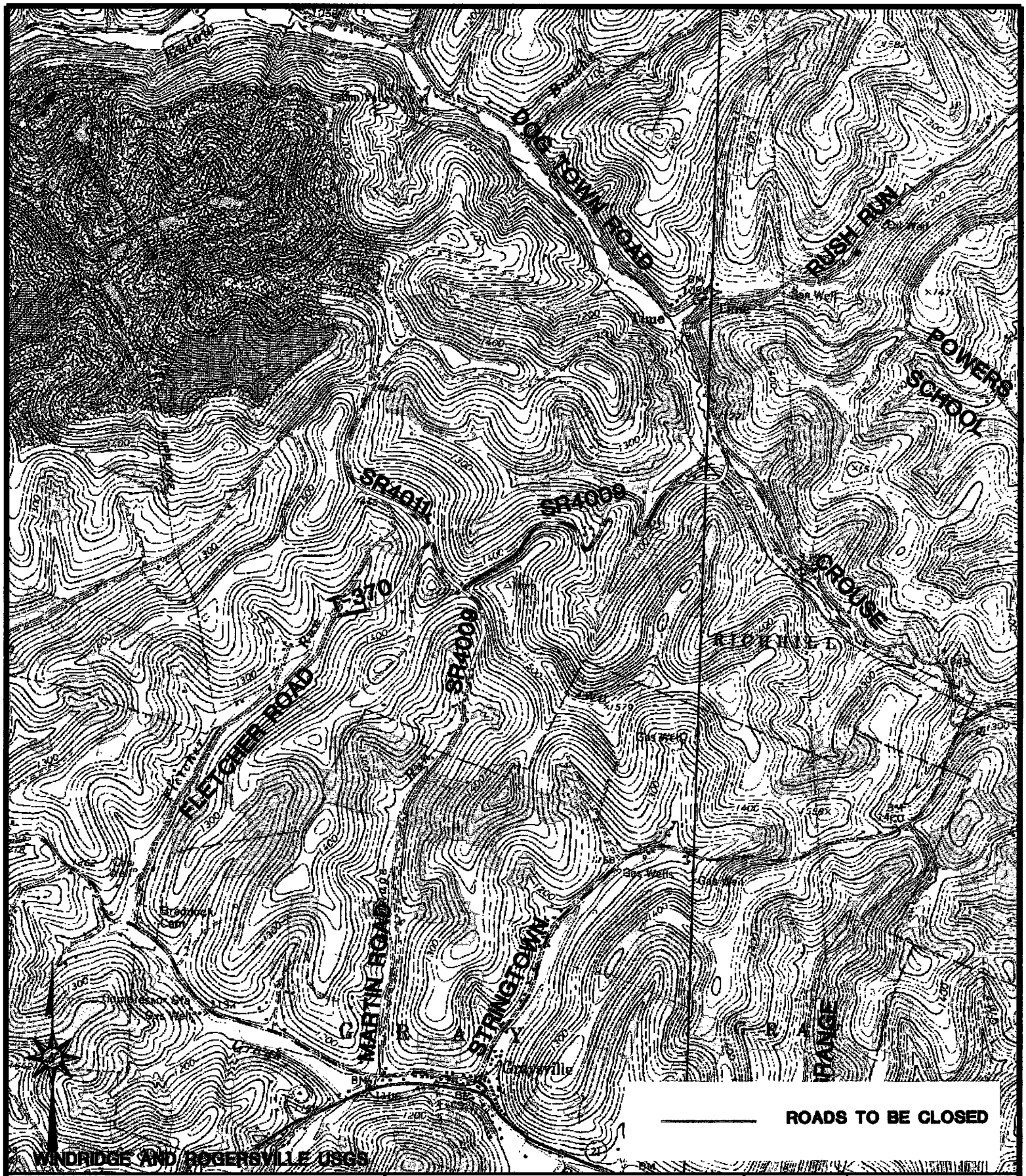
The Closure Plan that was presented identified the temporary closure start date on January 15th, 2004 and the existing emergency routes that would be affected. After lengthy discussions, alternative emergency routes for Wind Ridge and Graysville were designated. Exhibit 3.0: Proposed Emergency Response Routes delineates the proposed emergency routes. As previously stated, no changes to West Finley or Morris Township would occur as a result of the Closure. The result of this meeting concluded that the Closure impacts to an Emergency Response would be negligible provided Consol would perform the following:

- Have a contractor assist in snow removal on Crouse Road during the winter months.
- Assist in widening Crouse Road where feasible and agree to reimburse Richhill Township for material to improve Crouse Road.
- Top coat Powers School Road in the next paving season.
- Conduct a public open house to answer questions with the area residents prior to the Closing.

Consol agreed they would perform these activities.

4.0 Conclusion

The temporary Closure will not affect ambulance (EMS) services. The Closure will have no effect on the response routes from either the Morris Township VFD or the West Finley VFD to an emergency in or around the village of Time. Consol agreed to perform the activities listed in Chapter 3.0 of this report: accordingly, the Closure will have minimal impact on an emergency response from either the Wind Ridge VFD or the Graysville VFD.



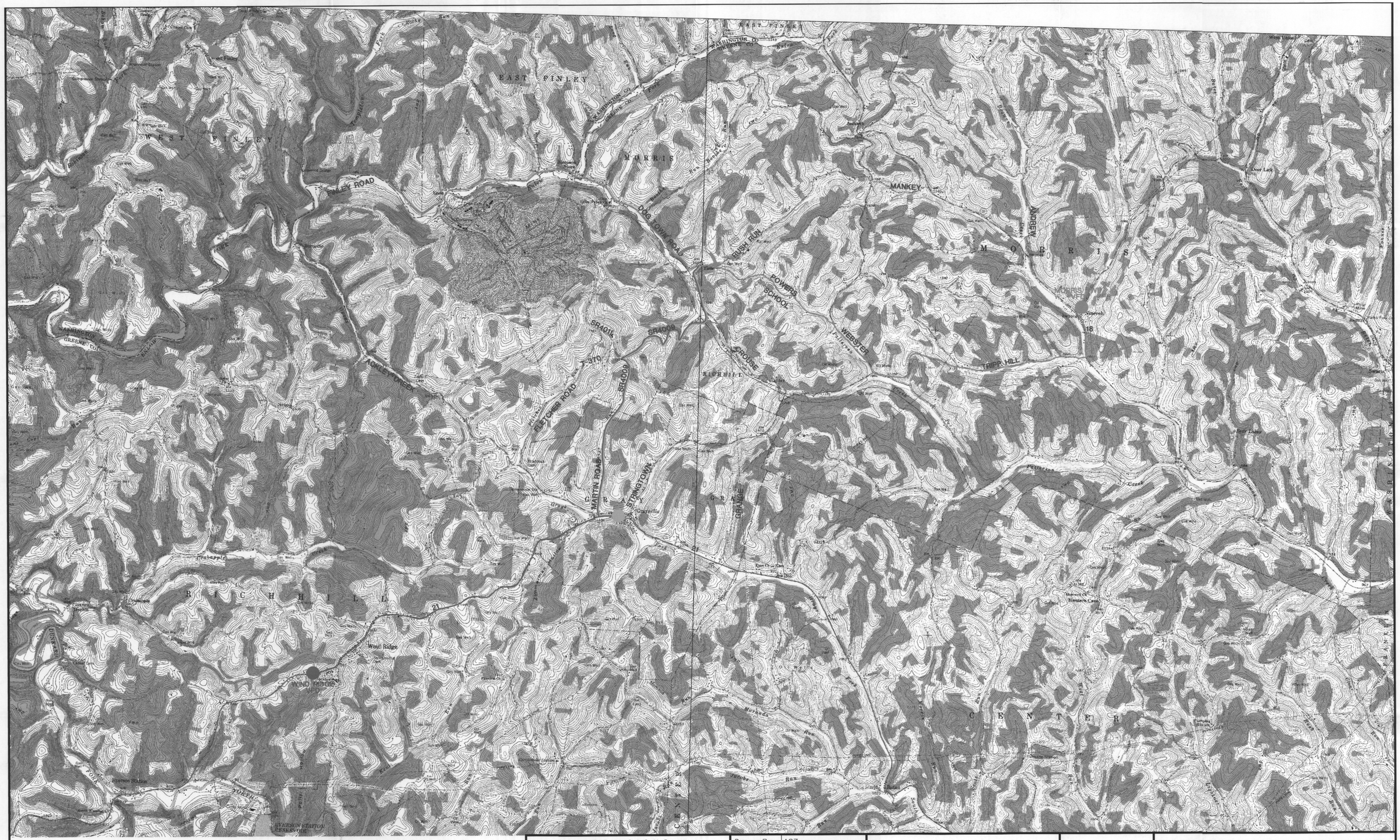
CME ENGINEERING

Civil Mining Environmental Engineering, Inc.
165 E. Union St., Suite 100, Somerset, PA 15501
814-443-3344 FAX: 814-444-0365 E-MAIL: info@cmeeinc.com

EXHIBIT 1- SITE LOCATION MAP
for
CONSOL PA COAL CO.

MORRIS AND RICHHILL TOWNSHIP
GREENE COUNTY, PENNSYLVANIA

Drawn By:	AGZ
Checked By:	MRT
Date:	12/10/2003
Scale:	1" = 2000'
Project No.:	357-01
File Name:	BAILY-RD.DWG



WEST FINLEY VFD. ——— EXISTING TRAVELWAYS TO TIME

WIND RIDGE VFD. ——— EXISTING TRAVELWAYS TO TIME

GRAYSVILLE VFD. ——— EXISTING TRAVELWAYS TO TIME

MORRIS TWP. VFD. ——— EXISTING TRAVELWAYS TO TIME

REVISIONS			
No.	By	Date	Description

Drawn By:	AGZ
Checked By:	MRT
Date:	12/10/2003
Scale:	1" = 2000'
Project No.:	357-02
File Name:	ROAD-RELOCATION.DWG
Drawing:	1 of 2

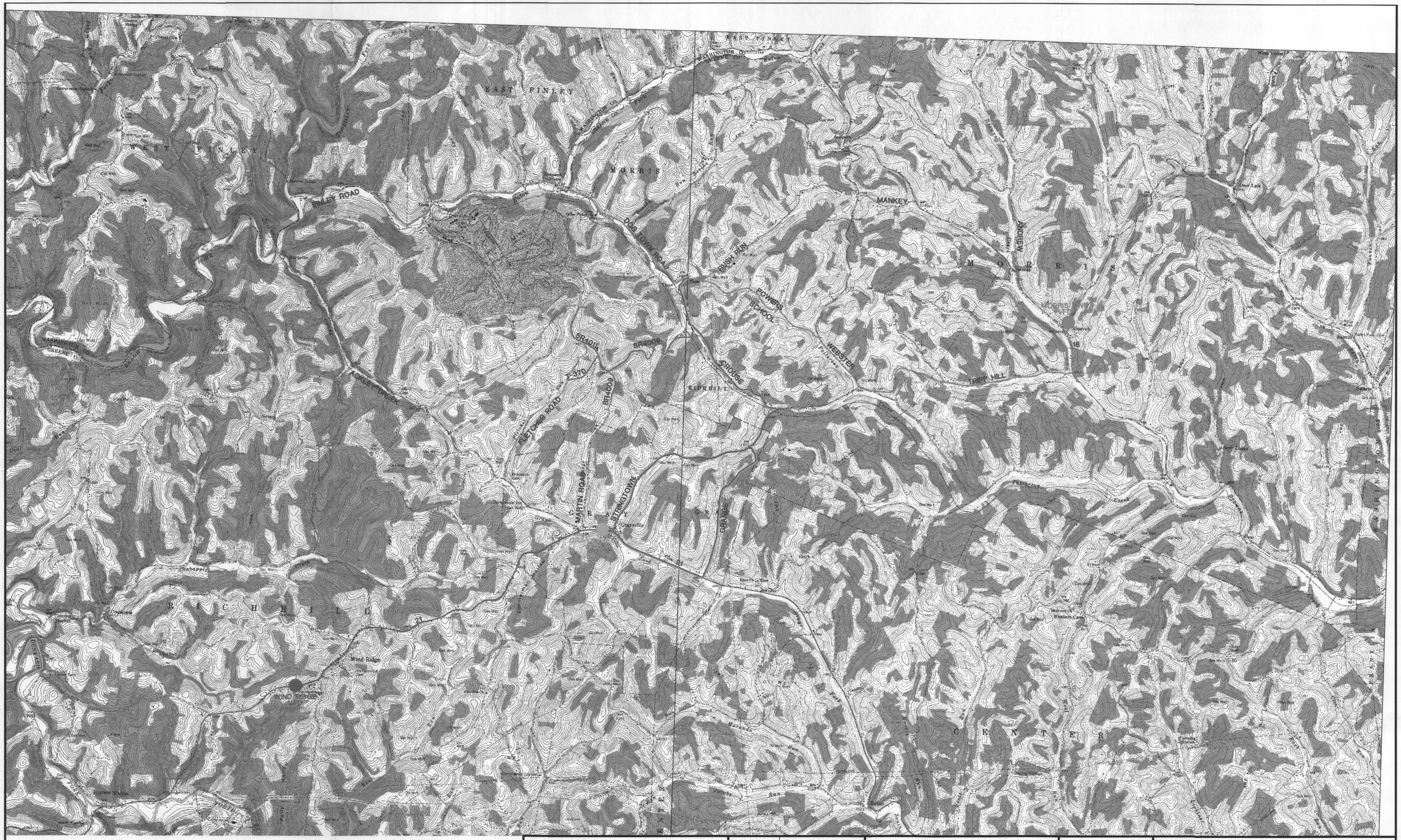
CME
ENGINEERING
Civil Mining Environmental Engineering, Inc.
165 E. Union St., Suite 100, Somerset, PA 15501
814-443-3344 FAX: 814-444-0365 E-MAIL: info@cmeeinc.com

Seal

EXHIBIT 2.0: EXISTING EMERGENCY RESPONSE ROUTES
for

CONSOL PA COAL CO.

RICHHILL, MORRIS, GRAY, AND WEST FINLEY TOWNSHIP
GREENE AND WASHINGTON COUNTY, PENNSYLVANIA



WEST FINLEY VFD. — EXISTING TRAVELWAYS TO TIME

WIND RIDGE VFD. — EXISTING TRAVELWAYS TO TIME

GRAYSVILLE VFD. — EXISTING TRAVELWAYS TO TIME

MORRIS TWP. VFD. — EXISTING TRAVELWAYS TO TIME

ROADS TO BE CLOSED

REVISIONS			
No.	By	Date	Description

Drawn By:	AGZ
Checked By:	MRT
Date:	12/10/2003
Scale:	1" = 2000'
Project No.:	357-02
File Name:	ROAD-RELOCATION.DWG
Drawing:	2 of 2

CME
ENGINEERING
Civil Mining Environmental Engineering, Inc.
165 E. Union St., Suite 100, Somerset, PA 15501
814-443-3344 FAX: 814-444-0365 E-MAIL: info@cmeeinc.com

Seal

EXHIBIT 3.0: PROPOSED EMERGENCY RESPONSE ROUTES
for

CONSOL PA COAL CO.

RICHHILL, MORRIS, GRAY, AND WEST FINLEY TOWNSHIP
GREENE AND WASHINGTON COUNTY, PENNSYLVANIA

Road Relocation Meeting 3/31/04

Jim Goroncy	Consol	724-206-2057
Jo Lewis	911/EMA	724-852-5205
Kenneth Baldwin	Gray	724-428-3702
Dave Bauer	Gray	724-428-4173
Doug Grim	Richhill	724-428-4465
Tom Cohoo	Richhill Twp	724-428-446
Harold Finnegan	" "	" " "
Harold Whyel	Pennsbury	724 429 7136
Ron Clark	"	724-430-4499
Dave Whitlatch	"	724-439-7357
Jeff A Mooney	Morris Twp	724-627-9844
Pam Blaker	Gr Co. Commissioners office	724-852-5210
Sharon Kodavich	Wm DeWeese Office	
Joyce Stewart	CONSOL	412-831-4068
Glenn Adamson	Morris Twp	724-627-9844
Bob Keller	Morris Twp.	724-627-9844
J. William Hook	Solicitor Morris Richhill Gray	(724) 627-614
Christina Schroeder	USACE	412-395-7375
JOHN PAXTON	PA DEP	412-442-5245
MARK TERCEK	CME	814-443-3344
RON LEHMAN	CONSOL	724-206-2035
Joe Cerenzia	CONSOL	412-831-4062
Joe Wilcoy	CONSOL	724-206-2004
TOM SHOTTS	CONSOL	(412) 831-4457

12/11/03 SIGN IN

NAME	LOCATION	PHONE
Tom Sparts	Consol	(412) 831-4457
Steve Emery	West Finly VFC	(724) 428-4128
Jim Enman	Graysville VFD	(724-428-4196
Mark Curtis	" "	724-428-4268
Harold Finnegan	Richhill Twp	724 428 4465
Bob Keller	Morris Twp	724-627-9844
Judy Moninger Sec	Morris Twp	724-627-3096
Doug Grim	Richhill Twp	724-428-4465
Jeff A Mooney	Morris Twp	724-627-9844
Tom Chess III	Richhill Twp	724-4445
Joe Cerenzia	CONSOL	412-831-4062
Dave Whitlatch	PennDOT	724-439-7357
Ron Lehman	Consol	724-206-2036
Mark Tercek	CME	814-443-3344
Jim Goroncy	Consol	724-206-2057
Rick Weaver	Consol	724-206-2029
Joe Wilcox	Consol	724-206-2033
Eric S. Bedilion	Richhill V.F.D.	724-428-3839
Travis Jones	Richhill VFD	724 428-9859
Jo Lewis	911	724-852-5205

U.S. Fish & Wildlife Service

The Value of Headwater Streams: Results of a Workshop, State College, Pennsylvania, April 13, 1999

April 2000

Sponsored by:

Pennsylvania Field Office,
Suite 322, 315 South Allen Street,
State College, Pennsylvania

THE VALUE OF HEADWATER STREAMS

Results of a Workshop
State College, Pennsylvania
April 13, 1999

Sponsored by:

U.S. Fish and Wildlife Service
Pennsylvania Field Office
State College, Pennsylvania

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University of Georgia, Athens, Georgia

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Stroud Water Research Center, Avondale, Pennsylvania

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Stroud Water Research Center, Avondale, Pennsylvania

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The Pennsylvania State University, University Park, Pennsylvania

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FOREWORD

The U.S. Environmental Protection Agency, U.S. Office of Surface Mining, U.S. Army Corps of Engineers, U.S. Fish and Wildlife Service, and West Virginia Division of Environmental Protection are cooperating in the preparation of an Environmental Impact Statement (EIS) on mountaintop mining operations and valley fills in the Appalachian coal fields. As announced in the *Federal Register*, the purpose of the EIS is to:

> ...consider developing agency policies, guidance, and coordinated agency decision-making processes to minimize, to the extent practicable, the adverse environmental effects to waters of the United States and to fish and wildlife resources from mountaintop mining operations, and to environmental resources that could be affected by the size and location of fill material in valley fill sites.

As a result of the public EIS scoping process, the potential for valley filling to adversely affect streams emerged as a priority issue. The multi-agency EIS steering committee identified the following questions, among others, that need to be addressed during preparation of the EIS:

- How will we measure the effects (impacts) of mountaintop mining operations and associated valley fills on streams and aquatic life?

- What are the short- and long-term effects of individual mountaintop mining operations and associated valley fills on the physical, chemical, and biological conditions of affected streams and their watersheds, both within the area of direct impact and downstream? In answering this, consider water quality and quantity, changes in aquatic habitat, and stream use.

- What are the expected effects likely to be on aquatic species of federal and state concern (i.e., listed and proposed threatened and endangered species, candidate species, and species of special concern)?

- What are the relative individual and cumulative effects of a single large valley fill versus multiple small headwater fills? In answering this question, assess the relative value of headwaters and their contribution to the physical, chemical, and biological health of the larger watershed.

- How do we reach a better scientific consensus on the water quality/aquatic habitat values of valley headwater streams so that the on-site impacts of fills, and the resulting mitigation, restoration, and reclamation requirements can be judged more effectively -- both in the fill area and downstream? What does "minimize" environmental damages mean in this context?

- What criteria should be used to determine whether a fill may be placed in a stream?

- What is a stream? The agencies should develop a mutually acceptable approach for reconciling the interagency and interstate differences concerning the definition of streams.

To gather information relative to these questions, a one-day invitational meeting was organized by the Pennsylvania Field Office of the U.S. Fish and Wildlife Service to discuss the value of headwater streams. Experts from industry, government, and academia attended. In advance of the meeting, participants were sent the following list of questions, to be discussed at the meeting:

- What is a stream?
    - At what point in the upper reaches of a stream do regulators stop regulating?
    - How far upstream should we regulate to ensure that downstream functions and quality are maintained?

- Are stream classifications such as perennial, intermittent, or ephemeral ecologically useful or even relevant in this context?

- What indicators do we use to define these conditions? Flows? Fish presence? Invertebrate abundance and/or diversity?

- What can we afford to lose?

  - In evaluating the cumulative impacts of more than one valley fill, what size watershed do we evaluate?

  - How many streams can be eliminated by valley filling in a given watershed before the downstream aquatic ecosystem is unacceptably impaired?

  - If we assume that the amount of overburden material that needs to be disposed of is a constant, is one valley fill or a few very large valley fills better for the environment than more numerous small valley fills at the upper reaches of more valleys?

The meeting was held on April 13, 1999, in State College, Pennsylvania. Participants were informed that the meeting was being tape-recorded, and that the transcript would become part of the formal EIS record.

This report constitutes the meeting record, compiled from notes recorded during the meeting by EPA's Rebecca Hanmer, text slides or overheads used by presenters, and transcription of the meeting tapes by FWS's Cindy Tibbott. In addition, each presenter was given the opportunity to edit a draft transcript of his presentation. The meeting was informal and interactive, so discussions of various technical and regulatory issues are interspersed throughout the speakers' presentations and are delineated by use of a "SMALL CAP" font. Due to space limitations, many of the presenters' slides are not included here.

The State College meeting agenda also included a discussion of technical issues related to the EIS work plan for studying the effects of valley fills on streams. Because that discussion occurred early in the development of the study, and resulted in numerous follow-up discussions and iterations of the work plan, it is not included here.

The EIS steering committee extends its sincere appreciation to the speakers and participants for taking the time to share their expertise and insights on this important issue.

List of Participants

John Arway, Pennsylvania Fish and Boat Commission, Bellefonte, PA
Frank Borsuk, Potesta and Associates, Inc., Charleston, WV
Robert Brooks, The Pennsylvania State University, University Park, PA
Hope Childers, EPA, Wheeling, WV
David Densmore, U.S. FWS, State College, PA
Larry Emerson, Arch Coal, Huntington, WV
Diana Esher, EPA, Philadelphia, PA
Jim Green, EPA, Wheeling, WV
Steven N. Handel, Rutgers University, Bridgewater, NJ
Rebecca Hanmer, EPA, Washington, D.C.
Dave Hartos, OSM, Pittsburgh, PA
William Hoffman, EPA, Philadelphia, PA
Steve Kepler, Pennsylvania Fish and Boat Commission, Bellefonte, PA
George Kincaid, U.S. Army Corps of Engineers, Apple Grove, WV
Fred Kirschner, U.S. Army Corps of Engineers, Apple Grove, WV
Jerry Legg, Virginia DMME, Big Stone Gap, VA
Bernie Maynard, OSM, Pittsburgh, PA
Dan McGarvey, The Pennsylvania State University, University Park, PA
Dennis Newbold, Stroud Water Research Center, Avondale, PA
Maggie Passmore, EPA, Wheeling, WV
Ken Politan, WV DEP, Nitro, WV
Randy Pomponio, Canaan Valley Institute, Valley Forge, PA
Dan Ramsey, FWS, Elkins, WV
David Rider, EPA, Philadelphia, PA
Mike Robinson, OSM, Pittsburgh, PA
Craig Snyder, U.S.G.S. - BRD, Kearneysville, WV
Jay Stauffer, The Pennsylvania State University, University Park, PA
Don Stump, OSM, Pittsburgh, PA
Bernard Sweeney, Stroud Water Research Center, Avondale, PA
Cindy Tibbott, FWS, State College, PA
J. Bruce Wallace, University of Georgia, Athens, GA
John Wirts, WV DEP, Charleston, WV
John Young, U.S.G.S. - BRD, Kearneysville, WV

About the Presenters . . . .

Larry Emerson is Director of Environmental Performance with Arch Coal, Inc., in Huntington, West Virginia. He has a Bachelors degree in Agronomy from Virginia Tech (1978) and has been in the coal mine reclamation and environmental compliance field for 21 years. His professional affiliations include membership in the West Virginia Association of Professional Soil Scientists and the American Society for Surface Mining and Reclamation.

Denis Newbold is a Research Scientist at the Stroud Water Research Center where he studies nutrient cycling, organic particle transport, and riparian zone influences in stream ecosystems. He received a B.S. in engineering from Swarthmore College in 1971, an M.S. in hydrology from Cornell in 1973, and a Ph.D. in aquatic ecology from the University of California in 1977. From 1977 through 1983 Denis worked in the Environmental Sciences Division at Oak Ridge National Laboratory, where he was involved in both theoretical development and experimental analysis of the nutrient spiraling concept. Since joining the Stroud Center (then part of the Academy of Natural Sciences of Philadelphia) in 1983, his work has included modeling temperature influences on insect life histories, experimental studies of the spiraling of dissolved and particulate organic carbon, and investigations of the role of riparian forest buffers in mitigating nonpoint source pollution.

Jay R. Stauffer, Jr., has been working on the systematics, ecology, distribution, and behavior of stream fishes for more than 25 years. He received his B.S. from Cornell and his Ph.D. from Virginia Polytechnic Institute and State University. He co-authored a text on the Fishes of West Virginia, and is currently revising the Fishes of Pennsylvania. He has published some 140 articles in referred journals and is currently Professor of Ichthyology at the Pennsylvania State University.

Bernard Sweeney is presently Director, President, and Senior Scientist at the Stroud Water Research Center in Avondale, Pennsylvania, and an adjunct Professor at the University of Pennsylvania. The Stroud Center was founded in 1967 and is focused on producing new knowledge, greater understanding, and better appreciation of streams, rivers, and their watersheds through programs emphasizing basic and applied research and environmental education. Bernard has a Ph.D. from the University of Pennsylvania (1976) in Zoology and has published research papers on the following topics: Population and community ecology of aquatic invertebrates, the role of streamside forests in the structure and function of stream and river ecosystems, the effects of global warming on stream ecosystems, genetic variation and gene flow among populations of stream insects, factors affecting the growth and development of aquatic insects, bioenergetics and secondary production of aquatic insects, and the bioassay of toxic materials in aquatic systems.

J. Bruce Wallace received his B.S. from Clemson University, and M.S. and Ph.D. from Virginia Tech. He is currently Professor of Entomology and Ecology, University of Georgia, Athens, Georgia, where he teaches courses in stream ecology, aquatic entomology, and immature insects. He has served as major professor of some 38 graduate students at Georgia. Dr. Wallace is author, or co-author, of some 150 scientific papers, including book chapters concerned with various aspects of stream ecology, or aquatic entomology. Much of his research during the past 25 years has been conducted on southern Appalachian streams at the Coweeta Hydrologic Laboratory (U.S. Forest Service) in western North Carolina and supported primarily by the National Science Foundation. His primary research areas include: linkages between streams and terrestrial ecosystems; role of aquatic invertebrates in stream processes; effects of disturbance and recovery of streams from disturbance; secondary production and aquatic food webs and energy flow; and organic matter dynamics in headwater streams. Dr. Wallace is a past president (1991-1992) of the North American Benthological Society. He was the recipient of the 1999 Award of Excellence in Benthic Science from the North American Benthological Society.

EXECUTIVE SUMMARY

Mountaintop mining is a form of strip mining that uses large equipment to access multiple coal seams across large tracts of land. The terrestrial landscape is dramatically altered, and streams are filled with overburden material. Over the last approximately 20 years, the size of individual operations has increased, as has the number of mountaintop removal mines, leading to public concern over the cumulative environmental and social impacts of this mining method across Appalachia.

To help assess the potential impact of stream filling activities on the aquatic ecosystem, a one-day invitational meeting was organized by the Pennsylvania Field Office of the U.S. Fish and Wildlife Service to discuss the value of headwater streams. The speakers focused on the description of the mining method and the headwaters environment in which it is carried out. Special emphasis was placed on the ecological context and importance of headwater streams within the larger aquatic ecosystem.

Larry Emerson (Arch Coal) provided an overview of large-scale mountaintop mining as it is practiced in West Virginia. The demand for low-sulfur coal is the purely economic force driving the increase in mountaintop mining. This mining method allows companies to recover 85 to 90 percent of the coal resource. Companies are able to use large-scale mining because of their ability to put together large, contiguous tracts of land in West Virginia. Production costs are primarily in moving rock. This mining method is best employed on coal seams within the Stockton level and above, in southern West Virginia. These areas have already been deep- and contour-mined in the past, so there are few untouched coal reserves remaining. The estimated life of large-scale mining in the state is about 15 more years.

Mr. Emerson stated that, in the creation of the post-mining topography, there is real potential for water resources to be maximized so that wetlands and stream channel areas with biotic communities can be created. In addition, there is a great potential for re-mining pre-SMCRA mine sites, reclaiming them and bringing them up to today's standards in the process.

Bruce Wallace (University of Georgia) has been studying headwater streams at the Coweeta Hydrologic Laboratory in western North Carolina for 30 years. He has conducted a number of experiments that demonstrate the reliance of stream biological communities on inputs from the surrounding forests. For example, when leaf litter was excluded from a stream, the primary consumer biomass in the stream declined, as did invertebrate predators and salamanders (there are no fish in these small streams; salamanders are the only vertebrate predators). Overall, leaf litter exclusion had a profound effect on aquatic productivity, illustrating the direct importance of terrestrial-aquatic ecotones. Other experiments illustrated the fact that, while invertebrates and microbiota in headwater streams are only a minute fraction of living plant and animal biomass, they are critical in the export of organic matter to downstream areas by converting leaf litter to fine particulate organic matter, which is much more amenable to downstream transport than the leaves themselves are. Organic matter transport to downstream reaches totals about 1 kg of export per meter length of stream on an annual basis, and comprises a large proportion of the food supply for invertebrate populations downstream, which in turn become food for fish populations.

Dr. Wallace raised the concern that stream thermal regimes, which can have important influences on microbial activity, invertebrate fauna and fish egg development, larval growth, and seasonal life cycles, may be affected by valley fills and sedimentation ponds at the base of the valley fills. In addition, with the documented increases in nitrogen deposition that are occurring in eastern North America, we need to understand what is happening to nitrate concentrations in streams emerging from valley fills.

Dr. Wallace expressed concern that this mining practice is eliminating first order streams with no requirement for pre-impact biological inventories. Streams in the southern Appalachian region have been found to harbor outstanding biological diversity, with rare species known to occur in only one or two springbrooks or seepage areas.

Bernard Sweeney (Stroud Water Research Center) provided insights into the value of headwater streams based on research in southeastern Pennsylvania that has been ongoing since 1968. The Center's Robin Vannote formulated

what has become known as the "River Continuum Theory," which views the stream ecosystem as a continuum from the first order headwater streams down through the larger order rivers. Results from the first few years of research at the Center demonstrated that first order streams are both abundant and crucial to the overall function of the ecosystem.

Dr. Sweeney emphasized the relationship between streams and the surrounding terrestrial environment. As wet depressions in the landscape, leaves tend to blow across the forest floor and get stuck in the streams. Very little of this coarse organic material (leaves) is transported downstream; most is processed by living organisms. Streams flowing through grassy areas have much lower inputs of coarse organic material than streams flowing through forests; this is a concern regarding the concept of reconstructing streams in grassy reclamation areas. Different kinds of leaves (from different species of trees) affect the production and biomass of invertebrates. In addition, as precipitation percolates through leaves on the forest floor, it extracts organic compounds from the leaves, similar to the effect of steeping a tea bag in hot water. These dissolved organic compounds -- "watershed tea" -- are carried to the stream by groundwater and drive a major portion of the aquatic system's productivity.

The stream bottom is the crucial site of biological and biochemical activities in stream systems. About 32 percent of the total bottom area in the White Clay Creek watershed is in first order streams. High species diversity is typical of benthic invertebrate populations in small headwater streams. Densities of invertebrates are similar in small, first order streams and larger streams, but the fact that there is so much benthic area available in small streams, and there are so many of them, mean that collectively the headwaters account for abundant production in the system.

The turnover of benthic invertebrate species is high as you travel down through the river continuum; there are few species in the headwaters that also occur downstream in a large river. This raises the question of what happens if headwater streams are eliminated. If a species occurs only in first, second and third order streams, and the first and second order streams are eliminated, how long can the third-order population persist? Because human developments typically concentrate along third, fourth, and fifth order streams, this is where accidents will happen that destroy aquatic life. Recolonization would occur through organisms moving in from the upstream, smaller tributaries -- but only if the tributaries still exist.

Dr. Sweeney cautioned that the area of eastern West Virginia and western Virginia are hotspots of new species discovery, due to thermal diveristy, and the lack of glaciation which allowed time for species to evolve. The aquatic insects of this area haven't even been fully characterized yet, and we can't afford to destroy what we don't know.

Denis Newbold (Stroud Water Research Center) discussed Webster and Wallace's concept of nutrient spiraling, which is a way of assessing the effectiveness of an ecosystem at processing nutrients. The tighter the nutrient spiral, the more effective the ecosystem is at trapping and reusing organic matter and nutrients as you move downstream. The spiraling length is relevant to the mountaintop removal issue, because it gets at the question of where, if you're an organism living in a downstream ecosystem, your nutrients originated.

In a typical stream carbon cycle, much of the dissolved organic carbon (DOC) in a stream is refractory (it doesn't get used very fast, and is transported great distances downstream). On the other hand, a significant portion of the DOC is labile, and it cycles within the stream ecosystem. About half of the labile DOC produced within any given reach of stream will be utilized within that reach, while the remainder is passed to a larger downstream reach. The next reach (the next order stream) will have a proportionately longer turnover length. Each downstream reach uses a portion of the labile DOC passed from upstream, and passes the remainder downstream. The downstream transfer and utilization of carbon successively cascades downstream. Turnover lengths also vary depending on the type of material being transported. Very fine particulate organic matter can move 10,000 km downstream, generally putting it into the ocean; refractory can move even farther, and on its way it feeds larger streams, rivers, and estuaries. While there is a wide range of stream ecosystem efficiency, the median is about 50% regardless of the size of the watershed.

Dr. Newbold discussed a possible scenario for the organic content of streams emerging from the toe of a valley fill. Precipitation will pick up organic matter from the revegetated valley fill surface, percolate through the fill, and eventually emerge below the fill as water with low-concentration refractory, possibly even at concentrations similar to what would have been there without the fill. However, the stream emerging from the fill will be missing the labile

dissolved and particulate organic matter that would have been produced by the stream that is now buried, and it is this labile portion, produced by the stream itself, that supports downstream metabolism.

Summarizing, Dr. Newbold explained that a significant portion of exported organic matter originates within the stream and is labile. Soil and riparian areas next to the stream are major sources of carbon, and the decomposition of litter and the primary production of material in the stream are also important sources of organic matter that get exported downstream. Most of the organic matter inputs to mid-order streams originated from first and second order streams; between 60 and 80% of the water feeding a fourth-order stream came from first and second order streams. If you're in a fourth order basin, and you eliminate the first and second order streams, you eliminate half of the water and drainage area and stream bed area to the downstream larger order.

Jay Stauffer (Pennsylvania State University) discussed eliminating headwater streams from the standpoint of fish populations that occur in these areas.

Dr. Stauffer discussed many factors that lead to speciation in fish in headwater streams. It is a common misconception that fish fauna are well-known, and that there are no unique fish present in the coalfields' headwater streams. In fact, many headwater streams have fish populations that have become isolated due to any number of causes, and minimal gene flow with the main population results in the development of new species. These species may occur only in one or two small streams, and nowhere else.

These streams may even support populations of migratory fish, such as lampreys. Other species may move into headwater streams at certain times of the year, but won't be found there at other times.

Dr. Stauffer discussed the concepts of ecosystem inertia and elasticity. Inertia concerns the ability of a stream to withstand stress before structural components of the ecosystem change. Headwater streams may only have two or three species of fish, so there is little functional redundancy built into the fish community. The loss of one species would mean the loss of one-third of the fauna, which is a structual change. This causes a more drastic impact on the ecosystem than it would if a species were lost in a larger stream that supported many species. Other factors, such as buffering capacity, or how close the stream is to a major ecological threshold -- such as thermal limits -- are involved in determining a stream's inertia.

The elasticity of the system considers such factors as whether or not there are epicenters nearby that could provide organisms to reinvade a damaged ecosystem. In many headwater streams with unique fish or invertebrate species, there simply are no epicenters from which recolonization can take place -- these organism may only occur in one place. These headwater streams are very fragile and have very low inertia, and their ability to recover from stress is probably compromised because they are so unique and so different. Dr. Stauffer argues that we should not be taking chances with streams that support genetically unique aquatic life, because we can't risk losing that genetic diversity.

Dr. Stauffer discussed the possibility of "recovery" of stream ecosystems by trying to recreate streams on the mine benches, stressing that the goals of the recovery effort must be clearly articulated in advance: Do we want the stream or ecosystem back to the way it used to be? Is it satisfactory if something can just live in the system? If something different lives in the system, is it satisfactory if it serves the same basic functions as the original?

Larry Emerson, Arch Coal, Inc., Huntington, West Virginia

I'd like to first, illustrate in schematics and photos the process of large-scale mountaintop mining as it's practiced today in West Virginia, with particular emphasis on valley fills, which seem to be the focus of all these efforts. Secondly, to point out the relative value of some of these reclaimed sites with respect to water resources, and also to emphasize the potential of some of these post-mining sites to have some water resource value. Also, to touch on the reality that some mountaintop mining operations in existence today are going in and remining previously-mined, pre-law sites, and there is yet additional potential to remediate past mining scars from back in the '40's and '50's. I also have a slide on the areal extent of mountaintop mining in West Virginia from the West Virginia Geological and Economic Survey. Also, I can offer some of our mines for consideration as sites to be studied during the process. Should they fit the criteria, we offer them for consideration.

With respect to Arch's West Virginia operations, we have four of the six largest mining complexes in West Virginia. These four sites have walking draglines -- the large-scale equipment which allows us to compete under today's economic conditions. Just so everyone understands, the reason for mountaintop mining in West Virginia today is purely economics and markets. Demand for low sulfur coal is driving the eastern coal market. The other large deposits of low-sulfur coal are in the Powder River Basin which is very cheap to produce, due to thick coal seams, some reaching 68 feet. West Virginia's seams are more like 4 - 6 feet. With mountaintop removal, we can recover 85 to 90 percent of that coal resource, whereas with other mining methods it's sometimes significantly less than that. It is the large-scale ability to put together contiguous leased tracts of land in West Virginia (and there are historical reasons for that) that have allowed this type of large-scale mining to take place.

This is a schematic showing a typical dragline operation in West Virginia. The analogy I like to make is with a layer cake. If you take a slice through these mountains, it's like a layer cake with the fudge icing being the coal seams and the sandstone and shale strata in between the coal seams representing the cake. Some of these mountains contain 11 - 12 coal seams, mostly oriented horizontally, but there is some localized roll and dip in the seams. The first stage in the mining operation is to clear the area of vegetation (usually the landowner is responsible for this stage). The upper elevations of the mountain are then drilled, blasted, and excavated to recover the first coal seam. That overburden is deposited in the only available, stable place to put it, which is in the adjacent valley. That process proceeds downward to the lower elevations until you reach a certain coal seam elevation where the dragline is then deployed. The dragline then excavates down to the bottom two coal seams. The function of the dragline is basically to pick up the rock strata from point A and moves it to point B. The dragline excavation moves laterally through the mountain, uncovering these coal seams. Smaller equipment extracts the coal. Reclamation follows with bulldozers, resculpting the area to its post-mining topography with some rolls and undulations. It is possible to do a fair amount of creation in terms of how you re-grade to the post-mining topography. There's real potential here for post-mining water resources to be optimized so that there can be some addition of stream channel areas with which there could be some biotic communities restored.

Here's how it works operationally, at the Catenary Mine in Kanawha County: The upper horizons are excavated with smaller equipment, such as loaders and trucks. Then the electric shovel excavates down through the middle horizons, uncovering one or more coal seams from the top downward. Finally the dragline is utilized to uncover the lower coal seams. The dragline and shovel only move rock. We're basically rock miners, because we move multiple cubic yards of rock to recover one clean ton of coal, so our production costs are mainly in moving rock. Finally, the overburden is re-graded and shaped to its post-mining topography, which can be gently rolling with undulations and watercourses that approximate the pre-mining topography. So it's in this post-mining topography where we have a real potential to put in basins, check dams, stream channels, to recreate water areas where you can capture rainwater, allow it to accumulate or pool up, and there's potential to create wetland resources.

Now for an explanation of valley fill construction, the first order of business is sediment control. You go into your permitted valley fill area and construct the sediment control structure, which is designed on the maximum amount of the disturbed watershed behind it. West Virginia requirements are 0.125 acre-feet of sediment storage capacity for each acre disturbed. The actual construction of the fill begins at the headwaters; the excavated rock material is placed first at the headwater areas, then progresses downstream. Proceeding on, this is your classic end-dump valley fill, where the larger rock, just by shear gravity and segregation, rolls down to the bottom, creating internal drainage through the fill. There are still going to be some perched aquifers on either side of the hollow, and there will also be

some surface runoff -- this reality is accounted for in the design process and the result is that these structures are somewhat porous and there's a fair amount of infiltration. The big rocks that roll down to the bottom provide void spaces and places for water to be stored. When you reach the permitted extent of the valley fill, you put in post-mining sediment control and drainage ditches. These are generally 50-foot vertical lifts with 20-foot horizontal benches, with a certain percentage grade down to the center (this is the center core fill). Some fills are side drained fills, with groin ditches on each side (different fill design). The final stage requires certification by a registered professional engineer and revegetation.

During the active phase of mining, the area is open to the elements and weathering. This phase can run from 6 to 18 months in length. However, all surface runoff is channeled through a sediment control structure and regulated as a point source under the Clean Water Act. After final reclamation, the post-mining topography lends itself to re-creation of water resources. Ponds, basins, check dams, and bench sediment control structures are all designed to handle the surface runoff from predetermined rain events under the Surface Mining Act. It is with these structures that wetland resources could be created on the mine site.

There's also a lot of potential to remine previously mined areas (pre-law) -- these can be reclaimed and brought up to current standards. These examples are from the Catenary site. Old refuse fills that have been abandoned prior to 1977 can be capped over and reclaimed using modern mining methods [showed slide of reclaimed area]. Old slurry impoundments have been eliminated as part of the mitigation process; when some of these sites are reclaimed, current law allows mitigation credits. There are opportunities for creating wetlands for treating pre-law discharges. There's a substantial body of knowledge out there on re-creating wetlands, and there's lots of potential to do this on older mine sites.

This slide is another illustration of some of the post-mining water resources suitable for aquatic life. Some of them are even flowing. The top of a valley fill is shown on the slide, with a wide bench on the perimeter. SMCRA does not allow standing water on valley fills, but there are a lot of other areas of the reclaimed site that lend themselves very well to wetland resources. We can construct basins and settling ponds to capture rainfall, and over time infiltration occurs through the backstack that ultimately can provide a post-mining spring in certain limited circumstances. Another example is a perimeter ditch around the periphery of the mine site.

The Hobet 21 site was the first area to use a walking dragline in West Virginia, in 1983. We've had 15 years of large-scale mining at that site. The area now has over 50 valley fills. It lies in the upper Mud River drainage. This site may provide opportunities for study.

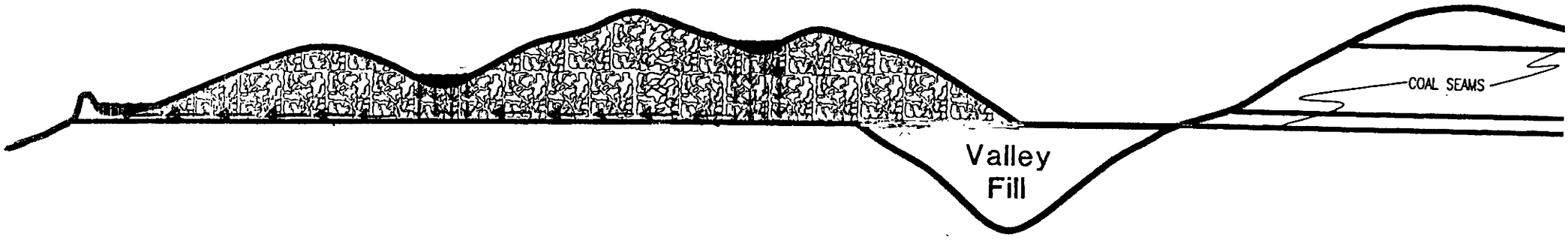
This overhead (Figure 1) reinforces the concept of back-filled areas and valley fills to present opportunities for post-mining water resources. We have found through experience that valley fills are porous in nature and water becomes stored within the fill. This stored water is continuously released to the receiving stream, and provides significant flow during extended dry periods.

This overhead (Figure 2) shows a typical cross section of a valley fill, using center core construction method, where you're dumping from the headwaters and on each side laterally as this is constructed from the headwaters on down to the mouth. As you can see, the larger rocks roll to the center and to the bottom and creates that porous area. There is water flowing from the toe of these areas. With regard to the backfill areas, this overhead represents the undisturbed solid area just below the lowest coal seam that was mined. This barrier acts as an aquaclude and prevents the downward infiltration of water. As we construct basins, channels, and ponds on top, some water infiltrates, reaches the shale underlying the lowest coal seam, and stops there and flows down-gradient and pops out at the toe of one of the outslopes, and in several occasions there is flowing water coming out of these sites.

KINKAID -- DEFINE BACKFILL. EMERSON -- BACKFILL IS ROCK STRATA THAT IS REMOVED DURING THE MINING PROCESS TO UNCOVER THE COAL SEAM, AND IS DEPOSITED ON TOP OF THE SOLID BENCH WHICH IS REPRESENTED AS THE HORIZONTAL DISTANCE FROM ONE SIDE OF THE MOUNTAIN TO THE OTHER. BY CONTRAST, THE VALLEY FILL MATERIAL IS DEPOSITED ADJACENT TO THE BENCHED BACKFILL AREA (SEE DRAWING). BACKFILL IS COMPOSED OF SANDSTONE, SHALE AND OVERBURDEN, OR INTERBURDEN WHICH IS ROCK FROM IN BETWEEN COAL LAYERS. THIS MATERIAL IS PICKED UP BY THE DRAGLINE AFTER IT'S BEEN DRILLED OR BLASTED, THE DRAGLINE TURNS AROUND 90 DEGREES, AND DEPOSITS THE MATERIAL SOME 200 FEET TO THE SIDE. THIS "SPOIL PILE" IS THEN RESCULPTED TO ITS POSTMINING

EXPLANATION

Backfill Material
Water Percolation Path
Undisturbed Rock Strata (barrier to downward percolation of water)
Direction of Groundwater Flow

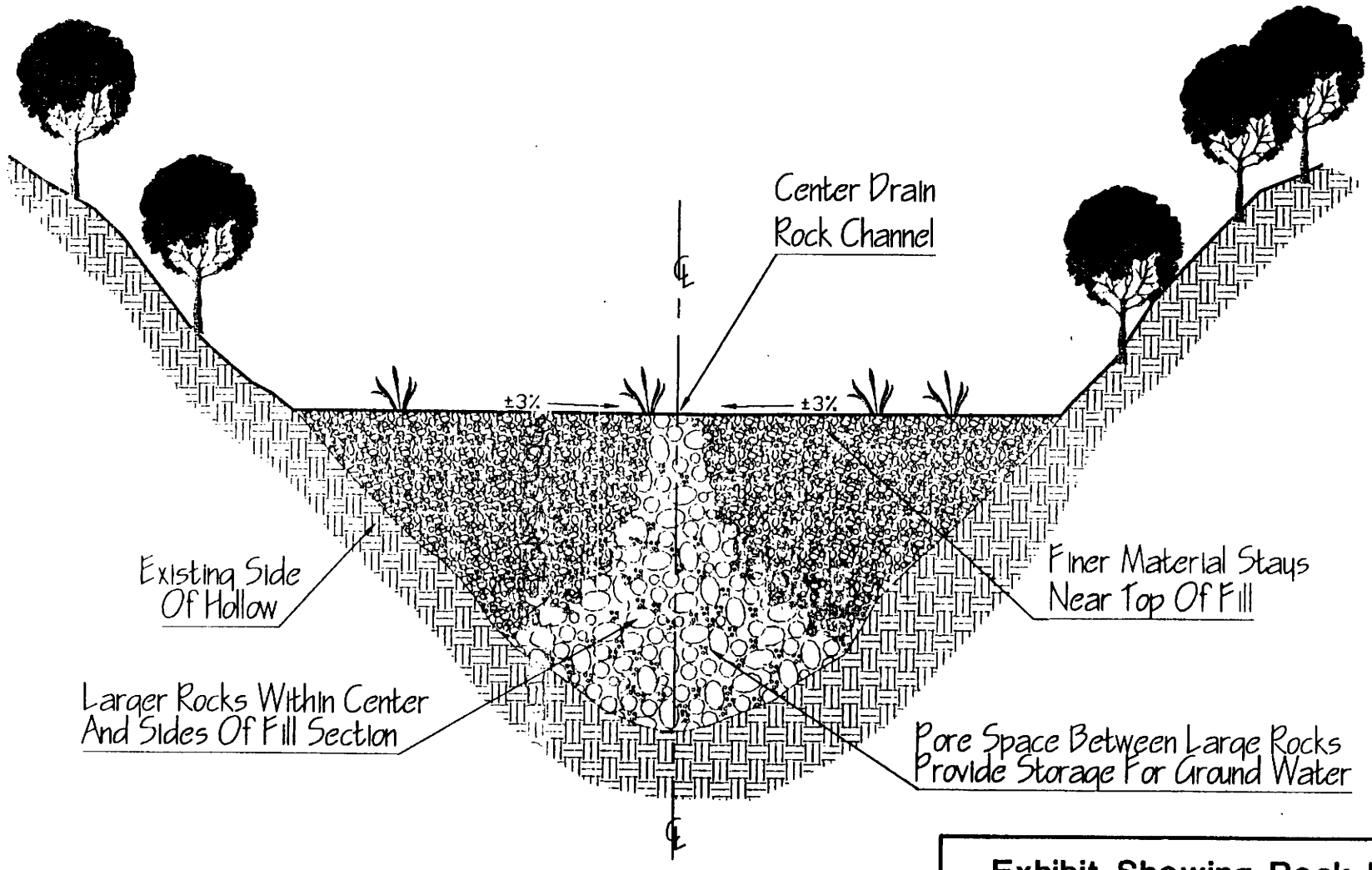


REGRADED SECTION OF BACKFILL ON SOLID BENCH

Backfilled rock material is very permeable and allows rainwater to percolate through and become stored as groundwater. This new recharge area then becomes the source of water for post mining streams and seeps.

FIGURE 1.

Typical Cross Section Of Finished Valley Fill



Valley Fill Section

Exhibit Showing Rock Blanket And Ground Water Storage Capacity Of Fill

FIGURE 2.

TOPOGRAPHY. **KINKAID** - IS IT COMPACTED OR JUST DROPPED? **EMERSON** - IN THE CASE OF THE DRAGLINE EXCAVATION, IT'S JUST DROPPED. WITH RESPECT TO COMPACTION, THERE'S SOME COMPACTION GOING ON WHEN YOU'RE RESCULPTING THIS, WHEN YOU PUT A DOZER ON THERE. REMEMBER THE SPOIL PILES ARE FAIRLY SHARP WHEN YOU FIRST DEPOSIT THEM, THEN YOU PUT BULLDOZERS ON THEM TO SHAPE THEM OFF, MAKE THEM SMOOTHER, AND PREPARE THE SEED BED. THERE'S AT LEAST SOME COMPACTION THAT GOES ON THERE WHEN YOU HAVE THE BULLDOZERS RESHAPING.

KINKAID - WITH SANDSTONE AND SHALE, THERE IS SOME POTENTIAL FOR ACID LEACHING, GIVEN THE COMPOSITION OF THE 5 BLOCK COAL. WHAT IS PUT ON THE SURFACE FOR REVEGETATION? **EMERSON** - SOMETIMES, TO THE EXTENT NATIVE SOILS CAN BE SALVAGED AND REDISTRIBUTED, THAT HAPPENS, BUT THAT'S MORE AN EXCEPTION RATHER THAN THE RULE. THERE IS A PROVISION IN THE REGULATIONS THAT ALLOWS FOR AN ALTERNATE TOPSOIL MATERIAL TO BE USED IF CAN BE TESTED AND SHOWN TO BE THE "BEST AVAILABLE" THAT IS WITHIN THE STRATA. IF IT'S TESTED AND SHOWN TO HAVE GOOD SOIL MEDIUM CHARACTERISTICS AND YOU PUT TOGETHER A HANDLING PLAN THAT SHOWS HOW YOU RECOVER THOSE PARTICULAR STRATA AND USE THEM AS SOIL MEDIUM, THIS TENDS TO BE THE RULE: WE'RE BASICALLY CREATING NEW TOPSOILS FROM SHALE AND SANDSTONE THAT EXISTS WITHIN THE MOUNTAIN PRIOR TO MINING. IT'S BEEN OUR EXPERIENCE THAT IT'S VERY CALCAREOUS IN NATURE (PASTE pH BETWEEN 6.5-7.5), WITH A FAIR AMOUNT OF CALCIUM AND MAGNESIUM, WHICH DOES CERTAINLY INCREASE THE TDS OF POST-MINING WATER QUALITY. THERE'S NO DOUBT ABOUT THAT. IT DOES INCREASE THE BUFFERING CAPACITY AS WELL.

KINKAID - YOU'RE PLACING SOIL OVER THE VALLEY FILL AND BACKSTACK MATERIAL? **EMERSON** - YOU MEAN SALVAGING NATIVE TOPSOILS? **KINKAID** - I'M WONDERING WHAT'S ON TOP OF THE BACKSTACKED MATERIAL AND VALLEY FILL FOR THINGS TO GROW? **EMERSON** - IT'S GENERALLY A MIXTURE OF SANDSTONE AND SHALE THAT'S IN THE INTERVAL BETWEEN THE 5 BLOCK AND STOCKTON FORMATIONS WHICH IS A MIXTURE THAT WINDS UP ON TOP OF THE SPOIL PILE AS A RESULT OF THE EXCAVATION. WE HAVE FOUND THAT SINCE pH IS FAIRLY HIGH AND THE MATERIAL WEATHERS FAIRLY READILY, THAT PARTICLE SIZE DISTRIBUTION, ALTHOUGH FAIRLY SANDY, STARTS TO APPROACH LOAM IN MOST CASES. WE ADD NITROGEN, PHOSPHOROUS, AND POTASSIUM AND SEED MIXTURE, MOSTLY THROUGH HYDROSEEDING. IT ACTUALLY GROWS HERBACEOUS COVER VERY WELL. WHAT GOES ON THERE IS PART OF THE PROCESS OF EXCAVATING THE MATERIAL. AFTER THE STRATA HAS BEEN BLASTED AND RE-HANDLED, YOU PUT THE BULLDOZERS ON TO RE-SCULPT IT, YOU GET A FAIR AMOUNT OF FINE MATERIAL DURING THE PROCESS. WE THEN SPRAY OUR MIXTURE OF GRASSES, LEGUMES, FERTILIZERS AND MULCH AND IT GROWS THAT GRASS/LEGUME MIXTURE VERY WELL. SO OVER TIME YOU'RE BASICALLY CREATING A NEW SOIL AS A RESULT OF USING THIS BRAND-NEW PARENT MATERIAL. **KINKAID** - DO TREES GET ESTABLISHED? TREES ARE HAND-PLANTED AFTER HERBACEOUS COVER IS ESTABLISHED, BECAUSE OF EROSION CONTROL REQUIREMENTS. THAT DOES PRESENT SOME PROBLEMS IN GETTING TREES ESTABLISHED QUICKLY. WE HAVE FOUND THAT PIONEER SPECIES TEND TO COMPETE WELL WITH GRASSES AND THEY HAVE AN EDGE OVER NATIVE HARDWOODS. GENERALLY POPLARS, MAPLES, ASH, BIRCH, BLACK CHERRY, ETC., WILL GROW FAIRLY WELL AND COMPETE WITH THE GRASSES AND LEGUMES THAT ARE ALREADY ESTABLISHED. IT'S GENERALLY MUCH MORE DIFFICULT TO ESTABLISH HARDWOODS. WE HAVE FOUND THAT BY GOING TO OLDER SITES THAT WERE MINED IN THE MID-70S, ON THE OUTSLOPES WHERE MATERIALS WERE PUSHED OVER AND NOT COMPACTED, AND NOT ANY KIND OF POST MINING SEEDBED PREPARATION TOOK PLACE, WHERE IT'S LEFT LOOSE AND ROUGH -- THOSE GENERALLY WERE MUCH MORE CONDUCIVE TO NATURAL SUCCESSION OF HARDWOODS ONTO THESE SITES. ON TOP OF THE OLDER 20-YEAR OLD SITES, WHERE THERE WAS A FAIR AMOUNT OF COMPACTION, NATIVE TREES HAD A HARDER TIME. SO COMPACTION PLAYS IN A ROLE IN THAT.

KINCAID - WHEN MATERIALS ARE RELOCATED TO VALLEY FILL AND BACKSTACK LOCATIONS, HOW ARE THEY CHARACTERIZED AS TO ACID-BASE ACCOUNTING AND THE PHYSICAL CHARACTERISTICS OF THE ROCK -- WHAT ABOUT THE MATRIX WHICH CEMENTS THE SANDSTONE. IS THE MATRIX SUBJECT TO ATTACK BY NATURAL WATERS OR WATERS THAT MAY BE ALTERED AS A RESULT OF FLOW-THROUGH? **EMERSON** - THERE'S A FAIR AMOUNT OF PREMINING GEOLOGIC CHARACTERIZATION DURING THE APPLICATION PROCESS. CORES ARE DRILLED PRIOR TO MINING, AND ALL OF THE ROCK STRATA GO THROUGH AN ACID-BASE ACCOUNTING TO DETERMINE THE ACID-PRODUCING POTENTIAL FOR EACH STRATA. THERE IS A NET BALANCE DETERMINED TO DETERMINE WHETHER STRATA IS A NET NEUTRALIZER OR NET ACID PRODUCER. IF YOU FIND AREAS THAT ARE NET ACID PRODUCERS, YOU HAVE TO SPECIAL HANDLE THOSE LAYERS OF ROCK AND SEGREGATE THOSE AND HANDLE THEM THROUGH A SPECIAL HANDLING PLAN. GENERALLY, IN SOUTHERN WEST VIRGINIA, THESE HAVE BEEN DESCRIBED BY GEOLOGISTS AS MARINE DEPOSITS AND IN MOST CASES ARE CALCAREOUS. THE MATRIX IS CALCIUM CARBONATE BASED; NOT LIMESTONE, BUT IT DOES HAVE A FAIR AMOUNT OF CALCAREOUS MATERIAL AS A CEMENTING AGENT. THE SHALES TEND TO BREAK DOWN READILY WITH WEATHERING

AND ARE ALSO CALCAREOUS IN NATURE, SO IN MOST CASES THERE IS RAPID DETERIORATION OF THE STRUCTURE, FORMING A FAIR AMOUNT OF SAND- AND SILT-SIZE MATERIALS FOR PLANT GROWTH.

KINKAID - IT WOULD SEEM THESE MATERIALS COULD CRUMBLE IN A WAY THAT COULD AFFECT SLOPE AND STABILITY OF THE FILL. **POLITAN** - WE HAVE DURABLE ROCK TESTS, TOO. FOR DURABLE ROCK FILLS, THEY HAVE TO PASS CERTAIN TESTS TO BE PLACED IN A VALLEY FILL. **EMERSON** - SLAKE DURABILITY TESTS ARE DONE ON MATERIALS THAT ARE GOING TO BE PLACED IN THE VALLEY FILLS; THEY HAVE TO STAND UP TO A CERTAIN AMOUNT OF ABRASION AND WEATHERING. IF THEY PASS THE SLAKE TEST, YOU'RE ALLOWED 80% DURABLE ROCK IN FILLS. REGARDING STABILITY OF THE BACKFILL, THE SLOPES ARE NO GREATER THAN 2:1 AND IN MOST CASES ARE MORE GENTLE SLOPES POST-MINING THAN PRIOR TO MINING. **KINKAID** - SO VALLEY FILLS HAVE STEEPER SLOPE? **EMERSON** - THE FACES OF THE VALLEY FILL ARE STAIR-STEPPED, AND THERE ARE ENGINEERING CALCULATIONS WHICH GO INTO SAFETY FACTORS WHICH DETERMINE THE FINAL SLOPE OF THE FACE, AND FOUNDATION STUDIES ARE DONE PRIOR TO MINING. YOU KNOW WHERE THE VALLEY FILL IS GOING, YOU KNOW WHAT THE SUBSOILS ARE IN THE CRITICAL AREA DOWN AT THE TOE, WHICH IS THE MOST IMPORTANT AREA TO BE AWARE OF, AND THERE ARE SOIL TESTS DONE THERE TO MAKE SURE IT HAS THE BEARING CAPACITY TO SUPPORT THESE STRUCTURES. INTERNAL DRAINAGE OF THESE STRUCTURES IS ALSO DESIGNED INTO THEM. ALL THAT IS LOOKED AT IN THE APPLICATION PROCESS AND REVIEWED, AND IF IT MEETS CERTAIN SAFETY CONSIDERATIONS, THEN THAT PARTICULAR CONFIGURATION IS PERMITTED. **KINKAID** - ARE TESTS DONE THAT RELATE TO LONG-TERM GEOCHEMICAL STABILITY OF THE FILL MATERIAL? **EMERSON** - IF IT MEETS THE SAFETY FACTORS, IT IS PRESUMED IT WILL BE STABLE LONG-TERM. (CONCERNING REFUSE FILLS AND SLURRY IMPOUNDMENTS, ADDITIONAL SAFETY FACTORS ARE ENGINEERED, E.G., EARTHQUAKE FACTORS.) VALLEY FILLS HAVE BEEN CONSTRUCTED IN THE SOUTHERN PART OF THE STATE FOR OVER 20 YEARS AND TO MY KNOWLEDGE THERE HAS NOT BEEN A SINGLE DOCUMENTED FAILURE OF ANY OF THESE STRUCTURES. THERE MAY HAVE BEEN A FEW MINOR SLUFFS AT THE FACE OF THE FILLS, BUT NO DOCUMENTED FAILURES, PRIMARILY BECAUSE OF THE SAFETY FACTORS INVOLVED IN THE ENGINEERING AND PRE-MINING PERMITTING REQUIREMENTS. **KINKAID** - SO IT WOULD BE FAIR TO SAY THAT THE EXISTING REGULATIONS ADDRESS THE PHYSICAL, MECHANICAL STABILITY. **EMERSON** - THAT WOULD BE A FAIR STATEMENT, YES.

With respect to the areas in West Virginia that are susceptible to, or available for large-scale mining, the West Virginia Geologic and Economic Survey has issued a report to the Governor's Task Force last October that indicated that most of the large-scale mountaintop mining takes place in the Allegheny and upper Kanawha formations, which have a geographic extent within the State where the coal seams lie relatively close to the top and are conducive to this type of mining (Figure 3). With respect to what can be mined using these methods, it's generally from the Stockton level up. In a few cases you can surface mine the Coalburg, but generally it's a deep mine. Everything below that is either below drainage or too deep to be economically recoverable with large-scale surface mining.

Regarding the areal extent, the Geologic Survey mapped southern West Virginia -- the elevation of coal seams are proximate enough to the top of the mountains so it's potentially viable economically (Figure 4). Keep in mind these areas have been extensively deep-mined and contour-mined in the past. Over the long run, there are not many untouched coal reserves remaining; we think existing operations could go for another 15 to 20 years and then large-scale mining, by economic forces and depletion of reserves, will cease to exist as viable mining method.

DENSMORE - THE AREA YOU SHOW THERE IS AREAS OF MOUNTAINTOP REMOVAL MINING PRIMARILY? **EMERSON** - THAT'S CORRECT. **DENSMORE** - IF YOU LOOKED AT ALL SURFACE MINING (NOT JUST MOUNTAINTOP REMOVAL) THAT MIGHT INVOLVE VALLEY FILLING AND THEREFORE HEADWATER STREAMS/AQUATIC IMPACTS, HOW BIG AN AREA WOULD WE BE TALKING ABOUT? **EMERSON** - IF YOU LOOK AT CONTOUR MINING, WHERE YOU JUST TAKE A SLICE OUT OF THE SIDE OF THE MOUNTAIN AND FOLLOW THE OUTCROP AROUND THE MOUNTAIN, YOU COULD GO MUCH FARTHER INTO THE CENTRAL AND SOUTHERN AREA OF STATE, PERHAPS AS FAR NORTH AS CLAY AND BRAXTON COUNTIES. BUT BEAR IN MIND THAT THE "HINGE LINE," NORTHERN PART OF THE STATE HAS HIGHER-SULFUR RESERVES, WITH SOUTHERN WEST VIRGINIA HAVING THE LOW-SULFUR RESERVES. SO MOST OF THE DEMAND IS IN SOUTHERN WEST VIRGINIA BECAUSE OF THE CLEAN AIR ACT, OTHERWISE THE COAL NEEDS TO GO TO PLANTS WITH SCRUBBERS.

ROBINSON - DOES ARCH HAVE LONG TERM PLANS ON RESERVES FOR THIS 15-YEAR PERIOD? IS THERE DATA TO SUPPORT THIS? **EMERSON** - WE DON'T OWN THE LAND, IN MOST CASES WE LEASE. THESE ARE LARGE TRACTS OF

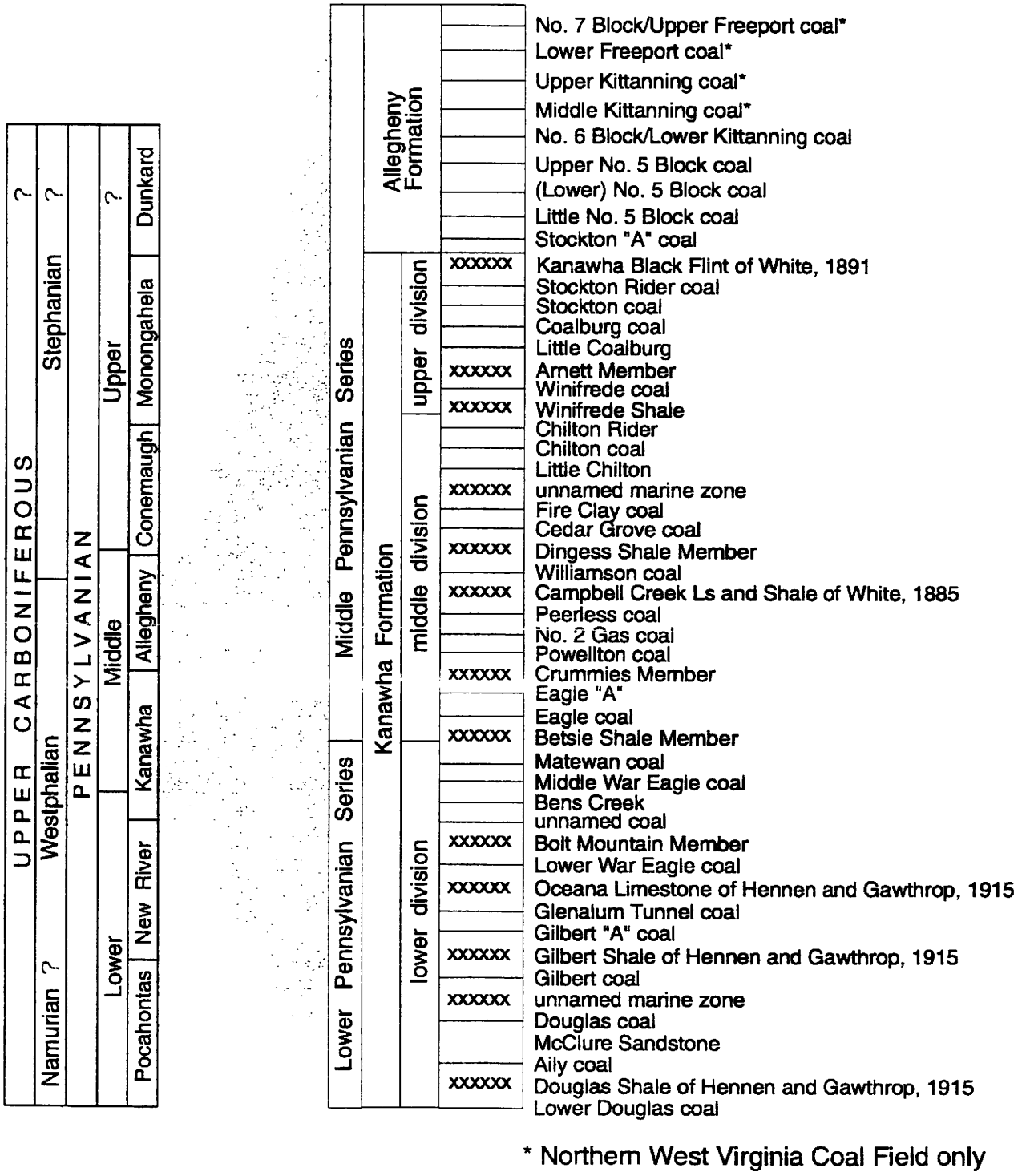

UPPER CARBONIFEROUS
?
Namurian ?
Westphalian
Stephanian ?
PENNSYLVANIAN
Lower
Middle
Upper
?
Pocahontas
New River
Kanawha
Allegheny
Conemaugh
Monongahela
Dunkard
Lower Pennsylvanian Series
Middle Pennsylvanian Series
Kanawha Formation
Allegheny Formation
lower division
middle division
upper division
No. 7 Block/Upper Freeport coal*
Lower Freeport coal*
Upper Kittanning coal*
Middle Kittanning coal*
No. 6 Block/Lower Kittanning coal
Upper No. 5 Block coal
(Lower) No. 5 Block coal
Little No. 5 Block coal
Stockton "A" coal
Kanawha Black Flint of White, 1891
Stockton Rider coal
Stockton coal
Coalburg coal
Little Coalburg
Arnett Member
Winifrede coal
Winifrede Shale
Chilton Rider
Chilton coal
Little Chilton
unnamed marine zone
Fire Clay coal
Cedar Grove coal
Dingess Shale Member
Williamson coal
Campbell Creek Ls and Shale of White, 1885
Peerless coal
No. 2 Gas coal
Powellton coal
Crummies Member
Eagle "A"
Eagle coal
Betsie Shale Member
Matewan coal
Middle War Eagle coal
Bens Creek
unnamed coal
Bolt Mountain Member
Lower War Eagle coal
Oceana Limestone of Hennen and Gawthrop, 1915
Glenalum Tunnel coal
Gilbert "A" coal
Gilbert Shale of Hennen and Gawthrop, 1915
Gilbert coal
unnamed marine zone
Douglas coal
McClure Sandstone
Aily coal
Douglas Shale of Hennen and Gawthrop, 1915
Lower Douglas coal
* Northern West Virginia Coal Field only

FIGURE 3.

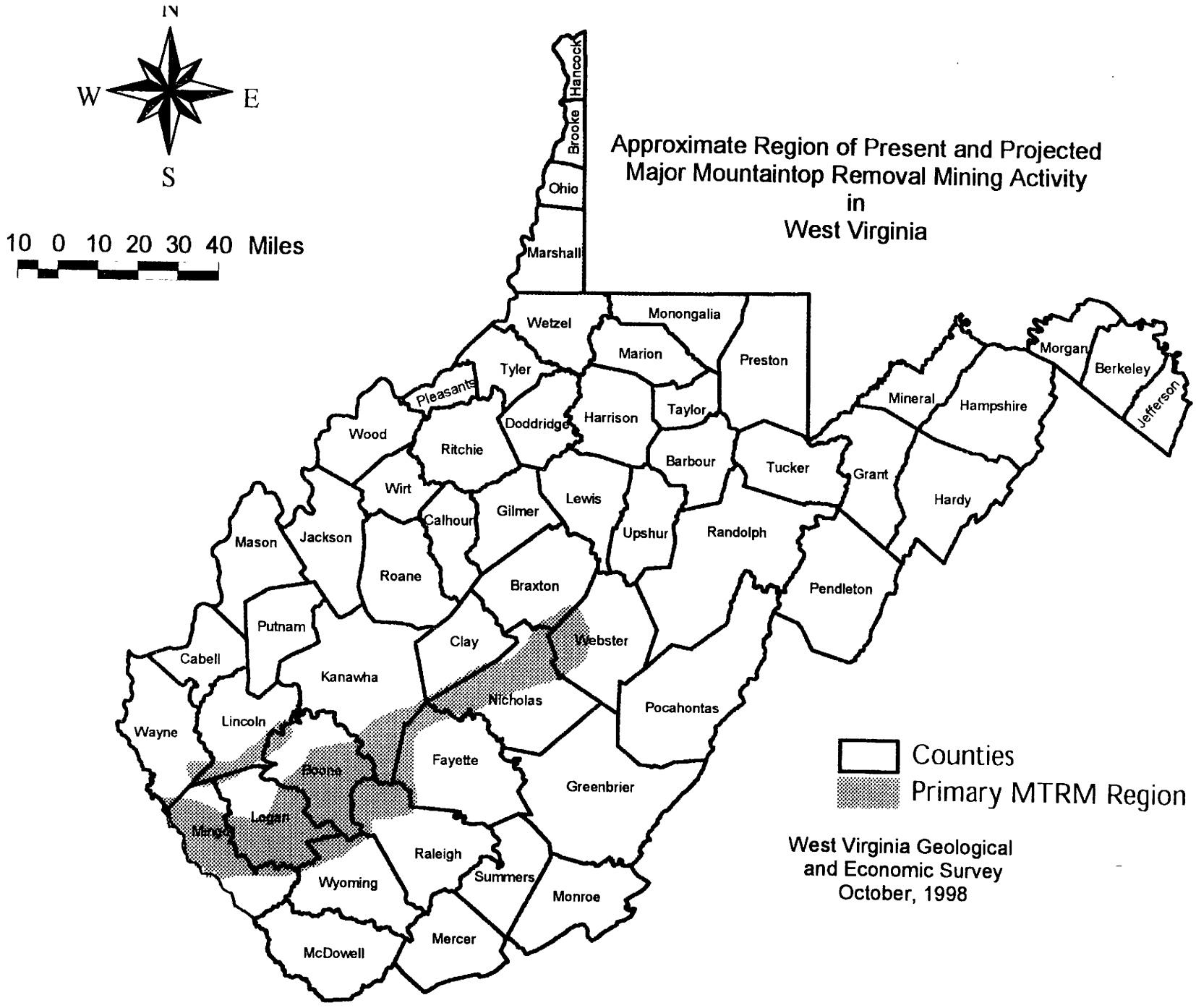

N
W
E
S
10 0 10 20 30 40 Miles
Approximate Region of Present and Projected
Major Mountaintop Removal Mining Activity
in
West Virginia
Hancock
Brooke
Ohio
Marshall
Wetzel
Monongalia
Marion
Preston
Tyler
Pleasants
Doddridge
Harrison
Taylor
Wood
Ritchie
Barbour
Tucker
Wirt
Calhoun
Gilmer
Lewis
Upshur
Randolph
Mason
Jackson
Roane
Braxton
Putnam
Clay
Webster
Cabell
Kanawha
Nicholas
Pocahontas
Wayne
Lincoln
Boone
Fayette
Greenbrier
Logan
Mingo
Raleigh
Summers
Wyoming
Monroe
Mercer
McDowell
Morgan
Berkeley
Jefferson
Mineral
Hampshire
Grant
Hardy
Pendleton
Counties
Primary MTRM Region
West Virginia Geological
and Economic Survey
October, 1998

FIGURE 4.

10,000 - 15,000 ACRES. WE HAVE SOME CORE DRILLING DATA ON RESERVES THAT INDICATE 10 TO 15 YEARS OF RESERVES USING LARGE-SCALE EQUIPMENT UNDER PRESENT ECONOMIC CONDITIONS.

POMPONIO - ARE SEAMS BENEATH THE STOCKTON BEING MINED? **EMERSON** - YES, DEEP, CONTOUR AND AUGER MINING ARE ALSO GOING ON.

HARTOS - WHAT TYPE OF SITE CONSTRUCTION CRITERIA GO INTO PLANNING A VALLEY FILL? **EMERSON** - THAT'S A VERY LARGE QUESTION AND WOULD TAKE LOT OF TIME. I COULD IDENTIFY THOSE AREAS FOR YOU LATER.

Dr. Bruce Wallace, Department of Entomology and Institute of Ecology, University of Georgia, Athens, Georgia

The problem here, as I see it, is that it is a difficult question how much headwaters need to be protected to really ensure integrity of downstream reaches (Figure 1). The problem is that we stream ecologists study one or two streams, maybe adjacent waters, or streams in longitudinal linkage. Rarely do we look at drainage networks. I have been working for 28 to 30 years at the Coweeta Natural Research Laboratory in western North Carolina. The Coweeta basin is slightly larger than the controversial Pigeonroost watershed. Over the years we've studied a number of things at Coweeta, such as replacing hardwoods with conifers; we've done some clearcutting experiments to study the response of the stream to clearcutting.

One of the things that I hope to convince you is that there are some things happening in headwater streams that are important, some of the processes there are important, some invertebrates are important and some of the things they do are important. First of all, is the reliance of the stream community on inputs from surrounding forests. One of the ways we've been testing this hypothesis for a number of years is by a litter exclusion project, where we've constructed a canopy over an entire reach of a headwater stream which excludes terrestrial litter inputs so we can see what happens to stream productivity. We also have lateral fences along the sides to keep lateral movement of terrestrial organic matter out of the stream. So we're looking at linkages between invertebrates and what's happening in the stream with detrital inputs from the forest. These detrital inputs are very important to the biology of the stream. The question we're testing is: What happens if this linkage is broken or severely curtailed (we can't eliminate all inputs to the stream). How dependent are these headwater stream invertebrates on detrital inputs? Are detritivores, as a group, food limited (Figure 2).

This slide shows the standing crop of detritus in the stream from the start of treatment (litter exclusion) over 1,460 days (Figure3). The treatment stream has a large amount of stored detritus in it, and has been losing detritus at a rate of about 0.8 grams/m^2/day for the first 4 years of this experiment. So these streams are very retentive, they have a lot of detritus in them and store a lot of material.

This slide shows a reference stream with a lot of leaf material. The next slide shows a litter-exclusion stream, where we've actually excluded the terrestrial inputs to the stream. There's little, in fact hardly any, litter in the stream. We still have large, woody debris in the stream which we removed last summer, so I don't have all those data complete for the past year. However, I do have the results of four years of litter exclusion (Figure 3) which included one year

A difficult question: How much headwaters need to be protected to ensure sustained integrity of downstream reaches?

Stream ecologists primarily study single streams, few streams, or a few streams along a continuum.

How do we incorporate the branching pattern into large-scale patterns and non-linear aspects of the basin?

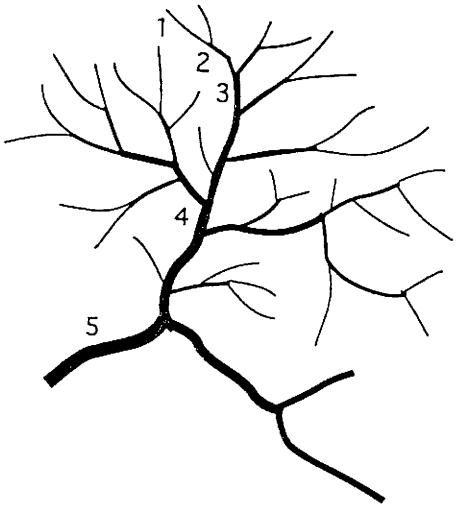
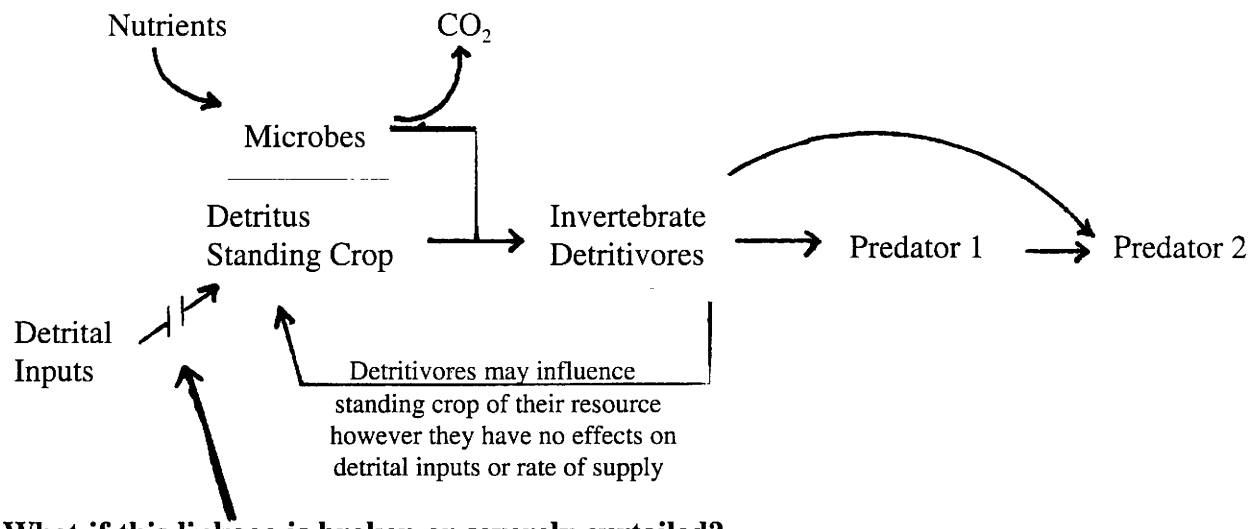


FIGURE 1.



What if this linkage is broken or severely curtailed?
How dependent are headwater stream invertebrates on detrital inputs?
Are detritivores as a group, food limited?
What type(s) of currency do we use to measure invertebrate response?

FIGURE 2.

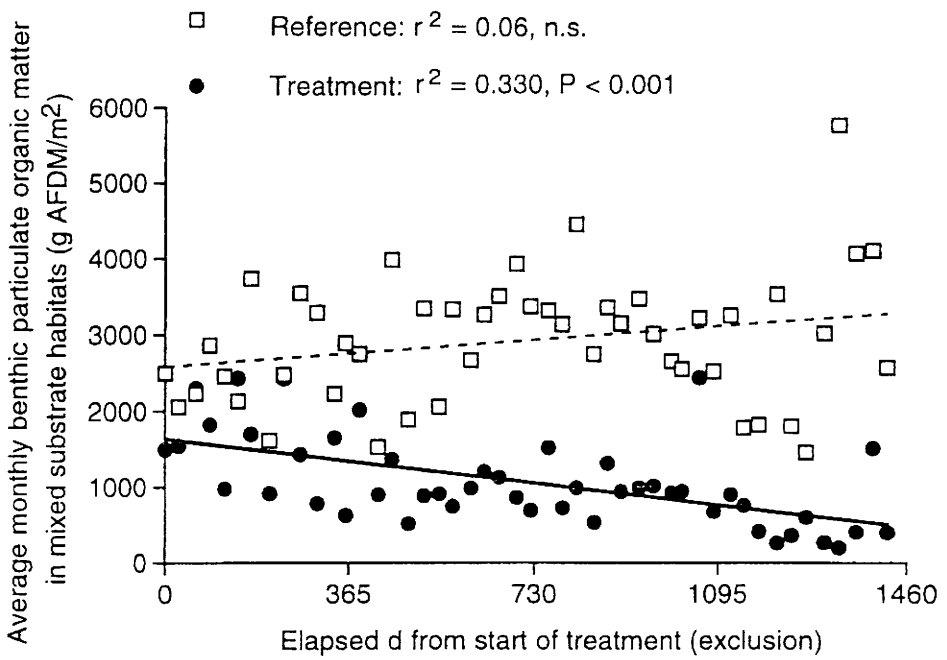


FIGURE 3.

of removal of small woody debris, which decomposes very slowly. What we found was, after we excluded the litter input, that we still had this woody debris which still served as a food resource to certain invertebrates; a few of them were able to switch over to use the biofilm which accumulates on the wood as a food resource.

This slide shows total primary consumer biomass for the first 365 days (pretreatment), during three years of litter exclusion, and during the period of small woody debris removal plus litter exlusion (Figure 4). You can see what's happening to invertebrate biomass: the primary consumer biomass is going down whereas the reference stream biomass remained basically the same. (There was one treatment stream and one reference stream used in this study. We can get away with that by using a randomized intervention analysis technique which uses extensive pretreatment period data compared with post-treatment.)

We also saw a decrease in invertebrate predators and salamanders over time (Figure 5). (There are no fish in these streams; salamanders are the only vertebrate predators.)

I want to point out that there are a couple of functional groups of invertebrates that are very directly dependent on this allocthonous input. One is the shredders, another the gatherers, in fact the primary consumers as a group, invertebrate predators, and this carries all the way up to the salamanders -- significant decreases.

These data are for the mixed substrate habitat, which represents about 87% of the stream area. On the other hand, you have high gradient bedrock substrates, which are dominated primarily by scrapers, filterers, some gatherers, some shredders (Figure 6). No change in abundance or biomass over time occur on the bedrock habitat, suggesting a somewhat different food web that relies on transported organic matter rather than on material that's actually stored there as benthic organic matter through time.

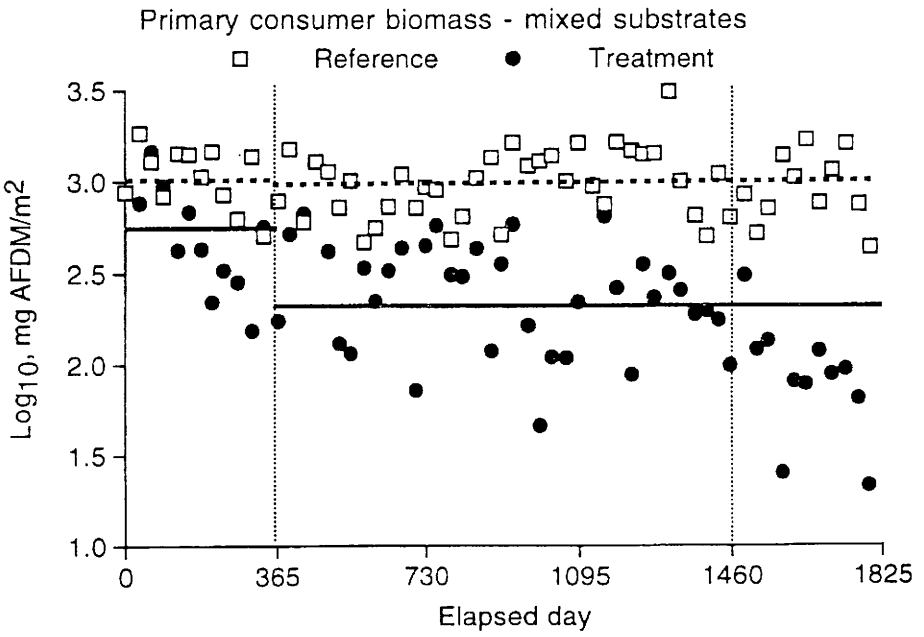


FIGURE 4.

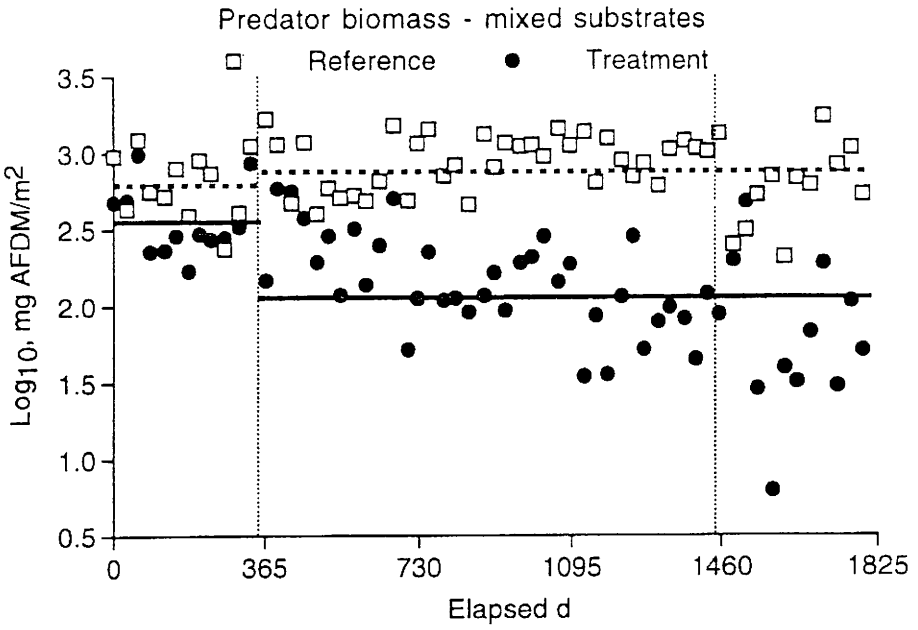


FIGURE 5.

FIGURE 6.

Randomized Intervention Analysis testing probabilities of change between reference and treatment stream for benthic abundance and biomass. Values are probabilities that observed differences were significant.

	-------- Mixed substrates --------		---- Bedrock substrates ----	
Group	- Abundance -	- Biomass -	-Abundance-	- Biomass -
Scrapers	0.408	0.670	0.782	0.822
Shredders	<0.0000001	0.012	0.400	0.574
Gatherers	<0.0000001	0.001	0.752	0.994
Filterers	0.174	0.326	0.227	0.916
Primary consumers	<0.0000001	0.006	0.863	0.612
Invert. Predators	<0.0000001	<0.0000001	0.317	0.399
Salamanders	0.009	0.010	1.000	0.863

We had a period of five pre-treatment years, and if we examine total secondary production vs. predator production in that pre-treatment period, you can still see a relationship (Figure 7). A lot of that is related to nothing more than the storm hydrograph in a particular year. In those years with many storms, we found that storms remove a lot of leaf material from the stream bed; it's not all exported downstream, but a lot is deposited laterally onto the stream banks, not downstream. Those are years when we see some of the lowest levels of secondary production.

We can show through studies that you can have many anthropogenic disturbances such as clearcutting, fire, agriculture, and mining that disrupt detrital inputs to streams. Assessing the significance for the stream community is difficult in the face of multiple effects that confound the analysis; e.g., with clear-cutting, you can get altered hydrology, altered thermal regimes, enhanced sediment, nutrient and solar inputs, and shifts in the relative importance of detrital inputs and within-stream primary production.

These studies show that litter exclusion alone, without considering the multitude of potential direct and indirect effects, has a profound effect on aquatic productivity. Litter inputs alone influence abundance, biomass, and production of invertebrates. This emphasizes the direct importance of the terrestrial-aquatic ecotones. Therefore, maintaining or reestablishing riparian inputs are an important aspect to consider in the conservation and restoration of streams.

Here's a myth we need to discuss - "Invertebrates and microbiota in these headwater streams represent a minute fraction of living plant and animal biomass (true); therefore, they are not important in the export of organic matter to downstream areas (myth)". We tested this at Coweeta through the application of pesticides to a headwater stream. We found we had to treat seasonally (every 3 months) because there's a lot of recolonization. This slide shows shredder production vs. insecticide treatment (Figure 8). The pre-treatment production of shredder biomass was 3.5 g/m^2 for the year. Following the first year of insecticide treatment, this dropped to 0.4 g/m^2. Most of the Plectopterans and caddisflies were eliminated. Tipulids are very resistant (you have to kill them with rocks); even with litter exclusion they were the last shredders to leave. They switch over and start eating the wood.

This is a slide of a leaf (Figure 9) that had been fed on by a shredding insect, a peltoperlid stonefly. One of the ways you can follow leaf decomposition in streams is to put known amounts of leaf material in a bag -- coarse-meshed, that allows animals to colonize the leaves. Then you can follow the rate of loss of that leaf litter in the stream through time. We did that in the stream that we treated with insecticide. (We also looked at microbial respiration rate on leaves in insecticide-treated and untreated streams. There was absolutely no difference in microbial respiration; therefore, differences in decomposition of leaves were due strictly to the animal community.) Our results

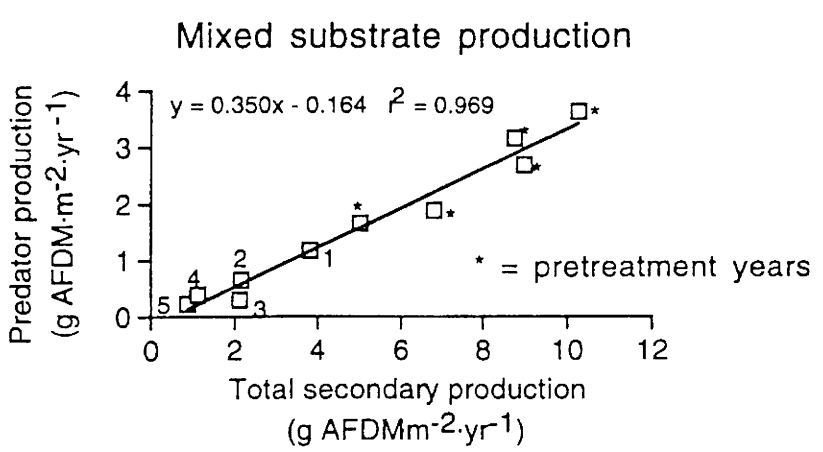


FIGURE 7

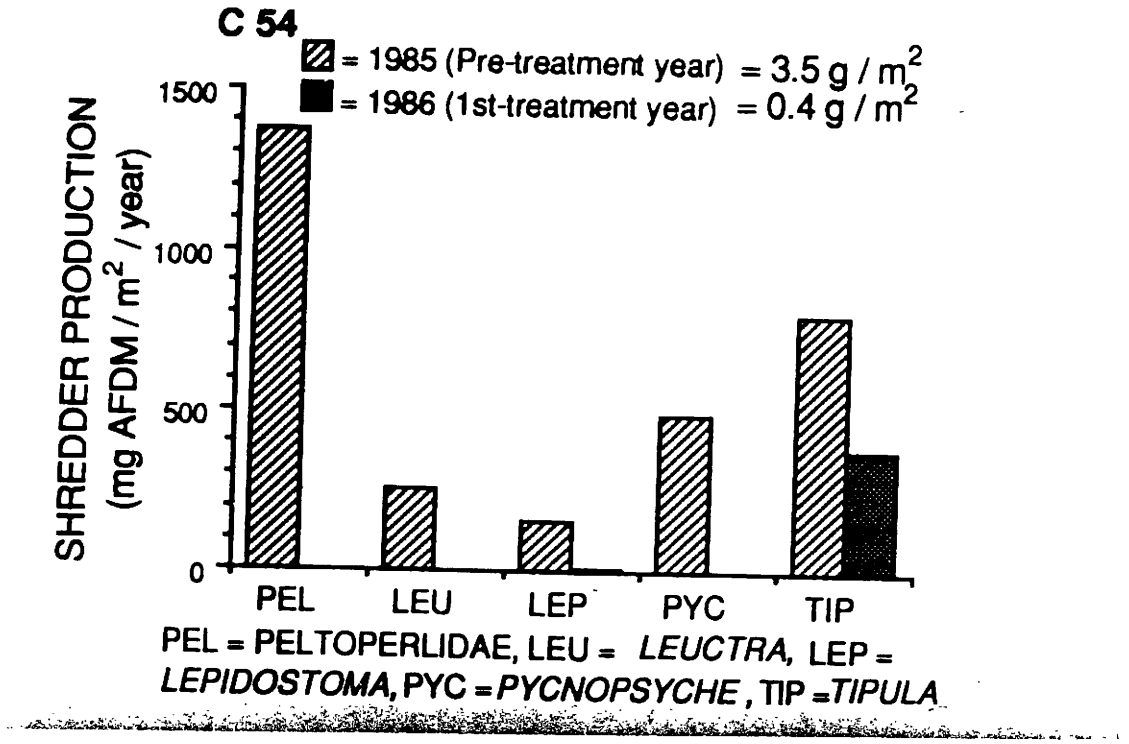


FIGURE 8.

FIGURE 9.

are based on 11 years of data for untreated streams, with 95 to 100 litter bags per year, so this is a pretty extensive study. The average breakdown time for red maple leaves where invertebrates were present (untreated) was 275 days (Figure 10). On the other hand, if you treat and remove most of the invertebrate shredders (with the exception of Tipulids!), you end up with about 575 days. In other words, it takes much longer to break that material down when you remove the invertebrates.

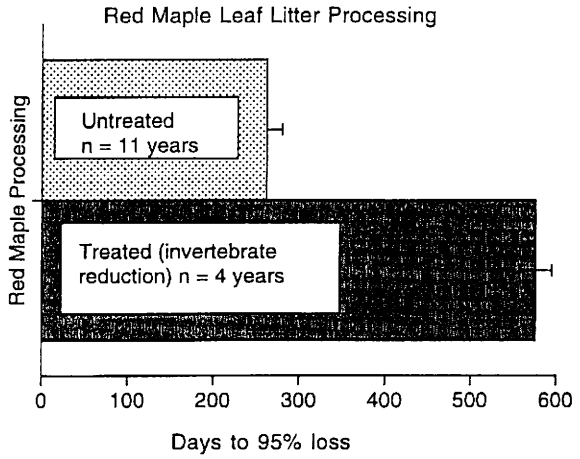


FIGURE 10.

These data show the same for rhododendron (Figure 11). Rhododendron is a thick, leathery leaf, very resistant to decomposition. It takes about 750 days to break down with invertebrates. With removal of large shredding invertebrates, it takes almost 1,800 days. The point is that the invertebrates are very important in the breakdown of some of this material.

Another thing to keep in mind is that invertebrates tend to have very low assimilation efficiencies -- about 90% of everything that enters the anterior end of the body (through the mouth) comes out the rear end as fine particles. In other words, they will assimilate about 10% of material intake and 90% is egested as fine particles. So they are actually grinding up this material into small particles which are more amenable for downstream transport. This slide on seston (organic matter suspended in the water column) concentration shows the effect of insecticide treatment (removal of most of the invertebrates) (Figure 12). During a three-year treatment with insecticides, seston was very low. It increased again after treatment ended, but it took about one year to recover.

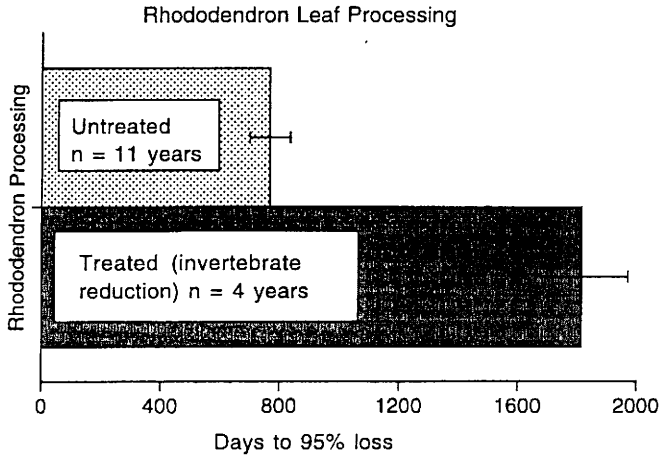


FIGURE 11.

Problem: We know a large amount of export occurs with individual storms. If you do continuous export as opposed to grab samples of export, you will find that continuous export is usually 30 to 40% higher, because with grab samples you're missing the little storm events (Figure 13) that transport much of the organic material. We also know there's a strong relationship between the amount of organic matter exported (coarse particulate organic matter or CPOM, or fine particulate organic matter, or FPOM), with maximum discharge during a given sampling interval. Export of material (Figure 14) is greater with high discharge.

Based on secondary production, the benthic macroinvertebrate production in the insecticide-treated stream was reduced by 1.2 kg/year for the entire stream. Also, the loss of invertebrate production over three years is 3.6 kg. We constructed models of FPOM export, incorporating discharge during each sampling interval, for each of the two reference streams and the treatment stream during the pretreatment year. Based on three-year treatment periods, we saw a reduction of 170-200 kg of FPOM export to downstream reaches in the insecticide-treated stream. With recovery of invertebrate populations (about 1.5 to 2 years), FPOM export approached pre-treatment levels.

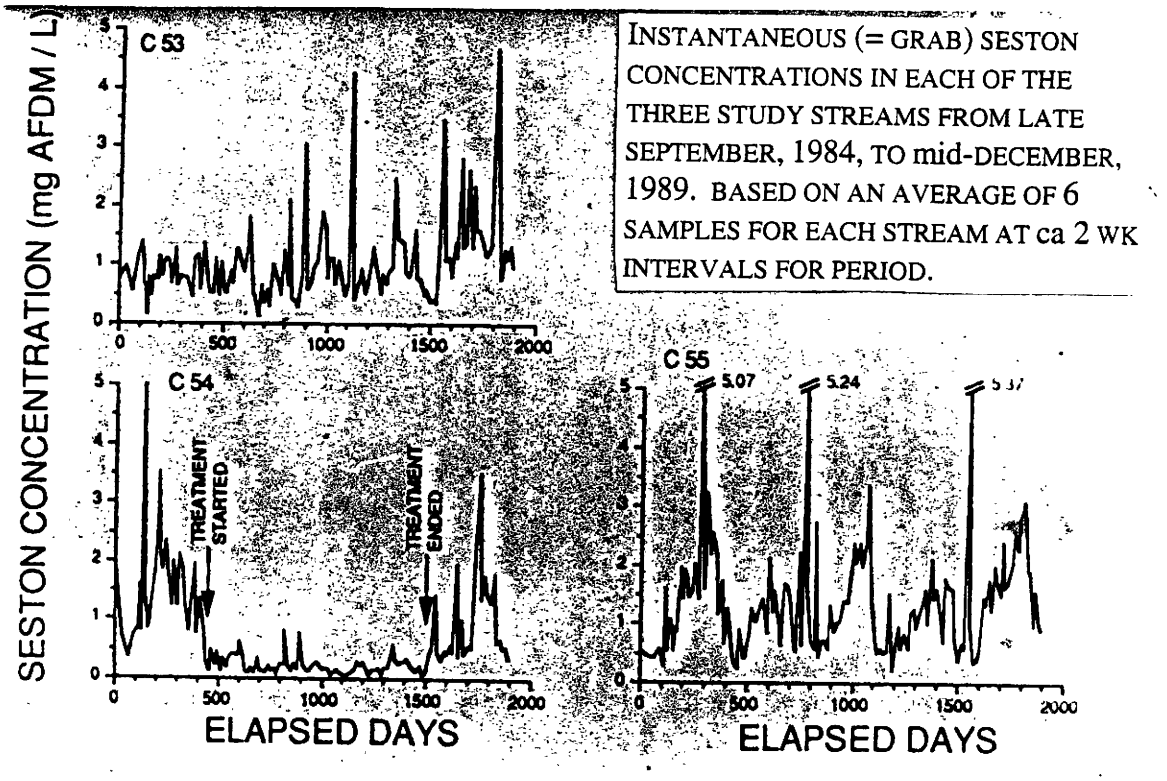


FIGURE 12.

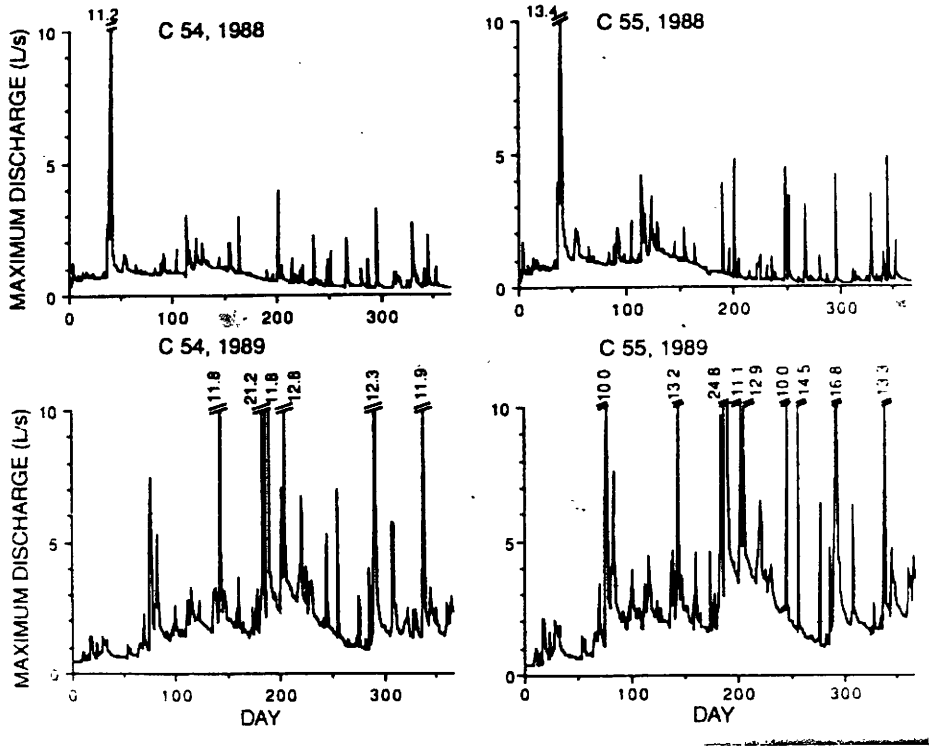


FIGURE 13.

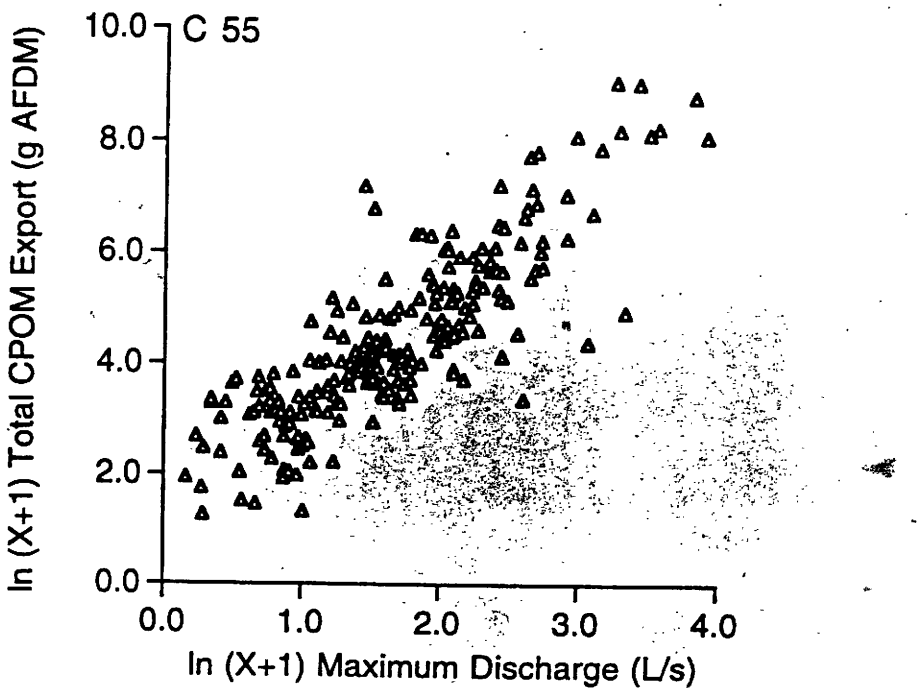


FIGURE 14.

I also want to emphasize that this is invertebrate reduction, and not complete extirpation, as animals recolonized between treatments or survived treatments. For example:

- Scrapers production reduced by ≈ 71%
- Shredders production reduced by ≈ 88%
- Gatherers production reduced by ≈ 21%
- Filterers production reduced by ≈ 98%
- Predators production reduced by ≈ 71%

So the roles for invertebrates in forested headwater streams are:

a) processing of CPOM to FPOM
b) increase downstream breakdown rates of leaf material
c) enhance downstream transport of organic matter as FPOM is more amenable to downstream transport than CPOM.

Leaves are not very amenable to downstream transport because of high retention of large particles.

Here is a quote from a consultant's report: "As a general rule, most small headwater streams have their organic import equal to their organic uptake, allowing the system to exist in a relatively steady state. The energy used just maintains the status of the existing benthics leaving little or no material for active transport (as averaged on an annual basis)." I'm not aware of any stream that works that way. In fact, it would not be a stream if it did.

Example: At Coweeta, Catchment 55, I want to point out that about 80% of the total input of that stream is CPOM from the surrounding forest. You can get about 10% as dissolved organic matter; you get a certain amount of

through-fall as well as particulate inputs from the soil, which we have measured. There is very little primary production in these headwater streams as they are usually heavily shaded. The total annual input of organic matter is about 720 g/m^2 or so; keep in mind that 80% is CPOM input, and only 2 to 5% of the output is CPOM (Figure 15). Most of the material, about 56 - 62%, is exported as FPOM, and 30-40% as dissolved organic matter. So, these headwater streams are very important as sites of deposition, transformation, and subsequent export to downstream reaches.

If we look in terms of the total export (in terms of ash-free dry mass, kg/year; Figure 16) (Remember that these are extremely small streams , 0.035 cfs to 0 .061 cfs), the total export is 145 - 167 kg/year. Another way to look at this is annual export per m length of stream. We get about 1 kg of export per m length of stream. Looking at total lengths of first and second order streams found in the Coweeta basin, there are about 44.7 km. You can estimate values of the export of this organic matter to downstream reaches: 44 to 45 metric tons, or 50 U.S. tons, per year. And this estimate is low because of underestimation of stream length from maps.

I did a similar analysis for all the streams I could find in the eastern U.S. (Appalachian, ridge and valley, piedmont (White Clay); Figure 17). Note that none of the streams on the slide approach 5 cfs. As you see, by examining total annual organic matter export, with increasing discharge and increasing stream length, there's a general tendency toward more annual organic export per linear m as you go into larger streams. Not surprising -- discharge increases, stream width increases, and stream power increases, but certainly there is this tremendous increase as you go downstream. So headwater streams can be very important sites of organic matter deposition and subsequent export to downstream reaches.

Is this stuff important downstream? You bet. Example: For a fifth order reach of Coweeta Creek, amorphous detritus makes up the large portion of flow of food through different groups of aquatic invertebrates (Figure 18).

Some other concerns from the point of view of stream ecologist: We are seeing increased nitrogen deposition in eastern North America (Figure 19); it's a major problem in some of the forests. What's happening to nitrate concentrations in streams coming out of valley fills, where you no longer have some of these forest activities and microbial populations that might be playing a very important role in the nitrogen cycle?

Annual sources and input (g m^{-2} yr^{-1}) of organic matter to the stream draining Catchment 55 at Coweeta (prior to litter exclusion).

Allochthonous sources	**g m^{-2} yr^{-1}**	**% of total**
Direct fall[1]	492	68.6 %
Lateral movement[1]	137	19.1%
Dissolved organic matter ([DOM] soil water)	62*	8.6%
Throughfall (DOM) ≈	16*	2.2%
Particulate input from soil ≈	4*	0.5%
Total allochthonous =	**711**	**99.2%**
Autochthonous sources		
Primary production (algae) ≈	3.8	
Aquatic moss ≈	2	
Total autochthonous =	**5.8**	**0.8%**
Total annual input =	716.8	

[1] primarily leaves and woody debris

* inputs not curtailed by litter exclusion, in addition the efficiency of exclusion of the direct fall canopy and lateral movement fence was = 95%.

FIGURE 15.

How much organic matter is exported from forested headwater streams in the southern Appalachians? Data are based on 9-y of continuous measurements at the Coweeta Hydrologic Laboratory in western North Carolina.

	WS 53 Reference	WS 55 Reference
Watershed area ha (acres)	5.2 (12.9)	7.5 (18.6)
Stream length (m)	145	170
Avg. discharge L/s (CFS)	1.06 (0.035)	1.72 (0.061)
Annual range (L/s) [a]	0.33 to 1.56	0.52 to 2.48
Years of data	9	9
Export mg AFDM/L (total)	4.358	4.06
CPOM (% of total expt.)	0.106 (2.4%)	0.159 (5.2%)
FPOM (% of total expt.)	2.452 (56.3%)	1.904 (61.7%)
DOM[b] (% of total expt.)	1.800 (41.3%)	1.023 (33.9%)
Avg. export (g AFDM/d)	399.1	458.6
Export (kg AFDM/y)	145.7	167.4
Annual export (kg AFDM) per m length of stream	1.004	0.985
1st - 2nd order streams (m)[c]	44,700	44,700
Total estimated annual organic export (kg AFDM/y)	44,979	44,030
Export (metric tons/y)	~ 45	~ 44
Export (U.S. Tons/y)	~ 49.6	~ 48

[a] Includes record drought and wet years (65 years of record)
[b] DOM = assumes dissolved organic carbon (DOC) = 50% of DOM
[c] Includes a conservative measure of only total length of 1st and 2nd order streams in Ball Creek and Shope Fork Basins (1,483 ha or 3,673 acres) and does not include an additional 11 km of 3rd and 4th order streams.

FIGURE 16.

What are some other measures of export per length of stream channel in eastern North American Streams?

Stream and Location	Physiographic Region	Avg. Annual Flow L/s (CFS)	Stream Order	Total Annual Organic Export (kg AFDM)	Annual Organic export (kg/linear m)
Catchment 53, NC	Appalachian	1.1 (0.04)	1st	399	1.0
Satellite Branch, NC [a]	Appalachian	1.7 (0.06)	1st	459	0.99
Walker Branch, TN [b]	Ridge & Valley	12 (0.43)	1st	2,010	5.9
Hugh White Creek, NC [c]	Appalachian	19 (0.67)	2nd	6,122	5.4
White Clay Creek, PA [d]	Piedmont	115 (4.06)	3rd	83,200	6.6

Sources: [a] Wallace et al. (1997); [b] Mulholland (1997); [c] Webster et al. (1997); and [d] Newbold et al. (1997) *in:* Webster, J. R., and J. L. Meyer (editors). 1997. Stream organic matter budgets: Journal of the North American Benthological Society 16:3-161.

FIGURE 17.

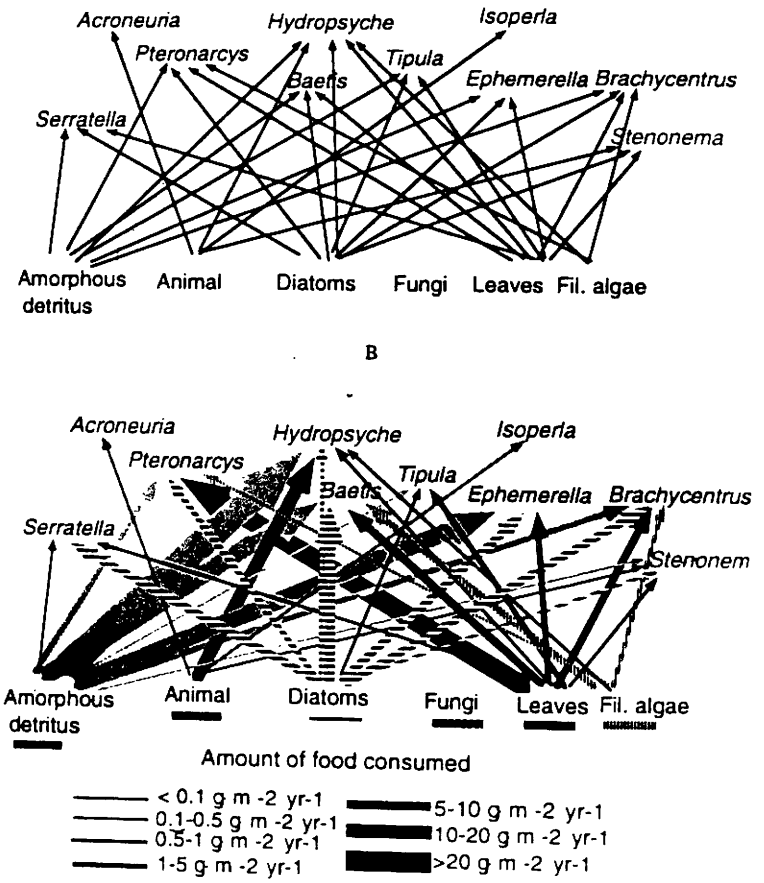
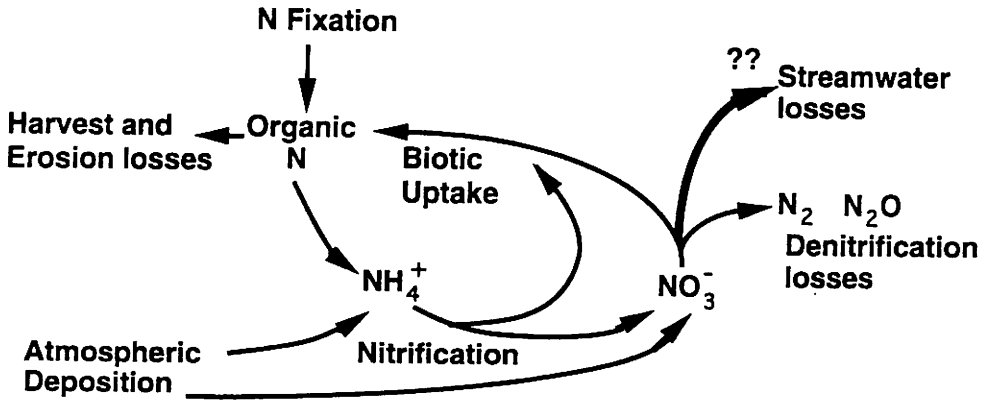


FIGURE 18.



- Primarily as a consequence of fossil fuel combustion, nitrogen deposition is increasing in much of eastern North America.
- Biotic uptake by vegetation, transformation by microbes in soils, riparian zones and streams, especially in the presence of available carbon are important mechanisms controlling the export of nitrogen from watersheds.
- How does mountain top removal and valley filling influence downstream nitrate concentrations?

FIGURE 19.

Another myth is that only flows greater than 5 cfs are streams. Only a lawyer would debate this question. How much is 5 cfs? - over 1 billion gallons of water per year. The average city in the U.S. uses 100 gal/day/per capita for personal use. In other words, if you looked at this in terms of how many people's water needs this could supply in a year, it's 32,300 people. Or, it would supply the personal and industrial needs of 16,000 people. If you could sell this water in Saudi Arabia, you'd be well off!

Another important point of concern: Stream thermal regimes can have important effects on microbial activity, invertebrate fauna, and fish. For example, for invertebrates these effects include eggs, larval growth, life histories, and seasonal cycles. What are the effects of valley fills and sediment ponds at the base of valley fills on downstream temperature regimes with respect to annual degree days, daily max-min (diel fluctuation), or seasonal temperature patterns? These things have a very important influence on the life cycles of aquatic insects.

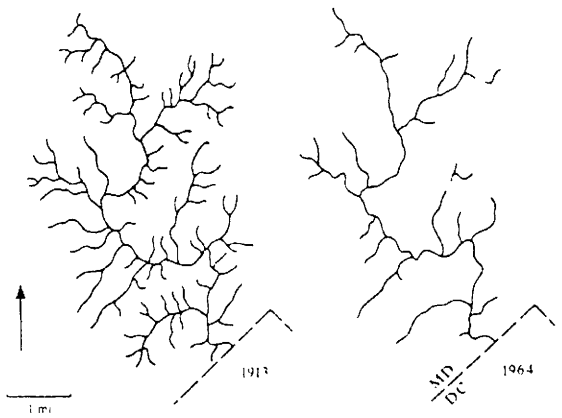
Another myth - There are so many kilometers of first order streams in Appalachia that destroying a small portion does not represent any potential threat to biodiversity. In fact if you look at papers by Morse, Stark and McCafferty - they make a point that the southern Appalachian region and the Appalachians in general are regions of outstanding biodiversity. Morse et al. (1997) consider 19 species of mayflies, seven species of dragonflies, 17 species of stoneflies, and 38 species of caddisflies to be vulnerable to extirpation at present in the southern Appalachians. They suspect the numbers may be considerably higher than these; why? Many of the rare species are known from only one or two locations in springbrooks or seepage areas. Furthermore, many small streams, seeps, and springbrooks have been poorly explored. To add to the problem, immature (aquatic) stages usually cannot be readily identified to species; adult (aerial-terrestrial) males are often required for accurate identification. There are few taxonomic specialists for various groups. Knowledge of their distribution, ecology, life history, and habitat requirements is sorely lacking.

As a closing thought to this biodiversity question, especially because of the potential importance of small springbrooks and spring seeps to southern Appalachian biodiversity, I would like to leave you with a question: Can we continue to destroy and entomb, forever, potential important habitats for life on this planet -- without requiring extensive pre-impact inventories by competent biologists? I think it's a very dangerous thing for life on this planet to do that, and to destroy streams where there is no complete biotic inventory.

I realize that valley fills by coal mining is not the only process that eliminates streams. This overhead shows the effect of urbanization on Rock Creek in Washington, D.C., 1913 to 1964, as you vary and extirpate first and second order streams (Figure 20). We need to be considering some of the hydrologic consequences downstream. It's not fair to equate these [valley fills] to what happens with urbanization, but with Rock Creek, the creek became muddy and silty, there was an increase in annual flood frequency (it's increased 10 to 20 times since about 1913), and downstream increase in channel width and depth associated with increased peak discharge.

PASSMORE - A LOT OF STREAMS DOWNSTREAM OF VALLEY FILLS HAVE RIPARIAN ZONES, SO LEAF LITTER IS PRESENT IN LOT OF CASES. BECAUSE OF THAT, HOW DO YOU ESTIMATE WHAT'S LOST FROM WHAT'S NO LONGER THERE, HOW IMPORTANT IS THAT FOR THE DOWNSTREAM REACHES, AND HOW DO YOU MEASURE IT? **WALLACE** - IT WOULD DEPEND ON THE SITE, AND YOU NEED TO MEASURE EACH ON ITS OWN. DOWNSTREAM OF WHERE WE'VE BEEN EXCLUDING LEAF LITTER AT COWEETA, WITHIN 100 M WE CAN FIND A FULL COMPLEMENT OF INVERTEBRATES AGAIN. **TIBBOTT** -- MAGGIE, WHAT YOU'RE SAYING IS, WE HAVE TO FIGURE OUT WHAT THE IMPACT IS ON THE DOWNSTREAM AREA FROM THE LOSS OF ALL THOSE TONS OF FINE PARTICULATE ORGANIC MATTER PRODUCTION IN THE BURIED REACH, RIGHT? **PASSMORE** -- WELL, I GUESS YOU'RE MOVING EVERYTHING DOWNSTREAM. **WALLACE** -- WELL, IF YOU MOVE EVERYTHING DOWNSTREAM, OVER THE LONG HAUL YOU GREATLY REDUCE THE AMOUNT OF EXPORT TO DOWNSTREAM REACHES IN TERMS OF PARTICULATE ORGANIC MATTER AND DOM, BUT I HAVE NO DATA ON DISSOLVED ORGANIC MATTER.

HANDEL - TO TIE IN WHAT YOU'VE TALKED ABOUT WITH THE PREVIOUS TALK ABOUT CURRENT PRACTICE AND HOW THESE LANDS ARE REVEGETATED: THE COMMON PRACTICE IS TO REPLACE MATURE HARDWOOD FORESTS WITH GRASSLANDS, WITH AN OCCASIONAL SMALL SEEDLING, AND THIS HAS ENORMOUS IMPACT ON PRIMARY PRODUCTION. AS WE LEARNED AT THE KENTUCKY MEETING SPONSORED BY OSM A FEW WEEKS AGO [THE TECHNICAL INTERACTIVE FORUM ON ENHANCEMENT OF REFORESTATION AT SURFACE COAL MINES, MARCH 23-24, 1999, IN FORT MITCHELL, KENTUCKY], THESE LANDS UNDER CURRENT PRACTICE RARELY DEVELOP INTO A FOREST -- THE PRODUCTIVITY RATE IS MUCH, MUCH LOWER BECAUSE OF COMPACTION, ETC. THE LINKS BETWEEN UPLAND PRACTICE AND STREAM BIOTA: SOIL REPLACEMENTS WHICH ARE PUT ON THESE MINES ARE TYPICALLY ENGINEERED FROM SUBSOILS, AND EVEN



Drainage basin of Rock Creek upstream of the District of Columbia in 1913 (left) before extensive urbanization and again in 1964 (right)(USGS, Dept. Interior 1964).

Note extirpation of many first and second order channels.

FIGURE 20.

THOUGH THEY HAVE SOME OF THE IONS THAT ARE APPROPRIATE, PARTICULARLY FOR GRASSLAND GROWTH, THEY LACK SOIL BIOTA WHICH ARE NECESSARY FOR PROCESSING AND FOR BIOTIC PRODUCTION THAT EVENTUALLY GETS DOWN INTO THE STREAM. SO I WOULD HOPE THAT THE APPROPRIATE AGENCIES PAY ATTENTION TO THE QUALITY OF SOIL ABOVE AND BEYOND pH AND CHEMICAL CHARACTERISTICS. YOU'VE CLEARLY SHOWN THAT WITHOUT PROCESSING OF THE ORGANIC PRIMARY PRODUCTIVITY, THE EVENTUAL BIODIVERSITY WILL BE AFFECTED. ALSO, THERE HAVE BEEN MANY ATTEMPTS IN RESTORATION OF COMMUNITIES NEAR STREAMS. IT'S BEEN SHOWN WITH SOME WONDERFUL STUDIES THAT THE KIND OF VEGETATION PUT NEAR STREAMS -- WETLAND SHRUBS AND HERBS -- REALLY AFFECTS THE KINDS OF ORGANISMS THAT LIVE IN THE STREAMS. EVEN THE SPECIES OF WILLOW THAT WILL GROW NEXT TO THE STREAM AND WHEN THEY LEAF OUT WHAT KIND OF INSECTS LIVE ON ITS NEW LEAVES AFFECTS THE FOOD WEB FURTHER ON. SO THERE'S A TREMENDOUS AMOUNT OF SUBTLETY ABOVE AND BEYOND JUST HOW MUCH PRIMARY PRODUCTIVITY IS THERE. ARE THERE ORGANISMS IN THE SOIL THAT CAN ILLUMINATE A TRUE BIODIVERSITY IN THIS REGIONAL AREA?

WALLACE (TO HANDEL) - ANOTHER POINT OF CONCERN -- DO YOU HAVE ANY FEEL, AS A TERRESTRIAL ECOLOGIST, FOR WHAT'S HAPPENING WITH NITROGEN? **HANDEL** - THE BEST STUDIES ARE IN WATERSHEDS THAT ARE HIGHLY DISRUPTED. I BELIEVE CLEARCUTS ARE MUCH MORE BENIGN THAN 5,000 ACRES OF SURFACE-MINED LAND, IN THE SENSE THAT SOIL STRUCTURE IN A CLEARCUT IS RELATIVELY UNIMPACTED COMPARED TO ENGINEERING A WHOLE BASIN. **WALLACE** - CLEARCUTTING IN COWEETA SAW INCREASES IN NITROGEN FOR A COUPLE OF YEARS, UNTIL REGROWTH, SO YOU HAVE NITROGEN UPTAKE WITH NEW GROWTH; BUT I HAVE NO IDEA WHAT'S HAPPENING WITH VALLEY FILLS; I HAVEN'T SEEN THE DATA. **HANDEL** - BASED ON INFORMATION IN THE FORT MITCHELL SYMPOSIUM, PRE-SMCRA PRACTICES MAY BE MORE EFFECTIVE FOR NATURAL REINVASION. BUT MOST OF THE NATURAL REINVASION WAS ON THE EDGES, WITHIN 100 YARDS OF THE EDGE - IT'S VERY UNCLEAR WHAT'S HAPPENING MORE TOWARDS THE CENTER OF VERY LARGE, ENGINEERED SITES.

HARTOS - HOW ACTIVE ARE BENTHIC CRITTERS IN EPHEMERAL OR INTERMITTENT PARTS OF STREAMS? **WALLACE** - I WOULD QUESTION, LOOKING AT SOME OF THESE THINGS THAT ARE CALLED "INTERMITTENT," LOOKING AT WHAT THEY'VE DONE WITH SOME OF THE PIGEONROOST SURVEYS. THE FAUNA THERE ARE VERY SIMILAR TO WHAT WE HAVE AT COWEETA. THESE AREN'T WHAT I'D CALL INTERMITTENT TAXA; THEY HAVE LIFE CYCLES IN SOME CASES THAT ARE UP TO 18 MONTHS OR LONGER, WHICH SUGGESTS THAT THERE'S WATER THERE FOR AT LEAST 18 MONTHS, OR THEY WOULDN'T BE THERE. **HARTOS** - SO THE LIMITING FACTOR ISN'T WATER, SO LONG AS THEY CAN BE INUNDATED AT CERTAIN PARTS OF THE YEAR? **WALLACE** - NO, THEY NEED CONTINUOUS WATER.

POMPONIO - YOU'VE DONE A GREAT JOB OF EXPLAINING THE PROCESSES, ETC. MY PROBLEM IS YOU DON'T GO FROM BUGS TO FISH. **WALLACE** - IT'S OBVIOUS! I CAN GO ON DOWN TO THE LITTLE TENNESSEE RIVER, DOWNSTREAM OF COWEETA, AND SHOW THAT 60% OF THE TOTAL INVERTEBRATE CONSUMPTION IS ATTRIBUTED TO AMORPHOUS DETRITUS (Q - WHAT'S AMORPHOUS DETRITUS? **WALLACE** - ORGANIC MATTER OF UNRECOGNIZABLE ORIGIN -- OFTEN HAS MICROBES ASSOCIATED WITH IT; MAY HAVE BEEN LEAF MATERIAL, ALGAL, WOOD, ETC.). A LARGE PORTION OF THE LITTLE TENNESSEE RIVER BUG PRODUCTION IS MADE UP OF AMORPHOUS DETRITUS. IT'S ONE OF THE MOST PRODUCTIVE LOCATIONS I'VE SEEN FOR A LARGE RIVER ANYWHERE IN THE WORLD. IT ALSO HAS 44 SPECIES OF FISH, A VERY PRODUCTIVE FISH COMMUNITY, INCLUDING A RIVER REDHORSE THAT'S THE LARGEST NEW SPECIES OF FISH DESCRIBED IN RECENT YEARS FROM NORTH AMERICA. **POMPONIO** - ....FEEDING OFF THE BUG COMMUNITY PRODUCED BY THE AMORPHOUS DETRITUS? **WALLACE** - YES. **POMPONIO** - THAT'S THE WHOLE THING!

KINKAID - IS IT YOUR SENSE THAT AS MATERIALS EVOLVE TOWARDS SOILS, ORGANIC MATERIALS WOULD BUILD UP? **WALLACE** - AS HANDEL JUST SAID, THERE'S VERY LITTLE ORGANIC MATTER. **KINCAID** - AS SOILS FORM AND WEATHER, THEY WILL BECOME INHABITED BY PLANTS AND MICROORGANISMS AND AS THESE MATERIALS BUILD, THEY'LL PROVIDE A SOURCE OF CARBON WHICH CAN INTERACT WITH RAINWATER PERCOLATING THROUGH. MY CONCERN IS THAT THE SAME MECHANISM THAT RESULTS IN THE FORMATION OF KARST TOPOGRAPHY WOULD BE ACTIVE OVER A PERIOD OF TIME, AND THIS IS A PROBLEM THAT NEEDS TO BE ADDRESSED IN TERMS OF STABILITY.

HANDEL - EARLIER, THE IDEA OF CREATING ENGINEERED STREAMS ON TERRACES WAS BROUGHT UP. WHAT MIGHT THE QUALITY OF STREAMS ON TERRACES BE VS. NATURAL? **WALLACE** - YOU COULD MAKE SOMETHING DIFFERENT; YOU COULD CONSTRUCT A WETLAND THAT WOULD BE DIFFERENT BUT CONSTRUCTING A STREAM, SOMETHING THAT RESEMBLED THE ORIGINAL -- I DON'T SEE IT. **HANDEL** - THE STRUCTURAL COMPLEXITY IS SO DIFFERENT ...

WALLACE - IT'S NOT GOING TO BE ANYTHING LIKE WHAT YOU STARTED OUT WITH; I'M NOT SURE IT'S FEASIBLE TO EXPECT SOMETHING THAT RESEMBLES THE ORIGINAL STREAM.

HANDEL - WOULD YOU CHARACTERIZE THE BIODIVERSITY OF AN ENGINEERED STREAM ON A MINING SITE COMPARED WITH A FORESTED NATURAL STREAM. **WALLACE** -- IT WOULD BE VERY DIFFERENT. IT MIGHT BE FAIRLY DIVERSE, BUT IT MIGHT BE EXOTIC SPECIES COMPARED TO WHAT WOULD NORMALLY BE THERE.

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Morse, J. C., B. P. Stark, W. P. McCafferty, and K. J. Tennessen. 1997. Southern Appalachian and other southeastern streams at risk: implications for mayflies, dragonflies, stoneflies, and caddisflies. Pp. 17-42 in G. W. Benz, and D. E. Collins (eds.), Aquatic Fauna in Peril: The Southeastern Perspective. Special Publication 1, Southeastern Aquatic Research Institute, Lenz Design and Communications. Decatur, GA. 554 pp.

Dr. Bern Sweeney, Stroud Water Research Center, Avondale, Pennsylvania

The Stroud Center has been studying the structure and function of stream ecosystems since 1967. During the first five years after opening its doors, the research team at the Center completed an intensive study of White Clay Creek, a small piedmont stream in a quasi-natural state. From those data, Robin Vannote, the Director and team leader at the time, formulated what has been referred to as the "River Continuum Hypothesis" -- a conceptual model viewing the stream ecosystem as a continuum from the first order headwater streams down through larger order rivers (Figures 1 and 2). One of the important things that impressed the team early on was the relationship between the stream and the terrestrial environment. This slide (Figure 3) shows leaf litter on a square meter of forest floor; the leaves were taken out of the square meter and weighed, and found to weigh 203 g. Leaf litter blows across the forest floor and into the streams. Because our streams are wet depressions in the landscape, you get a lot more organic matter in the stream than on the terrestrial floor. The leaves tend to accumulate behind things in the stream and don't go far in the stream; what does go far is the processed leaves. This slide (Figure 4) shows the standing stock of coarse particulate organic matter (CPOM) in a wooded area of our stream. Remember that the forest floor had around 200 g/m^2, in the stream in November we have a standing stock of about 800 to 1,000 g/m^2, about four times more in the stream channel than on forest floor, because as the leaves blow across the forest floor, they hit the stream, and they stay, and they accumulate in the stream channel.

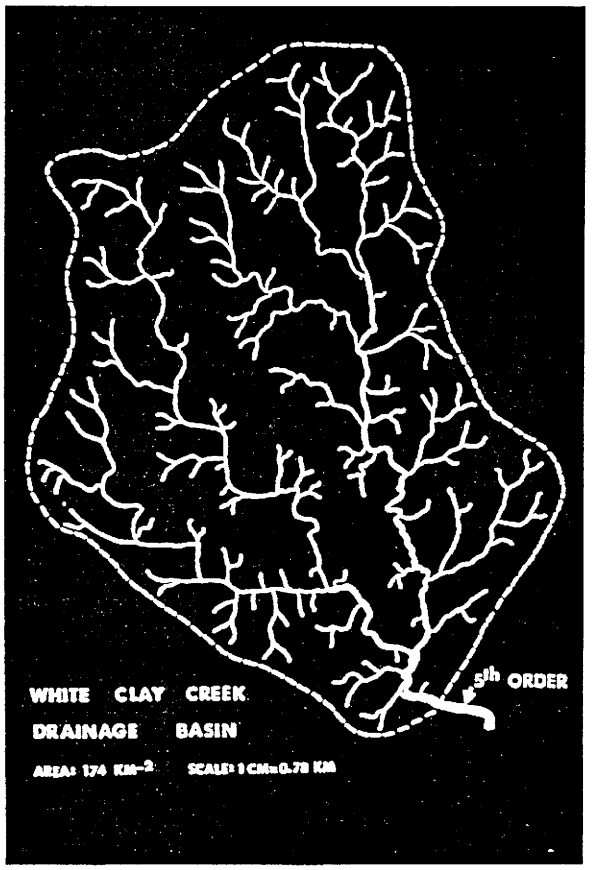

FIGURE 1.

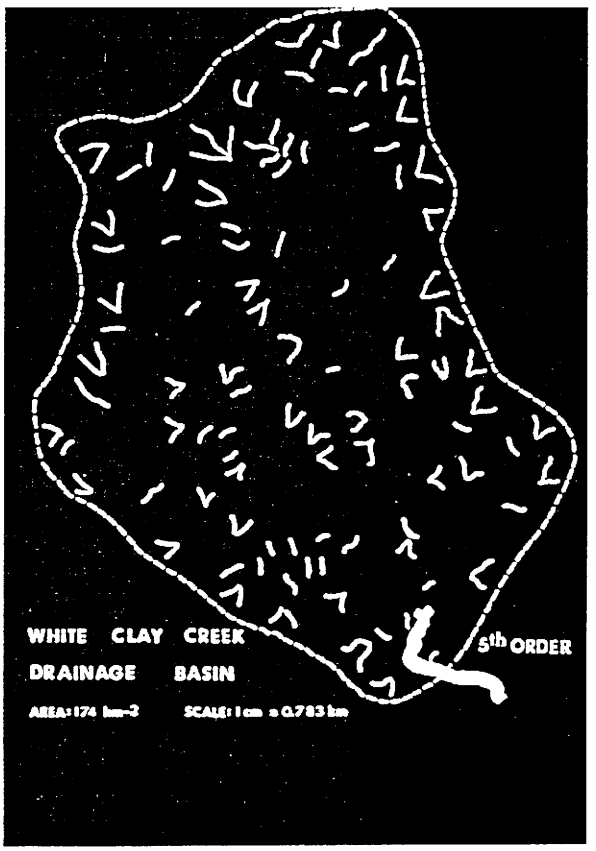

FIGURE 2. FIRST ORDER STREAMS ONLY.

FIGURE 3.

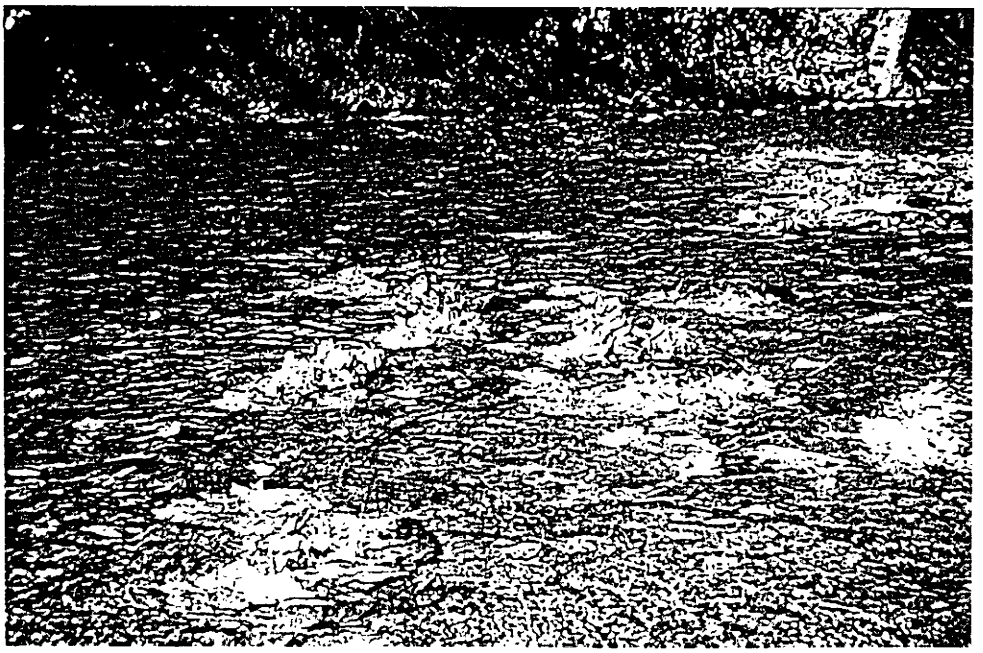

FIGURE 4.

Notice that this stream is flowing [from the forest towards a meadow (no animals in the meadow)] (Figure 5), and standing stock estimates were made in a downstream direction. The wooded section is very retentive; there is very little export of the coarse leaf litter down to the meadow. So you have two orders of magnitude lower leaf litter standing stock in the meadow. We just don't get the input of coarse organic matter in our grassy meadows that we do in our wooded areas. This is a concern regarding reconstructing streams in grassy reclamation areas.

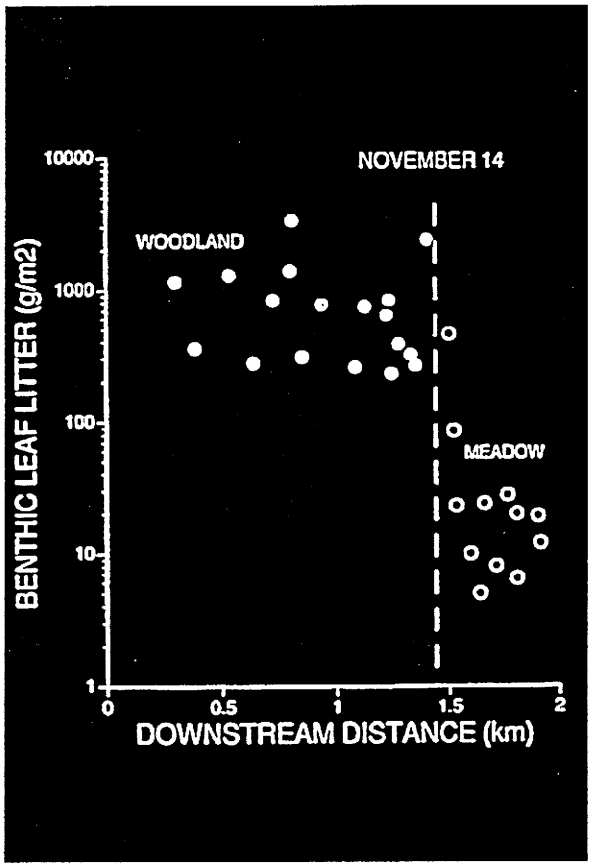

FIGURE 5.

HARTOS - HOW DOES LEAF LITTER CHANGE OVER TIME? **SWEENEY** - THIS TIME OF YEAR (APRIL/MAY) THERE'S VERY LITTLE OF THIS COARSE PARTICULATE ORGANIC MATTER IN THIS WOODED REACH OF STREAM. IT'S ALL BEEN PROCESSED. **HARTOS** - DOES IT SEEM TO WEIGH OUT WITH THE MEADOW BEING MORE CONSTANT? **SWEENEY** - I DON'T KNOW THAT. BASICALLY, THE PROCESSING OF THIS MATERIAL OCCURS IN THE FALL AND WINTER MONTHS BY INVERTEBRATES; BY THIS TIME YOU'RE LUCKY TO FIND A LEAF PACK, LET ALONE A SINGLE LEAF, IN THE STREAM.

This slide (Figure 6) shows leaf litter that's been processed by a lot of invertebrates. We measured production in our stream as Wallace did at Coweeta, and got the same kinds of values. We're getting about 5 g/m^2 (dry biomass) for this one species of stonefly on a mixed deciduous diet. We've also done exclusion experiments in our small, first order streams. We've shown that if you change the kind of tree species that go into the first order stream, you can dramatically affect the production and biomass of various invertebrates. For a particular stonefly, with a mixed deciduous leaf diet, we got about 5 g/m^2 of production, but when fed only on red oak leaves in a first order stream, we got only 1 - 2 g/m^2. So, the type of tree species growing next to these streams is really very critical to many of these invertebrates.

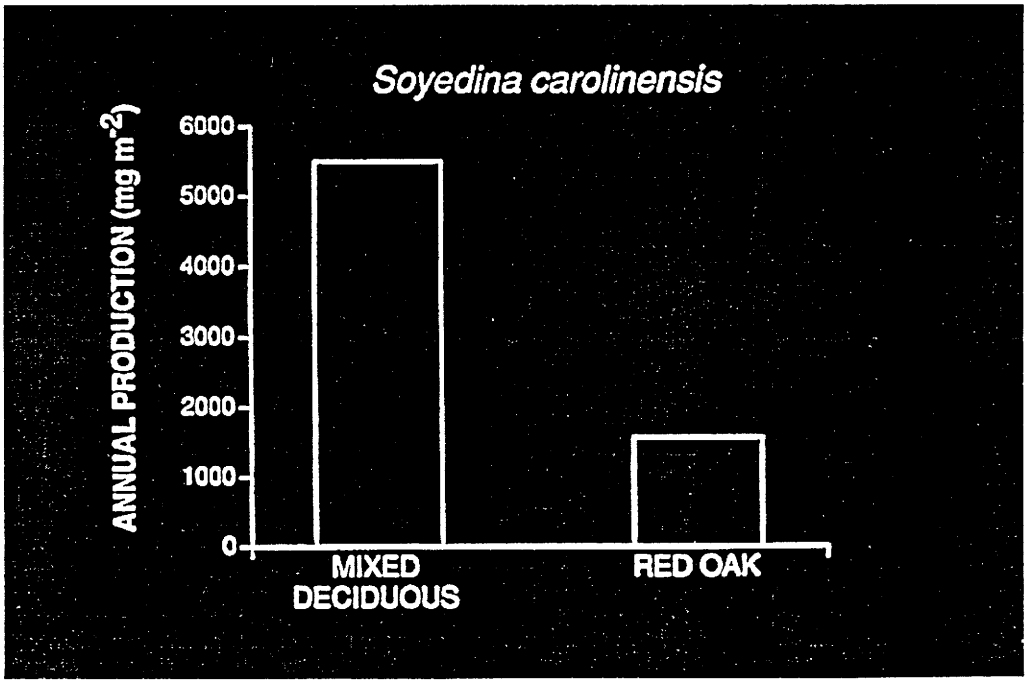

FIGURE 6.

The next slide (Figure 7) is an analysis of how much area there is in different order streams in our White Clay Creek basin. The slide shows how many streams of each type we have in the basin: 147 first, 47 second, 9 third, 2 fourth. It also shows the average width of the streams in a forested condition, and also the average lengths of tributaries in general in the United States. This is an attempt to try to calculate how much benthic area is available for production for biological and biochemical activities, because in streams a lot of the biological or biochemical action is taking place on the bottom substrates. This is very different than in a lake ecosystem or marine environment where there's a lot of water column processes. In a stream it's on the bottom -- benthos -- that's where the action is. So how much benthic area you have per unit length of stream makes a big difference per unit order of stream. You can see from this analysis that about 32% of total bottom area in our watershed available for macroinvertebrate production or any kind of production is in first order streams; this is a striking thing. First order streams are the heart and soul of a watershed. They're the place where the groundwater interfaces with the surface water. They're the collectors of materials on the landscape. First order streams are scattered all over the landscape. They're the first places where the terrestrial and the aquatic environment interface. (**Q**: HOW DID YOU MEASURE THE WIDTH? **SWEENEY** - THE WIDTHS SHOWN HERE ARE THE AVERAGE BASE-FLOW WETTED PERIMETER OF THE STREAMS.)

WHITE CLAY CREEK

ORDER	NUMBER	WIDTH (M)	LENGTH (M)	AREA (M^2)
1	147	3.0	1,609	704,838 (32.5%)
2	47	3.0	3,701	520,055
3	9	4.9	8,529	369,988
4	2	14.7	19,312	568,545
TOTAL				2,163,426

FIGURE 7.

In our experimental watershed, we have a lot of forest canopy which restricts light levels in the system, but in our first and second order streams we still get some significant primary production going on, because at certain times of year, especially this time of year, before leaf-out, when stream temperatures are high enough, we have enough light levels, we can get significant primary production. We can get up to 100-150 species of diatoms living on the surface of a rock in these smaller streams, tens of thousands of individuals, in this kind of area of stream bottom. Most of these algal species are diatoms because they can live at this time of year and under low light conditions in summer when the trees are shading the stream. This kind of algae is very important in these small-order streams because this was the dominant kind of algae, at least in our area, because it's a shade-loving kind of algae -- it competes well in shaded conditions -- and historically most streams were shaded in our region because it was part of the eastern deciduous forest biome. Consequently, most native species in our small streams that eat algae have mouth parts and digestive systems that are adapted to eating this type of algae (as opposed to filamentous green algae).

This slide (Figure 8) shows some old data (1972-1973) that are some of the first stream metabolism measurements ever made on a stream anywhere. The data are of dissolved oxygen measurements on small-order streams. You can see that in April and May, you have a time where you get a pulse of primary production. During shaded months, the streams are heterotrophic, but in late fall/early winter, when the canopy is gone and you have high sunlight, the temperatures

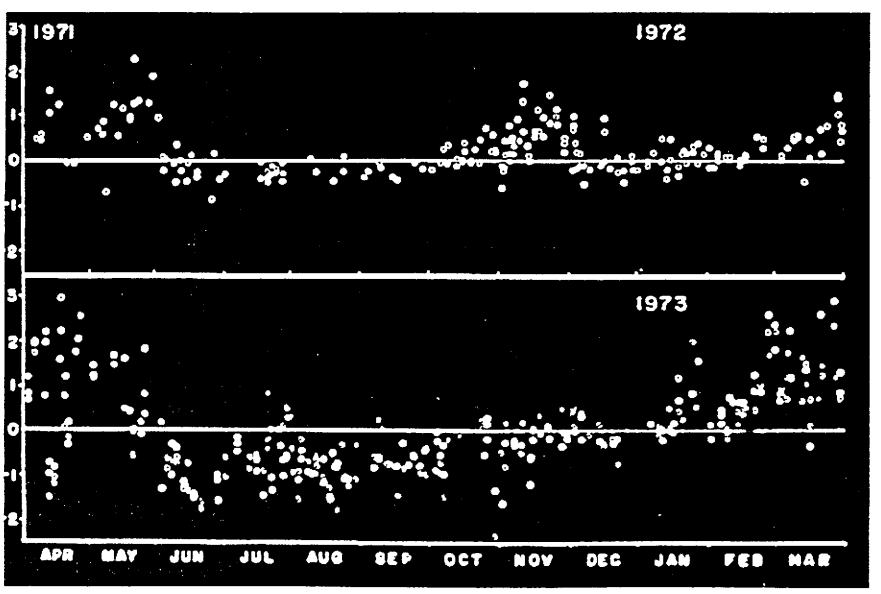

FIGURE 8.

are suitable and you get more primary production. Consequently, even in these small-order streams, besides the detritivores, you have a lot of herbivores. We have species that go through their life cycles that are timed very specifically to the availability of this primary production. So species like this will put on most of their biomass at a very narrow time of year and it has to coincide with that period of maximum primary production.

The next slide shows again that 203 g of leaf litter on the forest floor. One of the things that was recognized by our organic chemists after the first year or two of study on the White Clay was the importance that this leaf litter plays in the export of dissolved organic carbon to our low-order streams. When rainfall percolates through this leafy matrix on the forest floor, enters the ground as groundwater, and then flows to the stream, it picks up a lot of the organic compounds out of the leaves; at the Stroud Center, we call this "watershed tea." Just like the dark color you get when you steep a tea bag in hot water is the release of dissolved organic compounds that are food -- we drink it as food -- in a watershed, instead of having tea leaves you have hickory leaves, beech leaves etc., but it's the same thing. You have materials coming out of the leaf litter, and the leaves don't have to fall into the stream directly. These compounds go into the groundwater and are carried to the stream by the groundwater. We estimate in our system that this dissolved organic carbon fraction in our low-order streams represents a tremendous piece of the total food pie in the system (Figure 9). This is something which has to be looked at carefully in the mountaintop removal/valley fill situation.

This dissolved organic carbon drives a tremendous amount of productivity in the system. Our microbiologist tells us that in 1 square inch of stream bottom of the White Clay Creek, we have about 6.6 billion bacteria being fed by that dissolved organic carbon, 6 million flagellates (little microscopic animals), and 64,000 ciliates. Of course, this provides the basis for a good part of the food web that in turn gets exported up to larger invertebrates and fish.

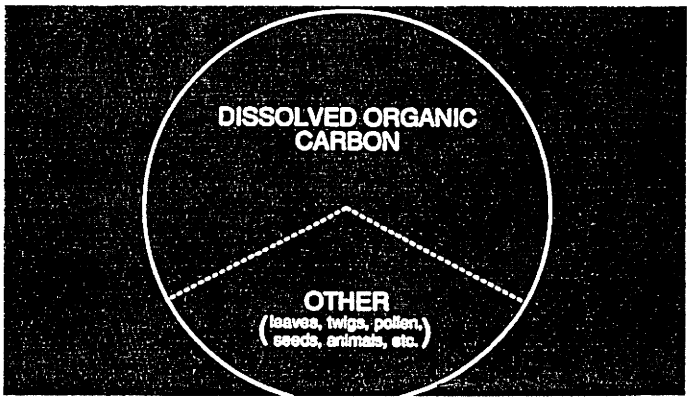

FIGURE 9.

The next slide (Figure 10) shows a schematic of a cross-section through a stream channel to show that streamside areas (wetland areas) along first and second order streams are extremely important not only for the dissolved organic carbon which comes through them, but also because they are zones of nutrient processing. Groundwater brings with it not only dissolved organic carbon, but also nitrogen and other types of nutrients. In our wetland areas, especially the wet soils in first and second order streams, we get a significant amount of denitrification going on. Shallow groundwater is moving through the streamside wetlands and into our streams.

The next slide (Figure 11) shows an analysis of nitrate levels in deep wells, surface springs, in the stream itself, and in shallow streamside wells. You can see that a lot of the nitrogen is being removed in shallow streamside wetland areas before it gets to the stream. This is another issue we've talked about this

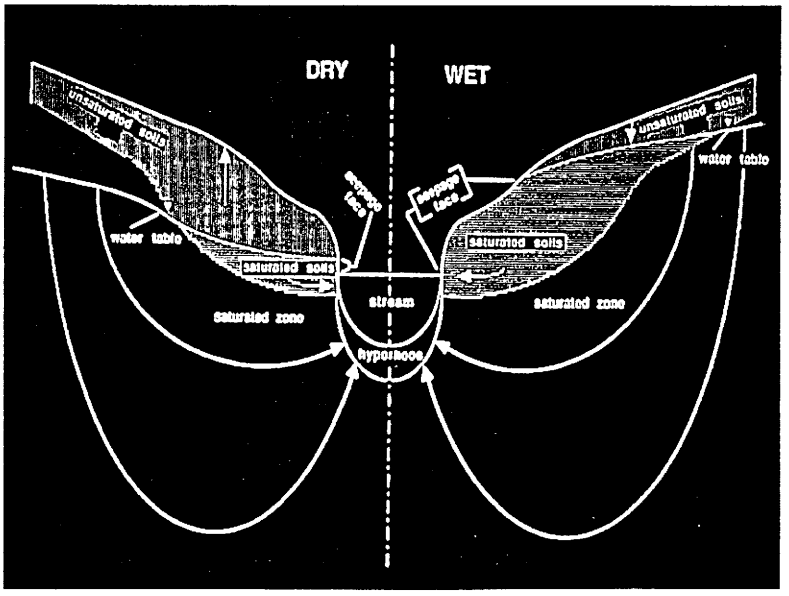

FIGURE 10.

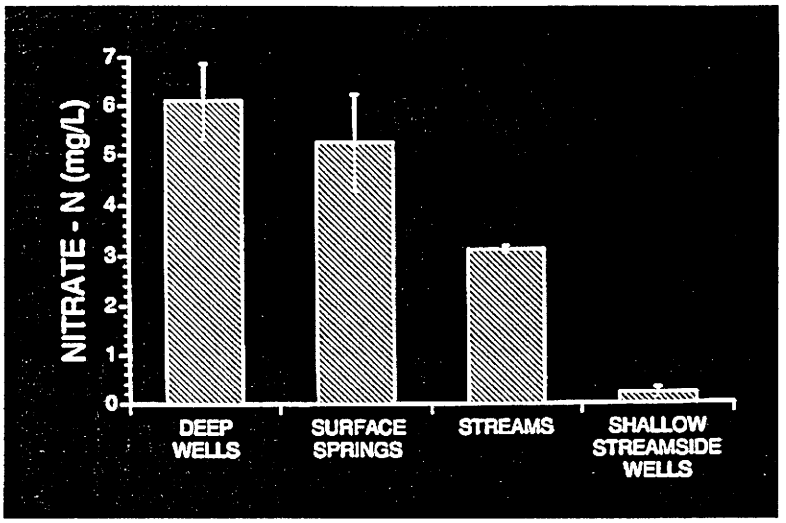

FIGURE 11.

morning: How different will these systems be without these kinds of processing areas for nutrients? We certainly have a lot of atmospheric nitrogen loading on our watersheds.

The next slide (Figure 12) is a schematic illustrating the connectivity between what's going on on the surface with water percolation and the dynamics of small streams. These small first order streams are really tightly connected to what's going on on the landscape through this internal plumbing network.

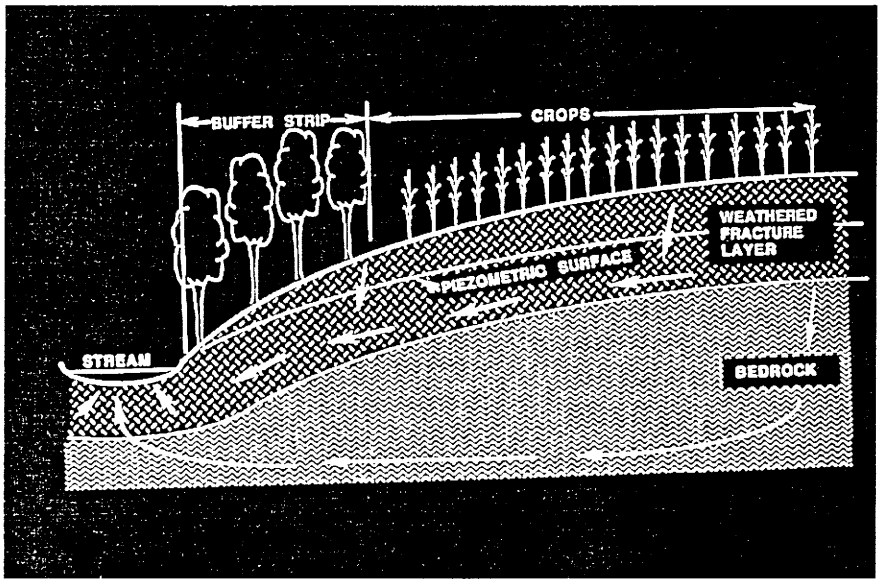

FIGURE 12.

The next point concerns the biota of these systems. The Center has been running Malaise nets which collect adult flying aquatic insects. It's the way that you inventory what species you have there. (You can't tell the species apart from the aquatic larvae for most taxa -- you need to get the adults.) We've been at this for 32 years, and have found up to 304 species in these small streams (Figure 13). We've done a poor job with dipterans, and I suspect that triple these numbers are really there, and the actual total species number will be over 600 when we're done. So we have a tremendous number of species brought in a very small linear length of stream channel.

The next slide (Figure 14) shows the Breitenback Creek in Germany. They've been working on this stream for about 50 years, and they're up to 881 species of macroinvertebrates. So high species diversity in these small streams is not uncharacteristic -- I think it's the norm.

SPECIES RICHNESS OF AQUATIC INSECTS

Insect Order	White Clay Creek* PA
Odonata (dragon/damselflies)	15
Ephemeroptera (mayflies)	50
Plecoptera (stoneflies)	14
Trichoptera (caddisflies)	52
Megaloptera/Neuroptera (hellgrammites, spongillaflies)	5
Hemiptera (water boatmen,striders)	10
Lepidoptera (aquatic moths)	3
Coleoptera (aquatic beetles)	18
Diptera (midges, craneflies, blackflies)	137
Total	304

* Stroud Water Research Center Survey

FIGURE 13.

BREITENBACH CREEK, GERMANY*

Macroinvertebrates	No. Species	% of Total
Insect	642	73%
Non-Insect*	239	27%
Total	881	100%

* Cited in Allan 1995; non-insect macroinvertebrates include Mollusca, Annelida, Crustacia, Hydracarina, Nematoda

FIGURE 14.

One thing we and others have discovered is that not only do you have high alpha diversity (that is, diversity at a given point in stream, so there's high diversity in first order streams, high diversity in sixth order streams, there's high diversity in the big river) but there's high beta diversity -- the turnover of species as you go down through this river continuum. It's extensive enough that there are very few species that you would find up in the headwaters of a system that also live downstream in the big river -- in fact, I can't even think of any. This is true for invertebrates and somewhat true for fish. My point is there's a continuum of species that have distinct distributions within the river continuum. In other words, a headwater species may only occur in first, second, and third order streams; you don't find it in fifth, sixth or seventh order streams. It doesn't have the right habitat, the right food, whatever. Also, there are species in a big river that you don't find in the headwaters. The point is - what happens when you clip off the top part of this continuum? What happens to a species that happens to only have a distribution in first, second, and third orders? You clip off first and second orders, and you have a much more affected population, restricted only to the third order. How long can that population persist? What happens if there's disturbance in middle of this continuum, say in a third or fourth order stream? What happens to the recolonization process? Are you going to get taxa from downstream going upstream? I don't think so, because organisms in the higher orders probably don't want to live in the lower orders. A lot of third, fourth and fifth order streams are where people like to live and develop the land -- this is where the housing developments are, this is where there's disturbance, and this is where accidents are going to happen -- this is where you'll need recolonization. Recolonization is going to come in from these smaller tributaries, if they exist. We need to think about these things in terms of the persistence of the system as a whole, not just as individual tributaries.

We haven't talked much about densities of invertebrates -- we've talked about production. In this system and others that we've studied, there's a tremendous density of macroinvertebrates and algae on the bottom of the streams. The density isn't really that size dependent. In these small first order streams, we get macroinvertebrate densities of 8,000 - 20,000 individuals per m^2. Down in our bigger watersheds, we get the same densities. So it's not the case that if you have a bigger stream you have more bugs per unit area. The kind of bugs are very different downstream (species are different), but the densities are pretty equal. So, a lot of people think of first order streams as a lot of "nothing" -- not much water in them, probably not much living in them. But in fact, the amount of organisms living per unit area is just as much as down in the bigger system. And the fact is that there is so much benthic area in these small streams, and there's so many of them, that collectively a lot of this "nothing" is worth something, and it's something very special -- it's very abundant.

This slide shows a first order stream bordered by grass. We've been studying paired reaches of these low order streams, reaches bordered by forest compared to reaches bordered by grass. In the grass section, the stream is not functionally as well off; the stream is only one-third as wide as the forested reach. A terrestrial forest will shade out grasses; if there is sunlight enough for grasses, they'll put roots in the stream which trap sediments, narrowing the stream bed in two to three years. Because organisms live on the stream bottom, and the productivity and biochemical processing is associated with the bottom area, narrowing will have a tremendous impact on stream productivity.

The last slides show the quality of the populations in a given stream and in broad sense. We have some genetic data published on mayflies in eastern North America. We're one of the few labs to study the genetic structure of aquatic insects. This slide (Figure 15) shows one of the species, which shows very different genes, moving from north to south. These data tell us that there's not a lot of gene flow occurring on a big scale. Gene flow in these insect populations occurs in a stepping stone fashion, as insects fly from one stream to another. What that means is that species like this which are occurring in first and second order streams need to have streams nearby for genetic exchange. So if there are gaps in the network, what are the implications for gene flow across the whole population? What we don't know may be very important. We don't even know what species are in these first order streams in the area [the mining region] we're talking about. The area of eastern West Virginia/western Virginia is a real hotspot of new species discoveries (Figure 16). It's unusual, non-glaciated, there's been a lot of time for populations to persist and evolve. Thermally, it has lot of diversity. We don't know what's in this area yet, and we don't know its importance to stream ecology.

We can't afford to destroy what we don't know. As a professional who has worked for 30 years in this field, should we be concerned about first and second order streams? We don't draw the line anywhere - we can't sacrifice a single first order stream (Figure 17).

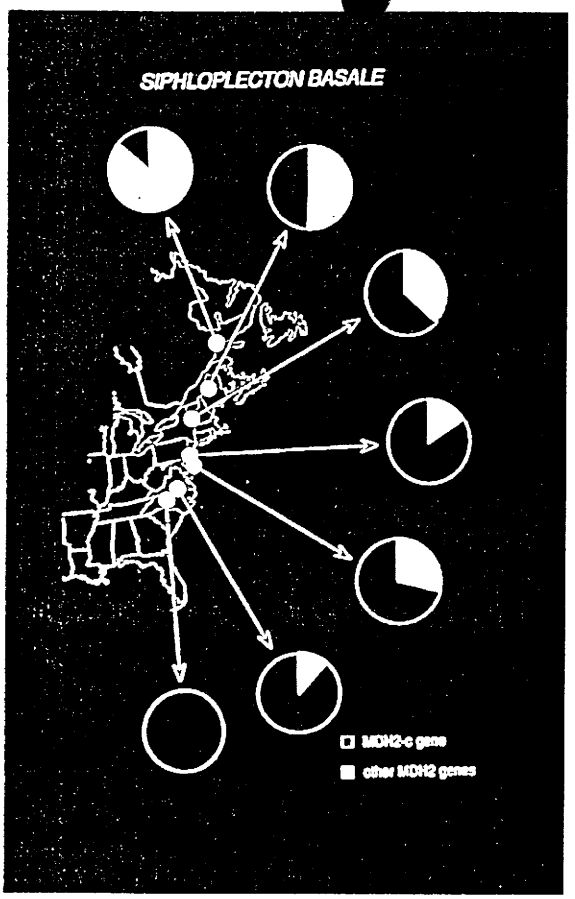

FIGURE 15.

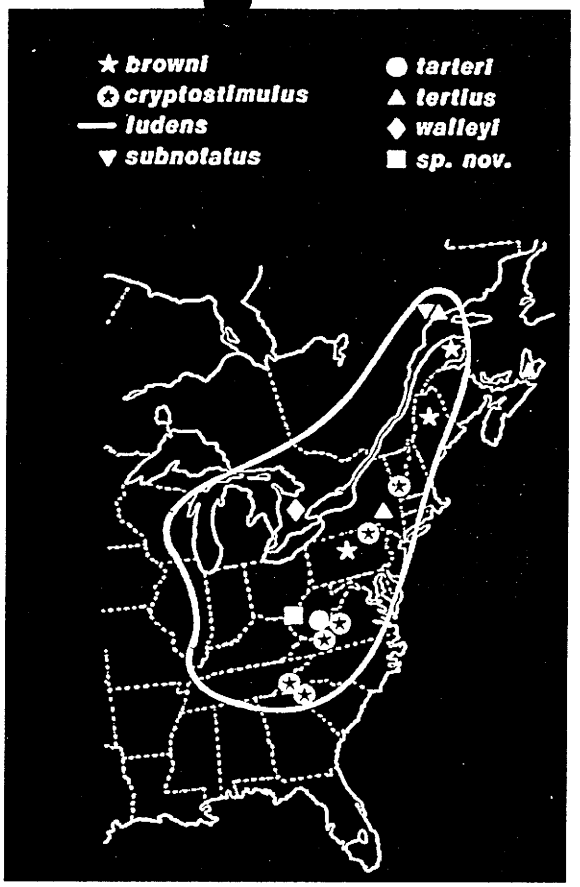

FIGURE 16.

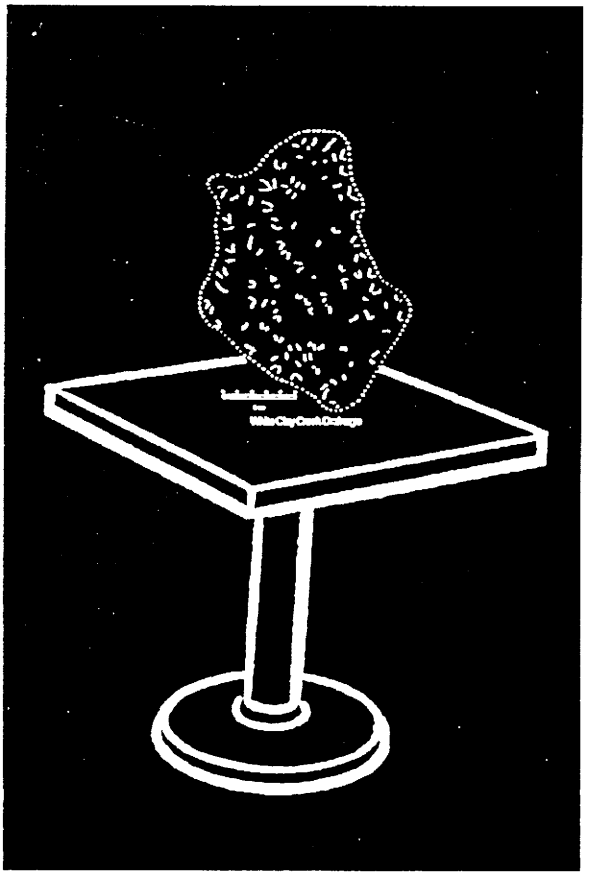

FIGURE 17.

KINCAID - GIVEN THE SHORT TIME FOR EIS STUDIES, AND THE CURRENT DROUGHT SITUATION, DO YOU HAVE ADVICE ON THINGS NOT TO DO? **SWEENEY** - GO ABOUT DATA COLLECTION VERY CAREFULLY. IF A STREAM IS DRY, DON'T ASSUME NO DATA CAN BE GATHERED. THERE ARE SOME GOOD PAPERS ON THIS REGION AND HOW TO SAMPLE QUANTITATIVELY. I THINK WE HAVE TO RELATE NUMBERS WITH PRODUCTION. YOU ALSO NEED SOME DATA FROM SOME OF THE ALREADY-DISTURBED SITES, SUCH AS THE TEMPERATURE REGIME FROM VALLEY FILLS AND HOW THEY ARE LIKE OR DIFFERENT FROM NATURAL STREAMS. TEMPERATURE DRIVES THE LIFE CYCLE OF MANY OF THESE SPECIES; MANY SPECIES HAVE EVOLVED SOPHISTICATED RESPONSES TO TEMPERATURE CHANGES. ALSO CHEMISTRY DATA ON WHAT IS BEING EXPORTED - NITROGEN, DISSOLVED ORGANIC CARBON.

Q: IF ONE WOULD RANDOMLY SAMPLE 20 STREAMS IN AN AREA, HOW DIVERSE DO YOU THINK THESE STREAMS WOULD BE ONE TO ANOTHER? **SWEENEY** - I'M NOT SURE WE KNOW. THE POTENTIAL IS TREMENDOUS. FOR EXAMPLE, BILL KAUFFMAN HAS DONE STUDIES WITH US IN COSTA RICA ON TWO LOW-ORDER STREAMS THAT ARE SEPARATED FROM EACH OTHER BY ONLY A KILOMETER. IN ONE, THERE WERE 200 SPECIES OF CHIRONOMIDS, IN THE OTHER THERE WERE 200 SPECIES OF CHIRONOMIDS, BUT THE DEGREE OF OVERLAP WAS LESS THAN

50 PERCENT. Q - SO THE UNIQUENESS THAT EACH OF THESE STREAMS REPRESENTS IS GOING TO HAVE TO BE ADDRESSED. **SWEENEY** - I THINK SO. THE PROBLEM, THAT I'VE TRIED TO CONVEY AND THAT BRUCE HAS TRIED TO CONVEY, IS THAT IT'S NOT EASY TO DO A TAXONOMIC INVENTORY OF THESE SYSTEMS. BUT JUST BECAUSE SOMETHING ISN'T EASY DOESN'T MEAN THAT IT SHOULDN'T BE DONE, OR THAT YOU SHOULD ALLOW SOMETHING ELSE TO HAPPEN BEFORE IT'S DONE.

POMPONIO - IS THERE ANYTHING IN YOUR STUDIES WHICH HAS LOOKED AT THE USE OF THOSE SYSTEMS BY TERRESTRIAL CRITTERS LIKE BIRDS? **SWEENEY** - YES, WE HAVE SOME DATA ON EXPORT OF AQUATIC LIFE. THE MALAISE TRAPS WOULD GIVE YOU DATA ON WHAT'S EXPORTED. ALSO WE KNOW THAT THERE'S A GREAT DEAL OF INTERACTION BETWEEN BIRDS AND INSECT POPULATIONS IN TERMS OF MAINTAINING SOME OF THE INTEGRITY OF THE LIFE HISTORIES, FOR EXAMPLE, EMERGENT SYNCHRONY. YOU HAVE A SPECIES THAT LIVES IN THE STREAM FOR A WHOLE YEAR, AND THEN ALL OF A SUDDEN IT EMERGES ON APRIL 10, AND ONLY APRIL 10-15 AND REPRODUCES. WHAT MAINTAINS THAT KIND OF SYNCHRONY? WE PUBLISHED INFORMATION SHOWING THAT TERRESTRIAL BIRDS FEEDING ON THE TAIL ENDS OF THE EMERGENCE PERIODS CAN MAINTAIN OR SELECT AGAINST INDIVIDUALS THAT EMERGE TOO EARLY OR TOO LATE. THERE'S A LOT OF THAT KIND OF THING THAT GOES ON. **POMPONIO** - I THINK IT'S IMPORTANT TO FOCUS NOT ONLY ON THE AQUATIC SPECIES, BUT ALSO WHAT'S USING THEM THAT'S AN IMPORTANT PART OF LANDSCAPE -- THE WHOLE INTERACTION. **SWEENEY** - WELL, I CAN TELL YOU THAT WHEN YOU GO OUT COLLECTING EMERGENT MAYFLIES AT CERTAIN TIMES OF THE YEAR, YOU'RE REALLY COMPETING WITH THE BIRDS.

[Note: Dr. Sweeney sent a letter to the Fish and Wildlife Service after the symposium, summarizing many of the points in his presentation. The letter is reproduced on the following pages.]

STROUD WATER RESEARCH CENTER

970 Spencer Road
Avondale, Pennsylvania 19311

Telephone 610-268-2153 610-268-0490 Facsimile

May 11, 1999

Mr. David Densmore
Supervisor
Pennsylvania Field Office
U. S. Fish and Wildlife Service
Suite 322, 315 South Allen Street
Sate College, PA 16801

Dear Mr. Densmore:

One of the key issues with respect to the Mountain Top Mining debate is whether small (first and second order) streams are important and worthy of unconditional protection and preservation? I offer the following thoughts in an attempt to convince you and others associated with the debate that the answer is an emphatic and unqualified YES!

The Stroud Water Research Center has been studying the structure and function of small tributaries of the White Clay Creek (WCC) Watershed since 1968. Results from the first few years of study quickly established the tiniest of streams (first order) as being both abundant and crucial to the overall function on the ecosystem. Vannote's "River Continuum Theory," which was first developed out of the early studies on the WCC, made special note of the importance of first order streams and their physical, chemical, and biological connectivity to the larger downstream tributaries.

Numerous studies over the years at the Center have shown that first order streams occur throughout the watershed, interface clearly with the landscape, and are the primary collectors of material and energy for the stream ecosystem. Under natural conditions, small streams receive leaf litter directly from the forest canopy and, because they are wet depressions in the landscape, often trap leaves blowing across the forest floor. Thus, small streams in WCC can have an average 800-1000 g/m^2 standing stock leaf litter in November even though the surrounding forest floor only averages about 200 g/m^2. These leaves are processed (eaten) by a variety of aquatic macroinvertebrate species and converted to animal biomass by some species at a rate of 5-8 g/m^2/year. Given that the WCC watershed contains about 147 first order streams which collectively contain about 700,000 m^2 of bottom area for macroinvertebrate production, the amount of animal biomass and smaller particles of food produced from leaf litter processing alone is staggering. Over 32% of the total benthic surface area in WCC is represented by first order streams. This is especially important because most of the structural and functional activity in a stream ecosystem is associated with benthic substrata (bottom areas) as opposed to water column processes.

Although small, natural streams in the WCC often flow through forest, seasonal openings in the canopy (Spring and Fall) and the occurrence of shade tolerant algae (diatoms) enable significant levels of primary production to occur. Studies at the Center have not only documented that each square meter of first order stream bottom is capable of producing significant levels of algae (~0.2 - 0.4 g C m^{-2} d^{-1}), but that individual rocks can often contain over 100 species of algae (diatoms) representing thousands of individuals.

Significant biological productivity in tiny first order streams of WCC is also associated with bacterial communities which are feeding on large amounts of dissolved organic compounds (DOC) carried to the stream by groundwater. The DOC, which effectively can represent up to 60% or more of the total

food base of a small stream, originates from rainwater percolating through the organic matter (leaves, twigs, etc.) of the floor of the watershed. A square centimeter of stream bottom substrata in a small tributary of WCC can support a community consisting of about 1 billion bacteria being fed on by 1 million microflagellate and 10,000 ciliated invertebrates --- all supported to a large extent by DOC.

Thus, the in-stream biological productivity of first order streams is significant and certainly non-trivial compared to larger streams. In fact, widely accepted models of ecosystem structure and function (e.g. River Continuum, nutrient spiraling) strongly connect the productivity and structure of downstream communities with their smaller upstream tributaries.

In similar fashion, the chemical fingerprint of downstream reaches is determined in large part by the fingerprint of upstream tributaries. In WCC, for example, the wetland areas adjacent to first order streams are critical areas of denitrification for groundwater flowing into the system. Thus, despite high levels of nitrate in watershed groundwater (e.g. > 5-6 mg/l), nitrate levels in low order streams average < 3 mg/l.

The unique physical, chemical and biological conditions of low order streams supports not only a productive fauna and flora but a high level of diversity. In WCC, well over 300 species of aquatic insects alone co-exist in a small tributary. Both alpha and beta diversity are high in the system. Thus, species occurring in the small tributaries typically do not occur in the larger downstream reaches and vice versa. This means that eliminating first order streams greatly jeopardizes the ability of certain species to maintain local populations and provide propagules for recolonizing disturbed areas. In Appalachian mountain watersheds, the biological diversity of small order streams has not been studied extensively. Recent studies, however, indicate a substantial level of endemism and a disproportionately high level of species new to science associated with these small stream systems.

The abundance and proximity to one another of first order streams have also been shown to have important implications with respect to maintaining levels of genetic diversity in natural populations. For example, a comparison of the genetic structures of certain WCC populations with populations elsewhere (north or south) in their geographic range suggest that gene flow occurs in a "stepping stone" fashion (i.e. occasional short distance migration as opposed to long distance genetic exchange). Elimination of first order steams, or a portion of the "stepping stones", has obvious negative consequences for dispersal and gene flow of species uniquely adapted to these systems.

In conclusion, small first order streams form the heart and soul of the functional stream ecosystem in WCC and every watershed that has been carefully studied. They are small but numerous and collectively represent a significant part of the system with respect to its physical, chemical and biological characteristics. They support a wide variety of unique species that do not occur in larger streams. The structure and function of small streams is not only important locally (to the reach itself) but critical to the productivity of larger downstream tributaries. Clearly, any discussion of destroying even one first order stream is out of order. Rather, first order streams should be placed on a pedestal, protected at all cost, and treated with reverence in the sense of respect co-mingled with awe.

I hope that these comments are helpful to you and your staff.

Sincerely,

Bernard W. Sweeney
Director and Curator

Dr. Denis Newbold, Stroud Water Research Center, Avondale, Pennsylvania

This slide (Figure 1) shows the conceptual diagram of nutrient spiral in the stream. That concept was developed by Jack Webster of VPI, who published it with Bruce Wallace. The spiral tells you how effective the ecosystem is at processing nutrients. The tighter the spiral, the more effectively the ecosystem is trapping and reusing organic matter and nutrients as you go downstream stream. But there's another side of this: The tightness to the spiral which we measure with length (the distance something has to move downstream in order to be processed in some way) (Figure 2). This spiraling length (or "turnover length" when referring to carbon) has particular relevance to the question we face. If you're sitting in a downstream ecosystem, where did your nutrients come from -- how far upstream did they come from?

The original work on spriraling looked at the cycling of phosphorus. This slide (Figure 3) shows an upstream and a downstream caddisfly. In these original examinations of nutrient cycling, we could see evidence of spiraling taking place: a downstream caddisfly that collects particles in its net is actually getting labeled with radioactive phosphorus relative to the one upstream, providing the evidence that this downstream animal is depending on an upstream source.

I'm going to focus mostly on carbon, and shift to what we've learned in studies of White Clay Creek (but there have been a lot of studies at Coweeta and elsewhere showing similar things). A simple carbon cycle here (Figure 4) involves algae on the stream bottom, and/or microbes. As microbes decompose organic matter, or as algae produce organic matter through photosynthesis, they release a lot of dissolved organic carbon to the water column, which then moves downstream. Traditionally we viewed the organic matter in the stream, the dissolved organic matter especially, as refractory (i.e., it doesn't get used very fast; it eventually gets to the ocean where it may last a hundred years) (Figure 5). Much of the dissolved organic carbon (DOC) is, in fact, refractory, but there's also a significant labile component to that carbon which cycles within the stream ecosystem.

This slide (Figure 6) shows dissolved organic carbon cycling in White Clay Creek; it shows the fate of dissolved organic matter (in this case produced by algae, but it would be similar to that produced by microbes decomposing litter that falls into the stream). Based on our experimental results, the labile component of the DOC produced by the algae will travel 2 km downstream before being taken up and utilized by the streambed microbes. The refractory component will travel much farther. The estimate shown here of 144 km actually means that it would travel an average of 144 km downstream if the stream were not to grow any larger. But of course, the stream -- in this case, the White Clay Creek -- does grow larger, and in fact enters the Delaware Estuary in much less than 144 km. Thus, the 144 km actually means that nearly all of the refractory component will reach either the estuary or the ocean before being utilized. These estimates were based on the third order reach of the White Clay, and the 2-km turnover length for the labile DOC is about the same length as the reach. In fact, it turns out that the way these distances scale, the turnover length for labile DOC in a reach of any given order, will be comparable to the average length of a segment of that order (Figure 7). Thus in a first order reach, which is typically about 1 km long, the turnover length for labile DOC would be about 1 km. This means that we can normally expect about half of the labile DOC produced within any given reach to be utilized within the reach, while the remainder will be passed to a larger downstream reach. The next reach, which is typically second order with a length of 2 to 3 km, will have a proportionately longer turnover length, so the downstream transfer and utilization successively cascades downstream. Each downstream reach will utilize a portion of the labile DOC passed from upstream, and pass the remainder downstream.

The next slide (Figure 8) emphasizes the production of dissolved organic phosphorous, which has a lot of the same characteristics as dissolved organic matter.

Now I want to discuss the transport of fine particulate organic matter, or seston. We've been involved in a number of studies of how particles move downstream through a system. This is a diagram (Figure 9) of how particles might settle and be resuspended in the water column. We put radioactively-labeled particles in streams, along with red dyes to serve as tracers, and then sampled over several months after that in the sediments. From this work you get a picture of how much of these particles that are in the water column are settling, how long they stay on the bottom, and when they come back up, how far downstream they go. In a third order stream (Smiley Creek) in Idaho the

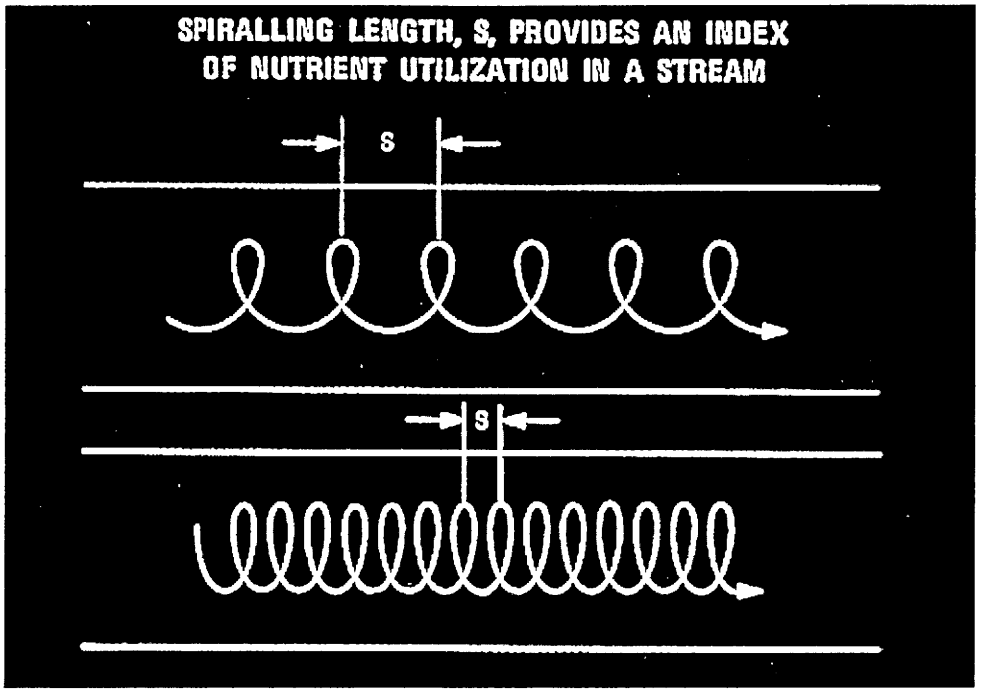

FIGURE 1.

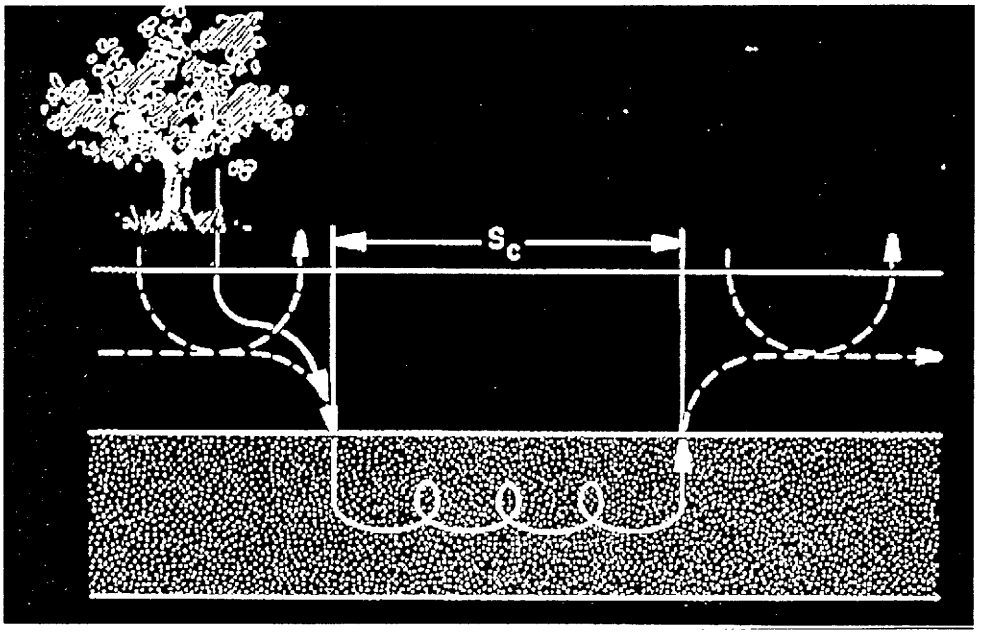

FIGURE 2.

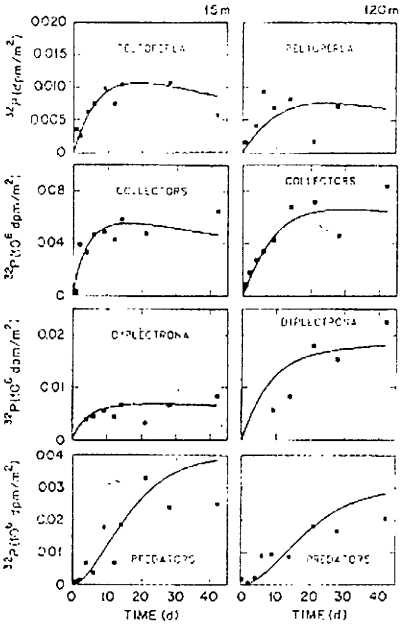

FIGURE 3.

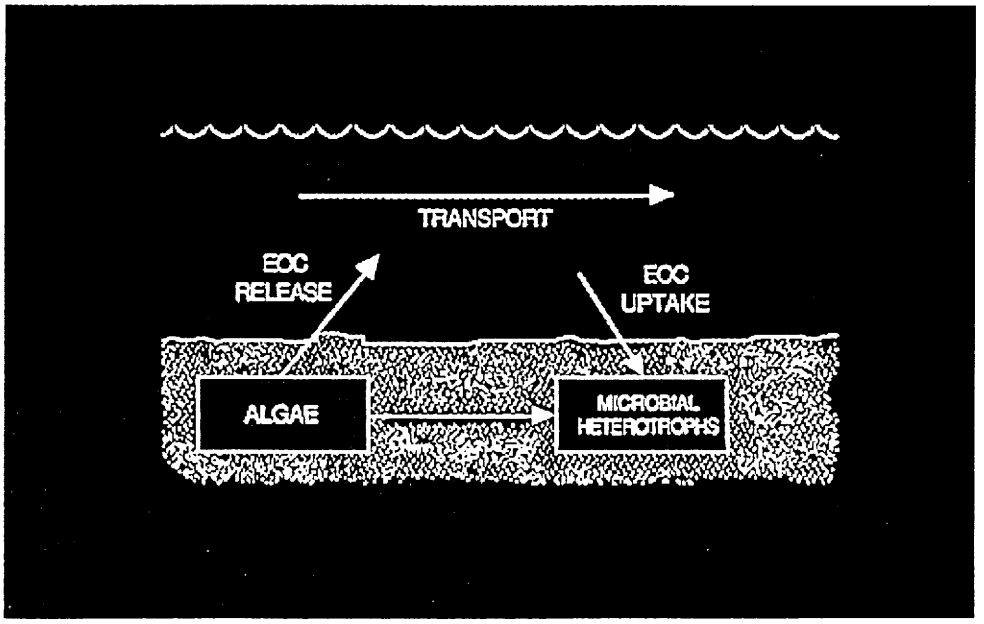

FIGURE 4.

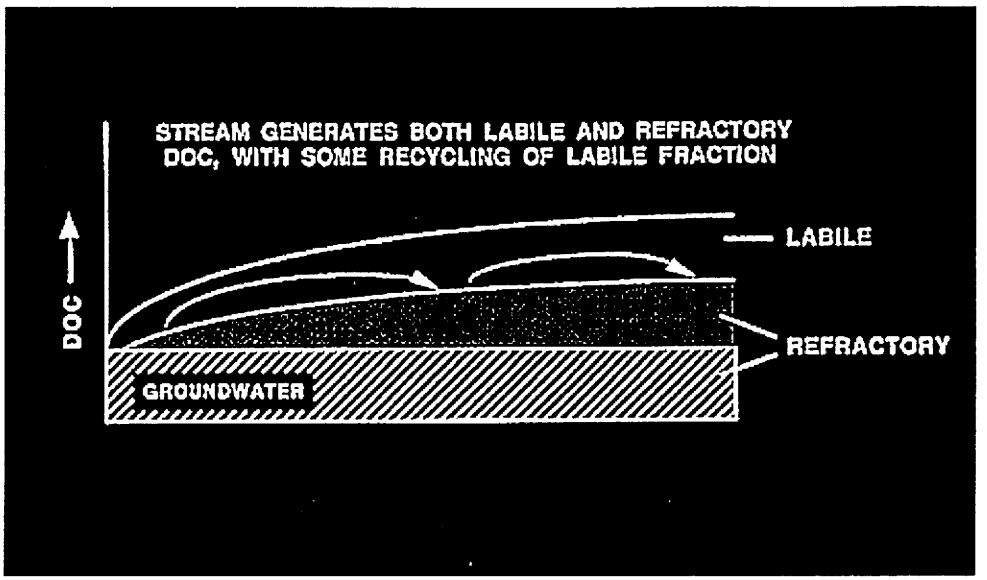

FIGURE 5.

DOC CYCLING IN WHITE CLAY CREEK

THIRD-ORDER REACH:
DEPTH, d= 0.2 m
VELOCITY, v_w = 0.12 m/sec
LENGTH, L = 4 km

	LABILE	REFRACTORY
Mass transfer coefficient for uptake (from chambers) v_f	.04 h	0.0006 h
Turnover time, $T = d/v_f$	5 h	14 d
Turnover Length, $S = v_w T$	2 km	144 km
EOC Utilized within 3rd order reach	57%	1%
labile + refactory	35%	
Theoretical peak EOC Concentrations	0.4 mg/L	0.4 mg/L

FIGURE 6.

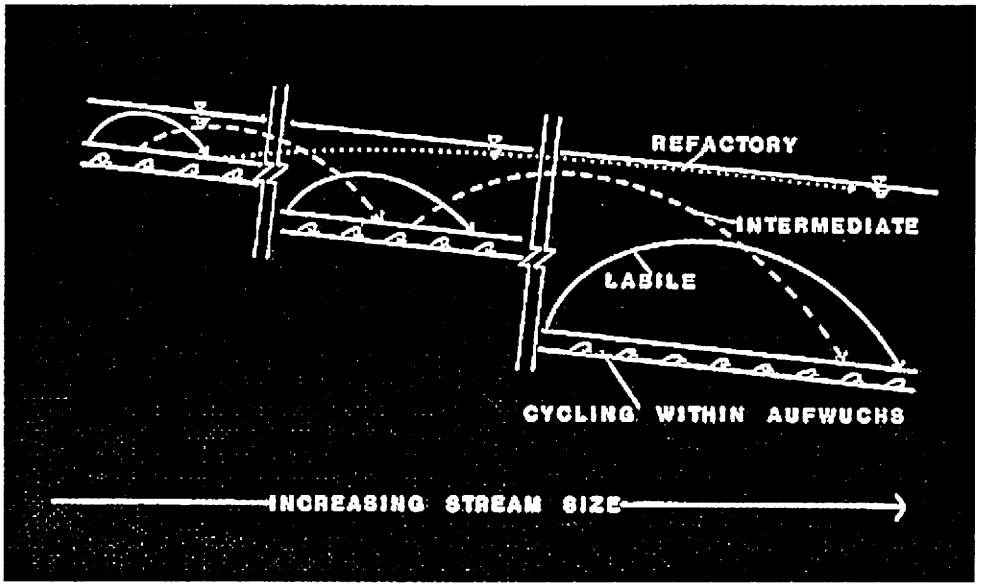

FIGURE 7.

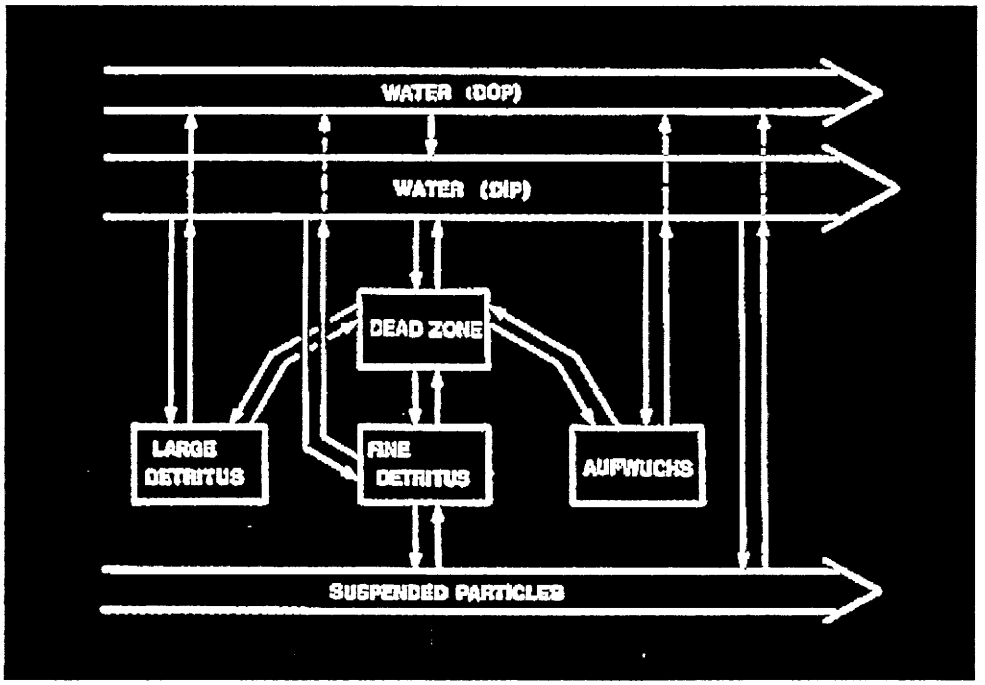

FIGURE 8.

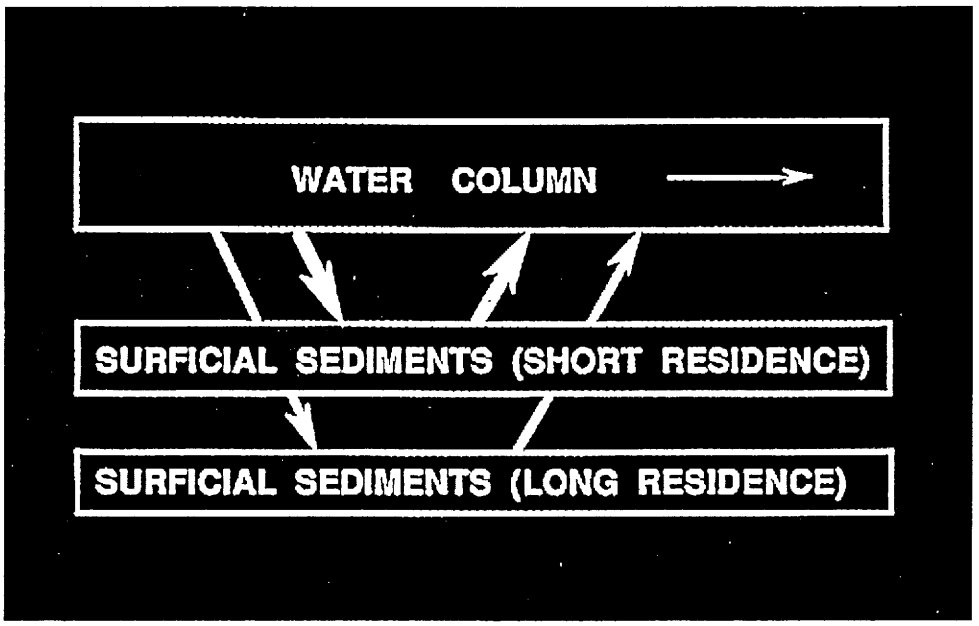

FIGURE 9.

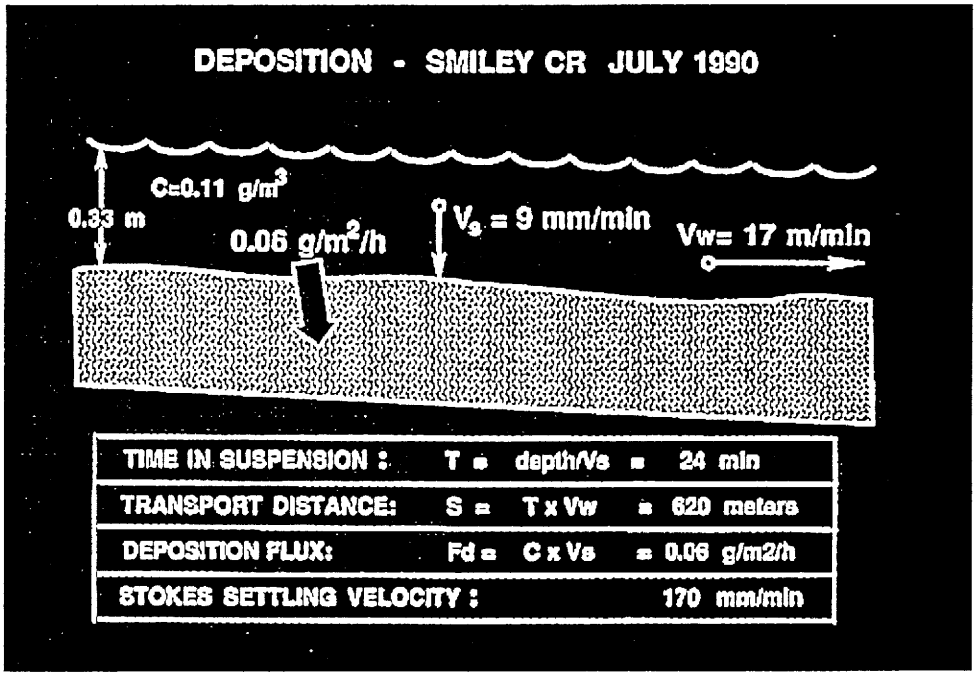

FIGURE 10.

transport distance for seston was 620 m (Figure 10). Again, this distance is on a scale with the length of stream we're talking about. By following these particles, we can say that a particle moves downstream 620 m, sits on the bottom for a period of 24 minutes (part of the fraction stays much longer), then it's resuspended and moves downstream another 620 m. So this material can move downstream great distances.

We know that downstream waters in estuaries are heavily dependent upon allochthonous carbon from upstream. This slide (Figure 11) shows a summary way of looking at turnover length concept. We can look at how long something lasts (wood lasts a long time, labile dissolved organic carbon may last only a few minutes, everything else is somewhere in between), vs. how fast it moves downstream; wood doesn't move very fast, both kinds of dissolved organic matter move downstream just as fast as the water moves. Different kinds of materials show tremendous ranges of turnover lengths. Drifting macroinvertebrates tend to stay put. Very fine particulate organic matter can move 10,000 km downstream, generally putting it into the ocean, refractory even farther, and on its way it feeds larger systems, rivers and estuaries.

[Overheads]:
1.

$$\text{Stream Ecosystem Efficiency} = \frac{\text{Inputs - Outputs}}{\text{Inputs}} = \frac{\text{Respiration}}{\text{Inputs}}$$

This reiterates some of the material Bruce was talking about. This is a basic way that we have of looking at processing in headwater systems: Stuart Fisher's concept of stream ecosystem efficiency.

2. The interesting thing is that while stream ecosystems tend to have a range of efficiencies, the basic median stream ecosystem efficiency is about 50% regardless of the size of the watershed. Stream ecosystem efficiency is not terribly dependent on size. We don't see a real trend, which is counter to what a lot of us thought earlier on... some thought that the bigger the stream, the more efficient.

3. As a general rule of thumb, about half of all the inputs to any stream get exported downstream, although it does have a range of 10 to 80 percent at the extremes. **Q** - AND IT CHANGES OVER THE YEAR, RIGHT? **NEWBOLD** - THIS IS AN IDEALIZED, LONG-TERM AVERAGE. THE NUMBER MAKES NO SENSE ON AN INSTANTANEOUS BASIS, BECAUSE YOU HAVE STORAGE, ETC. IT ONLY MAKES SENSE ON A 10-YEAR TIME SCALE. UNFORTUNATELY IT HASN'T BEEN MEASURED ON A 10-YEAR TIME SCALE; THESE ARE APPROXIMATIONS.

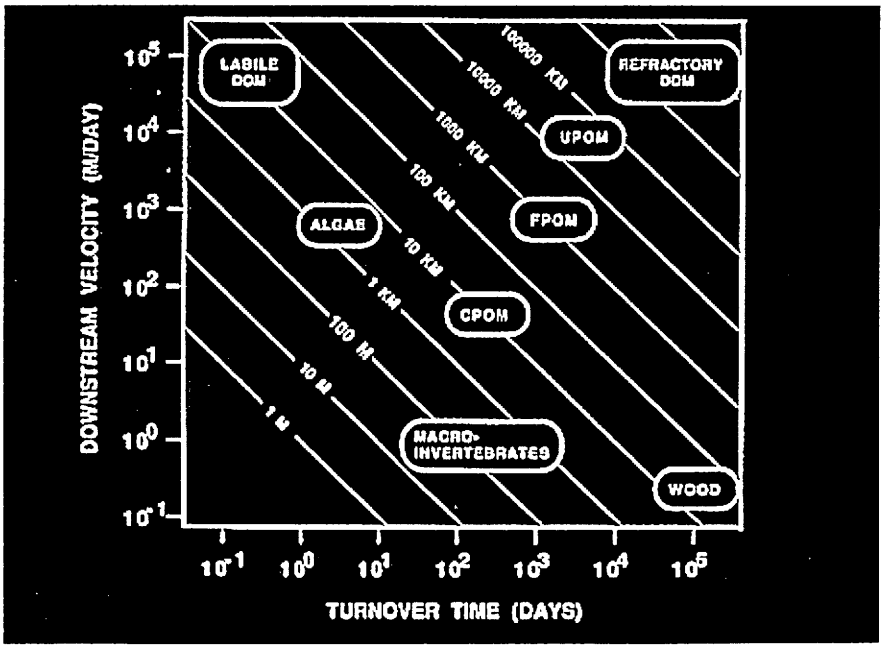

FIGURE 11.

4. This is something Bruce laid out, and I want to make a point on the issue of the inputs. We have litterfall, primary production (which now that we know how to measure it, can be more important in shaded streams than we had thought), and groundwater dissolved organic matter. Deep groundwater sources almost everywhere have low concentrations of dissolved organic matter, and that tends to be highly refractory because it's already been processed; it's been through the ground and there's not much left. But when you look at a stream, it has lots more kinds of dissolved organic matter, there's what's coming from the stream bed and the soil and riparian drainage that tends to be higher concentration and labile.

I don't know much about these fills, but when you think about a fill, you can think about rain coming onto the ground, picking up organic matter from grasses leaching down through, going through the standard process that happens to organic matter as it goes through the ground; it becomes this low-concentration refractory. Even though there's not a stream there, it will go through the ground, and eventually it will emerge below the fill, yielding low concentration refractory; it might be at about the same concentration it would have been without the fill. Yet the water emerging from the fill would be missing the labile dissolved and particulate organic matter, that would have been produced by the stream that is now buried, and it is this labile portion, produced within the stream itself, that supports downstream metabolism. We've calculated in the White Clay Creek that this labile fraction can account for about 20-30% of the metabolism of the stream in the reach.

5. Turnover length and stream organic matter budgets. As you get into larger and larger streams, the turnover length increases. In the smallest streams (10 liters per second down to 1 liter per second), turnover length tends to be about 1 kilometer. This material, even from these smallest streams, tends to move downstream about a kilometer, and feed the downstream reach. In terms of budgets, about half of it makes it that far down.

6. Turnover length of carbon is 1 kilometer or longer in first and second order streams. Turnover length increases with stream size. Organic matter cascades in increasingly larger systems.

7. Summary: A significant fraction of exported organic matter (OM) originates within the stream ecosystem and is labile. This is a combination of the point that says that the soil and the riparian areas next to the stream are a major source of organic carbon. And also, the decomposition of the litter and the primary production of material are also important sources of organic matter that get exported downstream. Most of the OM inputs to mid-order streams originated from first and second order streams. Based on these concepts, Bruce and Bern showed some data showing the frequency of first and second order streams. Between 60 and 80% of the water feeding a fourth-order stream came from first- and second-order streams. You can work this math out for any drainage basin. If you go all the way back to the geomorphology text of Leopold et al., and work out their miles of stream length against the stream sizes, each order has about the same bottom area and drains about the same drainage area as every other order. First, second, and third order streams are all roughly equivalent, to within an order of magnitude. So, if you're looking at fourth order basins, and you're potentially eliminating the first and second order streams, you find that they are contributing at least half of the water and drainage area and stream bed area to the downstream larger orders. Through this "50 percent rule" they are fully contributing their share, if not more, of the carbon in the system (it tends to be a little more because of the specialized habitat of the first-order systems). So we can calculate what this carbon influence is -- it's large --a large amount of the carbon is delivered downstream. We know that it's labile. There are some missing links -- such as exactly how that feeds back up into the food web in the downstream waters. But we can come to reasonable conclusions about the likely importance on all these points.

Dr. Jay Stauffer, The Pennsylvania State University, University Park, Pennsylvania

I'd like to talk about freshwater fishes and their role in headwater streams. Most of the time we're talking about brook trout, and *Cottus* (sculpins). We look at these as species that are common throughout their range, and in fact a lot of fish and game commissions will stock brook trout. In work that we did in the Potomac River in Maryland, we found brook trout in first and second order streams feeding the Potomac River (which had a pH of 4 or 5 on good days) that had been isolated populations for 150-200 years. We could distinguish these brook trout populations -- we could tell which stream a brook trout came from with about 98% probability. At the time I thought it was because they were isolated by the main channel Potomac River and its low pH. Now I think there are a lot of headwater streams that maintain discreet populations. There was discussion about reduction in genetic flow among aquatic insect populations. For fish, that reduction is even exacerbated because they do not have an aerial stage to their life histories -- they must migrate through water to get from one stream to another -- they can't fly over land barriers. So I think a lot of these populations are very much isolated. A former student of mine, Rich Raisley, who is now at Frostburg State University (University of Maryland) is describing many species of *Cottus* -- sculpins -- from many of the headwater streams in Pennsylvania, Maryland, Virginia, and West Virginia. At one time we thought all of these populations were conspecific, but it turns out they're not. So I'd like to talk about these fishes and ways of evaluating the potential for these stream systems to be harmed and then their potential to recover.

A lot of fishes that live in riffles are darters (*Etheostoma* or *Percina* spp.) -- they seem to be unique to particular stream systems. We've done a lot of instream, behavioral studies (many funded by the U.S. Fish and Wildlife Service) looking at the impact of introduced species on these darter communities -- where they breed, where they live, and what they eat.

The banded darter (*Etheostoma zonale*) was introduced into a headwater stream, Pine Creek in Pennsylvania, about 1950, and stayed there for a long time. It wasn't until Hurricane Agnes hit in the '70's that this fish was distributed throughout the Susquehanna River. When this happened, the other fishes (e.g., tesselated darter, *Etheostoma olmstedi*), hybridized with fishes all through the system. Many of you might be familiar with the Maryland darter (*Etheostoma salare*), which occurred in Deer Creek and Swan Creek in the Susquehanna River drainage, just over the Pennsylvania border. This species now, I'm confident, is extinct. We last had a siting of that fish about 10 years ago and we haven't found it since then. Its disappearance was coincident with the introduction of *E. zonale* into Deer Creek and Swan Creek by Hurricane Agnes. Once it got into that part of the Susquehanna, *E. salare,* the Maryland darter, disappeared.

These headwater streams are particularly important, because if you study evolution and are familiar with the work of Mayr and some other people, you find a founder effect, which is very important in the evolution of species. In many of these headwater streams we have isolated populations that are separated, or sometimes disjunct, sometimes with minimal gene flow with the main body of the population. So these fish are a little bit different anyway, they're on the edge of their range. So they're very much subject to natural selection, and different forces which probably drive speciation and evolution of these fishes. So these headwater areas contain what Mayr and others have called "semi-species," or "incipient species." There might be a population where some taxonomists would not give it species status at the time, but maybe 10 years from now, 100 years from now, or 1000 years from now the speciation process would take place. So these fishes are very important, because they're slightly genetically distinct, they're certainly phenotypically distinct -- they look different -- because they're under different selection pressures and environmental pressures that cause phenotypic plasticity.

So these fishes are a little bit different, and they need to be preserved. I think we need to look very carefully at what's in these headwater streams. One of the speakers this morning talked about it's a mistake to go in and alter these things before we know what's in them. We think fish fauna are well-known, and I'll talk about that more later. We have other fish species that have pockets in headwater streams -- they're just isolated in these headwater streams, and there's probably very little gene flow that takes place from one headwater stream to another headwater stream, even within the same drainage area. Even in the White Clay Creek basin, you'll find populations in first order streams that don't exchange gene flow with similar fishes in first order streams in the same drainage basin.

Not all headwater streams are fast-moving, high gradient; we have pools, wetlands areas, we have mud minnows and sticklebacks in there. We have them in West Virginia and Pennsylvania. These are very cold, slow-moving pools

where fish live. We talked about differences and comparisons. Many of these fish are the same species that occur at other end of drainage, where they go into the Chesapeake Bay or the Gulf of Mexico -- forms which are sort of saltwater forms but their cousins or brothers or maybe even the same species occur at other end of the drainage. But again, there's very little gene flow or no gene flow from one population that lives in the first order stream and the population living near the Bay or Gulf.

We also find fishes in these headwater streams that are migratory. A lot of the lampreys, for example, occur in these small streams. In doing surveys in Pennsylvania, we're finding that a lot of lamprey populations have been deleted or extirpated -- some because of lampricide, some because of habitat changes that have occurred. We may not find adults there, but ammocoetes, which bury into the mud banks, are present. You'll find the adults there at certain times of the year when they migrate to breed. Some of the redhorse suckers you would also find in small headwater streams, especially those streams that empty directly into large rivers. We're doing some surveys of small streams that empty directly into the Allegheny, and the redhorse suckers, even the juveniles, are out of there by June or July. But early in the Spring, you can go to these streams that you wouldn't think would harbor fishes, and you'll find very large redhorse suckers, white suckers, hogsuckers, whatever.

We also have a series of madtoms. These are small catfish (*Noturus* sp.), and these fishes are unique and a lot of the populations are isolated from one another and are genetically and morphologically distinct -- we can tell them apart; and if they are isolated in these headwater streams they become particularly important.

This slide shows a *Phoxinus* species, a dace that appears in headwater streams. This form occurs in Tennessee, in just two small tributaries. Last week somebody sent me a *Phoxinus* from Virginia to identify, and it turned out to be an undescribed new species. A lot of us have spent a lot of time studying the fish in streams all over Virginia. You take a State with a well-described fish fauna like Virginia, and all of a sudden you come up with a whole new species! It was from a second-order stream. It's probably confined to that second-order stream, it probably occurs in no other second-order stream in the Clinch River.

We also have a series of dace - *Clinostomus* spp., a species that is found in first, second, and third order streams. Many of the populations are disjunct; you'll find them in one stream and you don't find them in another stream. So, there are a lot of fishes that are unique to these areas and we're making a mistake deciding to go into these areas and alter these streams until we have a really good knowledge what the fauna is, not just the insects but the fish. Fish are thought to be better known (fewer species, there's not so many life stages, it's easier to identify juveniles, etc.), and so on the surface you think, Oh, the fish fauna's pretty well known, and so if we wipe out this headwater stream we're not doing anything we're not going to be able to live with; we're not going to extirpate a species; and I just ask you to be a little cautious when you make that decision, because there are a lot of these unique populations that are called the same species but are different phenotypically, different genetically, and may in fact be a semi-species or even have achieved specific status at some point, maybe not in your lifetime but maybe in your grandchildren's lifetime. So it's something we need to preserve and something we need to examine.

I mention that and you might think, "Things don't evolve that fast." I also do a lot of work in Lake Malawi in Africa, and I'll tell you this quick story just to drive home my point. There's an island in Lake Malawi about 500 m from where my research station is. There are women in the village that talk about their fathers farming the land between where my research station is and that island. The island isn't very old; the lake water came up and made it an island. There are species of fish that occur at that island that occur nowhere else in Lake Malawi. We're talking about speciation that occurred within two generations of humans. So these things can happen very quickly.

When we look at assessment of ecosystems, the evolution assessments went from species/area curves, diversity indices, oligotrophic/heterotrophic ratios, Karr's biotic indices, etc.. When we look at flowing systems, we classify based on calcium content, distribution of fauna. First order streams generally have higher gradients than other orders, but we find exceptions. I studied a stream in the Conowingo Creek basin where the highest gradient was just where it went into the Susquehanna. We found headwater-type organisms -- so gradient has had a profound effect on the fauna found.

Why use fishes for study? Factors: they occupy the top of the food chain; they pass through other trophic levels; they are taxonomically well studied; there's generally more information available on life history.

Species succession in stream fishes is usually a factor of species addition rather than one of replacement.

I have been studying common shiners and striped shiners in headwater streams, in an area where there has been quite a lot of stream capture events among Atlantic Slope, Allegheny river, and Great Lakes drainages. In these areas I postulated that there would have been mixing of the populations and subsequent gene flow among them. I also found some other areas where we find a sibling species (one that morphologically resembles the common or striped shiner) where none of these so-called intergrades occur; thus, a distinct form is present. I have what I think is a new species where none were ever caught before. This occurred in headwater streams.

When looking at streams, as we go down through the drainage basin, we talk about the potential recovery of systems that have been damaged. I was successful in implementing such a program when I was at the University of Maryland, relative to giving mine permits. I persuaded the Maryland Bureau of Mines to give permits for one headwater area, and insisted that it be reclaimed, before a permit in an adjacent headwater area was granted, so we could save refugia in the system.

Cairns and Dickson proposed the concept of inertia -- how hard could we shove this system in terms of stress before structural components of the ecosystem change. They also talk about elasticity: How many times can we shove a system, how will that system recover. Another term is resiliency, defined as a rubber band snapping back. We can stretch the rubber band many times and it comes back; but we get to a point where the band breaks. Do streams act the same way? We don't understand that very well.

Considerations associated with the concept of "inertia":

1. Are the indigenous organisms accustomed to variations? Headwater streams are fairly stable, compared, for example, to estuarine environments. Estuarine organisms would be more used to varying conditions, and thus perhaps contribute more inertia to the system.

2. Structure - is there a lot of structural redundancy in the stream? I've been studying French Creek, a fourth order stream in northwestern Pennsylvania, one of the most diverse streams in the State. There's a lot of structural redundancy. In a particular riffle there are thirteen species of darters. There's a lot of functional redundancy -- they overlap a lot, do a lot of the same things. If you lose one species, it would probably not be as critical to French Creek as it would be to a headwater stream. A lot of these headwater streams (first and second order) have only two or three species of fish -- if you lose one of those species, you lose a third of your fauna, which is a structural change, and you lose a lot of functions as well, because there's not a lot of overlap. There's only one species of darter, or only one *Cottus* -- there's not thirteen of them. So it makes a more drastic impact.

3. The presence of buffered water antagonistic to toxic substances. Headwater streams don't have nearly the built-in protection -- physically or environmentally -- as fourth or fifth-order streams. A lot of these streams don't have the safeguards built into them to resist a functional or structural change.

4. How close the system is to a major ecological transitional threshold. We have a lot of headwater streams where the canopy has been removed, where the temperature in summer gets close to the lethal limit for brook trout; the winter limit gets close to the upper limit of egg production and embryo development. So that stream is close to a transitional threshold, and it won't take a lot of environmental change to push it over the edge.

5. The presence of a drainage basin management group with a water quality monitoring program. Headwater streams are vulnerable because they don't get a lot of attention from fishermen, biologists, etc., compared with larger downstream areas. A fish kill could happen in a headwater stream, and no one would know or call for remediation action.

Considerations associated with the concept of "Elasticity" (the parameters that play an important role in the ability of an ecosystem to recover once it's been damaged.)

1. Existence of nearby epicenters for providing organisms to reinvade a damaged ecosystem.

We can say that the Atlantic Ocean has a lot of inertia -- it's so big, it's well buffered, it can take a lot of stress without showing a change. What happens if the Atlantic Ocean is damaged - if it shows a structural and functional change? Where are the epicenters from which recolonization would take place? There aren't any. Take a headwater stream where *Phoxinus cumberlandensis* occurs. Talk about the unique insects that were talked about today -- they only occur in one place. There aren't other epicenters from which recolonization can take place if that stream is shoved functionally or structurally. Look at Pennsylvania, look at the stream maps. Some have dendritic networks; it looks like there are a lot of streams that could be a source for recolonization to take place. But what if that new species of mayfly only occurs in two of them? Where's recolonization going to take place? These streams are very fragile and have very low inertia, and I would also argue that their ability to recover is also compromised because they're so unique and so different.

2. Another thing that affects elasticity is mobility of any disseminules (life stages) of the organisms present. As I alluded to earlier, in those streams that were clearcut and flowing into the Potomac River in Maryland and West Virginia, the fish fauna was eliminated and so were aquatic insects. You can go back today and can find good aquatic insect populations, but they're still devoid of fish. Aquatic insects can fly and recolonize to some extent and even some of them are confined. Recolonization of fish could not take place, because they had to come up from one headwater stream to another and migrate through the Potomac River. With a pH of 4, that didn't happen very often. So, you have to look at the mobility of the life stages of the critters that inhabit these streams and the potential for them to get from one stream to another.

3. We have to look at the condition of the habitat following the stress. Question: if you put a stream on one of these benches, is it going to be the same? The condition of the habitat is going to be different -- you're not going to have the canopy, the gradient, the soils that you had. If you're a fish, you're not going to have the insects to support you -- it's going to change. So, those kinds of changes make a big difference on this recovery. And so, people say "recovery": Are we satisfied if something can live in the system? Are we satisfied if something different lives in the system but serves the same basic functions? Or do we want to define recovery as putting that stream or that ecosystem back to the way it used to be? These are several different levels that have quite different answers.

4. Elasticity -- The presence of residual toxicants. If you change the substrate, the soils, does that affect the ability of a particular stream to recover to the way it was before?

5. Chemical, physical environmental quality after the stress: How did we alter the system, and how is it physically or chemically different from the way it used to be?

6. Management or organizational capabilities for immediate control of the damaged area. Are there organizations there that will reintroduce the fauna? Are there organizations that know enough about how to introduce the native fauna? If we take brook trout and scatter them all over Pennsylvania and they interbreed with native brook trout populations, have we somehow diluted the gene pool of the native brook trout? Have you changed the ability of the native trout to inhabit that particular system?

These are all things that need to be considered in making a decision about the EIS, about recovery. You need to define recovery, and put in your minds "What kind of chance am I going to take with this ecosystem if I structurally or functionally change it?" and if I get to the probability where I do change it, no matter how small that probability may be, are there other refugia or other ways I can rehabilitate the system or reintroduce the fauna and flora to bring it back to its natural condition, or isn't this even an important question to ask? It makes a big difference if there are unique fauna in that stream. I would argue that, if there's a headwater stream that's the only stream in the world that contains this particular species, we're not going to take any chance with it. And if you want to mine coal or gold or silver or whatever under that stream, we're not going to allow you to do that, because we're not going to take a chance that we're going to lose that genetic diversity of this fish, this mayfly, or this stone fly, or whatever.

WALLACE - I WOULD ADD ANOTHER VERTEBRATE TO THAT GROUP -- SALAMANDERS. THEY ARE VERY LIMITED TO A FEW LOCATIONS IN THE APPALACHIANS. **STAUFFER** - RIGHT. A LOT OF HELLBENDER POPULATIONS ARE REALLY ISOLATED AND DISJUNCT FROM ALL OTHER POPULATIONS.

HANDEL - IS THERE A MINIMUM SIZE STREAM THAT CAN SUPPORT A FISH COMMUNITY? **STAUFFER** - NO. THERE ARE SOME SMALL STREAMS THAT DON'T SUPPORT FISH COMMUNITIES, BUT I'VE FOUND FISH COMMUNITIES IN BASICALLY SINKHOLES. WE WERE SPEAKING OF INTERMITTENT STREAMS, WHERE THE STREAMS DRY UP AND YOU THINK THERE'S NO FISH IN THEM, BUT YOU KEEP GOING BACK YEAR AFTER YEAR, AND YES THERE ARE. THERE ARE SOME FISHES IN FLORIDA (*JORDANELLA*) THAT HAVE -- FOR LACK OF A BETTER TERM -- ANIMAL SEED, AND CAN LIVE FOR ONE YEAR IN TRULY INTERMITTENT STREAMS. THEY LAY THEIR EGGS, THE EGGS SINK DOWN INTO THE MUD, THEY AESTIVATE AND DRY UP. WHEN THE RAINS COME AGAIN THE EGGS HATCH, AND *JORDANELLA* ARE BACK IN THE STREAM. SOME OF THE WORK THAT WE DID IN DROUGHT PERIODS, WHERE WE FOUND RIFFLE SECTIONS IN WEST VIRGINIA, WE FOUND A STREAM THAT HAD A POOL HERE, AND A POOL THERE, BUT NO RIFFLE CONNECTING THE POOLS. I THOUGHT THE DARTERS HAD TO BE IN THE POOLS. WE SAMPLED AND WE DIDN'T FIND THEM. I THOUGHT SURELY THE DARTERS HADN'T BEEN ELIMINATED FROM THE SYSTEM, AND OUT OF DESPERATION I STARTED SHOVELING RIFFLES: ABOUT 5 HOURS AND 2 FEET LATER, I FOUND THE DARTERS AMONG THE GRAVEL. **HANDEL** - WOULD YOU POINT-BLANK SAY THAT IN APPALACHIA THERE IS NO STREAM SYSTEM TOO SMALL TO BE IMPORTANT FOR FISH CONSERVATION? **STAUFFER** -YES, I WOULD MAKE THAT STATEMENT.

DISCUSSION: WHAT IS A STREAM. WHAT KIND OF INPUT DO THE REGULATORY AGENCIES NEED FROM THIS ASSEMBLED GROUP TO MAKE THE DECISIONS THEY NEED TO MAKE ON PERMITS IN THE INTERIM WHILE THE EIS IS BEING DEVELOPED?

PASSMORE - FOR OUR WORK THAT WE'VE DONE IN PERMIT REVIEWS AND PRELIMINARY DATA COLLECTION THAT WE'VE DONE, WE'VE USED WEST VIRGINIA'S DEFINITION IN THEIR WATER QUALITY STANDARDS WHEN THEY DEFINE INTERMITTENT AND PERENNIAL. WE KNOW THAT FLOW ALONE IS NOT A GOOD INDICATION OF THE FUNCTION OF STREAMS. WEST VIRGINIA WATER QUALITY STANDARDS DEFINE INTERMITTENT STREAMS AS STREAMS WHICH HAVE NO FLOW DURING LONG PERIODS OF NO PRECIPITATION, AND DO NOT CONTAIN AQUATIC ORGANISMS WHOSE LIFE HISTORIES REQUIRE MORE THAN 6 MONTHS IN FLOWING WATER. FOR ONE OF THE PERMITS, WE LOOKED AT A LOT OF STREAMS THAT WERE INTERMITTENT IN TERMS OF FLOW, WITH A FEW RESIDUAL POOLS HERE AND THERE, BUT WE DIDN'T CLASSIFY ONE OF THOSE AS INTERMITTENT UNDER WEST VIRGINIA STANDARDS. THEY ALL CONTAINED MANY AQUATIC ORGANISMS, AND CERTAINLY MANY WHOSE LIFE HISTORIES REQUIRE MORE THAN 6 MONTHS OF FLOWING WATER. THE WEST VIRGINIA WATER QUALITY STANDARDS HAVE AN ECOLOGICAL CONNECT TO THEM.

TIBBOTT - IS THAT CONSISTENT ACROSS ALL OF THE STATES THAT WE'RE DEALING WITH IN THIS EIS?

HANMER - NO. THE WEST VIRGINIA AND THE PENNSYLVANIA STANDARDS ARE THE ONES WE FOUND THAT TRY TO MIX FLOW REGIME AND BIOLOGY, AND WHAT THEY'VE WOUND UP DOING IS BASTARDIZING THE ENGLISH LANGUAGE, BECAUSE BY TRYING TO DISTINGUISH BETWEEN PERENNIAL AND INTERMITTENT -- FOR EXAMPLE, THE SURFACE MINING REGULATIONS ARE THE ONES THAT MAKE DISTINCTIONS BETWEEN PERENNIAL, INTERMITTENT, AND EPHEMERAL. NOW HOW THESE DEFINITIONS AFFECT THE REGULATORY REGIME IS UNKNOWN. MOST WATER QUALITY AND ENVIRONMENTAL REGULATIONS DON'T USE THESE TERMS IN A REGULATORY SENSE. SO, ONE OF THE THINGS WE'RE STRUGGLING WITH IS, RATHER THAN TRY TO SAY THAT SOMETHING IS "PERENNIAL AND THEREFORE . . .," MEANING ANYTHING DIFFERENT THAN WHAT IT SAYS IN THE DICTIONARY, WHICH IS THAT IT FLOWS ALL THE TIME, IS TO FIND ANOTHER WAY OF TALKING ABOUT THE BIOLOGICAL VALUES THAT DON'T TRIP OVER THESE OLDER TERMS AND OLDER WORDS. SO, I THINK WE DO NEED TO LOOK FOR SOME LANGUAGE.

TENNESSEE IS INTERESTING BECAUSE THEY DON'T HAVE ANY DEFINITION, OTHER THAN "WATERS." THEY'RE TRYING TO DEFINE SOMETHING CALLED A "DE MINIMIS" STREAM, AND TRYING TO DEFINE THAT RIGHT NOW. THEY'RE THINKING OF IT IN TERMS OF HAVING A DRAINAGE AREA OF 20 ACRES.

FROM THE STANDPOINT OF THE 404 PROGRAM AND WATER QUALITY STANDARDS, IT'S MORE IMPORTANT TO DESCRIBE THE FUNCTIONAL VALUES, RATHER THAN TRYING TO PUT A NAME ON IT LIKE PERENNIAL OR INTERMITTENT. FROM THE STANDPOINT OF REVIEWING REGULATIONS, WE DON'T HAVE GOOD DEFINITIONS. IT WOULD BE NICE TO HAVE AN "APPALACHIAN COAL FIELD" DEFINITION, OR A COMMON SENSE DEFINITION BASED ON SOME OTHER GEOGRAPHIC SCALE. IN KENTUCKY, ACCORDING TO PEOPLE WE TALKED TO, THEY DEFINE REGULATED SURFACE WATERS OF THE COMMONWEALTH AS THE BLUE LINE STREAMS ON A USGS TOPO MAP, OR A DISCRETE CONVEYANCE WITH A DEFINED CHANNEL, FIELD-CONFIRMED. STATISTICAL RECURRENCE OF LOW FLOW DOES NOT ENTER INTO THE DEFINITION OF A STREAM. SO, THERE'S NOT A SINGLE STATE IN THIS REGION THAT DOES IT THE SAME WAY [AS ANOTHER STATE].

WALLACE - DOES EPA HAVE A DEFINITION OF A STREAM, OTHER THAN ARMY CORPS STANDARDS? **HANMER** - WE HAVE A DEFINITION OF WATERS OF THE UNITED STATES IN CORPS AND EPA REGULATIONS. BUT, YOU HAVE TO GO OUT AND DEFINE WHAT YOU'RE TRYING TO PROTECT ON AN AREA BY AREA BASIS. OUR DEFINITIONS TENDED TO BE BROAD, TO ALLOW FOR GOING OUT AND MAKING MORE SPECIFIC DEFINITIONS.

WALLACE - LUNA LEOPOLD IN 1994 POINTED OUT IN HIS BOOK "A VIEW OF THE RIVER" THAT ALL OF THESE BLUE LINES ON USGS MAPS ARE MUCH SMALLER THAN ACTUAL STREAM FLOWS, ACTUALLY MUCH SMALLER THAN PERENNIAL FLOW. THEY WERE NOT DONE BY FIELD WORK, THEY WERE DRAWN IN THE LABORATORY. THEY BASICALLY ASSIGNED "WHAT IS A STREAM" TO SOMEONE SITTING INSIDE IN A LABORATORY DRAWING A MAP.

HANMER - I THINK YOU DO WANT TO SAY WHAT IS THE IMPACT? BEFORE YOU DEFINE "WHAT IS A STREAM," YOU ASK "WHY DO I CARE?" AND THE REASON YOU CARE, FROM A REGULATORY STANDPOINT, IS THAT YOU'RE TRYING TO

FIGURE OUT HOW TO REGULATE SOME KIND OF PERTURBATION. MINING COMPANIES ARE IRRITATED THAT SOME OF THE SAME PERTURBATIONS ARE DEFINED AS NON-POINT SOURCES UNDER THE CLEAN WATER ACT AND THEREFORE NOT REGULATED, AND ARE DEFINED AS POINT SOURCES UNDER THE CLEAN WATER ACT AND ARE REGULATED, AND IT SEEMS ARBITRARY. AND IT IS, TO A CERTAIN DEGREE, ARBITRARY. HERE WE'RE TRYING TO DISCUSS PHYSICAL PERTURBATIONS. WATER QUALITY STANDARDS WERE DEVELOPED WITHOUT MUCH CONSIDERATION FOR PHYSICAL IMPACTS, THEY WERE DEVELOPED TO CONTROL CHEMICAL INPUTS, AND THEY WERE MOSTLY CONCERNED WITH DEFINING LOW FLOW FOR THE PURPOSE OF SAYING WHEN STANDARDS WOULD BE ALLOWED TO BE VIOLATED. SO THE HISTORY OF THIS WAS A DEVELOPMENT UNDER A "LOGIC STREAM" FOR A PURPOSE. NOW WE NEED A NEW "LOGIC STREAM" THAT SAYS WE'RE CONCERNED ABOUT PHYSICAL PERTURBATIONS, PHYSICAL DESTRUCTION, AND THEREFORE, YOU SAY WHAT KIND OF LOGIC, WHAT KINDS OF DEFINITIONS DO YOU WANT TO CONSTRUCT IN A CASE LIKE THAT. AND THE MOST IMPORTANT QUESTION FOR US IN TERMS OF MITIGATION AND PREVENTION IS THE WORD "SIGNIFICANCE" -- IN OTHER WORDS, IT'S NOT THE MERE EXISTENCE, IT'S ALSO THE SIGNIFICANCE, BECAUSE AT THE END OF THE DAY IF YOU WANT TO STOP SOMETHING FROM HAPPENING, THEN YOU HAVE TO TALK ABOUT SIGNIFICANT ENVIRONMENTAL IMPACT AND WHAT DO YOU MEAN BY THAT.

PASSMORE - IN WATER QUALITY STANDARDS, THERE ARE FOUR COMPONENTS: NARRATIVE CRITERIA (SEDIMENTS, SOMETIMES TOXICS), NUMERIC CRITERIA (MORE TRADITIONALLY WHAT PEOPLE THINK ABOUT AS WATER QUALITY STANDARDS, FOR EXAMPLE DISSOLVED OXYGEN CAN'T BE LESS THAN 5 MG/L), AND DESIGNATED USES, WHICH IS VERY IMPORTANT AND OFTEN WHAT WE'RE TRYING TO PROTECT AND MOST STATES HAVE A BLANKET DESIGNATED USE FOR ALL OF ITS WATERS THAT SAYS THAT THE STREAM HAS TO SUPPORT THE AQUATIC LIFE THAT SHOULD BE THERE. THE AQUATIC LIFE DESIGNATED USE IS OFTEN THE STANDARD WE USE WHEN WE THINK ABOUT WHAT WE'RE TRYING TO PROTECT. IF THE AQUATIC LIFE IS THRIVING AND DOING WELL, WE FEEL THAT THE OTHER PARAMETERS ARE PROBABLY DOING WELL. AND THE FOURTH IS ANTIDEGRADATION. SO, THERE ARE AT LEAST FOUR ELEMENTS OF WATER QUALITY STANDARDS, AND THE TRADITIONAL CHEMISTRY IS ONLY A TINY PART OF WATER QUALITY STANDARDS.

QUESTION - WHAT ARE SOME OF THE CRITERIA THE EPA USES FOR THE BIOLOGICAL ASSESSMENT? A SIGNIFICANT CHANGE FROM WHAT WOULD BE NORMAL? THERE REALLY AREN'T ANY ESTABLISHED BIOLOGICAL CRITERIA.
PASSMORE - MOST OF THE STATES HAVE SOME TYPE OF NARRATIVE CRITERIA THAT COVERS AQUATIC LIFE.

HANMER - WHEN YOU ARE CONTEMPLATING THE PHYSICAL DESTRUCTION OF A STREAM, WHICH IS WHAT YOU HAVE WHEN YOU HAVE A FILL, THERE'S ANOTHER SECTION OF THE LAW WHICH CONTAINS THE RULES, AND IT'S SECTION 404. THE FIRST THING YOU HAVE TO CONSIDER ARE THE 404(B)(1) GUIDELINES, WHICH ARE AVOIDANCE- OR TECHNOLOGY-BASED: WHY IS IT THAT YOU HAVE TO FILL IN THE STREAM? WHAT ARE THE ALTERNATIVES? WHAT CAN YOU DO TO AVOID THE IMPACT? SO YOU DRIVE MINIMIZE, MINIMIZE, MINIMIZE AS FAR AS YOU CAN GO, AND THEN YOU SAY WELL, THIS ACTIVITY HAS TO TAKE PLACE HERE (FOR EXAMPLE, THIS IS WHERE THE COAL SEAM IS), AND THIS IS THE SIZE OF THE OPERATION YOU GET TO THE POINT WHERE YOU ARE CONVINCED THAT THE ECONOMICS OF THE OPERATION WOULD NOT TAKE PLACE BUT FOR THE FILL. AT THAT POINT, YOU'VE FINISHED THE MINIMIZATION JOB, AND YOU SAY WHAT CAN BE DONE TO AMELIORATE THE IMPACTS TO TRY TO DETERMINE WHAT IS THE LONG-TERM, PERMANENT IMPACT HERE (WHICH GIVES YOU AN INTENSE INTEREST IN QUESTIONS LIKE WHAT IS THE EFFECTIVENESS OF LONG-TERM RESTORATION TECHNIQUES). AND THEN FINALLY, ONCE AN APPLICATION PASSES THROUGH ALL OF THOSE TRIGGERS, THERE MAY BE A CIRCUMSTANCE WHEN THE GOVERNMENT WILL STILL NOT ALLOW THE IMPACT TO TAKE PLACE: THAT'S WHERE YOU GO TO THE ENVIRONMENTAL TRIGGER, AND THAT TRIGGER HAS THE WORD "SIGNIFICANT" IN IT, AND NO ONE KNOWS HOW TO DEFINE IT EXCEPT ON A CASE-BY-CASE BASIS. THIS IS WHY WE'VE BEEN ACCUSED OF NOT CARING ENOUGH ABOUT INSECTS, BUT GENERALLY "SIGNIFICANCE" IS NOT A SCIENTIFIC TERM; IT'S A VALUE-LADEN, PUBLIC-RELATIONS... IT HAS A LOT IN IT BESIDES SCIENCE. BUT THE KIND OF CONVERSATION WE'VE HAD THIS MORNING IS INFORMING THE WHOLE CONVERSATION ABOUT WHAT SIGNIFICANCE IS. BUT THE WATER QUALITY STANDARDS BASICALLY GO AWAY, ONCE YOU HAVE SAID "YES" UNDER 404(C), YOU'VE TURNED A WATER OF THE UNITED STATES INTO A LAND OF THE UNITED STATES -- IT NO LONGER IS A WATER OF THE UNITED STATES -- AND THEN THE WATER QUALITY STANDARDS PICK UP BELOW. THERE'S ONLY ONE CIRCUMSTANCE UNDER THE CLEAN WATER ACT WHERE WATER QUALITY STANDARDS CEASE TO EXIST, AND THAT'S WHEN WATER CEASES TO EXIST, AND IT'S ONLY SECTION 404 WITH ITS OWN SET OF REGULATIONS AND GUIDELINES, THAT DEFINES THE CIRCUMSTANCES UNDER WHICH ECONOMIC ACTIVITY IN THE UNITED STATES WILL BE ALLOWED TO DISPLACE A WATER. UNFORTUNATELY, THERE IS MUCH OF THIS GOING ON THAT'S UNREGULATED, BECAUSE IT'S CALLED NON-POINT SOURCE. THERE ARE LOOPHOLES UNDER THE LAW WHERE STATES ARE SUPPOSED TO BE REGULATING, FOR EXAMPLE AGRICULTURE OR OTHER ACTIVITIES -- BUT THEY AREN'T. THERE ARE LOSSES -- DRAINAGE IS OCCURRING IN NORTH CAROLINA ON AN ABSOLUTELY AWESOME SCALE --

AND THAT'S LOSS BY SUCKING IT OUT RATHER THAN FILLING IT IN. IT'S OFFENSIVE, BUT UNDER THE LAW YOU'RE SUPPOSED TO GET A 404 PERMIT AND IF YOU GET ONE YOU COULD BE ALLOWED TO FILL AND THEREFORE IT BECOMES A LAND OF THE UNITED STATES.

WALLACE -EXPLAIN NATIONWIDE 26? **HANMER** - ALL OF THE REGULATORY AGENCIES, THE CORPS AND EPA, BEGAN TO LOOK FOR WAYS TO PERMIT LARGE GROUPS OF WHAT WE CONSIDERED DE MINIMIS ACTIVITIES, OR ACTIVITIES THAT WERE SO SIMILAR TO EACH OTHER THAT YOU COULD WRITE A BLANKET REGULATION RATHER THAN HAVE TO ISSUE HUNDREDS OF THOUSANDS OF INDIVIDUAL PERMITS. THE CORPS STARTED OUT WITH 5 CFS, BY TRYING TO DEFINE DE MINIMIS IN TERMS OF THE GEOGRAPHIC AREA AFFECTED, WHICH COULD BE AFFECTED BY A VARIETY OF DIFFERENT FILLING TYPES OF ACTIVITIES. NATIONWIDE 21 IS FOR SURFACE MINING ACTIVITIES REGULATED UNDER SMCRA. IT WAS DONE WHEN SMCRA WAS STILL LARGELY A FEDERALLY-REGULATED PROGRAM. THE RATIONALE WAS THAT THE SMCRA PROCESS AND NEPA SHOULD INCORPORATE ALL THE TYPES OF CONSIDERATIONS THAT WERE RELEVANT TO PROTECTING THE ENVIRONMENT, AND IF IT DID, THEN THE CORPS WOULD NOT IMPOSE A SECOND NEW NEPA REVIEW ON EVERYTHING, BUT WOULD ACCEPT THE RESULTS OF THE SMCRA PROCESS AND AUTOMATICALLY PERMIT. NP 21 SEEMS TO BE A MOSTLY AUTOMATIC PERMIT THAT WAS TACKED ONTO THE END OF A SMCRA PERMIT. THE PROBLEM WAS (THIS IS NOT A CRITICISM OF THE STATES) THAT AS WE DELEGATED TO THE STATES, SOME OF THE ENVIRONMENTAL REQUIREMENTS ASSOCIATED WITH NEPA "FELL OFF," AND A FEW QUALITATIVE DIFFERENCES OCCURRED, AND THE FEELING WAS THAT WE WERE LOSING SOMETHING, PERHAPS.

POLITAN - BEFORE A SECTION 404 PERMIT IS VALID, A STATE MUST ISSUE 401 WATER QUALITY CERTIFICATION FOR THE PROJECT, AND CERTIFY THAT THE PROJECT COMPLIES WITH STATE WATER QUALITY STANDARDS. SO EACH STATE CAN MANAGE ITS RESOURCES THAT WAY. THAT'S WHERE WE GET INTO THE DIFFERENT TERMS, DOES IT COMPLY WITH WATER QUALITY STANDARDS?

HANMER - ONE OF THE FACTORS WITH SECTION 404 IS THAT THE STATE HAS AN EFFECTIVE VETO OVER THE ISSUANCE OF A 404 PERMIT. TAKE TROUT STREAMS -- FOR EXAMPLE, IF STATES TRY TO USE THEIR WATER QUALITY STANDARDS TO SAY NO TO ALL TYPES OF FILL, THE STATE LEGISLATURE PROBABLY VERY QUICKLY DOES SOMETHING TO THAT STATE AGENCY. BUT THE STATES ARE EXPECTED TO IDENTIFY SPECIAL WATERS, AND YOU GET INTO WHAT DO YOU MEAN BY THAT, TROUT STREAMS? WHAT HAVE PEOPLE BEEN WILLING TO DESIGNATE IN THEIR STANDARDS AS SPECIALLY-PROTECTED WATERS.

AS A REGULATOR, THE QUESTION IS, WHAT DO BIOLOGISTS HAVE TO TELL US THAT CAN BE USED TO DETERMINE SIGNIFICANCE OR VALUES THAT NEED TO BE PROTECTED? SO IT'S A WAY OF DEFINING, BUT IT'S NOT THE SAME THING AS A DEFINITION.

QUESTION - IS THERE AN UNDERLYING ASSUMPTION IN THIS APPLICATION OF THE LAW THAT HEADWATER STREAMS ARE LESS IMPORTANT THAN LARGER STREAMS? **HANMER** - YES, IN MY EXPERIENCE OVER THE LAST 25 YEARS, I WOULD SAY THAT IS DEFINITELY THE CASE. **COMMENT** - IN WEST VIRGINIA, UNTIL RECENTLY, THOSE HEADWATER STREAMS WERE ALSO GIVEN A DIFFERENT DESIGNATED USE (THEY WERE CALLED "BAIT MINNOW STREAMS") WHICH DIMINISHED THEIR IMPORTANCE. **PASSMORE** - BUT, THEY STILL HAD TO MEET ALL THE AQUATIC LIFE CRITERIA. **QUESTION** - SO IF THERE WERE A PERMIT APPLICATION TO DESTROY A FOURTH-ORDER STREAM, THERE WOULD BE A DIFFERENT SET OF CRITERIA APPLIED? **HANMER** - I WOULD SAY AUTOMATICALLY YES, BECAUSE THE NATIONWIDE PERMIT ORIGINALLY SAID THAT IF THE WATER BODY FLOWED LESS THAN 5 CFS, IT WAS A DE MINIMIS WATER BODY, AND A DE MINIMIS WATER BODY TRANSLATED INTO A DE MINIMIS EFFECT. I THINK THAT WAS SCIENTIFIC IGNORANCE -- THAT'S WHAT YOU'RE TRYING TO TELL US. I MUST TELL YOU THAT HEADWATER STREAMS ARE BEING DESTROYED EVERYWHERE -- FOR WATER SUPPLY RESERVOIRS, EVER PLACE YOU LOOK. IT'S AN AREA THAT BEGAN TO WORRY US SOME YEARS AGO BUT WE DIDN'T KNOW WHAT TO DO WITH IT. WE STILL HAVEN'T KNOWN QUITE WHAT TO DO WITH IT UP UNTIL TODAY, WHICH IS WHY THIS MEETING IS A GOOD MEETING.

POMPONIO - A COUPLE OF POINTS: THE CORPS DID WHAT THEY DID BECAUSE THE VOLUME OF PERMITS THE CORPS EXPECTED TO HAVE TO PROCESS IF THEY HAD TO DO PERMITTING WORK ON ALL THE LOCAL LITTLE THINGS THAT WENT ON, AND THE CONCERN THAT THE FEDERAL GOVERNMENT DIDN'T REALLY BELONG WAY UP IN THE LITTLE HEADWATER STREAMS REGARDLESS OF THE ECOLOGICAL REASONS, BASED ON WHERE FEDERAL INTERVENTION SHOULD OCCUR. IT WASN'T A TOTALLY ECOLOGICAL DECISION ONE WAY OR ANOTHER -- IT WAS A PRACTICAL DECISION. ALSO, THE NATIONWIDE PERMITS NEVER SAID THEY WEREN'T WATERS OF THE UNITED STATES, AND THAT THE CORPS COULDN'T

REGULATE THEM, THE CORPS CAN TAKE DISCRETIONARY AUTHORITY ON ANY AREA. NP 26 GAVE EVERYONE CARTE BLANCHE TO WORK ABOVE THE HEADWATERS, AND NP 21 GAVE MINING COMPANIES EVEN MORE OPPORTUNITY TO DO THINGS IN EVEN LARGER STREAMS.

COMMENT - SO IF THERE'S AN UNDERLYING BIAS AGAINST HEADWATER STREAMS THAT DOES NOT COME FROM A SCIENTIFIC BASIS, THEN THIS ISN'T A SCIENTIFIC ISSUE SINCE DESTROYING THE WATERS OF A SMALL STREAM, FROM A SCIENTIFIC STANDPOINT, ISN'T ANY DIFFERENT THAN DESTROYING THE WATERS OF A LARGE STREAM. IN A SENSE, WE'RE BEING ASKED AS SCIENTISTS TO COUNTERACT A MAJOR SOCIAL BIAS OR A BIAS CONSTRUCTED FOR PURELY ECONOMIC REASONS, THAT HAS NOTHING TO DO WITH THE SOCIAL VALUE OF THE SYSTEM, OR THE SCIENTIFIC VALUE.

HOFFMAN - BUT THE 404 PROGRAM WAS THOUGHT ORIGINALLY TO EXTEND ONLY TO NAVIGABLE WATERS, SO THERE WAS ALWAYS A BIAS AGAINST HAVING FEDERAL INTERVENTION IN THE UPPERMOST HEADWATER AREAS. THAT COUPLED WITH THE WORK LOAD ISSUE, DROVE THE CORPS TO DEVELOPING NP 26. BUT NP 26 ALSO HAS THE PROVISION OF BEING REVIEWED EVERY SO MANY YEARS, AND AS A RESULT OF THE AGENCIES PROVIDING INFORMATION ON THE IMPACTS, AND DEMONSTRATING THAT THEY WERE CUMULATIVELY SIGNIFICANT, THAT'S WHY THEY WENT INTO REVISING THE EXISTING NP 26 INTO THE FORM THAT IT HAS NOW, WHICH IS GOING TO BE ARGUED AGAIN. WHAT THEY'RE DOING NOW IS CONSIDERING EXPANDING IT INTO ALL HEADWATER AREAS, BUT SAYING THAT ANYTHING LESS THAN AN ACRE IS OK TO FILL.

POMPONIO- ONE OF THE REASONS THE FEDERAL GOVERNMENT COULD GET AWAY WITH EXEMPTING ALL OF THAT ACTIVITY ABOVE THE HEADWATERS IS THAT NO ONE CONVINCED THE DECISION-MAKERS WHO WERE NOT FIELD BIOLOGISTS OR AQUATIC SCIENTISTS, THAT THERE WAS ANYTHING SPECIAL ABOUT THOSE AREAS. COMMON KNOWLEDGE AND SCIENTIFIC RESEARCH ALWAYS SEEMED TO BE FOCUSED ON THE LARGER WATERS. ALTHOUGH THEY HAD AN INTUITION ABOUT THE VALUE OF THOSE AREAS, THEY COULD EASILY DISMISS AREAS ABOVE THE HEADWATERS. NEED TO DO A BETTER JOB OF EXPLAINING WHY THEY'RE IMPORTANT. IF THERE'S MORE UNDERSTANDING OF THE VALUE OF THESE AREAS, IT WILL EXTEND FAR BEYOND JUST MINING ISSUES.

HANMER - THERE'S UTILITY VALUE, TOO. ENVIRONMENTAL PROGRAMS, OLDER ONES, EVEN GOT PAID FOR, MAYBE EVEN STILL DO, GOT PAID FOR FROM SALES OF FISHING LICENSES. CORPS OF ENGINEERS BENEFIT STUDIES: YOU WEREN'T JUST LOOKING AT FISH, YOU WERE LOOKING AT WHETHER THERE WAS FISHING; NOT JUST WHETHER IT WAS SWIMMABLE, BUT WHETHER THERE WAS SWIMMING. COULD YOU ASSIGN ECONOMIC VALUES TO THESE WATER BODIES THAT WOULD THEN INCREASE THEIR "VALUE" THAT WOULD THEN OFFSET THE OPPORTUNITY COSTS YOU WOULD HAVE OF REFUSING TO ALLOW THEM TO BE EXPLOITED FOR MINING OR OTHER PURPOSES. BECAUSE A LOT OF THE DECISION-MAKING PROCESS IS SOCIO-ECONOMICS.

EVERY TIME WE GET CLOSE TO FARMING AND FORESTRY WITH THE CLEAN WATER ACT, WE FIND OURSELVES IN POLITICALLY DANGEROUS TERRITORY, SO THESE HEADWATERS STREAMS PROBABLY LOOK LIKE SOMEBODY'S FARM OR SOMEBODY'S SACRED PROPERTY.

WE NEED TO TELL A BIOLOGICAL VALUE STORY THAT WILL ENRICH OUR UNDERSTANDING OF STREAMS, IF NOT OUR DEFINITION. "A STREAM LOOKS LIKE A PILE OF WET LEAVES," RIGHT?

HARTOS - WHAT DOES THE CORPS RELY ON TO DEFINE A JURISDICTIONAL STREAM? DO YOU RELY ON THE STATE STANDARDS? **POLITAN** - DON'T THEY USE THE ORDINARY HIGH-WATER MARK? [IN RESPONSE, CORPS PERSONNEL INDICATED THAT THEY PERSONALLY ARE NOT INVOLVED WITH PERMITTING, AND COULDN'T REALLY ANSWER THE QUESTION.]

HANDEL - WE HAVE FORMAL DEFINITIONS OF WETLANDS, A FEDERAL MANUAL THAT'S ENORMOUS THAT DEFINES WETLANDS BY HYDROLOGY, VEGETATION, AND SOIL CHARACTERISTICS. MANY SMALL STREAMS HAVE WETLANDS ASSOCIATED WITH THEM. ARE THERE STREAMS THAT DON'T HAVE WETLANDS? SO IS THE ISSUE REALLY TO DEFINE THOSE HEADWATER STREAMS THAT DON'T HAVE WETLANDS ASSOCIATED WITH THEM? **HANMER** - PROBABLY YES. **POMPONIO** - IF WE CAN DEFINE WETLANDS BY SOILS, VEGETATION AND HYDROLOGY, IS THERE AN ANALOGOUS SET OF PARAMETERS WE CAN USE TO DEFINE A STREAM? SOMETHING ANALOGOUS TO AN OBLIGATE HYDROPHYTE? LIKE FLOW REGIME, ETC.? **WALLACE** - THE WEST VIRGINIA DEFINITION IS VERY GOOD, IT MAKES A LOT OF SENSE, IT MAYBE EVEN TOO RESTRICTIVE!

HANMER - THE PROBLEM IS THAT THEY USED IT IN ASSOCIATION WITH THE WORD INTERMITTENT -- KIND OF A NON-DEFINITION, IT SAYS IT'S NOT INTERMITTENT, BUT IT DOESN'T REALLY SAY WHAT IT IS.

TIBBOTT - SHOULD WE HAVE A BIOLOGICALLY-BASED DEFINITION? **COMMENT** - A FUNCTIONAL DEFINITION. **POLITAN** -- IF WE USE A BIOLOGICAL DEFINITION, WHAT HAPPENS TO STREAMS DEVOID OF LIFE DUE TO AMD? **ANSWER** - THAT'S AN IMPAIRMENT. **HANMER** - ARE ANY OF THOSE SITUATIONS NATURALLY-OCCURRING? **POLITAN**-- I'VE NEVER SEEN A NATURAL AMD SITUATION THAT WIPED OUT A STREAM. **POMPONIO** - EVEN THE WETLANDS DEFINITION INCLUDES THE PHRASE "UNDER NORMAL CIRCUMSTANCES."

TIBBOTT - I WOULD THINK THAT ONE OF THE RECOMMENDATIONS WHICH COULD COME OUT OF THE EIS WOULD BE A DEFINITION OF A STREAM ACROSS PROGRAMS AND ACROSS STATES. **WALLACE** - IT'S VERY DANGEROUS TO HAVE ONE DEFINITION THAT COVERS ALL TYPES OF AREAS. THERE ARE SOME AREAS IN THE COASTAL PLAIN OF GEORGIA WHERE STREAMS ARE DRY FOR PART OF THE YEAR. **COMMENT** - BUT IF WE'RE JUST DEVELOPING A DEFINITION FOR THE AREA OF STEEP SLOPE MINING, IS IT POSSIBLE TO DO? **HANMER** - AS A PRACTICAL MATTER, I CAN'T SEE HOW WE'RE GOING TO GET ALL THE STATES IN THIS REGION TO CHANGE ALL THEIR REGULATIONS TO A CONFORMING DEFINITION. IT WOULD BE A WASTE OF TIME TO TRY THAT, BUT IT WOULD BE USEFUL TO COME UP WITH A GUIDELINE FOR ALL THE STATES TO DETERMINE WHEN THEY SHOULD BE CONCERNED ABOUT THESE STREAMS AND WHY. REOPENING THEIR WATER QUALITY STANDARDS IS DANGEROUS. **POLITAN** - WE DO IT EVERY THREE YEARS ANYWAY. **HANMER** - YES, BUT YOU DON'T OPEN UP THE DEFINITION OF WHAT IS A STREAM EVERY THREE YEARS.

ARWAY - I DON'T KNOW WHY YOU CAN'T USE THE SAME SYSTEM AS WHEN REGULATING DISCHARGERS -- THAT IS, TO ASSIGN THE "POINT OF FIRST USE" -- WHEREVER THERE IS A USE IS WHERE THE STREAM STARTS FROM A REGULATORY PERSPECTIVE. **QUESTION** -- WHAT IS THE "POINT OF FIRST USE" IN PENNSYLVANIA? **ARWAY** - IT'S A VERY SUBJECTIVE DEFINITION EMBODIED WITHIN THE REGULATORY PROGRAM THAT ALLOWS THE FIELD BIOLOGIST TO USE PROFESSIONAL JUDGEMENT TO ASSIGN WHERE A PERENNIAL STREAM STARTS AND WHERE THE WATER QUALITY STANDARDS ARE APPLIED. **RAMSEY** - IN WEST VIRGINIA, THAT "BEST PROFESSIONAL JUDGEMENT" BECAME 250 ACRES, SO THERE'S A REAL DANGER IN DOING THAT. **HANMER** - AND IN KENTUCKY, IT'S THE BLUE LINE. SO, IF YOU WANT TO WORK ON THIS, WHEN IS IT YOU KNOW YOU'RE SEEING SOMETHING YOU WANT? I DON'T THINK THAT ANY OF THESE DEFINITIONS IS THE PROBLEM. THE PROBLEM IS ASSIGNING VALUE FOR MITIGATION AND FOR MAKING PERMITTING DECISIONS.

COMMENT - THERE ARE SCIENTISTS HERE THAT TALK ABOUT HEADWATER STREAMS DISTRIBUTING NUTRIENTS, ETC. -- THAT'S NOT A SOCIETAL VALUE JUDGEMENT ABOUT WHAT'S IMPORTANT. WE KNOW THINGS WILL CHANGE WITH THIS TYPE OF ALTERATION OF THE LANDSCAPE, BUT WHETHER OR NOT SOCIETY WILL ACCEPT IT . . . THAT'S ALL WE CAN DO AS SCIENTISTS. **HANMER** - THAT'S RIGHT, BUT THE INFORMATION THAT WAS PRESENTED THIS MORNING IS NOT GENERALLY KNOWN, SO THAT SIDE OF THE CONVERSATION NEEDS BEEFING UP, COMPARED TO PEOPLE WHO SAY THEY OWN THE LAND AND SOMETIMES IT'S WET AND SOMETIMES IT'S DRY. THERE'S A RICH OPPORTUNITY TO INFORM THIS DECISION-MAKING PROCESS FROM THE SCIENTIFIC PROCESS.

COMMENT - WHY ARE INTERMITTENT STREAMS ASSUMED TO BE UNIMPORTANT? **HANDEL** - IT'S ANALOGOUS TO VERNAL POOLS, WHICH HAVE CRITICAL ECOLOGICAL VALUE, BUT ONLY IN A CERTAIN SMALL TIME OF YEAR. THERE ARE CERTAIN STREAMS WHICH ARE DRY FOR MANY MONTHS, BUT STILL HAVE BIOLOGICAL INTEREST. **COMMENTER** - BUT IT'S AS IF WE'RE EXCLUDING INTERMITTENT AS BEING IMPORTANT, IN THESE DEFINITIONS. WHY ISN'T INTERMITTENT AS IMPORTANT AS PERENNIAL? **HANMER** - THAT'S A MISUNDERSTANDING. MOST OF THE STATE WATER QUALITY STANDARDS DO NOT DISTINGUISH -- THEY DON'T TRY TO DEFINE INTERMITTENT AND PERENNIAL AND EPHEMERAL FOR PURPOSES OF THE REGULATORY EFFECT. THE SURFACE MINING REGULATIONS DO -- I DON'T KNOW WHAT EFFECT THEY GIVE THOSE DEFINITIONS, BUT THE CLEAN WATER ACT DEFINITIONS ARE NOT BASED ON THE FLOW. MOST OF THE STATES DID NOT TRY TO DO THAT; WEST VIRGINIA IS ACTUALLY THE EXCEPTION IN THIS LIST OF STATES THAT USE THE TERM "INTERMITTENT" IN THEIR WATER QUALITY STANDARDS. THE REST JUST LEFT IT ALONE.

WALLACE - WHAT'S WRONG WITH THE WEST VIRGINIA DEFINITIONS? **HANMER** - WHAT IS THE DEFINITION USED FOR? THE DEFINITION IS "STREAMS WHICH HAVE NO FLOW DURING SUSTAINED PERIODS OF NO PRECIPITATION AND WHICH DO NOT SUPPORT AQUATIC LIFE WHOSE LIFE HISTORY REQUIRES RESIDENCE IN FLOWING WATERS FOR A CONTINUOUS PERIOD OF AT LEAST 6 MONTHS." WHY DOES WEST VIRGINIA USE THAT DEFINITION? **POLITAN** - IT'S WHERE WATER QUALITY STANDARDS APPLY. **HANMER** - SO YOU START WATER QUALITY STANDARDS AT THAT POINT? **POLITAN** - NO.

IF THERE'S AN AQUATIC INSECT THAT REQUIRES 4 MONTHS OF FLOWING WATERS, IT'S AN INTERMITTENT STREAM, THAT MEANS THAT IF YOU DO SOMETHING TO THAT STREAM, WE CONSIDER IT A SIGNIFICANT LOSS TO THE STATE, WE WANT COMPENSATION FOR IT, OR IT MANDATES PROTECTION -- WE MAY DENY YOU DOING ANYTHING IN THERE. **HANMER** - SO YOU USE IT KIND OF LIKE PENNSYLVANIA USES "POINT OF FIRST USE" -- IT'S YOUR POINT OF FIRST USE? **POLITAN** - KIND OF. WET WEATHER STREAMS ARE "STREAMS THAT FLOW ONLY IN DIRECT RESPONSE TO PRECIPITATION, OR WHOSE CHANNELS ARE AT ALL TIMES ABOVE THE WATER TABLE." **PASSMORE** - AND WHAT HAPPENS TO THOSE STREAMS IN YOUR REGS AS OPPOSED TO INTERMITTENT? **POLITAN** - IF WE FIND AQUATIC LIFE ... **PASSMORE** - I THINK PEOPLE IN THE ROOM ARE THINKING THAT THERE'S A DISTINCTION BETWEEN INTERMITTENT AND PERENNIAL, WHEN THERE ISN'T -- THERE'S A DISTINCTION BETWEEN INTERMITTENT AND EPHEMERAL, SO PEOPLE ARE MISUNDERSTANDING THAT THEY'RE CUTTING OFF INTERMITTENT STREAMS, WHEN THEY'RE NOT. **POLITAN** - ... AT LEAST IN WEST VIRGINIA.

COMMENTER - WELL, IN THE CASE AT HAND, ARE WE TALKING ABOUT BEING ABLE TO PREVENT VALLEY FILLS IN ALL STREAMS THAT ARE ACTUALLY CALLED STREAMS? MAYBE WE SHOULDN'T BE TALKING ABOUT THE DEFINITIONS, BUT WHAT WE CAN ACTUALLY DO HERE . . . IT'S NOT QUITE CLEAR TO ME WHETHER WE'VE COMPLETELY GIVEN UP THE PROBABILITY OF PUTTING AN END TO THIS PROCESS OF DESTROYING STREAMS. IT SEEMS TO ME THAT WE HAVE A REASONABLE CRACK AT MAKING A CASE, FROM THE STANDPOINT OF THE CLEAN WATER ACT AND THE VALUES TO THE ENVIRONMENT OF HEADWATER STREAMS, THAT THIS PROCESS SHOULDN'T OCCUR AT ALL. THAT'S THE FIRST STAGE. IF THE ENVIRONMENTAL IMPACT STATEMENT CAN FIND THOSE RESULTS AND ACTUALLY MAKE A CASE THAT THIS PROCESS SHOULD BE STOPPED, IT SHOULD BE STOPPED. OTHERWISE, THEN WE HAVE TO GET INTO ANOTHER LEVEL OF DISCUSSION, OF HOW YOU SORT OF LET SOMEBODY ROB $10 FROM A BANK, BUT NOT $1,000.

HARTOS - IT WAS RECOGNIZED THAT THERE ARE TIMES WHEN YOU NEED TO FILL IN STREAMS, FOR VARIOUS ACTIVITIES, AND THAT'S UNDER THE 404 PROCESS. YOU'RE ALLOWED TO FILL STREAMS. THERE ARE CERTAIN THINGS THAT NEED TO BE CONSIDERED WHEN YOU DO THAT -- THE BIOLOGICAL WEALTH OF THE STREAMS AND OTHER FACTORS. THE 404(B)(1) GUIDELINES APPLY IN THOSE CASES. IT'S A DECISION THAT NEEDS TO BE MADE. AN ARBITRARY "YOU CAN'T DO IT ANYMORE" . . . YOU WOULDN'T BE ABLE TO DO ANYTHING. **HANMER** - YES, OF COURSE YOU CAN IF YOU GET A 404 PERMIT YOU CAN FILL IN WETLANDS. **WALLACE** - YOU COULD FILL IN WHITE CLAY CREEK! **HANMER** - MINING IS ONE OF THE MOST DIFFICULT ACTIVITIES TO REGULATE, BECAUSE IT'S GEOGRAPHICALLY RESTRICTED -- IN OTHER WORDS, THE MINERAL RESOURCE SORT OF DICTATES WHERE YOU'RE GOING TO DO SOMETHING. USUALLY WITH BRIDGES OR HIGHWAYS OR PARKING LOTS OR FLOATING CRAP GAMES -- AND WE DO A LOT OF FILLING TO BUILD FLOATING CRAP GAMES IN MISSISSIPPI -- YOU TRY TO ARGUE THAT THEY DON'T HAVE TO PUT THEIR CASINO ON TOP OF THAT WETLAND, OR THEY DON'T HAVE TO PUT THEIR HOTEL ON TOP OF THAT BEACH. THAT'S PART OF THE ARGUMENT YOU HAVE UNDER 404(B)(1) -- WHY DO YOU HAVE TO DO IT THERE? YES, THE MINING COMPANY HAS TO SHOW YOU THEY ABSOLUTELY HAVE TO HAVE THAT VALLEY FILL IN ORDER TO EXPLOIT THAT RESOURCE. IF THEY WIND UP SHOWING YOU THAT THEY'VE GONE AS FAR AS THEY CAN GO ON MITIGATION, THEN THE BURDEN OF PROOF SHIFTS BACK TO SOCIETY TO SAY WHY IS THIS WATER BODY SO SIGNIFICANT THAT IT CAN'T BE SACRIFICED FOR THIS USE. AND STATES TRY TO GET AHEAD OF THAT -- WHICH WEST VIRGINIA HAS NOT -- BY TRYING TO DEFINE "AREAS UNSUITABLE FOR MINING" BASED ON SOME OTHER SYSTEM. BUT THAT'S HEAVY GOING. KENTUCKY HAS UNIQUE BIOTIC COMMUNITIES ON BLACK MOUNTAIN, WHICH IS ALMOST A TEST CASE IN TRYING TO SET ASIDE A LARGE AREA AND SAY "YOU CANNOT TAKE THIS RESOURCE." AND WHAT YOU GET BACK IS "BUT THERE'S A HUNDRED MILLION DOLLARS WORTH OF COAL THERE!"

STUMP - MAYBE WE SHOULD REORIENT OUR THOUGHTS TO THE DRAINAGE AREA IMPACTS VS. JUST THE STREAM CHANNEL -- FROM HERE DOWN I HAVE A BIOLOGICAL COMMUNITY. LOOKING AT A TYPE OF MINING FOCUSED ON MOUNTAINTOPS, ON FILLING FIRST ORDER STREAMS. MAYBE INSTEAD OF FOCUSING ON THE STREAMS WE SHOULD BE FOCUSING ON AMOUNT OF DRAINAGE AREA VS. STREAM CHANNEL. AND IF WE'RE LOOKING AT A DRAINAGE AREA IMPACTED BY MINING, AND THEN A POINT OF OBSERVATION OR EVALUATION DOWNSTREAM OF THAT, AND MAKING DECISIONS, VS. TRYING TO DETERMINE WHERE THE STREAM STARTS AND WHERE THE STREAM ENDS. BECAUSE I SEE THAT STARTING FROM THE RIDGETOP AND GOING ON DOWN, IT'S ALL A BIOLOGICAL COMMUNITY, AND VEGETATIVE COMMUNITY, ALL TOGETHER AND INTERRELATED, SO MAYBE WE SHOULD BE MAKING OUR CUTOFFS MORE ON A DRAINAGE AREA, OR PERCENTAGE OF DRAINAGE AREA, OF THE TOTAL DRAINAGE AREA CUTOFF, IN EVALUATIONS, AND POINTS OF OBSERVATION AND JURISDICTION. **WALLACE** - I LIKE DENNIS' ANALOGY -- IS IT OK TO STEAL $1, $10, OR $100 OR $1000 FROM A BANK? WHEN DO YOU DRAW THE LIMIT? **STUMP** - WELL, IN A REGULATORY FRAMEWORK WE'VE GOT LAWS THAT MINING IS ALLOWABLE WITH REGULATIONS, AND WE HAVE TO FIND THAT MIDDLE GROUND OF

HOW MUCH CAN YOU IMPACT BEFORE YOU'RE NOT ALLOWED TO DO ADDITIONAL IMPACTS? WE'RE NOT IN A "PRESERVATIONIST" MODE, EXCEPT IN AREAS WHERE IT'S BEEN DETERMINED UNSUITABLE FOR MINING. **DENSMORE** - IT'S AN ENTITLEMENT PROGRAM.

HANMER - NO, I DON'T THINK IT IS. WE'RE TALKING ABOUT HOW CAN BIOLOGISTS BE THE MOST USEFUL? I THINK THERE ARE A LOT OF PEOPLE WHO ARE GOING TO SIT AROUND AT THE END OF THE DAY MAKING DECISIONS, ECONOMIC, POLITICAL, SOCIAL. BUT HOW IS THE BIOLOGIST'S VOICE BEST HEARD? HOW IS THE SCIENTIFIC INPUT THAT YOU HAVE TO MAKE TO THIS DECISION MAKING PROCESS BEST EXPRESSED? **UNKNOWN COMMENTER** - FOR WHAT PURPOSE? **HANMER** -- TO HELP US. MAYBE YOU'RE UPSET ABOUT THE WORD "VALUE." MAYBE IT'S ONLY PEOPLE LIKE US REGULATORS OR MINING COMPANIES WHO USE THE WORD VALUE AND THAT "VALUE" IS ACTUALLY AN ANATHEMA TYPE WORD TO YOU. FUNCTION -- USE FUNCTION, BUT TO HELP US TO ENRICH THE UNDERSTANDING OF THE FUNCTIONS, SO THAT PEOPLE KNOW THEY'RE GIVING UP SOMETHING, AND NOT NOTHING.

KINCAID - WE DO FILL VALLEYS, WE FILL FOURTH ORDER STREAMS. THE CORPS OF ENGINEERS HAS DONE A PRETTY GOOD JOB OF IT. THE DIFFERENCE IS THAT, UNDER THOSE CIRCUMSTANCES, USING TAXPAYER MONEY, WE HAVE TO DO A COMPLETE, DETAILED ENVIRONMENTAL ASSESSMENT. I DON'T THINK IT'S HAPPENING, BUT ARE WE TRYING TO SWEEP THE SENSITIVITY OF THESE HEADWATER AREAS AND THEIR IMPORTANCE UNDER THE TABLE, AT THE EXPENSE OF RUBBER-STAMPING AN EIS? I DON'T THINK WE SHOULD GET INTO THAT POSITION. WE NEED TO DO GOOD SCIENCE, DESIGN THE EXPERIMENTS, COLLECT THE DATA, AND INTERPRET IT, BUT AS PART OF THAT INTERPRETIVE PROCESS WE NEED TO INCLUDE THE UNIQUENESS OF THESE HEADWATER STREAMS.

HANDEL - I THINK IT'S INTERESTING THAT THE CORPS DOES SOMETIMES FILL FOURTH ORDER STREAMS. BUT RECENTLY, SOME OF THE CORPS' OLD ACTIONS ARE BEING REVERSED, AS NEW KNOWLEDGE AND PUBLIC SENTIMENT CHANGE. WHETHER IT'S PULLING OUT DAMS ON SALMON RIVERS OUT WEST TO THE REMARKABLE ACTION IN THE EVERGLADES, THIS IS ILLUMINATED BY NEW KNOWLEDGE AND NEW ATTITUDES. THIS GROUP IS CHARGED WITH DEVELOPING A MODERN UNDERSTANDING OF THESE LITTLE STREAMS TO SAY TO THE GOVERNMENT: "WELL, THESE THINGS REALLY DO HAVE TO BE SAVED, EVEN THOUGH 25 YEARS AGO WE SAID, LOOK THEY'RE TOO SMALL TO EVEN WORRY ABOUT, OTHER VALUES ARE MORE IMPORTANT. IS THIS PARTICULAR REGIONAL PROBLEM GOING TO BE LIKE THE EVERGLADES AND SALMON STREAMS IN OREGON? I'M JUST A BOTANIST, BUT IT SEEMS LIKE A PRETTY STRAIGHTFORWARD PROBLEM. ARE WE AT STATE WHERE WE SAY THE OLD LAWS WERE WELL-MEANING, OF COURSE, BUT WE HAVE TO MOVE ON FROM THERE.

NEWBOLD - THE SENTIMENT OF PROBABLY MOST OF THE PEOPLE IN THIS ROOM IS THAT THIS VALLEY FILLING IS A BAD IDEA, AND THAT THE WEIGHT OF THE SCIENTIFIC EVIDENCE -- THE IMPACT YOU COULD DOCUMENT, ALTHOUGH IT MIGHT BE A LOT OF PROBLEM TO DO IT -- WOULD MAKE A STRONG CASE AGAINST DOING IT AT ALL. YET THE REALITY SAYS WE CAN'T STOP IT. SO, WE HAVE TO STEP BACK AND TAKE A COMPROMISE APPROACH, IN WHICH INSTEAD OF DOCUMENTING WHY IT SHOULDN'T BE DONE AT ALL, WE ARE IN A POSITION OF DECIDING WHICH WATERSHEDS TO SACRIFICE AND HOW MANY, AND COMING UP WITH A SORT OF "CALCULUS" TO DO THAT. THAT CALCULUS IS WELL BEYOND THE FIRST STEP. WE ARE, AS SCIENTISTS, IN A POSITION TO BE ABLE TO SAY THIS HAS A STRONGLY NEGATIVE IMPACT, AND LIST THE IMPACTS, AND SAY THIS IS A PRACTICE THAT SHOULDN'T BE DONE. WE DON'T HAVE THE TECHNOLOGY TO CREATE A CALCULUS TO DECIDE WHAT PERCENT CAN BE DESTROYED. WHERE YOU DO SEE THIS KIND OF REGULATION DEVELOPED, WHERE THERE IS A CALCULUS, IT'S ALMOST ALWAYS A JOKE. IT TYPICALLY IS THE RESULT OF SOME KIND OF POLITICAL COMPROMISE, AND BECAUSE YOU COULDN'T REALLY DO IT RIGHT YOU HAD TO COME UP WITH SOME CRAZY SCHEME OF ADDING A LOT OF DIFFERING COEFFICIENTS TOGETHER OR WORKING THROUGH SOME KIND OF A MATRIX THAT EVERYONE REALIZES DOESN'T MAKE SENSE, BUT IT WAS COME UP WITH AS A COMPROMISE TO COME UP WITH A SLIDING SCALE WHICH ENDS UP IN MIDDLE GROUND.

HANMER - DO YOU REMEMBER LEOPOLD'S "UNIQUENESS INDEX" FROM 1972? MY CHALLENGE TO YOU IS THAT CHANGES OCCUR. THAT DEVELOPMENT OCCURS, AND THAT EVEN BIOLOGISTS LIVE IN HOUSES AND BENEFIT FROM DEVELOPMENT. SO THEN, THE QUESTION FOR US IS, DO YOU WANT THAT TO JUST HAPPEN HELTER-SKELTER, OR DO YOU WANT TO TRY TO FIGURE OUT AND TAKE SOME RESPONSIBILITY FOR IT? THAT'S THE DILEMMA YOU'RE IN. YOU'RE SAYING "I DON'T WANT TO TAKE RESPONSIBILITY SAYING THAT FILLING 10% OF THE HEADWATER STREAMS IS OK" AND I CAN UNDERSTAND WHY YOU WOULDN'T WANT THAT KIND OF RESPONSIBILITY. BUT UNFORTUNATELY, SOME OTHER PEOPLE HAVE TO TAKE THAT RESPONSIBILITY AND IT WOULD BE NICE IF THEY COULD DO IT ON THE BASIS OF THE BEST KIND OF INFORMATION THEY CAN GET.

WALLACE -THERE'S ANOTHER DANGER HERE, ESPECIALLY WHEN YOU CONSIDER LONG-TERM NITRIFICATION OF CATCHMENTS. THERE MIGHT BE THINGS HAPPENING HERE THAT WE'RE NOT GOING TO SEE UNTIL 15 OR 20 YEARS DOWN THE ROAD. ARE YOU GOING TO LET THESE PROCEED NOW, AND THEN FIND OUT 15 OR 20 YEARS LATER THAT THERE'S SOMETHING AWRY HERE THAT YOU CANNOT CORRECT? AND I'M PARTICULARLY THINKING ABOUT POTENTIAL FOR NITRATES IN THE SURFACE WATERS. THAT CAN BE PRETTY DANGEROUS. **KINCAID** - THAT'S ALL THE MORE REASON WHY WE NEED TO DESIGN GOOD EXPERIMENTS RIGHT NOW. **WALLACE** - EXACTLY, THAT'S WHAT I'M SAYING. AND THESE SHOULD BE MINIMIZED UNTIL WE SOLVE THE PROBLEM AND HAVE SOME IDEA OF THE WHAT KIND OF DOWNSTREAM EFFECTS THEY HAVE. **ROBINSON** - THERE ARE SOME VALLEY FILLS WHICH HAVE BEEN IN PLACE FOR 15 YEARS, CAN'T THESE BE STUDIED?

KINKAID - WE'RE TALKING ABOUT PROBLEMS THAT CAN COME TO GET US DECADES DOWN THE ROAD. WE NEED TO DESIGN THE EXPERIMENTS NOW PROJECTING THE PROBABLE IMPACTS, AND DETERMINING THE SIGNIFICANCE OF THE IMPACTS. I DON'T THINK RIGHT NOW, OR EVEN AFTER A YEAR'S WORTH OF DATA, WE'LL BE ABLE TO SORT OUT WHAT WE FIND FROM ENVIRONMENTAL NOISE WELL ENOUGH TO SAY THAT THESE IMPACTS ARE GOING TO OCCUR NEVER, TOMORROW, OR IN 2050. WE NEED TO BUILD INTO THE PROCESS SOME MEANS OF CONTINUING THIS EVALUATION PROCESS, AT THE SAME TIME THAT WE MEET THE DEADLINE.

DENSMORE - I WANTED TO BRING UP HERE, THAT GETS BACK TO THE SORT OF ARTIFICIAL CONSTRUCT WE GET INTO AS LAWYERS AND REGULATORS -- RIGHT NOW WE ARE LOOKING AT A 250-ACRE THRESHOLD FOR "MINIMAL" IMPACTS FOR PURPOSES OF THE PERMIT SYSTEM. THAT IS A NUMBER THAT HAS A LONG HISTORY, AND RELATES HISTORICALLY TO "AT WHAT POINT DO YOU REQUIRE COMPENSATION FOR LOSSES," BUT IT HAS NOW SORT OF JUMPED OVER AND BECOME A THRESHOLD BELOW WHICH YOU DON'T HAVE A SIGNIFICANT IMPACT ON THE SYSTEM. THIS HAS THE DANGER OF BECOMING LAW, THE WAY IT'S BEING USED RIGHT NOW, BECAUSE IT IS BEING USED AS A PRIMARY BASIS FOR PROCESSING CORPS OF ENGINEERS PERMITS.

WALLACE - THIS MEANS THAT ON ANY GIVEN DRAINAGE BASIN, YOU COULD FILL IN A SERIES OF FIRST AND SECOND ORDER STREAMS -- YOU COULD RAID THE BASIN, BASICALLY, AS FAR AS THE HEADWATERS -- EACH WITH SEPARATE FILLS OF UP TO 250 ACRES. **HANMER** - YOU COULD. **DENSMORE** - IT'S BEING SO RIGIDLY ADHERED TO THAT YOU COULD FILL 20 BASINS, SO LONG AS YOU KEPT THEM TO 249 ACRES OR LESS. I'D BE INTERESTED IN THE REACTION TO THAT HERE.

STAUFFER - DEPENDS WHICH 250 ACRES YOU'RE TALKING ABOUT. IF IT'S 249 ACRES OF WHITE CLAY CREEK WHERE THIS ONLY MAYFLY OCCURS, SOMEONE'S GOING TO HAVE A PROBLEM. IF IT'S THE 249 ACRES WHERE MY ONLY *PHOXINUS* OCCURS, I'M GOING TO HAVE A PROBLEM.

ROBINSON - IT'S NOT THAT SIMPLE, BECAUSE THERE'S A CAVEAT THAT SAYS THAT IF WE CONSIDER THAT MULTIPLE 250 ACRES BECOME CUMULATIVELY SIGNIFICANT -- AND WE HAVE TO KNOW WHAT THAT MEANS. SO, HOW MANY 250'S DO WE DO BEFORE ... **HOFFMAN** - OR, THE 249 ON YOUR SENSITIVE CREEK IS SENSITIVE. **ROBINSON** - OR THERE'S A THREATENED OR ENDANGERED SPECIES OR A WETLAND OR A FEDERAL TRUST RESOURCE.

STAUFFER - SOMEBODY MIGHT NOT WANT TO WIPE OUT A SONGBIRD, SOMEBODY MIGHT NOT WANT TO WIPE OUT A SALAMANDER, AND SOMEBODY ELSE WANTS TO PROTECT A FISH, WANT TO PROTECT A MAYFLY, THEN THE DINOFLAGELLATE AND A BACTERIA, AND YOU'VE GOT A QUALITY JUDGEMENT THERE. I'M PRETTY SURE THAT ALL OF THESE SYSTEMS HAVE SOME UNIQUE ORGANISMS AT SOME LEVEL OR ANOTHER ASSOCIATED WITH THEM. **ROBINSON** - AND AS REGULATORS, WE LOOK FOR BLACK AND WHITE LINES, AND WE KEEP PUSHING PEOPLE TO TELL US WHERE THEY ARE, AND IT DEPENDS ON YOUR INTEREST AND WHAT PART OF SCIENCE YOU COME FROM AS TO WHAT YOU CARE ABOUT. **STAUFFER** - IT GETS BACK TO THE $10 OR $1,000: "I'M WILLING TO GIVE UP A FISH BUT NOT A SONGBIRD," OR "I'M WILLING TO GIVE UP A MAYFLY BUT NOT A FISH."

TIBBOTT - WE'VE TRANSITIONED TO OUR NEXT QUESTION: HOW MUCH CAN WE GIVE UP? HOW MUCH CAN WE AFFORD TO LOSE? THERE ARE 40 PERMITS THAT HAVE TO BE DEALT WITH. SIX OF THE 40 HAVE MULTIPLE FILLS UNDER 250 ACRES. THE FISH AND WILDLIFE SERVICE IS THE ONLY AGENCY AMONG THE FIVE AGENCIES THAT CONSIDERS THIS A SIGNIFICANT CUMULATIVE IMPACT; ALL THE OTHER AGENCIES WOULD JUST AS SOON LET THEM GO AS NATIONWIDE

PERMIT AUTHORIZATION. THE FISH AND WILDLIFE SERVICE IS INTERESTED IN YOUR REACTION TO WHAT DO WE DO WITH MULTIPLE FILLS?

ARWAY - JUST A COMMENT ABOUT CUMULATIVE IMPACTS. THERE'S A PROVISION IN SMCRA THAT DEALS WITH CUMULATIVE HYDROLOGIC IMPACT ASSESSMENTS. WHERE STATES HAVE DELEGATED PROGRAMS, THEY HAVE TO DO CHIAS. TO MY KNOWLEDGE, NO PERMIT HAS EVER BEEN DENIED OR ALTERED BECAUSE OF CHIAS. WE'VE BEEN DOING CHIAS FOR A LONG TIME, BUT I'VE NEVER SEEN ANY EFFECT ON THE PERMIT PROCESS. **TIBBOTT** - I DON'T THINK THEY'VE REALLY BEEN DONE. **ARWAY** - THE OBLIGATION OF THE AUTHORITY IS THERE, AND THE STATE HAS TO "CHECK THE BLOCK" WHEN IT ISSUES THE PERMIT THAT THE CHIA HAS BEEN DONE. **TIBBOTT** - ALTHOUGH THE BLOCK IS CHECKED, THEY'RE NOT DONE. **ARWAY** - WELL, THEY'RE REQUIRED TO BE DONE AND IN THEORY THEY ARE DONE. HISTORY TEACHES US THAT THEY'RE REQUIRED TO BE DONE, BUT THEY'RE NOT DONE, AND PERMITS ARE STILL ISSUED.

NEWBOLD - CAN WE GO DOWNSTREAM AND IDENTIFY THE RESOURCES ON WHICH THE CUMULATIVE IMPACTS MIGHT BE FELT; A SPECIFIC REACH OF STREAM, A LAKE, AN ESTUARY IF YOU GET FAR ENOUGH DOWN? IS THAT A USEFUL WAY OF LOOKING AT THE QUESTION? **ROBINSON** - IT GOES BACK TO WHAT ARE THE VALUES THAT YOU ASSESS, AT WHICH CUMULATIVE PROBLEMS START KICKING IN. **NEWBOLD** - IF WE GET IN A BOAT AND GO DOWNSTREAM, AND WE COME TO THIS STRETCH OF RIVER THAT'S USED FOR FISHING OR WHITEWATER RAFTING, OR COME TO A LAKE THAT HAS A FISHERY, THEN WE SEE THE RESOURCES AND WE SAY ARE THESE AT RISK OF BEING IMPACTED, SO INSTEAD OF WORKING FROM, "WELL, WE COULD HAVE ALL THESE KINDS OF IMPACTS DOWNSTREAM," AND WORKING THROUGH THAT, WE GO DOWNSTREAM AND SEE WHAT MIGHT BE VULNERABLE AND WHAT MIGHT BE THE IMPACTS. **ROBINSON** - REGULATORS STRUGGLE WITH "HOW FAR DOWNSTREAM" YOU'RE SUPPOSED TO DEFINE CUMULATIVE IMPACT AREAS. IS IT THE GULF OF MEXICO OR THE CLINCH RIVER OR THE CHEAT RIVER OR SOME TRIBUTARY OF THE CHEAT RIVER. **COMMENTER** - THE GULF OF MEXICO IS A CANDIDATE BECAUSE THERE ARE NUTRIENT PROBLEMS IN THE GULF OF MEXICO IN REGARDS TO NITRATES. **ROBINSON** - IF YOU CHOOSE THE GULF OF MEXICO AND WE HAVE TO LOOK AT WATER QUANTITY AND QUALITY AND WELLS AND THINGS, THE POOR CITIZEN WHOSE WELL IS IMPACTED BY UNDERGROUND MINING OR SURFACE MINING, IF YOU'RE LOOKING AT THE GULF OF MEXICO THAT BECOMES AN INSIGNIFICANT IMPACT AND SO YOU CAN WRITE IT OFF. SO WHERE YOU DRAW THE LINE SO YOU CAN EVALUATE IMPACTS IS SOMETHING THAT HAS TO BE DECIDED.

MRH

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REVIEW

A Position Paper on Selenium in Ecotoxicology: A Procedure for Deriving Site-Specific Water Quality Criteria

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This paper describes a method for deriving site-specific water quality criteria for selenium using a two-step process: (1) gather information on selenium residues and biological effects at the site and in down-gradient systems and (2) examine criteria based on the degree of bioaccumulation, the relationship between measured residues and threshold concentrations for reproductive effects in fish and wildlife, and any observed reproductive impacts. Several outcomes are possible-criteria can be left unmodified, adjusted upward by a fixed amount (50%), or adjusted downward by one of three amounts (25, 50, or 75%). A criterion (existing or proposed) is lowered or raised by an amount that is proportional to the magnitude of bioaccumulation and toxic effects present-i.e., the degree of biological hazard. Criteria can be modified under two circumstances: (1) diagnostic residues and toxic effects must be coupled (present) in order to lower a criterion or (2) diagnostic residues and toxic effects must be coupled (absent) in order to raise a criterion. Coupling residues and effects makes the procedure sensitive to the natural inter- and intraspecific variation in bioaccumulation and toxic responses exhibited by fish and wildlife in aquatic ecosystems. The goal is to establish criteria that keep food-chain bioaccumulation below levels that result in toxicity to fish and wildlife. Precautions are given for those attempting to apply the generic EPA model for implementing national water quality criteria to a site-specific selenium criterion. © 1998 Academic Press

INTRODUCTION

The United States Environmental Protection Agency (EPA) conducted a comprehensive review of information on selenium ecotoxicology and published revised national freshwater criteria for selenium in 1987 (USEPA, 1987). Since that time, two divergent lines of evidence and thought have emerged regarding whether the criterion for chronic exposure (5 μg/L) is adequate to protect aquatic life. The first line supports the position that the criterion is too high and should be lowered. For example, Winter Stress Syndrome in fish-a disruption of the normal annual cycle of metabolic and physiological changes in cold weather-can substantially increase their sensitivity to selenium and causeconcentrations approaching the criterion value to become toxic (Lemly, 1993a, 1996). In the western United States, selenium resulting from agricultural irrigation has bioaccumulated to toxic levels in food chains and poisoned fish and aquatic birds when waterborne concentrations were well below 5 μg/L (e.g., Hallock and Hallock, 1993; Hamilton *et al.*, 1996; Lemly, 1995a; Stephens *et al.*, 1992; Skorupa and Ohlendorf, 1991). The second line of evidence supports the position that the criterion is too low and should be raised. For example, faunal surveys in Colorado streams revealed the presence of abundant fish populations where waterborne selenium consistently exceeds the criterion. These observations have led some to conclude that the national criterion is overly conservative and that it should be relaxed by as much as 26 μg/L in some locations (e.g., Guglielmone, 1995; Canton and Van Derveer, 1997; Van Derveer and Canton, 1997). The principal disagreements between these two schools of thought were recently discussed by Hamilton and Lemly (in press).

The ongoing controversy over whether the EPA criterion is too high or too low makes a very important point. Regardless of what the national criterion is, there will likely be a concerted effort by some to raise or lower it. EPA policy allows the national criterion to be modified by states on a site-specific basis when biological evidence warrants it (Stephan et al., 1985; USEPA, 1985). Such modifications have been pursued; local criteria-below 5 μg/L in some instances and above 5 μg/L in others-are being considered or have been adopted in several western states, for example, Arizona, California, Colorado, and New Mexico (Arizona, 1992; CEPA, 1992; CSWRCB, 1987; Guglielmone, 1995; New Mexico, 1995). However, there is no widely accepted or published method for site-specific criterion revision-by EPA or other sources-that is targeted specifically at

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selenium. Consequently, criteria are being developed with little pertinent direction or guidance, which has caused some to use insufficient data and make assumptions about fish and wildlife exposure/effects that could introduce significant error into the derivation process (Lemly, 1997a; Hamilton and Lemly, in press). This type of error has important implications. A derivation might indicate that changing a criterion is appropriate when, in fact, it is not environmentally acceptable (raising) or biologically necessary (lowering) to do so. A scientifically credible method is needed that can be broadly and uniformly applied, yet is sensitive to selenium's site-specific variations in environmental cycling and biological effects. The procedure described in this paper was developed to address that information need.

RATIONALE

There are two primary considerations in developing site-specific water quality criteria for selenium: (1) local conditions must be evaluated and the resultant information used to decide if a modified criterion is necessary and (2) if changes are warranted, the existing or proposed criterion must be modified by an appropriate amount. A simple, two-step process is proposed for deriving criteria for chronic exposure.

The major principle underlying this process is that reproductive effects in fish and aquatic birds are the most sensitive biological indicators of aquatic ecosystem-level impacts of selenium (Lemly, 1993b,c,1997b,c; Ohlendorf, 1989; Skorupa *et al.*, 1996). Selenium is passed from parents to their offspring in eggs, where it can kill developing embryos outright or induce a variety of lethal or sublethal teratogenic deformities (e.g., Hoffman *et al.*, 1988; Lemly, 1993c). However, parents can consume a selenium-laden diet and experience partial or complete reproductive failure without exhibiting symptoms of selenium toxicosis themselves (Lemly, 1985a,1997c; Ohlendorf, 1989). Moreover, aquatic food organisms of wildlife strongly bioaccumulate selenium—hundreds to thousands of times the waterborne concentration-but are unaffected by tissue residues that are high enough to cause reproductive failure when consumed by fish and aquatic birds (Lemly, 1985a). Thus, bioaccumulation in aquatic food chains and dietary transfer to eggs cause otherwise innocuous concentrations of waterborne selenium to become toxic. Establishing water criteria that prevent this degree of bioaccumulation in aquatic food chains is the goal of the procedure given in this paper.

The presence or absence of reproductive effects, coupled with information on the degree of accumulation in major ecosystem components, can be used to precisely evaluate local conditions and derive an appropriate site-specific water quality criterion for selenium. This process can be applied consistently and uniformly, regardless of location or habitat type-i.e., in wetlands (seasonal or permanent), streams, rivers, lakes, reservoirs, and other impoundments.

PROCEDURE

Step One

The first step involves gathering information on selenium residues and biological effects. This is done to provide an empirical foundation for evaluating a criterion, which may be national, state, or local, and which may be currently in place or under consideration. A decision tree (Fig. 1) is used to guide the process. It specifies what types of information are necessary for the evaluation and also identifies conditions under which the criterion should be modified. The selenium criterion value is examined in the context of site-specific selenium concentrations and observed or potential toxicity to fish and aquatic birds. Several outcomes and conclusions are possible-the criterion may be appropriate as it is, or it may be inappropriate and need to be raised or lowered. Guidance for measuring selenium residues and interpreting tissue concentrations and biological effects thresholds is available in Table 1 and Fig. 1. If the empirical evidence indicates that a revised criterion is necessary (guided by the decision tree), the investigator should proceed with step two.

Step Two

A simple procedure is followed to determine what the new criterion should be. This technique is based on relationships between the degree of bioaccumulation present at the site (measured selenium residues), the known threshold concentrations for reproductive effects in fish and wildlife (diagnostic residues for teratogenesis and embryo mortality), and any observed reproductive impacts at the site (teratogenesis or embryo mortality).

A more restrictive (lowered) criterion is indicated when the existing or proposed criterion value for waterborne selenium is *not* exceeded, but site-specific residues equal or exceed diagnostic toxic thresholds and reproductive effects are observed. The criterion value should be lowered by an amount that corresponds to the magnitude of bioaccumulation present. Three sets of conditions are possible-each signifies a different level of toxic threat which, in turn, indicates a different amount of revision to the criterion: (1) If residue values fall partly below the threshold toxic ranges (see Diagnostic residue, Table 1) and partly withm the threshold toxic ranges, then the criterion should be lowered by 25%; (2) If residue values fall entirely within the threshold ranges or span the ranges such that some are below, some are within, and some are above, then the criterion should be lowered by 50%; or (3) If all of the residue values exceed the upper end of the threshold ranges then the criterion should be lowered by 75%. Criteria are lowered by an amount that is proportional to the degree of biological hazard present. This process is followed in each instance when a more restrictive criterion is indicated.

No change in the criterion is necessary if: (1) the criterion is not exceeded and no selenium problem is suspected; (2) the criterion is not exceeded, a selenium problem is suspected (diagnostic residues may or may not be present), but there are no reproductive effects; (3) the criterion is exceeded and residues exceed or fall within the toxic threshold ranges or are above the ranges for uncontaminated aquatic systems (Table 1); or (4) the criterion is exceeded, residues are within the ranges for uncontaminated systems, but down-gradient impacts are possible (Fig. 1).

If the residues fall within the ranges of values for reference conditions in uncontaminated systems, yet the existing or proposed criterion value is exceeded, then it may be reasonable to consider raising it. However, raising a criterion is contingent upon firmly establishing that there would be no down-gradient impacts to other aquatic systems, wetlands, or selenium-sensitive species of fish and aquatic birds. If these requirements are met, then the criterion should be raised by 50%. In summary, criteria can be left unmodified, adjusted upward by a fixed amount (50%), or adjusted downward by one of three amounts (25, 50, or 75).

Modified criterion values should be rounded to the nearest 0.5 μg/L. A criterion that falls equidistant from two values is rounded down if the criterion is being lowered and up if the criterion is being raised. For example, a criterion of 5 μg/L that is lowered by 25% (1.25 μg/L) becomes 3.5 μg/L (5.0–1.25 = 3.75, rounded down to 3.5). Lowering the same criterion by 50% yields a value of 2.5 μg/L, and lowering it by 75% results in a final criterion of 1.0 μg/L (1.25 rounded down to 1.0). Criteria that are raised are modified by adding 50% of the criterion value and then rounding up, if necessary, to determine the final value. In theory, criteria could be set at smaller intervals, e.g., 0.1 μg/L. However, it would likely be impossible to scientifically justify or reliably monitor and enforce such criteria. For example, the range of bioaccumulation and effects displayed among fish and aquatic birds (even among the most sensitive species) would offset the perceived benefits of setting criteria at 2.2 and 2.6 μg/L rather than 2.0 and 2.5 μg/L. Rounding to 0.5 μg/L intervals should accomplish the goal of criterion revision—i.e., achieve the desired reduction or prevention of selenium bioaccumulation/effects in aquatic ecosystems—yet also be practical for monitoring, compliance, and treatment/remediation considerations. Diagnostic selenium residues and examples of measured concentrations/effects and appropriate modifications to criteria are given in Table 1.

JUSTIFICATION

What Is an Appropriate Modification of a Criterion?

The main objective of the procedure given in this paper is to modify a criterion (by default, the EPA national criterion) by an *appropriate* amount. Appropriate, as used here, is the extent necessary to prevent bioaccumulation from reaching levels that induce toxic effects in fish and wildlife. A criterion that is appropriate will be both effective and reasonable—i.e., it will provide the needed level of protection to on-site biota and down-gradient habitats without being too conservative or too liberal. This translates to a criterion which neither requires that reference conditions be achieved in every instance nor permits toxic impacts to biota. For example, in situations when a criterion is not exceeded and diagnostic residues are present but no effects are evident, the decision tree indicates that no modification is necessary (Fig. 1). Conversely, when diagnostic residues are present without effects but the criterion is exceeded, no change is indicated. This, in effect, sets two major conditions for triggering criterion modification: (1) diagnostic residues and toxic effects must be coupled (present) in order to lower a criterion, and (2) diagnostic residues and toxic effects must be coupled (absent) in order to raise a criterion. Coupling residues and effects makes the procedure sensitive to the natural inter- and intraspecific variation in bioaccumulation and toxic responses exhibited by fish and wildlife in aquatic ecosystems.

An additional precaution is necessary if the scenario under evaluation consists of nonexceeded criterion, diagnostic residues present, but no observed toxic effects. In this case the recommended decision is to monitor reproduction but not lower the criterion. However, it is essential that all of the fish and aquatic bird species that are characteristic of the site—i.e., typical for the habitat type and are commonly found in nearby reference locations-be included in the assessment of "effects." Selenium-sensitive species can experience reproductive failure and be virtually eliminated, while at the same time some of the most tolerant species remain and only exhibit elevated tissue residues (Lemly, 1985a). This scenario could lead to the false impression that there are no effects and thus no need to lower the criterion when, in fact, selenium-sensitive species have been severely affected. This type of error is also possible when the scenario consists of exceeded criterion but no diagnostic residues or toxic effects among the species that are present. It is possible that sensitive species have been eliminated and the tolerant species that remain exhibit very low bioaccumulation, which may partially explain their ability to tolerate selenium. This could lead to the false assumption that increasing the criterion is appropriate. Thus, in certain situations the biota that "should be pesent" must be considered, particularly if they represent known selenium sensitive species, in addition to what is actually present.

Why Use Percentages and Ranges.7

Percentages are used because this appears to be the simplest practical way of modifying criteria while also addressing the main objective from both an ecological and

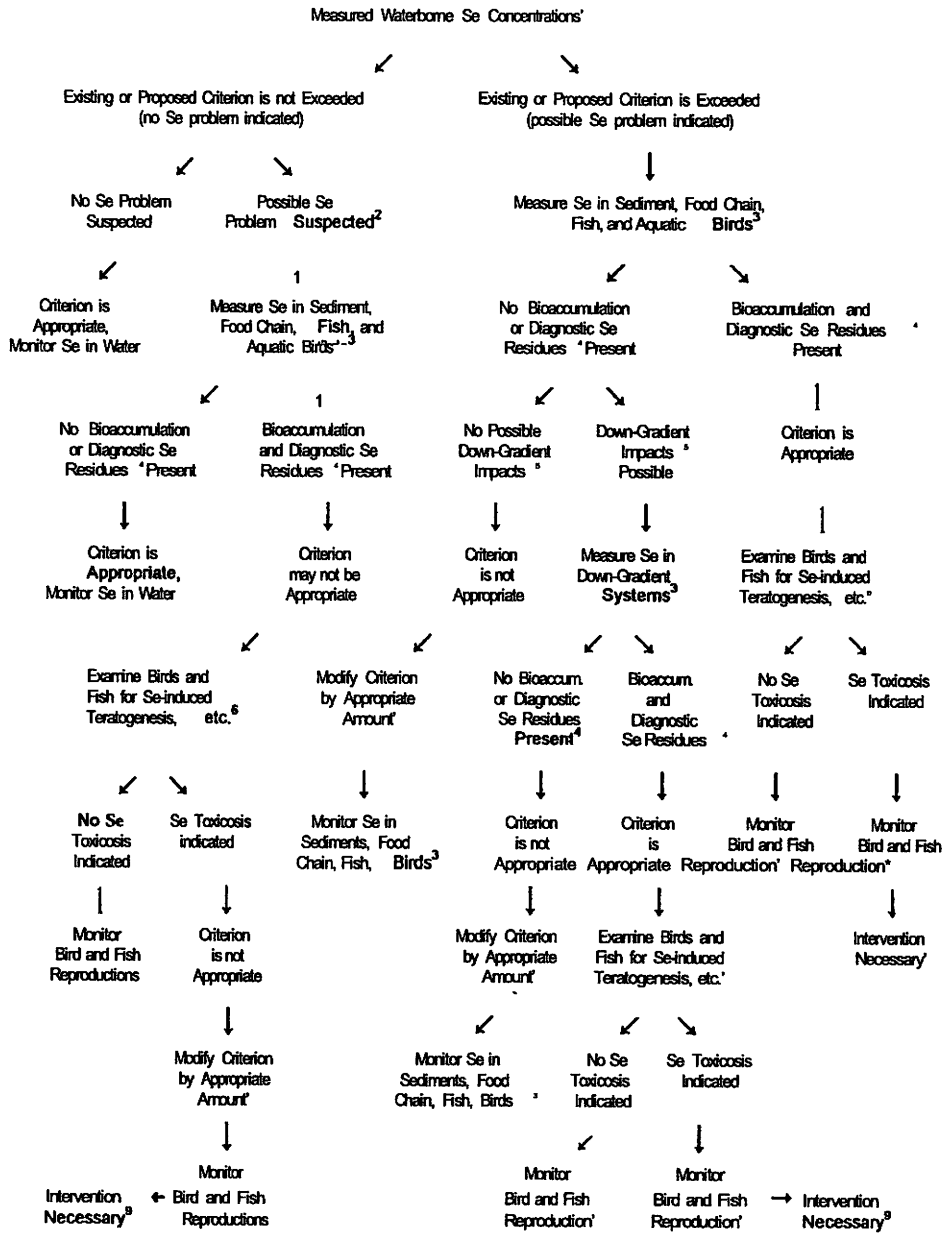

FIG. 1. A decision tree for determining if modification of a selenium water quality criterion is necessary. Numbers indicate the following: '[1]A sufficient number of samples to provide some spatial and temporal integration; '[2]Possible problem suspected based on observations and available mformation collected from the site: '[3]Measurements according to guidelines and procedures given by Lemly (1995b) and Skorupa and Ohlendorf (1991); '[4]Residues that equal or exceed the toxicity thresholds given in Table 1; '[5]Down-gradient impacts to other aquatic systems, wetlands, or selenium-sensitive species in the watershed, including confluence with receiving waters that cross state lines or other Jurisdictional boundaries; [6]Teratogenic deformities and/or embryo mortality, measured according to guidelines and procedures given by Lemly (1993c, 1997b), Hoffman *et al.* (1988), and Ohlendorf et *al.* (1986a, 1986b, 1988); '[7]Modify according to procedures given in the text: '[8]Monitor for evidence of teratogenic deformities and/or embryo mortality and associated selenium residues in eggs, embryos, and larvae: and [9]Regulatory and management actions to effectively control or modify the source of selenium.

a regulatory perspective. The decision tree specifies that selenium concentrations and effects should be monitored in each case when criterion modification is indicated (Fig. 1). It will quickly become apparent if a criterion derived using the percentage method is too conservative or too liberal. The monitoring requirements in the decision tree function as feedback loops that provide an ongoing field test of the effectiveness of the criterion. On-site monitoring of residues

TABLE 1
Selenium Residues that Signify the Thresholds for Reproductive Effects in Fish and Aquatic Birds

Type of Sample	Diagnostic residue[a,b] (reference[c])	Measured concentration[b] and toxic effect	Appropriate change to a criterion of 5 μg/L[d]
Sediments	2–4 (< 1)	1–5, no effect	None
Food chain[e]	2–4 (< 2)	3–8, embryo mortality in birds	Lower by 2.5 μg/L (50% decrease)
Fish			
Whole-body	5–7 (< 3)	6–9, no effect	None
Muscle (fillets)	6–8 (< 3)	5–10, no effect	None
Liver	15–20 (< 8)	4–7, no effect	None
Eggs	5–10 (< 3)	6–17, terata	Lower by 2.5 μg/L (50%)
Larvae/fry	8–12 (< 3)	5–12, terata	Lower by 1.5 μg/L (25%)
Aquatic birds			
Muscle	15–20 (< 3)	7–19, no effect	None
Liver	20–30 (< 10)	23–32, terata	Lower by 2.5 μg/L (50%)
Eggs	6–15 (< 3)	4–9, no effect	None
Embryos	10–15 (< 3)	16–25, terata	Lower by 4.0 μg/L (75%)

Note. Site-specific concentrations and biological effects are compared to diagnostic residues to determine if modification of a water quality criterion is necessary. The measured concentrations and indicated changes are given as examples of how to appropriately lower a criterion of 5 μg/L, assuming that site-specific waterborne concentrations are below or equal to 5 μg/L. Consult Fig. 1 and the text for guidance on raising criteria.

[a]Residues that indicate ecosystem contamination is sufficient to cause reproductive impairment of fish and aquatic birds (teratogenic deformity and/or mortality of embryos and larvae/fry).

[b]All values are in μg/g (parts-per-million) dry weight. Values for reference and contaminated habitats were compiled from data given by Hoffman *et al.* (1988), Lemly (1985a, 1993b, 1993c, 1997b, 1997c), Ohlendorf (1989), Ohlendorf *et al.* (1986a, b, 1988), Skorupa and Ohlendorf (1991), and Skorupa et *al.* (1996).

[c]Concentrations typical for uncontaminated aquatic systems.

[d]Lowering a criterion is indicated only if reproductive effects are present in combination with diagnostic residues; raising a criterion is indicated only if there are no effects, reference levels of residues are present, and there are no possible down-gradient impacts (Fig. 1).

[e]Organisms commonly utilized as food by fish and wildlife, such as macroinvertebrates, aquatic plants and seeds, and forage fish.

and biological effects is an essential part of the validation process for site-specific criteria.

There is a very narrow range between typical reference waterborne concentrations of selenium in aquatic systems (0.1-0.3 μg/L), those that can cause bioaccumulation and toxicity in fish and wildlife (1–3 μg/L), and the current national and state criteria for selenium (2-20 μg/L). Moreover, the values for site-specific criteria that are likely to be developed by states and approved by EPA probably fall within the range 1-20 μg/L. Within this narrow range, the most straightforward way to address necessary changes in environmental selenium residues is by using percentages (25, 50 and 75%) that are linked to different degrees of biological effects. This technique is appropriate because the magnitude of teratogenic deformity and/or embryo mortality, and resultant ecosystem-level impacts to fish and aquatic birds, are distinctly greater in cases when a 75% reduction in a criterion is indicated (all residues greater than upper end of the toxicity threshold ranges) than when a 25% reduction is indicated (residues partly below and partly within the threshold ranges).

The use of ranges for threshold values rather than a single number makes the criterion modification process sensitive to natural variation in bioaccumulation and toxic responses of biota. It prevents the process from being overly conservative in cases when a lowered criterion is indicated. Using reference values prevents the process from being too liberal in cases when it is appropriate to raise a criterion. Increases are contingent upon finding reference levels of bioaccumulation. Thus, modification is always linked to a "no effect" range. Allowing a 50% increase in a criterion is reasonable if there is no evidence of bioaccumulation or threats to downgradient systems. Moreover, the feedback loop provided by monitoring will indicate if further revisions (upward or downward) should be undertaken once a criterion is raised by this amount. This is also true for criteria that are lowered. It is possible that more than one revision will be necessary before an appropriate criterion is achieved.

IMPLEMENTING CRITERIA

EPA provides states the option of developing site-specific criteria and regulations governing their implementation if adequate justification is given. Establishing criteria that are sensitive to selenium's local variations in aquatic cycling and toxic effects should be the goal of the derivation process at the state and local levels. The main purpose of this paper is to provide a procedure for deriving criteria at those levels.

However, it is also important to consider how criteria will be implemented and enforced-i.e., whether there will be provisions for averaging concentrations over several days in order to meet criterion levels, whether periodic exceedance of criteria will be allowed, and whether mixing zones will be used to dilute effluents and achieve criterion concentrations. In many cases, states may choose to follow the example set by EPA (e.g., Stephan *et al.*, 1985; USEPA, 1985, 1987), which allows averaging, exceedances, and mixing zones to factor into the implementation of criteria. However, the guidance provided by EPA is generic and can greatly reduce the effectiveness of site-specific selenium criteria. It is essential that selenium's profile of environmental cycling and toxicity be used to formulate implementation policies at state and local levels. There are several important precautions that should be taken by water quality regulators if they intend to rely on EPA guidance documents to implement site-specific selenium criteria.

EPA guidelines allow the national criterion for chronic exposure to be exceeded periodically (once every 3 years, on average) as long as the 4-day average concentration is 5 μg/L or less (USEPA, 1987). During exceedances, the permissible ambient (ecosystem-wide) waterborne concentration can be as high as 20 μg/L (Fig. 2). Stephan *et al.* (1985) gives the rationale for this approach: "the averaging period of four days was selected by the U.S. EPA on the basis of data concerning how rapidly some aquatic species react to increases in the concentrations of some pollutants, and three years is the Agency's best scientific judgement of the average amount of time aquatic ecosystems should be provided between excursions." The wording of the statement reveals that this is a generic model for contaminant exposure-response and associated derivation of criteria—i.e., the words "some aquatic species" and "some pollutants." The EPA model is flawed when applied to selenium because little, if any, data specific to selenium were used to develop it in the early 1980s, and no attempt has been made by the Agency to test or validate its assumptions using selenium data that have become available since that time.

Some of the specific flaws that invalidate the EPA model when it is applied to selenium are: (1) The EPA guidance document clearly indicates that the process for national criteria is molded to fit wastewater treatment facilities (POTWs) that discharge a point source into a flowing receiving water (Stephan *et al.*, 1985, pp. 11–12). However, the most widespread threats of selenium poisoning in aquatic life are in lentic systems (reservoirs, wetlands, and off-channel bays and impoundments) and are due to selenium sources other than POTWs (Lemly, 1993b). The environmental dynamics of selenium in lentic ecosystems are quite different than the riverine conditions used for the EPA model. (2) The 4-day average is based on organism responses to waterborne exposure alone. However, food chain bioaccumulation and dietary intake resulting from short-term pulses are

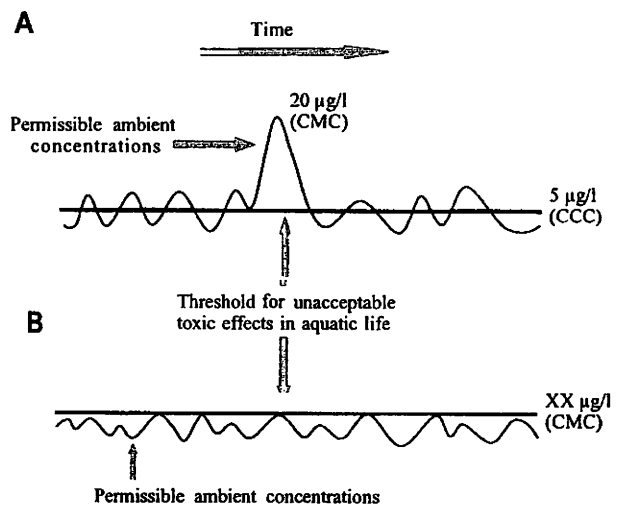

FIG. 2. Contrasts between the existing EPA national water quality criterion for selenium (chronic exposure, A) and the process for deriving site-specific criteria (this paper, B). A principal difference is that in implementing national criteria, EPA guidelines allow 4-day averages and exceedances up to the Criterion Maximum Concentration (CMC, 20 μg/L). This can offset the protection to aquatic life that is afforded by the Criterion Continuous Concentration (CCC, 5 μg/L). To provide full protection, site-specific criteria set biologically based concentration limits as the CMC and do not make provisions for averages, exceedances, or mixing zones (see text for details).

equally or perhaps more important in causing selenium toxicity to aquatic life (Lemly, 1985a, 1993b, 1997c). This component of selenium cycling is overlooked in the EPA model. Moreover, exposure-bioaccumulationresponse times for selenium in fish and aquatic birds (waterborne or dietary intake) are on the order of weeks or months rather than 4 days (e.g., Lemly, 1982, Heinz *et al.*, 1988; Coyle *et al.*, 1993; Heinz and Fitzgerald, 1993)—the EPA model assumptions are not correct. (3) The concentrations of waterborne selenium allowed by EPA during exceedances (up to 20 μg/L) are not environmentally acceptable for lentic systems or lotic systems that will deliver selenium into off-channel bays, wetlands, reservoirs, or other down-gradient lentic systems. Studies such as those by Cumbie and Van Horn (1978), Bryson *et al.* (1984), Lemly (1985), Gillespie and Baumann (1986), and Hamilton *et al.* (1996) reported that concentrations of 10–20 μg/L can quickly reach dietary levels that are toxic to fish and aquatic birds. Consider, for example, a scenario in which an exceedance causes waterborne selenium in a reservoir or wetland to reach 15 μg/L—an acceptable concentration in the EPA model (Fig. 2). By the time ambient locations reach this level, the entire "bioaccumulation engine" of the ecosystem will have been fueled by the influx of new selenium, which substantially escalates the toxic threat to aquatic life (Lemly, 1985b). (4) The 3-year period between excursions (exceedances),

although perhaps reflecting the best scientific judgement available for *some* pollutants in the early 1980s, is not appropriate for selenium. Once an aquatic ecosystem has captured the selenium dose delivered by an exceedance, it can continue to cycle it tightly within the system for many years. For example, studies indicate that the recovery period for reservoirs contaminated by 10 μg/L selenium could be > 10 years, perhaps several decades, due to recycling of selenium from sediments into benthic–detrital food chains and associated dietary and reproductive toxicity to fish (Garrett and Inmann, 1984; Lemly, 1997c).

Similar problems are evident with the use of dilution or mixing zones, which are areas exempt from ambient criteria. This concept was developed for application to flowing waters (Stephan *et al.*, 1985). It has no credible basis for application to selenium in lentic/wetland systems because the "dilution zone" may constitute the entire body of open water. Even in riverine habitats, the notion of mixing zones is a totally artificial process because EPA has not referenced data verifying that a mixing zone can effectively dilute a selenium-laden effluent and also be environmentally compatible with fish and wildlife habitat uses, which it must be under Federal statutes such as the Migratory Bird Treaty Act and the Endangered Species Act (Margolin, 1979). Selenium strongly bioaccumulates in food organisms and makes the dilution zone an area of extremely high exposure for fish and wildlife. On the contrary, several case studies found that using mixing zones to dilute seleniferous water creates more biological hazards than it resolves (e.g., Skorupa, 1998). The apparent benefits gained by achieving target concentrations in a mixing zone may be more than offset by detrimental effects that are caused by other aspects of the selenium cycle. The threat of toxic impacts overrides the need to attempt "dilution as a solution."

Given these flaws, it is important to closely examine the rationale for, and distinction between, national and site-specific criteria. EPA criteria are intended to provide protection for most aquatic species most of the time, not everything all of the time (Stephan *et al.*, 1985). Because of this basic caveat, as well as the fact that there are differences in ecosystem and aquatic species sensitivity to selenium, there may be a plausible argument for allowing some leeway in meeting the national criterion-i.e., a reasonable averaging of concentrations over time if monitoring indicates that there are no biological effects (but not 20 μg/L exceedances). However, at a local level, the national criterion's intent to protect "most species" still leaves large gaps that could lead to substantial inconsistencies (toxic effects at or below the criterion level, lack of effects above the criterion). Site-specific water quality criteria should reflect the sensitivity of local biota and close the gaps.

Site-specific criteria for selenium should designate a biologically based concentration limit using the procedure described in this paper (Figs. 1 2). If full protection of aquatic life is desired, then there should be no provision for averages, exceedances, or mixing/dilution zones in the implementation of criteria.

EXAMPLES OF CRITERION DERIVATION

Example 1-Lowering a Criterion

The existing criterion is 5 μg/L and the following site-specific information is available (μg/g concentrations are in dry weight):

Waterborne concentrations of selenium are 1–3 μg/L.

Concentrations of selenium in sediments are 224 μg/g.

Concentrations of selenium in aquatic food-chain organisms are 1–7 μg/g.

Concentrations of selenium in randomly sampled aquatic bird eggs are 4412 μg/g.

Teratogenic deformities occurred in 2% of randomly sampled aquatic bird eggs.

Embryo mortality occurred in 4% of randomly sampled aquatic bird eggs.

Concentrations of selenium in whole-body samples of fish are 6610 μg/g.

Teratogenic deformities occurred in 5% of fish from ichthyoplankton samples.

Concentrations of selenium in ichthyoplankton samples are 8-12 μg/g.

Evaluation. The site-specific residues span the toxic threshold ranges-some are below, some are within, and some are above-and reproductive effects are present.

Conclusion. These conditions warrant a 50% (2.5 μg/L) reduction in the criterion. The final criterion for chronic exposure is set at 2.5 μg/L.

Example 2—Raising a Criterion

The existing criterion is 5 μg/L and the following site-specific information is available (μg/g concentrations are in dry weight):

Waterborne concentrations of selenium are 5-12 μg/L.

Concentrations of selenium in sediments are < 1 μg/g.

Concentrations of selenium in aquatic food-chain organisms are < 2 μg/g.

Concentrations of selenium in randomly sampled aquatic bird eggs are < 3 μg/g.

Teratogenic deformities occurred in 0% of randomly sampled aquatic bird eggs.

Embryomortality occurred in < 1% of randomly sampled aquatic bird eggs.

Concentrations of selenium in whole-body samples of fish are < 3 μg/g.

Teratogenic deformities occurred in 0% of fish from ichthyoplankton samples.

Concentrations of selenium in ichthyoplankton samples are < 3 μg/g.

Evaluation. The site-specific residues were equivalent to reference levels and no reproductive effects were evident. Samples from down-gradient receiving waters and wetlands indicated the same pattern-no bioaccumulation or effects.

Conclusion. The criterion for chronic exposure should be raised by 50%, to a final value of 7.5 μg/L.

Example 3—No Modification Necessary

The existing criterion is 5 μg/L and the following site-specific information is available (μg/g concentrations are in dry weight):

Waterborne concentrations of selenium are 2-5 μg/L.

Concentrations of selenium in sediments are 1-4 μg/g.

Concentrations of selenium in aquatic food-chain organisms are 1-6 μg/g.

Concentrations of selenium in randomly sampled aquatic bird eggs are 2–8 μg/g.

Teratogenic deformities occurred in 0% of randomly sampled aquatic bird eggs.

Embryo mortality occurred in < 1% of randomly sampled aquatic bird eggs.

Concentrations of selenium in whole-body samples of fish are 3–6 μg/g.

Teratogenic deformities occurred in 0% of fish from ichthyoplankton samples.

Concentrations of selenium in ichthyoplankton samples are 3-8 μg/g.

Evaluation. Residues of selenium are at toxicity thresholds but no reproductive effects are evident (the fraction of a percentage of embryo mortality present is considered a background level and not due to selenium).

Conclusion. *No* change to the criterion for chronic exposure is indicated but monitoring of bird and fish reproduction—i.e., sampling for evidence of teratogenesis and embryo mortality-and associated selenium residues is recommended.

Example 4-Examining a Proposed Criterion

The proposed criterion for chronic exposure is 15 μg/L and the following site-specific information is available (μg/g concentrations are in dry weight):

Waterborne concentrations of selenium are 10–20 μg/L.

Concentrations of selenium in sediments are 1-2 μg/g.

Concentrations of selenium in aquatic food-chain organisms are 1–3 μg/g.

Concentrations of selenium, terata, and embryo mortality in randomly sampled aquatic bird eggs are unavailable because few aquatic birds nest at the site.

Concentrations of selenium in whole-body samples of fish are 2-5 μg/g.

Teratogenic deformities occurred in 0% of fish from ichthyoplankton samples.

Concentrations of selenium in ichthyoplankton samples are 3-6 μg/g.

Possible impacts to down-gradient systems-unknown.

Evaluation. *No* reproductive effects are evident in fish and potential threats to aquatic birds are likely minimal because few of them were found to nest or feed at the site. However, the habitat usage and selenium status of down-gradient receiving waters and associated wetlands have not been characterized. Moreover, concentrations of selenium in fish are at the lower end of the diagnostic toxicity range.

Conclusion. The proposed criterion of 15 μg/L is rejected because of possible threats to down-gradient systems, as well as the presence of elevated selenium residues in fish and food-chain organisms. Monitoring of selenium residues in fish and down-gradient systems is recommended.

CONCLUSIONS

During the past two decades, selenium has gained widespread attention as an important aquatic contaminant, and it is currently classified as one of EPA's priority pollutants. EPA published a revised (lowered) national freshwater criterion for selenium in 1987 but there is considerable disagreement as to the applicability of the national criterion at a state and local level-some believe it should be lowered, some believe it should be raised. This has led to more and more instances of states and municipalities attempting to develop site-specific criteria. However, there are no published or widely accepted methods available from EPA or other sources that give specific guidance for selenium. The procedure given in this paper should fill that information gap. It provides a simple, straightforward method for using information on the selenium status of aquatic ecosystems and resultant threats/impacts to biota as the basis for deriving criteria. The method should be a useful tool for those involved in water quality assessment and regulation throughout North America and abroad.

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A Procedure for Setting Environmentally Safe Total Maximum Daily Loads (TMDLs) for Selenium

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This article presents a seven-step procedure for developing environmentally safe total maximum daily loads (TMDLs) for selenium. The need for this information stems from recent actions taken by the U.S. Environmental Protection Agency (EPA) that may require TMDLs for selenium and other contaminants that are impairing water bodies. However, there is no technical guidance from EPA or elsewhere that deals exclusively with selenium. This leaves biologists and environmental contaminant specialists without the tools needed to effectively address the TMDL issue for selenium. This article provides guidance by laying out an assessment method that links the basic components of EPA's TMDL process to the contaminant-specific information required for selenium. The underlying principle in this process is that selenium concentrations be kept below levels that threaten reproduction of fish and aquatic birds. The steps are: (1) Delineate and characterize the hydrological unit (HU, i.e., water body) of interest. (2) Determine selenium concentrations and assess biological hazard. (3) Determine sources, concentrations, and volumes of selenium discharges; calculate existing selenium load. (4) Estimate retention capacity of HU for selenium. (5) Calculate the total allowable selenium load and specify reductions needed to meet the target loading. (6) Allocate selenium load among discharge sources. (7) Monitor to determine effectiveness of selenium load reduction in meeting environmental quality goals. Proper application of this procedure will ensure compliance with EPA regulatory requirements and also protect fish and wildlife resources. © 2002 Elsevier Science (USA)

INTRODUCTION

This article was prepared to provide field biologists, environmental contaminant specialists, and natural resource managers with a step-by-step procedure for developing total maximum daily loads (TMDLs) for selenium. The need for this information stems from recent actions taken by the U.S. Environmental Protection Agency (EPA) that may require TMDLs on impaired water bodies. For many years, water quality regulations in the United States have been implemented through point-source control programs such as the National Pollution Discharge Elimination System (NPDES) permit system. Recently, the USEPA has placed more emphasis on characterizing and reducing nonpoint sources of pollution to provide watershed-level improvement of water quality. This approach, know as total maximum daily loads, sets a limit on the total aggregate amount of a contaminant allowed in an aquatic system. The objective of TMDLs is to identify all pollution sources and then allocate/regulate discharges to meet the water quality needs of aquatic life within a watershed. The states are required to identify impaired water bodies to comply with Section 303(d) of the Clean Water Act. The USEPA is working with states and implementing the TMDL process as a way to gauge point and nonpoint sources of pollution, control/reduce discharges, and improve overall water quality pursuant to the requirements of Section 303(d). The EPA has requested that state and federal biologists provide input in this process for substances ranging from nutrients and sediments to pesticides and trace elements such as selenium. Every substance identified as a priority must be given a separate TMDL assessment, and this must be done independently for each impaired water body. The biologist's role may range from a simple review and recommendation based on available information to coordination/conduct of field work to assess contaminant cycling and fate, fish and wildlife exposure, toxicity, etc., involving considerable time and resources.

The magnitude of this effort becomes apparent when one considers that each state may have dozens to hundreds of impaired water bodies that will need TMDLs, many of which could involve selenium because of its widespread concern as a water quality issue (Lemly et *al.*, 1993; Lemly, 1999a). Although USEPA has published an overview document that explains principles underlying the development and implementation of TMDLs (USEPA, 1999), no procedures specific to selenium are given. This leaves biologists and environmental contaminant specialists without the assessment framework necessary to effectively address the TMDL issue for selenium. Due to selenium's propensity to

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bioaccumulate and cause reproductive impairment in fish and wildlife, and persist in the environment, selenium-specific methods are needed. It is critical to have a technically sound approach for evaluating selenium because it is considered a priority contaminant by natural resource managers and USEPA. Moreover, proposing TMDLs for this trace element is likely to generate attention by groups with widely divergent interests, who could challenge the validity of the techniques used. This article provides guidance by laying out an assessment method that links the basic components of EPA's TMDL process to the contaminant-specific information necessary for selenium. The hazard assessment procedures and interpretive guidelines used in the method have all been published in the peer-reviewed literature.

PROCEDURE

The method presented here is structured to answer two basic questions:

1. Is selenium impairing the water body based on biological criteria,
2. If so, what amount of selenium load reduction is necessary to correct the problem?

A seven-step procedure can be used to answer these questions and develop environmentally safe TMDLs for selenium. The basic premise in this approach is that selenium concentrations be kept below levels that threaten the reproduction of fish and aquatic birds.

Step 1: Delineate and Characterize the Hydrological Unit (HU) of concern

TMDLs for selenium should be based on an assessment of the degree of toxicological hazard to fish and wildlife, which is influenced by the hydrology of the site under consideration. The physical area from which measurements are taken to evaluate selenium concentrations and biological threats/effects, i.e., the database for setting TMDLs, must encompass more than an isolated segment of a river, a tributary stream, etc. Because of hydrological connections between the various aquatic habitats that may be present in a watershed basin-wetlands, rivers, streams, lakes, and impoundments- -the toxic threat from selenium contamination is also connected. For example, a TMDL that is set for a stream or river where low bioaccumulation occurs may result in *seemingly* harmless concentrations becoming a problem in downstream impoundments or in off-channel bays and wetlands where bioaccumulation is greater.

The hydrologically connected parts of a basin that are downgradient of a selenium input (natural or anthropogenic selenium source), extending to the point at which new sources of low-selenium water dominate the hydrology and

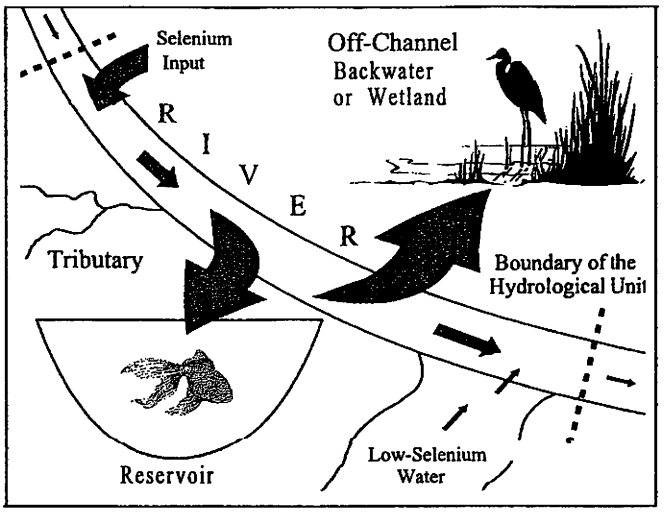

FIG. 1. Illustration of the "hydrological unit" principle. Arrows indicate the relative concentrations of selenium The interconnected parts of a unit may include several types of aquatic habitats, for example, a mainstem river, an off-channel wetland, and a reservoir. The hydrological connections transport selenium throughout the unit and thus greatly influence its bioaccumulation potential. Because of this, the entire hydrological unit should be the "water body" that is used to develop a TMDL for selenium.

lower concentrations below levels of concern (e.g., confluence with a larger tributary or river, spring or groundwater inflow), should be the area evaluated and given a specific TMDL, not isolated parts (Fig. 1). Thus, a hydrological unit (HU) should be identified and used as the "site" for the purpose of setting TMDLs. Importantly, TMDLs derived is this manner will reflect the transport and bioaccumulation of selenium within the entire HU rather than simply focusing on a small, artificially designated segment of the system. Failure to use a HU approach can set the stage for significant biological problems and undermine the intended outcome of the TMDL process. Consult Lemly (1999b) for more information on the rationale and justification for using HUs.

Substitute HU for the term "water body" used by states and USEPA in their TMDL documentation, and use the entire HU as a "mixing zone" for the purpose of evaluating potential selenium transport and bioaccumulation. Characterize and map the aquatic system of the HU using available information in combination with field reconnaissance to identify/verify hydrological connections. Identify all aquatic habitats within the HU: wetlands, streams, rivers, off-channel bays, lakes, reservoirs, other impoundments; map their spatial and gradient/hydrological relationships, i.e., know what flows where and into/out of what. Obtain information on trophic status, prevailing sediment type (organic, inorganic, mixed), and volume replacement times or flushing rates for lakes, reservoirs and other impoundments, bays oft' main-stem rivers, and wetlands; describe general level of primary productivity (low-oligotrophic, moderate-mesot-

rophic, high-eutrophic), predominant flow regime (slow, moderate, swift), and dominant sediment characteristics (depositional, erosional, particle size, organic, inorganic, mixed) of flowing-water habitats. Large rivers merit special attention to identify, map, and describe the variety of habitats that may be present, e.g., main-stem, off-channel bays, seepage or floodplain wetlands. Characterize fish and wildlife uses (feeding, spawning, nesting, migration, etc.) and identify biota of special concern, i.e., endangered or threatened species, management priorities, and selenium-sensitive species (e.g., centrarchid fishes, *Lepomis* sp., *Micropterus* sp.; waterbirds such as stilts, *Recurvirostra* sp.; and ducks, *Anas* sp.). Also, identify habitats where bioaccumulation would likely be greatest (e.g., wetlands, lakes, reservoirs, and other impoundments and off-channel backwater areas of rivers).

Step 2: Determine If Selenium Is Present at Hazardous Levels in the HU

Gather information on selenium concentrations. If there are no recent monitoring data (within the past 3 years), or if the data do not satisfy the following requirements, then it will be necessary to collect and analyze new samples. Selenium concentrations are needed for five ecosystem components: water, sediments, benthic macroinvertebrates, fish eggs, and aquatic bird eggs (use fish/bird tissue to egg conversion factor of 3.3 if no eggs are available; i.e., tissue concentration x 3.3 = approximate egg concentration (Lemly and Smith, 1987). If bird eggs or fish eggs cannot be obtained (but not both missing), a four-component assessment can be done. Collect a minimum of 10 samples of each component in each major habitat type present in the HU (stream, river, off-channel bay, wetland, lake, reservoir, other impoundment). Make sure to designate sampling sites throughout the HU to provide adequate spatial coverage. Maintain high quality assurance/quality control in all sampling and analysis; document QA/QC procedures for future reference. Evaluate selenium concentrations with hazard assessment protocol (Lemly, 1995 for five-component datasets; Lemly, 1996, for four-component datasets) to determine the hazard rating. A rating of low, moderate, or high hazard indicates that the TMDL process should continue. A rating of either minimal or no hazard indicates that TMDL calculations are not necessary, but the HU should bc monitored by applying the assessment protocol to selenium measurements made on a 3-year interval. If monitoring reveals that hazard has increased above the minimal level, TMDL reductions are needed.

Step 3: Determine Selenium Sources, Concentrations, and Discharge Volumes

Identify all possible sources of selenium (agricultural, industrial, petrochemical, mining, etc.) and map them in the HU, noting their proximity/discharge to specific habitat types, i.e., wetlands, streams, rivers, reservoirs. Determine/verify selenium concentrations from each source using existing data or by analyzing new samples; determine/estimate average discharge volume from each source. Calculate total existing selenium loading rate to the HU (kg/day).

TABLE 1

Retention Capacity (RC) Ratings for Selenium in Aquatic Systems Based on Habitat Type and General Biological/Physical Characteristics

	Habitat type		
	Stream, main-stem river	Lake, Reservoir, off-channel bay, impoundment	Wetland
Productivity			
High (eutrophic)	High	High	High
Moderate (mesotrophic)	Medium	Medium	Medium
Low (oligotrophic)	Low	Low	Low
Flow			
Swift	Low	Low	Low
Moderate	Medium	Medium	Medium
Slow	High	High	High
Sediment			
Inorganic	Low	Low	Low
Mixed	Medium	Medium	Medium
Organic	High	High	High

Step 4: Estimate the Retention Capacity of the HU for Selenium

A key part of the TMDL process for selenium is to estimate retention capacity (RC). This will determine the sensitivity of the HU to selenium and, thereby, serve as an indicator of how much selenium the system can tolerate. For the purposes of this paper, KC is defined as the propensity of a system to accumulate and conserve selenium. Components of RC include bioaccumulation, detrital retention, physical and chemical sequestration, and recycling within the HU. The more that selenium is held within a HU—whether incorporated in biota, deposited in sediments, etc.---the higher the RC. It is necessary to know RC to develop an environmentally sound TMDL because the higher the RC, the lower the TMDL has to be to prevent toxic threats to fish and wildlife.

To a large extent, RC depends on the degree of bioaccumulation and internal recycling in the HU, which is reflected in (1) primary productivity, (2) water flow regime, and (3) sediment type. From the characterization of HU done in Step 1 (above), information on these three factors should be available for each aquatic habitat. Use the matrix in Table 1 to assign each of these factors a separate RC rating: low, medium, or high. A rating should be done for

TABLE 2

Amount of Selenium Load Reduction Necessary for a Hydrological Unit (HU) Based on Hazard Rating and Retention Capacity (RC)[a]

	Hazard Rating		
RC of HU	Low	Moderate	High
LOW	Small	Medium	Large
Medium	Medium	Medium	Large
High	Medium	Large	Large

[a]Necessary load reductions = 10% for small, 25% for medium, 50% for large.

each distinct habitat in the HU, i.e., each main-stem river, off-channel bay, stream, wetland, lake, reservoir, and other impoundment.

An overall RC rating for each habitat is determined by combining the three factor ratings as follows:

3 low ratings = low RC
2 low and 1 medium = low RC
2 low and 1 high = medium RC
2 medium and I low = medium RC
2 medium and 1 high = medium RC
3 medium ratings = medium RC
2 high and 1 low = medium RC
2 high and 1 medium = high RC
3 high ratings = high RC

The final RC rating for the HU should be set equal to the highest individual habitat rating. For example, if there are two habitats with low RC and one with medium RC, the final RC rating for the HU is medium.

Step 5: Calculate the Total Allowable Selenium Load

Begin by plugging the hazard rating from Step 2 and the RC from Step 4 into the matrix in Table 2. The table indicates the appropriate amount of load reduction needed: small, medium, or large. The total existing selenium load should be reduced by 10% if the amount designated is small, 25% if it is medium, and 50% if it is large. Subtract the indicated amount from the total existing selenium loading rate (kg/day) calculated in Step 3. This will yield the total allowable selenium load for the HU.

Step 6: Allocate Total Allowable Selenium Load among Discharge Sources

Designate allowable discharges making sure to keep habitat type and sensitive species in mind. For example, it would be inappropriate to allow the largest loading to occur in habitats occupied by priority species (threatened or endangered, or management priority), selenium-sensitive species (e.g., centrarchid fishes, *Lepomis* sp., *Micropterus* sp.; waterbirds such as stilts, *Recurvirostra* sp.; and ducks, *Anus* sp.), or where bioaccumulation would likely be greatest (e.g., in a wetland, lake, reservoir, or off-channel backwater area of a river).

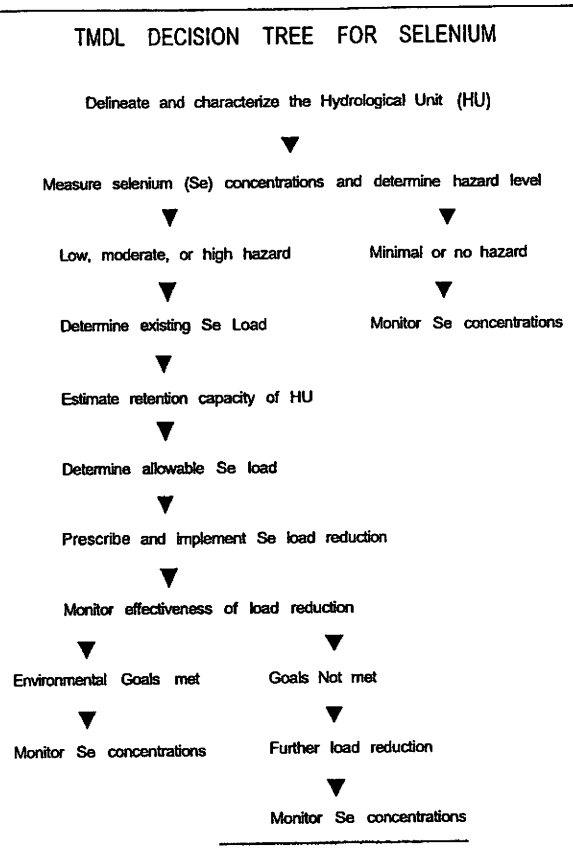

FIG. 2. Steps in the TMDL process for selenium.

Step 7: Monitor to Deter-mine Effectiveness of Selenium Loud Reduction in Meeting Environmental Quality Goals

The objective of the TMDL process is to keep selenium concentrations below levels that are toxic to biota. Therefore, it is important to use environmental quality goals as a guide in follow-up effectiveness monitoring. For this purpose, I recommend that the following guidelines be used as maximum allowable selenium concentrations (Lemly, 1993, 1995):

Water = 2μg/L, filtered samples (0.45 μm)
Sediment = 2 μg/g dry wt
Benthic invertebrates = 3 μg/g dry wt
Fish tissues: whole body = 4 μg/g dry wt
skeletal muscle (skinless fillets) = 8 μg/g dry wt

liver = 12 μg/g dry wt
ovary and eggs = 10 μg/g dry wt
Aquatic bird tissues: liver = 10 μg/g dry wt
eggs = 7 μg/g dry wt

These guideline values represent concentrations that are protective of fish and wildlife reproduction. Monitor selenium residues annually, and apply hazard assessment protocols (same as for Step 2) to determine if hazard is reduced to either the minimal or no hazard level. If it is, then no further load reductions are necessary; conduct environmental monitoring every 3 years. If it is not, repeat Step 5 to determine the additional amount of selenium load reduction necessary, implement load reduction, and monitor annually. The entire TMDL process is summarized in Fig. 2.

CONCLUSIONS

On the surface, the TMDL process may seem to be a formidable EPA regulatory requirement that generates uncertainty and apprehension, and is not easily addressed. Without adequate technical guidance, this may be true in many cases. However, the straightforward, seven-step procedure given in this article takes away the uncertainty and allows environmentally safe TMDLs to be set for selenium. It is important to use this specific method because it is tailored to account for selenium's ability to bioaccumulate and cause reproductive toxicity to fish and wildlife. A key part of the method is the identification and use of a hydrological unit (HU) as the basis for evaluation. The HU approach provides the contaminant-specific site characterization that is necessary for selenium. Proper application of this TMDL technique will ensure compliance with EPA regulatory requirements and also protect fish and wildlife resources.

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SELENIUM SEDIMENT TOXICITY THRESHOLDS AND DERIVATION OF WATER QUALITY CRITERIA FOR FRESHWATER BIOTA OF WESTERN STREAMS

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Abstract—Waterborne and sediment selenium (Se) data, in conjunction with selected physicochemical parameters, were collected from streams of the middle Arkansas River basin, Colorado, USA, to examine the factors affecting sediment Se accumulation in a lotic environment. An empirical model of dissolved-to-sediment Se transfer in western streams, as an interactive function of sediment organic carbon content ($R^2 = 0.78$, $p < 0.001$, $n = 34$), was developed and validated. Sediment Se and associated biological effects data were compiled from the literature, to provide an estimate of sediment Se concentration thresholds that have biological effects. Based on this preliminary analysis, sediment Se concentrations of 2.5 μg/g would be a threshold based on predicted effects and concentrations of 4.0 μg/g would be the observed threshold for fish and wildlife toxicity. The dissolved-to-sediment Se transfer model can be used to translate this type of sediment Se toxicity threshold to a site-specific chronic water-quality standard for western streams based on empirically derived sediment total organic carbon values.

Keywords—Selenium Sediment Toxicity thresholds Bioaccumulation Water quality criteria

INTRODUCTION

The primary environmental risk posed by selenium (Se) is a direct result of its propensity to cycle through the food web, its dominant exposure pathway, and its ability to cause reproductive impairment in fish and wildlife [1–3]. In a recent review of the adverse effects of Se on freshwater biota, Canton and Van Derveer [4] suggested that the degree of dietary uptake and subsequent toxic effects at a given site are a function of site-specific factors that affect the fate and bioavailability of Se through the sediment-to-diet pathway.

An implied role of sediment Se was noted as a potential causal factor for the impacted fishery within Belews Lake, North Carolina, USA [5]. Nonetheless, the current National Water Quality Criteria of 5 μg/L as the chronic level and 20 μg/L as the acute level for Se [6] are based upon waterborne Se data from Belews Lake. Despite the critical role of the sediment phase in the ecotoxicity of this element, sediment Se toxicity thresholds and a mechanism for translating them into site-specific water-quality standards (a necessary regulatory vehicle) have not been developed [4].

This study utilized a combination of site-specific data and data from existing studies to examine sediment Se speciation and factors affecting sediment Se accumulation in lotic environments, to develop sediment Se toxicity thresholds, and to derive a mechanism for translating a sediment Se threshold to a site-specific waterborne Se standard for lotic systems.

MATERIALS AND METHODS

Site description

Surface water and sediment samples were collected from a total of nine sampling stations in the middle Arkansas River basin of southeastern Colorado, USA, as part of a larger study (Fig. 1). Sample sites included four sites on the Arkansas River mainstem: upstream of Fountain Creek, at Avondale, at La Junta, and downstream of John Martin Reservoir (water only). In addition five tributary sites were sampled, including Fountain Creek at Piñon, Fountain Creek at Pueblo, the St. Charles River at Vineland, Turkey Creek near Pueblo Reservoir, and the Purgatoire River at Highway 101.

Streams in this region are characterized by broad shallow channels with high bedloads of sand and fine gravel. Organically rich depositional areas are rare as a result of a combination of frequent scouring and inorganic sediment deposition from flash-flood events. This basin was selected because there is a relatively high diversity and abundance of native fish species [7] (Colorado Department of Natural Resources, Division of Wildlife, unpublished data). In addition, waterborne Se concentrations consistently exceed the U.S. Environmental Protection Agency's (EPA) [6] chronic criterion and frequently exceed the acute criterion [8], suggesting that site-specific factors are playing an integral role in regulating the potential toxicity of Se in these streams [4].

Field collection methods

Cross-sectionally composited surface water samples were collected at each site during August and November 1994. Aliquots of surface water were grabbed at evenly spaced intervals of approximately 2 m and 1 m at mainstem and tributary sites, respectively, and composited in a polyethylene container. August samples for dissolved constituents were filtered in the Department of Wastewater Laboratory, Pueblo, Colorado, USA, within 24 h of collection using a 0.45-μm membrane filter. This method is consistent with clean metals handling for trace elements [9]. November samples were field filtered using

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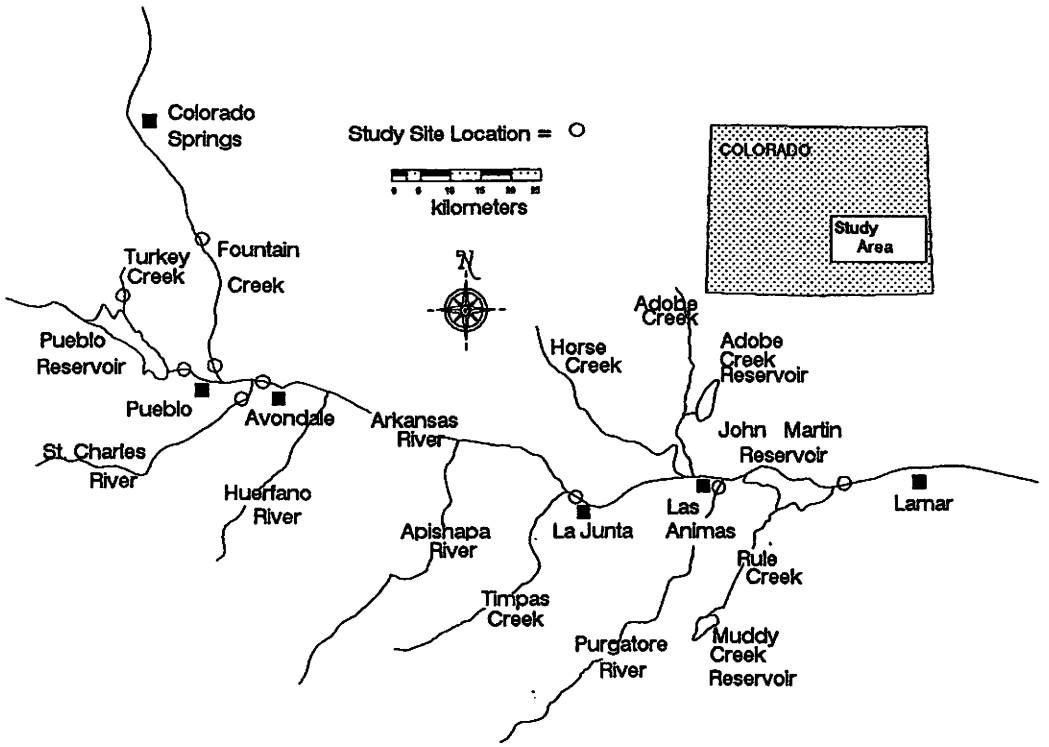

Fig. 1. Study site locations in the middle Arkansas River basin, Colorado, USA, 1994.

a 0.45-μm membrane filter. Samples for both total and dissolved Se were acidified to pH < 2.0 following filtration (note that field preservation of dissolved metal samples is not required if preservation is performed in the laboratory [9]). Samples were analyzed for total Se and dissolved Se speciation (selenite, selenate, organic Se, and total Se). Because dissolved Se accounted for >90% of the total waterborne Se concentrations, only dissolved Se results are presented. Field blanks were submitted for Se analysis during both sampling events (n = 6), and all water samples were stored at 4°C.

During November sampling, surficial sediment (approx. 0–5 cm) was composited from three depositional areas (i.e., areas with fine-grained sediment and slower current velocity) at each site utilizing a stainless steel hand trowel or an Ekman grab. Aliquots were removed for bulk Se speciation (selenite, selenate, elemental Se, organic Se, and total Se) and total organic carbon (TOC) analyses. Sediment samples for Se and TOC analyses were held at −20°C and 4°C, respectively.

Sample analyses

All surface water and sediment Se concentrations were determined by hydride generation atomic absorption spectroscopy. Speciation analyses of surface water for dissolved Se were performed in accordance with APHA Method 3500-Se C [10]. Using this method, selenite was measured directly, selenate was determined as the difference between selenite + selenate and selenite, and organic Se was determined as the difference between total Se and selenite + selenate. One duplicate Se speciation analysis was performed during the November sampling event. Duplicate procedural blank, laboratory control sample, and matrix spike/matrix spike analyses were run for total dissolved Se, selenite, and selenate.

Analysis of total sediment Se was performed in accordance with APHA Method 3500-Se B [10]. Sediment selenite and selenite + selenate analyses were performed using the methods of Cutter [11], with selenate determined as the difference between selenate + selenite and selenite. Sediment elemental Se analysis was performed using the method of Velinsky and Cutter [12]. Sediment organic Se was determined as the difference between total Se and selenate + selenite + elemental Se. Duplicate Se speciation analysis and matrix spike/matrix spike analyses were performed for total Se, selenite, and selenate + selenite. Sediment TOC was determined as the difference between total carbon and inorganic carbon using the methods of the U.S. Geological Survey [13]. The results of all sediment analyses are reported on a dry-weight basis.

Stream database compilation

In response to concerns about the Kesterson National Wildlife Refuge (NWR), California, USA, the U.S. Department of the Interior (USDOI) started a program in 1985 to identify the nature and extent of irrigation-induced water-quality problems that might exist in other parts of the western United States. Twenty-five areas in 17 states underwent reconnaissance investigations generally including analyses of water quality, sediment, and tissues, and, in some cases, a search for waterfowl deformities was also included [14].

To better analyze Se pathways in Colorado streams, a database of dissolved Se, sediment Se, sediment TOC, and related data was compiled from the present study and two of the USDOI studies conducted in Colorado [8,15]. This compilation is referred to in this paper as the "Colorado stream database" (see the Appendix). When data from multiple analyses at a single stream site were available, a site mean concentration was used to more closely approximate typical conditions. Because different sediment size fractions (i.e., coarse [bulk or <2.0 mm] and fine [<0.063 mm]) were collected among studies, mean sediment Se and TOC values were used. This computation was not expected to adversely affect the utility of the data.

Table 1. Dissolved Se speciation and total dissolved Se (μg/L) in the middle Arkansas River basin, August and November, 1994. (No Se species were detected in the field blanks [<1 μg/L] in August 1994 [n = 1] or November 1994 [n = 5].) Total Se in the field blanks (n = 6) and procedural blanks (n = 3) was below detection (<1 μg/L). Matrix spike recoveries (n = 3) for total Se = 105.3–114.5%, for selenite = 89.0–99.5%, and for selenate = 115.0–118.5%

	Selenate		Selenite		Organic Se		Total Se	
Station[a]	August	November	August	November	August	November	August	November
Arkansas River mainstem								
ARuf	6	6	<1	1	1	<1	7	7
ARav[b]	8	10	1	2	1	<1	10	11
ARlj	15	17	<1	2	2	<1	17	15
ARjm	1	14	3	<1	3	1	7	15
Tributary sites								
FCpñ	5	4	1	1	1	1	7	6
FCpu	17	8	<1	<1	1	<1	18	7
SC	21	40	<1	2	3	<10	24	30
TC	108	260	3	5	25	<20	136	240
PR	<1	7	<1	<1	2	<1	2	7

[a] Abbreviations for stations are as follows: ARuf, upstream of Fountain Creek; ARav, at Avondale; ARlj, at La Junta; ARjm, downstream of John Martin Reservoir; FCpñ, Fountain Creek at Piñon; FCpu, Fountain Creek at Pueblo; SC, the St. Charles River at Vineland; TC, Turkey Creek near Pueblo Reservoir; and PR, the Purgatoire River at Highway 101.

[b] Results of the duplicate November 1994 sample yielded identical concentrations.

Toxicity thresholds development

Sediment Se toxicity thresholds were approximated from a compilation of sediment Se concentrations and their associated predicted or observed biological effects. Both "predicted" and "observed" effects presented here are based on the original authors' reported determination. Each determination generally was based on comparisons of the authors' tissue or egg residue values to published threshold levels or direct observation of deformities. These data were derived from irrigation drainage studies conducted throughout the western United States and studies on coal-fired power plant reservoirs receiving Se-laden effluents. For each study, the lowest sediment Se concentration for a given sample area (e.g., a specific wetland or wetland complex within a larger study site), for either coarse or fine sediment, that was associated with an observed or predicted adverse effect on fish and/or birds was included in the compilation. When spatial or temporal replication was performed, the mean sediment Se concentration of those replicates was used in the compilation. This mean was assumed to improve the characterization of the extant sediment Se concentration for that sample area. Use of the lowest sediment Se concentration (or mean concentration) from a study imparts a strong degree of conservatism to the development of thresholds of effects from these data. If no adverse effects were observed or predicted, the highest sediment Se concentration was included in the compilation.

Because these data represent a compilation from a number of studies, it was not possible to determine an empirical concentration–response relationship between sediment Se concentrations and biological effects. For the purposes of this analysis, two types of thresholds were developed from these data using the approach of Long and Morgan [16]. Predicted effects values less than or equal to the 10th percentile were considered below the range where effects would be predicted to occur. Observed effects values less than or equal to the 10th percentile were considered below the range where effects would be observable. Given the variability in reported responses and the lack of direct experimental evidence, the 10th percentile is a conservative no-measurable-response level for either predicted or observed effects.

Data analysis

All statistical analyses were performed using SYSTAT® software [17]. Natural log transformation (ln) was applied in cases where assumptions of normality and homogeneity of variance were violated. A mean value was used in all calculations or analyses involving data from duplicate samples. A surrogate value of one-half the detection limit was used for nondetect data for any calculations or analyses [18]. Note that these surrogate values occurred in only the dissolved Se data and occurred at a very low rate (only 2%, or 3 of 155 measurements). Significance levels were tested at the $p < 0.05$ level.

Pearson product–moment correlation analysis was applied to the data from the present study to identify potential relationships among sediment Se and dissolved Se (mean of August and November 1994 combined), sediment TOC, and a dissolved Se × sediment TOC interaction term. Stepwise linear regression analysis of the Colorado stream database, using the variables listed above, was used to empirically describe the waterborne Se to sediment Se relationship in lotic environments. The resultant model was validated using stream data from four other USDOI irrigation drainage studies conducted in the western United States that had matching sediment Se, sediment TOC, and dissolved Se data.

RESULTS AND DISCUSSION

Waterborne Se

Except for Turkey Creek, dissolved Se concentrations at the sites ranged from 2 to 24 μg/L and 7 to 30 μg/L during August and November, respectively (Table 1). In contrast, Turkey Creek had levels as high as 240 μg/L (Table 1). This stream was almost intermittent in flow and collections were made as the water moved through a cattail flat. Selenate was the dominant dissolved species representing more than 67% of the total dissolved Se concentration, except at the Arkansas

Table 2. Sediment Se speciation and total Se (μg/g dry wt.) and total organic carbon (TOC) (% dry wt.) in the middle Arkansas River basin, November 1994. (Total Se in procedural blanks [n = 2] was below detection [<0.23 μg/L]. Recoveries for total Se in National Bureau of Standards Standard Reference Material (NBS SRM) 1646 estuarine sediment [0.6 μg/g dry wt.] [n = 5] = 92–110%. Matrix spike recoveries [n = 1] for total Se = 92.3%, for selenite = 90.0%, and for selenate + selenite = 90.5%)

Station[a]	Selenate	Selenite	Elemental Se	Organic Se	Total Se	% TOC
Arkansas River mainstem						
ARuf	0.06	<0.01	0.46	0.46	1.50	0.67
ARav[b]	0.03	<0.02	0.50	0.90	1.42	0.71
ARlj	0.02	0.04	0.17	0.11	0.33	0.17
Tributary sites						
FCpñ	0.02	0.03	0.18	0.18	0.40	0.26
FCpu	0.02	0.04	0.15	0.25	0.46	0.10
SC	0.02	0.18	0.55	0.49	1.23	0.18
TC	0.15	0.05	5.61	2.90	8.70	1.56
PR	0.03	0.05	0.11	0.15	0.34	0.07

[a] Abbreviations for stations are as follows: ARuf, upstream of Fountain Creek; ARav, at Avondale; ARlj, at La Junta; ARjm, downstream of John Martin Reservoir; FCpñ, Fountain Creek at Piñon; FCpu, Fountain Creek at Pueblo; SC, the St. Charles River at Vineland; TC, Turkey Creek near Pueblo Reservoir; and PR, the Purgatoire River at Highway 101.

[b] Mean results of duplicate Se analyses.

River mainstem site downstream of John Martin Reservoir where only 14% was selenate in August.

Those instances where the sum of the concentrations of all Se species was somewhat greater than the total Se concentration were likely associated with analytical variability; this variability does not affect the statistical analyses that employ only total dissolved Se concentration data. This difference in values is an inherent problem with selective hydride generation analysis of Se species, because selenate and organic Se are determined by difference [19].

Despite this wide range of dissolved waterborne Se concentrations, no significant relationship between fish species richness or abundance and Se concentration could be observed [4]. In fact, the St. Charles River and Fountain Creek, two of the tributaries with waterborne Se concentrations well above the current 5-μg/L criterion, had some of the highest abundance and richness of fish species of all the sites sampled.

Sediment Se speciation

Total sediment Se ranged from 0.3 to 1.5 μg/g at seven of the sites, with 8.7 μg/g found in the intermittent Turkey Creek (Table 2). The majority of the sediment Se was present in the elemental (mean ± SD, 42 ± 12%) and organic forms (mean ± SD, 42 ± 11%). Similar sediment Se speciation has been reported at numerous lentic habitats receiving Se from natural and anthropogenic sources [12,20–23]. Given the redox-dependent speciation behavior of Se, elemental Se has a tendency to predominate in reducing environments [20]. Generally, the sediment Se concentrations found in the present study are lower than those reported at Se-impacted sites, despite the relatively high waterborne Se concentrations. However, note that despite the predominance of different waterborne Se species (e.g., selenate in the Arkansas River basin and selenite in the power plant reservoirs), the sediment Se speciation (primarily elemental and organic Se) was consistent across habitats.

Sediment Se relationships with selected environmental variables

The sediment-Se-to-diet uptake pathway is important for predicting the potential toxicity to aquatic life [4], and sediment Se appears to behave similarly across habitats, despite differential waterborne Se speciation. Therefore the total Se concentration in water or sediments should be used in the development of any model to preclude the need for complex and expensive Se speciation analyses. Given this premise, total sediment Se concentrations were compared to a number of environmental variables to determine potential predictive relationships. Total sediment Se in the middle Arkansas River basin (this study only) exhibited positive ln–ln correlations (n = 8) with mean dissolved Se (r = 0.79, p = 0.02), sediment TOC (r = 0.86, p = 0.005), and the interaction term of mean dissolved Se × sediment TOC (r = 0.93, p = 0.001). This relationship between sediment Se and organic carbon or carbon-containing materials (i.e., detritus) has been widely reported in a variety of studies of freshwater environments [11,14,21,23–26].

Stepwise regression analysis of the Colorado stream database using the above variables indicates that the mean dissolved Se × sediment TOC interaction term explains the largest proportion of the variation in sediment Se concentration (R^2 = 0.81, p < 0.001, n = 21) (Fig. 2). This suggests, not unexpectedly, that neither waterborne Se concentrations nor the amount of organic carbon in the sediments alone can explain the sediment Se concentrations. This relationship is described by the following model:

$$\ln C_s = \ln(C_d \times f_{oc}) \cdot 0.671 - 1.088$$

where

C_s = sediment Se in μg/g dry weight
C_d = dissolved waterborne Se in μg/L
f_{oc} = sediment TOC expressed as a percentage of dry weight

This is certainly a simplified description of the complex biogeochemical processes associated with the movement of Se through a stream environment, such as the interaction of Se with other elements or the differential uptake by organisms of various Se species. However, this type of model can define the functional relationship between the measured variables and provide a straightforward depiction of the accumulation of sediment Se based on dissolved Se and organic carbon concentrations.

Sediment Se model validation

To validate this model, dissolved Se (detectable concentrations only) and sediment TOC (the mean of the <2.0-mm and <0.063-mm size fractions) stream data from four other USDOI studies performed outside of Colorado were used, including studies in South Dakota [27,28], Nevada [29], and Wyoming [30]. The ability of the model to predict sediment Se from mean dissolved Se and sediment TOC data was analyzed. A comparison of the predicted and measured sediment concentrations indicated that the model produced highly accurate predictions (ln–ln Pearson correlation, r = 0.94, p < 0.001, n = 13). These data show that the model is a good empirical representation of the sediment Se accumulation process.

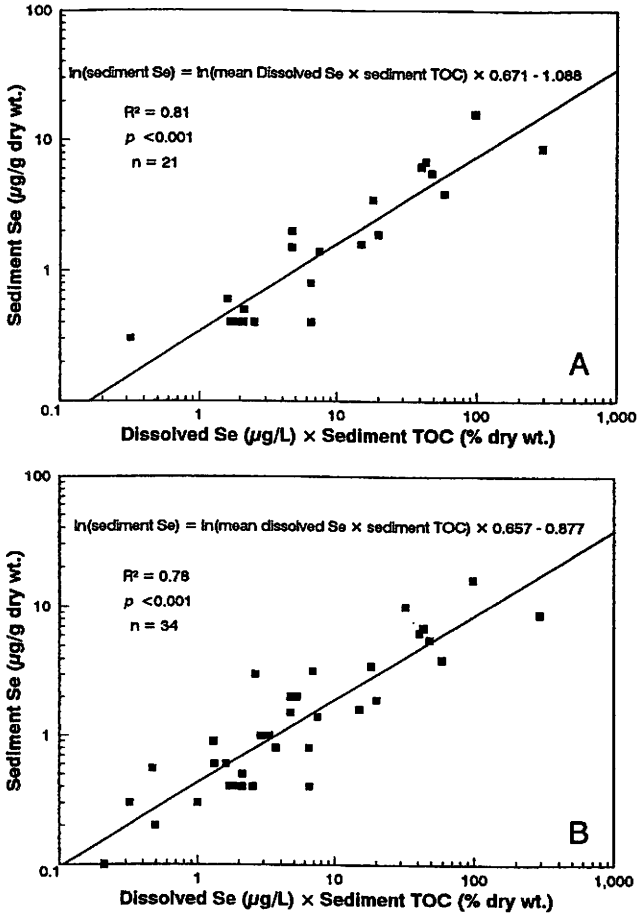

Fig. 2. Linear regression of sediment Se and a dissolved Se × sediment total organic carbon interaction term for the Colorado stream database (A) and for the Colorado stream database plus validation data (B).

With the model validated, additional data were incorporated into the Colorado stream database to increase the sample size (see the Appendix). After recalculation, the resulting model is still highly significant and explains a large proportion of the variance ($R^2 = 0.78$, $p < 0.001$, $n = 34$) (Fig. 2). The final sediment Se model proposed for use in western streams is

$$\ln C_s = \ln(C_d \times f_{oc}) \cdot 0.657 - 0.877 \qquad (2)$$

Although this model describes the sediment Se accumulation process as a basis for determining potential toxicity through dietary pathways in streams, probably it should not be used in standing waters. This model was derived solely from data derived in lotic environments, and the equation may not accurately represent the habitat and sediment accumulation process found in lakes, reservoirs, or wetlands.

Association between sediment Se and adverse biological effects

Particulate Se, as sediment, detrital, or suspended particulate Se, has been implicated repeatedly as a causal factor in food web contamination at sites including Belews Lake, North Carolina, USA [31]; Hyco Reservoir, North Carolina, USA [32]; Martin Creek Lake, Texas, USA [33]; Kesterson NWR, California, USA [21]; Sweitzer Lake, Colorado, USA [34]; and the lower San Joaquin River, California, USA [25]. An evaluation of the potentially causal association between sediment Se and adverse biological effects, using Hill's [35] criteria and existing literature, showed much stronger agreement with sediment Se rather than with waterborne Se [4].

Sediment Se toxicity thresholds

To use this model in the development of site-specific waterborne Se standards, sediment toxicity thresholds need to be determined. To accomplish this, sediment Se concentrations and their associated biotic effects (no effect, predicted effect, or observed effect) were compiled from 25 study sites throughout the United States (Table 3). Based on these data, the 10th percentile of sediment Se concentrations associated with predicted adverse effects is 2.5 µg/g (Table 3). The 10th percentile of sediment Se concentrations associated with observed adverse effects is 4.0 µg/g (Table 3). These findings suggest that there is little potential for observable adverse effects on fish or birds at sediment Se concentrations of about 4 µg/g or less. The predicted effects threshold concentration of 2.5 µg/g is only slightly above the 2.0-µg/g upper limit reported for uncontaminated sediment and soil [1,22]. This would tend to indicate that the predicted effects threshold is relatively conservative. The observed effects threshold of 4 µg/g has also been suggested by Lemly and Smith [1] as a sediment threshold level of concern for fish and wildlife. Sediment Se concentrations at many of the widely studied Se-contaminated sites (e.g., the Kesterson NWR and Belews Lake) were considerably greater than these effects thresholds.

Two toxicity thresholds or levels of concern for fish and wildlife may be derived from this analysis: sediment Se concentrations of 2.5 µg/g would be considered the predicted effects level, and sediment Se concentrations of 4 µg/g would be the observed effects level. These levels are consistent with the "low" and "high" hazard levels for reproductive failure in fish and birds proposed by Lemly [3]. Given that many of the effects in the low range of sediment Se concentrations are predicted rather than observed, these sediment thresholds should be considered preliminary until further effects data are developed.

Calculation of site-specific chronic dissolved Se stream standards

A sediment Se toxicity threshold can be translated to a site-specific chronic dissolved Se stream standard using the waterborne Se × sediment TOC interaction model for sediment Se described above (Eq. 2). The model is simply solved for waterborne Se by using a selected sediment Se toxicity threshold and the site-specific sediment TOC concentration as input for the model. The resulting predicted dissolved Se concentration could serve as a site-specific standard that would preclude accumulation of sediment Se to a level exceeding the selected toxicity threshold, thereby protecting fish and wildlife.

Example 1. Equation 2 is solved using a sediment Se toxicity threshold of 2.5 µg/g (predicted effects level) and a site-specific mean sediment TOC value of 0.5% (typical of Colorado streams) as input for the model as follows:

$$\ln 2.5 = \ln(C_d \times 0.5) \cdot 0.657 - 0.877$$

The resultant chronic dissolved Se standard would be 31 µg/L, based on the site-specific conditions and the selected threshold.

Example 2. Equation 2 is solved using the same conservative sediment Se toxicity threshold of 2.5 µg/g (predicted effects level) and a site-specific mean sediment TOC value of 5% (more typical of sites with adverse effects observed [e.g., Belews Lake, the Kesterson ponds], although outside of the

Table 3. Sediment Se concentrations and their reported biological effects

Sediment Se[a] (μg/g dry wt.)	Effect observed or predicted[b]		Site[c]	Station[d]	Reference
	Fish	Birds			
0.1	—	N	Volta Wildlife Area, CA	Site mean	[36]
≤0.4	—	N	Sacramento NWR, CA	5	[37]
≤0.4	N	N	Middle Rio Grande Valley, NM	B4/B12	[38]
≤0.6	N	N	Milk River basin, MT	10	[39]
≤0.6	N	N	Malheur NWR, OR	Malheur Lake	[40]
≤0.7	N	—	Lower Rio Grande, TX	6	[41]
≤0.7	N	N	Klamath basin, CA/OR	4	[42]
≤0.8	N	N	Pine River, CO/NM	N2/SB2	[43]
1.0	N	—	Philpott Lake, NC	2	[20]
≤1.4	N	N	Humboldt WMA, NV	11	[29]
≤1.8	N	N	American Falls Reservoir, ID	2	[44]
≥2.2	P	—	Kendrick, WY	KD02	[45]
≥2.3	—	P	Sun River, MT	22	[46]
≤3.0	P	N	Riverton, WY	16	[30]
≤3.4	N	—	Belews Lake, NC	158 (Reference)	[47]
≤3.5	N	—	Belle Fourche, SD	12	[28]
≥4.0	P	O	Kendrick, WY	KD07	[45]
≥4.0	—	P	Middle Arkansas River, CO	R4	[8]
≥4.0	—	P	Fernley WMA, NV	Massie Slough	[48, 49]
≥4.2	—	P	Middle Green River, UT	Marsh 4720	[26, 50]
5.0	O	—	Martin Creek Lake, TX	6	[20]
6.0	P	P	San Juan River area, NM	I-22	[51]
≥6.1	O	—	Belews Lake, NC	3	[47]
7.2	—	O	Tulare Lake bed, CA	Westfarmers	[52]
7.4	O	O	Kesterson NWR, CA	Site mean	[24, 36, 53]
≥8.6	O	P	Sweitzer Lake, CO	7	[54]
23	O	—	Hyco Reservoir, NC	Site mean	[20]

[a] Lowest concentration producing effects or highest concentration resulting in no effect presented when data were available for multiple sediment size fractions.
[b] Effects reported as N (no adverse effect predicted or observed), O (adverse effect observed), P (adverse effect predicted), and — (no data).
[c] NWR = National Wildlife Refuge; WMA = Wildlife Management Area.
[d] Station designation as provided by authors of each study and at which the listed Se concentration was reported.

range of data used to develop the model) as input for the model as follows:

$$\ln 2.5 = \ln(C_d \times 5)\cdot 0.657 - 0.877$$

The resultant chronic dissolved Se standard would be 3 μg/L, virtually matching the recommended waterborne Se thresholds based on data from these sites [1,22].

Example 3. The sediment toxicity threshold of 4 μg/g (observed adverse effects level) is used with a sediment TOC of 5% (again, similar to that found in Belews Lake or Kesterson ponds) as follows:

$$\ln 4 = \ln(C_d \times 5)\cdot 0.657 - 0.877$$

In this case, the resulting chronic dissolved Se standard would be 5 μg/L, matching the EPA's recommended criterion [6].

Thus, this model will produce chronic dissolved Se standards that are similar to the current EPA criterion and to others recommended in the literature, but only when appropriate sediment Se thresholds and site-specific sediment TOC conditions warrant. The model also shows that a 5 μg/L criterion would be considerably overprotective in other locations.

If the site-specific sediment TOC concentration is extremely low, it is plausible that a calculated site-specific chronic waterborne Se standard could exceed the current acute criterion. Under those circumstances, the site-specific chronic waterborne Se standard should not be set higher than an applicable acute standard.

CONCLUSIONS

Based on the review of recent literature, it is clear that particulate Se is a more reliable predictor of adverse biological effects than is waterborne Se [4]. Unlike waterborne Se, sediment or particulate Se satisfy all of Hill's [35] criteria for causal association. Sediment Se speciation is consistent across a wide range of habitat conditions, with the dominant sediment Se species (elemental and organic Se) typically accounting for nearly 85% of the total sediment Se burden. The results of the present study indicate that the accumulation of sediment Se in streams is a function of sediment organic carbon. These factors should permit the use of a total sediment Se concentration-based toxicity threshold without the added complexity and costs associated with Se speciation analyses.

An empirical model for predicting sediment Se accumulation in streams, on the basis of dissolved Se and sediment organic carbon content, was developed. The dissolved Se interaction with sediment organic carbon used in the development of our model provides a reasonable explanation for the variable biological response to waterborne Se reported in the literature. Organically rich sites (e.g., Belews Lake and the evaporation ponds at the Kesterson NWR) have a great potential for Se bioaccumulation, and in fact, significant biological effects have been recorded. In contrast, organically poor sites (e.g., Colorado streams) have waterborne Se concentrations consistently exceeding the 5 μg/L chronic criterion [6], yet apparently induce no adverse effects on fish populations.

Preliminary sediment Se toxicity thresholds were developed based on field data from throughout the United States. Based on this analysis, the following preliminary effects levels for fish and wildlife were derived: the predicted effect level of sediment Se concentrations is in the range of 2.5 μg/g and the observed effect level of sediment Se concentrations is in the range of 4.0 μg/g. The sediment Se model can be used to develop site-specific chronic water quality stream standards by using a desired sediment Se toxicity threshold and a site-specific empirically derived sediment TOC value in the model.

This study supports the concept that the existing chronic criterion of 5 μg/L Se may not fully protect fish and wildlife at some sites with organically rich sediments, although it may be considerably overprotective at sites with organically poor sediments. Standards or criteria that are intended to protect fish and wildlife from the bioaccumulative effects of Se should be expressed on a particulate basis, such as sediment concentration, using a model similar to the one described herein.

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Assessment of Tolerant Sunfish Populations (*Lepomis* sp.) Inhabiting Selenium-Laden Coal Ash Effluents

1. Hematological and Population Level Assessment

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Sunfish were collected from coal ash effluent-receiving streams and Ohio River watershed reference sites to assess the effects of exposure to low-level selenium concentrations. Selenium, copper, and arsenic concentrations were statistically higher in tissue samples from exposed fish than in reference fish. Leukopenia, lymphocytosis, and neutropenia were evident in exposed fish and were indicative of metal exposure and effect. White blood cell counts and percent lymphocyte values were significantly correlated with liver selenium concentrations. Plasma protein levels were significantly lower in exposed fish than in fish from the Ohio River, indicating that exposed fish may have been nutritionally stressed. Condition factors for fish from the ash pond-receiving streams were the same as, or lower than, those of fish from the reference sites. There was no evidence that the growth rate of fish in the receiving streams differed from that of fish in the reference streams. Despite liver selenium concentrations which exceeded reported toxicity thresholds and evidence of significant hematological changes, there were no significant differences in fish condition factors, liver–somatic indices, or length–weight regressions related to selenium. © 2001 Elsevier Science

Key Words: **coal ash; bluegill; selenium; hematology.**

INTRODUCTION

Coal combustion at electric generating plants produces a variety of waste products, including fly ash and bottom ash. The ash produced at many coal-burning power plants is sluiced to large settling ponds where the ash particles settle out and the effluent water is either discharged or reused. Ash disposal in settling ponds can affect adjacent aquatic ecosystems through effluent discharge, seepage, and groundwater infiltration. The potential toxic effects of coal ash effluents on aquatic ecosystems were reviewed by Carlson and Adriano (1993); effects can range from direct mortality (Cairns *et al.*, 1972) to reproductive failure and growth effects in fish (Lemly, 1985). Ecological disturbances, such as ash siltation of benthic habitat, heavy metal bioaccumulation in invertebrates and fish, and pH fluctuations have been caused by poorly operated settling pond systems. These effects can lead to simplification of food chains (Cherry and Guthrie, 1977), reduction in diversity and density of benthic invertebrate communities (Cherry *et al.*, 1979, 1984; Specht *et al.*, 1984), and reductions in fish populations (Cherry *et al.*, 1976, 1979, 1984, 1987).

Coal ash effluents are a primary source of metals such as copper, lead, selenium, and zinc to the environment (Cherry and Guthrie, 1977; Evans *et al.*, 1980). These metals, particularly selenium, are considered to be the most likely causative agent for coal ash toxicity. Hematological irregularities, reduced hematocrits, histopathological abnormalities, edema, uremia, egg follicle necrosis, and abnormal livers, ovaries, and gills have all been noted in fish from lakes receiving selenium-laden effluent from coal-fired power plants (Sorenson *et al.*, 1982, 1984; Sorenson and Bauer, 1983).

Despite the potential to be affected by hematological and biochemical changes, some fish populations exposed to ash pond discharges and high selenium levels are not always eliminated or otherwise adversely impacted (Reash *et al.*, 1988; Besser *et al.*, 1996). Cherry *et al.* (1979, 1984) found that the release of ash particulates did not affect mosquitofish (*Gambusia affinis*) populations in a South Carolina ash basin overflow. Selenium-enriched bottom ash effluent discharged into the New River, Virginia, was found to be nontoxic to bluegill sunfish (*Lepomis macrochirus*) and rainbow trout (*Salmo gairdneri*) (Cherry *et al.*, 1987). Clearly, the degree and extent of individual and population-level responses in fish exposed to coal ash effluents vary considerably. These differences may be due to differences in coal ash chemistry, receiving stream characteristics, or fish

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population exposures. Trophic status, habitat preference, and mobility may also modify selenium hazards in aquatic ecosystems. Therefore, it is difficult to draw conclusions concerning the relationships between exposures to coal ash effluents, individual fish health, and population-level responses.

A study was designed to assess the suborganismal responses of fish in streams receiving coal ash effluents and to evaluate their use as indicators of fish population health. A major goal of the study was to determine whether potential hematological, biochemical, and physiological disturbances in fish collected from ash pond effluent-receiving streams (Stingy Run and Little Scary Creek at the American Electric Power (AEP) General James M. Gavin and John E. Amos Plants) are sensitive indicators of coal ash exposure and effect. The assessment included metal analysis of water, sediment, and biota; evaluation of hematology, serum and tissue chemistry; and fish population endpoint assessments. This article presents the results of the hematological analyses and gives a perspective on the significance of these endpoints relative to fish health effects. The results of the remaining portions of the work are presented in accompanying articles (Lohner *et al.*, 2001a, b; Reash *et al.*, 1999).

METHODS

Study Sites

Stingy Run is the receiving stream of the American Electric Power Gavin Plant fly ash pond (Fig. 1). The Gavin Plant is a coal-burning facility with two generating units, each producing 1300 MW of electricity. The plant is located on the Ohio River at river mile (RM) 258 (415 km, measured downstream from Pittsburgh, PA) near Cheshire, Ohio, in Gallia County. Fly ash produced at the plant was sluiced with water to a fly ash reservoir. The plant has since been converted to dry ash disposal. The reservoir is an impoundment of Stingy Run, a third-order creek with its upper watershed now impounded. The stream is located in the Appalachian Plateau physiographic province and underlying bedrock consists of Pennsylvanian sandstone, limestone, shale, and coal seams. Kyger Creek, the receiving stream of Stingy Run, empties into the Ohio River about 4 km downstream of the Gavin Plant, at RM 259 (416 km).

Little Scary Creek is the receiving stream of the American Electric Power Amos Plant fly ash pond (Fig. 2). The Amos Plant is a coal-burning facility with three generating units and a combined plant capacity of 2900 MW. Fly ash from Unit 3, a 1300-MW unit, is sluiced with water, to a large settling pond at the headwaters of Little Scary Creek. Overflow of water from the fly ash pond is discharged through a structure which regulates pond level and retains any floating ash or debris by means of a surface skimmer. The overflow from the discharge structure flows into Little Scary Creek at its headwater, approximately 2.7 km from its confluence with the Kanawha River, which is approximately 61 km upstream from the Ohio River. The fly ash pond was formed by impounding the upper drainage basin of Little Scary Creek. The creek watershed is generally dissected by a series of relatively steep-sided valleys.

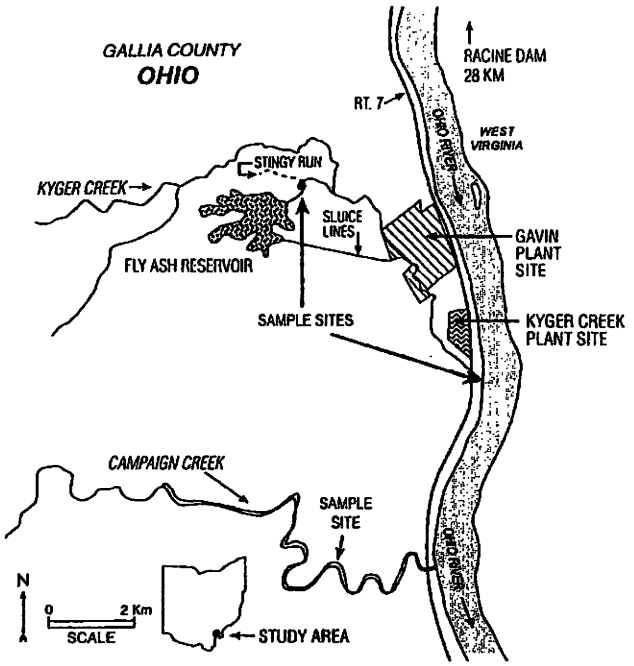

FIG. 1. Stingy Run study area.

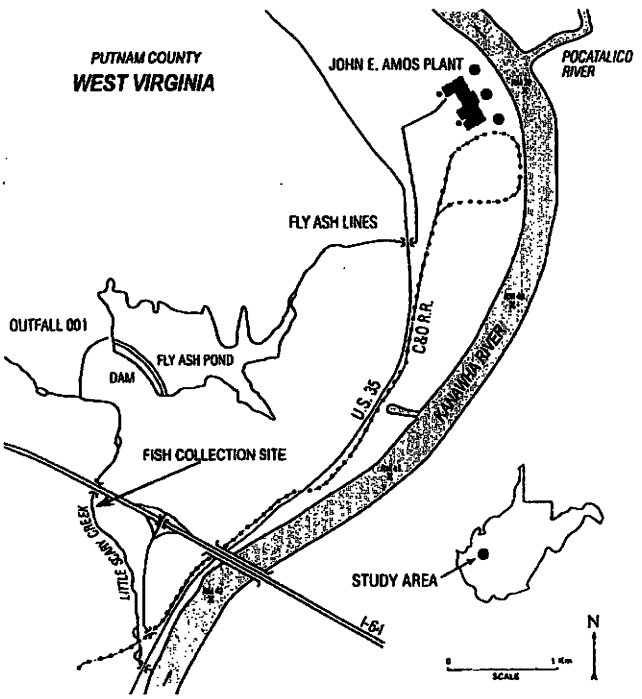

FIG. 2. Little Scary Creek study area.

Two reference streams, Campaign Creek and the Ohio River (Fig. 1), were selected for comparison to Stingy Run and Little Scary Creek. Campaign Creek is located in Gallia County, Ohio, and is a tributary of the Ohio River. Campaign Creek and Stingy Run/Kyger Creek have adjacent watersheds and drain portions of Gallia County. Campaign Creek empties into the Ohio River at RM 262.4, approximately 2.7 km downstream of Kyger Creek's confluence with the Ohio River. Fish were collected from Campaign Creek at a location approximately 4 km upstream of the Ohio River. Campaign Creek was chosen because of documented good water quality and biological communities (Ohio EPA, 1991). Due to difficulty in collecting adequate numbers of sunfish from Campaign Creek, fish were also collected from the Ohio River near the Kyger Creek confluence, 9.1 km upstream of the Kanawha River confluence. This site is near RM 260 on the Ohio River. Results obtained from both reference sites were compared to Stingy Run and Little Scary Creek data.

Fish Collection and Sampling

Adult and juvenile bluegill sunfish (*L. macrochirus*), green sunfish (*L. cyanellus*), and longear sunfish (*L. megalotis*) were collected by electrofishing in Stingy Run, Little Scary Creek, Campaign Creek, and the Ohio River. Not all species were collected in each stream. Fish were collected directly downstream from the discharge of the fly ash reservoir into Stingy Run in the fall of 1993 and 1994, May 1995, September 1995, and October 1997. Movement of fish from downstream areas is prevented by the presence of a culvert downstream from the discharge; therefore, this population of fish is relatively discrete from those downstream.

Fish from Little Scary Creek were collected downstream of a corrugated metal pipe in June 1996. Below the pipe is a concrete channel which ends in a drop of about 0.5 m to the creek below. This difference in elevation creates a small waterfall in the creek and prevents the upstream movement of fish past this point. Little Scary Creek ends at the Kanawha River by flowing through a 3.7-m-diameter corrugated metal pipe. The surface of the river can be as much as 15 cm below the bottom of the pipe 50% of the time. This separation effectively limits upstream movement of fish into Little Scary Creek. Fish were collected from Campaign Creek in fall 1994 and from the Ohio River in late summer 1995, August 1997, and October 1997.

Fish from Stingy Run, Little Scary Creek, and Campaign Creek were collected using pulsed DC backpack and longline electrofishing gear. Fish from the Ohio River were collected by boat electrofishing. All available habitats were sampled in stream lengths of 50–100 m. Sampling time was typically 20–30 min. All collected fish were placed in buckets and held until sampling was complete. Fish were allowed to recover from electroshocking and held in aerated, ambient-temperature stream water until they were processed, usually within 12 h of collection. Standard length and wet weight data were recorded. Blood samples were drawn from the caudal vein using EDTA-treated (lavender top) 3-ml Vacutainers with 21G × 1" needles (inserted ventrally, midline, posterior to the anal fin) or collected via pericardial puncture or dorsal gill incision (Watson *et al.*, 1989) into hepinarized 250-μL capillary tubes and preserved on ice. After blood removal, fish were examined externally and internally for evidence of lesions or other abnormalities. Dorso-anterior scales were removed from each fish for age determination by the scale method, using the annulus criteria given by Jearld (1983). Livers, spleens, and gill tissue were removed using acid-rinsed, stainless-steel instruments for metal analysis and placed in polyethylene bags and stored at −70°C until analysis.

Water Quality Monitoring

Water chemistry measurements were conducted on samples from Stingy Run, Little Scary Creek, Campaign Creek, and the Ohio River. Trace metals analyzed at the sites included arsenic, cadmium, chromium, copper, lead, nickel, selenium, and zinc. Weekly samples were collected at Stingy Run from April 1993 to December 1995. Monthly water samples were collected at Little Scary Creek starting in 1990. Ohio River trace metals (sampled at RM 258.6 and 259.9) were analyzed quarterly in 1993–1995, and Campaign Creek metals were analyzed once, in August 1994. Water grab samples (500 ml) were taken from the streams and preserved for metal analysis according to USEPA procedures (USEPA, 1983).

Metal Analysis

Total recoverable metal concentrations in the water were determined by inductively coupled plasma/atomic emission (ICP/AE) spectrometry (As, Cd, Cr, Cu, Ni, Pb, Zn) and furnace (Se), EPA method 220.7 (USEPA, 1983). In addition to total recoverable metal analysis, monthly discharge samples from the Amos Plant were collected in 1998 and analyzed for inorganic selenium species (Se^{+4} and Se^{+6}) using direct hydride generation (Cutter, 1986). The analyses were performed at the American Electric Power Dolan Laboratory in Columbus, Ohio. Duplicate samples, method blanks, and calibration standards were analyzed continually per standard laboratory procedures.

For tissue metal analysis, organs were weighed on an electronic balance and then subsampled as necessary. Organ samples were dried at 60°C, digested using the nitric acid–peroxide digestion procedure, filtered, and diluted with double distilled water (USEPA, 1991; ASTM, 1996). Metal determinations were performed on an ICP/AE spectrophotometer. All metal concentrations were reported as

micrograms per gram dry weight. Duplicate analyses were run on 10% of the samples in each batch. Quality control procedures consisted of quarterly accuracy-based performance evaluations and analysis of a Certified Reference Material (CRM). National Research Council of Canada dogfish liver (DOLT-1) was used as the CRM.

Hematology

Blood smears were prepared on-site, air-dried, fixed in methanol, and stained with Wright stain for cell differential analysis. Plasma protein, packed cell volume (PCV), hemoglobin, and leukocrit were determined according to established procedures (Houston, 1990) except that Natt & Herrick stain (0.01% methyl violet 2B) was used for leukocyte counts.

Data Analysis

Statistical analyses were carried out using SigmaStat statistical software (Jandel Scientific, 1995). Percent PCV, neutrophils, lymphocytes, and monocytes were arcsin square root-transformed and liver metal concentrations were $\log_{10}$-transformed. All data were tested for normality. Spearman rank order or Pearson product moment correlation analyses were used to test for significant associations between fish morphological, hematological, and liver metal data.

Condition factor was calculated for all fish using the equation

$$K = (W/L^3)\cdot 10^5,$$

where W = weight of fish in grams, L = standard length in millimeters, and 10^5 is a scaling constant to convert small decimals. Liver–somatic indices were also calculated (ratio of liver weight to body weight). Regression equations of fish age versus length were calculated for each stream. Growth rate of fish was defined as the rate of body size increase (length as a function of age). To test for differences of growth rate in the fish from the different streams, regression coefficients (slopes) of fish age vs length were evaluated. The length–weight relationship was evaluated using regression equations of fish length versus weight (log-transformed).

Condition factor was found to be significantly correlated with percent neutrophils and lymphocytes. This would normally necessitate a two-way analysis of variance (ANOVA) to compare blood parameters. Campaign Creek and Ohio River sample sizes, however, were too small to allow a meaningful two-way ANOVA. Consequently, a one-way ANOVA was done to compare hematology results between streams.

Possible statistical differences between hematology parameters, liver metals, and condition indices versus location were tested using a one-way ANOVA (when assumptions of data normality and equal variance were confirmed) or the Kruskal–Wallis test (nonparametric analog of one-way ANOVA). Tukey's (parametric) or a Dunn's (nonparametric) test for pair-wise comparison of means was used if the ANOVA test was significant ($P < 0.05$).

RESULTS

Summary of Metal Analyses

Results of water quality analyses indicated that all sites had similar routine water quality characteristics except for Stingy Run, which had markedly higher conductivity, hardness, and sulfate levels (Table 1). Elevated levels of total

TABLE 1
Representative Water Chemistry of Sampled Field Sites: Campaign Creek (Reference), Ohio River (Reference), Stingy Run (Effluent-Receiving Stream), and Little Scary Creek (Effluent-Receiving Stream)

	Campaign Creek 1994	Ohio River 1995	Ohio River (May–Aug) 1997	Stingy Run 1993–1994	Stingy Run (Jan–May) 1995	Stingy Run (Jun–Dec) 1995	Little Scary Creek 1990–1996[b,e]
pH	7.2	7.7	7.7 (19)	7.7	7.5	7.3	7.6 ± 4.0
D.O. (mg/L)	8	5.8–8.5[a]	9.3[c]	8.5	—	—	8.2
Cond. (Umhos/cm)	505	372	380 (19)	1,122	—	—	497 ± 126
TOC (mg/L)	—	3	—	3	2	—	3[d]
Hardness (mg/L)	—	131	137 (20)	484	—	—	196[d]
Alkalinity (mg/L)	—	58	65 (20)	36	—	—	48[d]
Sulfate (mg/L)	138	104	74 (20)	517	386	—	145 ± 37

Note. Mean ± SD is given; (n) = number of samples analyzed; to calculate means and standard deviations, samples less than method detection limit were set equal to the detection limit.

[a] Based on mean measurements at six shoreline sites in June and August, respectively.

[b] Based on monthly samples in 1990–1996.

[c] Mean of all measurements at ORERP electrofishing zones near Kyger Creek Plant in June and August 1997.

[d] Samples taken during semiannual biological monitoring, 1992–1994.

[e] From Reash *et al.* (1999).

TABLE 2
Representative Water Quality of Sampled Field Sites: Campaign Creek (Reference), Ohio River (Reference), Stingy Run (Effluent-Receiving Stream), and Little Scary Creek (Effluent-Receiving Stream)

Metal (μg/L)	Campaign Creek 1994	Ohio River 1995	Ohio River (May–Aug) 1997	Stingy Run 1993–1994	Stingy Run (Jan–May) 1995	Stingy Run (Jun–Dec) 1995	Little Scary Creek 1990–1996[a,b]
Arsenic	<4 (1)	4.2 ± 0.6 (66)	2.7 ± 1.7 (17)	14.3 ± 9.1 (69)	<4 (all values)	<4 (all values)	64 ± 40
Cadmium	<0.5 (1)	0.6 ± 0.4 (64)	<0.5 (all values)	0.8 ± 0.3 (70)	0.8 ± 0.1 (22)	0.7 ± 0.4 (17)	—
Copper	2 (1)	5.1 ± 3.5 (64)	5.4 ± 3.7 (17)	6.2 ± 2.9 (51)	5.1 ± 2.5 (22)	2.9 ± 1.5 (17)	13 ± 10
Chromium	<2 (1)	2.2 ± 1.7 (21)	1.5 ± 1.0 (4)	29.7 ± 12.1 (70)	2.6 ± 2.4 (22)	1.6 ± 1.5 (17)	—
Lead	<2 (1)	3.9 ± 3.2 (70)	3.3 ± 4.0 (17)	2.1 ± 0.3 (70)	<2 (all values)	<2 (all values)	—
Nickel	18 (1)	6.8 ± 4.2 (63)	5.0 ± 5.1 (17)	13.3 ± 6.9 (61)	17.9 ± 2.8 (22)	14.6 ± 5.3 (17)	—
Selenium	<5 (1)	1.4 ± 2.4 (7)	<0.5 (17)	11.8 ± 4.1 (84)	3.2 ± 1.2 (22)	3.8 ± 1.7 (17)	32 ± 13
Zinc	12 (1)	22.2 ± 10.3 (70)	17.8 ± 22.0 (17)	20.4 ± 14.3 (70)	22.5 ± 5.0 (22)	29.1 ± 12.2 (17)	—

Note. Mean ± SD is given; (*n*) = number of samples analyzed; to calculate means and standard deviations, samples less than method detection limit were set equal to the detection limit.
[a]Based on monthly samples in 1990–1996.
[b]From Reash *et al.* (1999).

dissolved solids and cations are typical of alkaline fly ash discharges (Carlson and Adriano, 1993). Both Stingy Run and Little Scary Creek had elevated levels of trace metals (Table 2). Stingy Run had elevated water column levels of arsenic, cadmium, chromium, copper, and selenium relative to those found in the Ohio River and Campaign Creek. Little Scary Creek had elevated levels of arsenic, copper, and selenium. Ohio River samples generally had higher concentrations of trace metals compared to Campaign Creek, but these levels were well below established water quality criteria for the Ohio River (ORSANCO, 1997). Speciation analysis for discharge samples taken in February–September 1998 from Little Scary Creek indicated that 90% of the total selenium was present as selenite (Se^{+4}) and 10% was present as selenate (Se^{+6}) (Reash *et al.*, 1999). The average Se^{+4} concentration in these eight monthly samples (42 μg/L) was well below acutely toxic thresholds (USEPA, 1995b).

Trace metal analysis of fish tissues from Stingy Run and Little Scary Creek indicated elevated levels of selenium and other metals. Bluegills collected from Stingy Run in September 1994 had significantly higher liver concentrations of arsenic, copper, and selenium relative to bluegill collected from Campaign Creek in October 1994 (Kruskal–Wallis Test, $P < 0.05$; Table 3). Bluegill sunfish from Little Scary Creek also had significantly higher levels of trace metals in liver tissues compared to sunfish from the Ohio River ($P < 0.05$; Table 3) (Reash *et al.*, 1999).

Hematology

Average plasma protein concentrations in fish collected from all sites ranged from 5.3 to 8.3 gm/dL and were significantly higher in fish from the Ohio River (1995) than in fish from Little Scary Creek (Table 4). Average packed cell

TABLE 3
Liver Tissue Metal Concentrations (μg/g Dry Weight) in Fish from Campaign Creek (CC), Ohio River (OR), Stingy Run (SR), and Little Scary Creek (LSC)

Location	Species	Arsenic	Cadmium	Copper	Chromium	Lead	Selenium	Zinc
CC 1994	Bluegill (4)	0.6 ± 0.4	0.7 ± 0.2	6.7 ± 0.4	1.0 ± 0.3	2.2 ± 3.3	2.8 ± 1.8	86.1 ± 7.3
OR 1995	Bluegill (14)	1.6 ± 2.4	0.9 ± 0.5	6.7 ± 3.7	1.8 ± 0.9	1.4 ± 1.5	6.0 ± 3.9	86.8 ± 16.6
OR 1997	Bluegill (8)	1.7 ± 1.2	0.9 ± 0.7	12.1 ± 6.1	0.7 ± 0.4	0.4 ± 0.4	8.2 ± 4.2	90.0 ± 23.4
SR 93–94	Bluegill (12)	4.7 ± 3.5	0.8 ± 0.4	33.0 ± 25.0	1.1 ± 0.3	3.2 ± 4.6	57.3 ± 24.1	97.7 ± 14.2
SR May-95	Bluegill (3)	1.7 ± 0.5	0.8 ± 0.6	4.6 ± 1.5	0.9 ± 0.2	11.5 ± 15	24.7 ± 9.1	93.8 ± 11.7
	Green sunfish (2)	0.5 ± 0.08	0.5 ± 0.2	1.8 ± 0.4	0.3 ± 0.0	0.3 ± 0.0	10.4 ± 1.8	91.8 ± 13.0
SR Sep-95	Bluegill (4)	2.1 ± 1.3	3.9 ± 0.7	12.1 ± 2.8	2.7 ± 0.9	0.7 ± 0.0	20.9 ± 6.0	84.7 ± 4.4
	Green sunfish (5)	1.7 ± 0.4	2.2 ± 0.5	19.7 ± 4.2	4.8 ± 1.9	2.1 ± 1.5	4.8 ± 2.3	86.8 ± 10.8
SR Oct-97	Green sunfish (2)	<1.7	4.9	18.1	1.3	<1.0	21.6	115.3
LSC 1996[a]	Bluegill (12)	5.38	4.18	33.5	3.54	1.2 ± 1.0	53.8	124.0 ± 6

Note. Mean ± SD is given; (*n*) = number of fish analyzed.
[a]From Reash *et al.* (1999).

TABLE 4
Terminal Blood Parameters for Sunfish from Campaign Creek (Reference), Ohio River (Reference), Stingy Run (Effluent-Receiving Stream), and Little Scary Creek (Effluent-Receiving Stream)

	Campaign Creek 1994	Ohio River 1995	Ohio River 1997	Stingy Run 1993–1994	Little Scary Creek 1996
Plasma protein (g/dL)	6.8 ± 0.8 (5)	8.3 ± 2.3 (5)A	6.3 ± 0.2 (4)	7.0 ± 1.0 (10)	5.3 ± 0.7 (4)B
PCV (%)	36.4 ± 6.8 (5)	42.4 ± 15.4 (5)	29.0 ± 7.4 (4)	35.0 ± 7.4 (10)	29.0 ± 12.6 (4)
Hb (g/dL)	—	7.6 ± 0.7 (5)	6.2 ± 1.2 (4)	9.0 (1)	6.4 ± 0.8 (4)
WBC (cells × 10^9/L)	89.8 ± 42.2 (3)A	35.2 ± 11.5 (5)A	8.6 ± 5.2 (3)	9.6 ± 6.5 (11)	5.0 ± 1.6 (4)B
Neutrophils (%)	4.7 ± 8.1 (6)A	83.4 ± 8.4 (5)B	60.3 ± 36.3 (4)B	14.4 ± 10.3 (13)A	67.8 ± 15.7 (6)B
Lymphocytes (%)	80.0 ± 28.8 (6)A	15.2 ± 7.3 (5)B	21.0 ± 8.8 (4)B	80.8 ± 10.7 (13)A	26.3 ± 17.7 (6)B
Monocytes (%)	18.4 ± 22.7 (5)	1.4 ± 2.2 (5)	4.0 ± 4.4 (3)	3.8 ± 4.5 (13)	6.5 ± 4.4 (6)

Note. Mean ± SD is given; (*n*) = number of fish analyzed; PCV, packed cell volume; Hb, hemoglobin; WBC, white blood cell count. Values with different letters are significantly different ($P < 0.05$).

volumes (PCV) ranged from 29% in 1997 Ohio River and Little Scary Creek fish, to 42% in fish collected from the Ohio River in 1995, but did not vary significantly between sites (Table 4). Attempts to collect sufficient volumes of blood to allow a determination of hemoglobin were partly successful. One sample was obtained from Stingy Run fish, nine were obtained from Ohio River fish, and four were collected from Little Scary Creek fish. Average hemoglobin concentrations ranged from 6.2 to 9.0 gm/dL, with no apparent differences between sites (Table 4). Average white blood cell (WBC) counts ranged from a high of 89.8×10^9 cells/L for fish from Campaign Creek to a low of 5.0×10^9 cells/L for fish from Little Scary Creek (Table 4). Fish from the Ohio River had variable counts with a mean of 35.2×10^9 cells/L obtained in 1995 and a mean of 8.6×10^9 cells/L obtained in 1997. The WBC counts of fish from Little Scary Creek were significantly lower ($P < 0.05$), and those of Stingy Run were lower (but not significantly) than those of fish collected from the Ohio River in 1995 and Campaign Creek.

Stingy Run and Campaign Creek blood smears had a significantly higher percentage of lymphocytes than those of fish from the Ohio River and Little Scary Creek (Table 4). The percentage of neutrophils found in Ohio River fish was significantly higher than those found in fish from Stingy Run or Campaign Creek (Table 4). Cell differentials in fish from Little Scary Creek were essentially the same as those from the Ohio River, with the percentage of neutrophils being the highest, followed by the percentage of lymphocytes and monocytes, respectively.

Slight to moderate polychromasia (the presence of blue red blood cells seen in blood films stained with Romanovsky stains, compared to the normal pink-stained red blood cells) was noted in the blood smears of fish from Campaign Creek, Ohio River, in 1997, and Little Scary Creek collections (Table 5). The cells that appear bluish are juvenile erythrocytes. Ohio River cell differentials from 1997 also revealed anisocytosis (cells of different sizes) while Ohio River fish collected in 1995 exhibited cytoplasmic basophilia and Dohle bodies. Polychromasia and anisocytosis are typically found in young animals or in cases of regenerating anemias. Cytoplasmic basophilia is a condition where the cytoplasma stains darker than usual and is generally associated with a diseased animal. Dohle bodies are structures found within the cell cytoplasm and are also associated with sick animals.

For all fish collected in the field, there was a significant correlation between WBC counts and liver concentrations of arsenic, copper, selenium, and zinc (Table 6). Leukopenia (reduction in the number of white blood cells) was evident with increasing liver selenium concentrations. WBC counts dropped quickly in the concentration range 0 to 20 μg/g. There was little change in WBC counts over the liver selenium concentration range of 20 to 100 μg/g. Percent lymphocytes and neutrophils were correlated with liver chromium levels, although not strongly. In general, WBC counts decreased, and the percentage of lymphocytes and neutrophils either increased or decreased, with exposure

TABLE 5
Occurrence of Atypical Blood Cell Types in Fish from Campaign Creek (Reference), Ohio River (Reference), Stingy Run (Effluent–Receiving stream), and Little Scary Creek (Effluent-Receiving Stream)

Site	Atypical hematology
Campaign Creek	Polychromasia
Ohio River 1995	Cytoplasmic basophilia,[a] dohle bodies[a]
Ohio River 1997	Polychromasia,[b] anisocytosis[b]
Stingy Run	Immature RBCs[b]
Little Scary Creek	Polychromasia[b]

[a]Typical in diseased animals.
[b]Typical in young animals or in regenerating anemias.

TABLE 6
Correlations between Hematology Biomarkers/Condition Indices, That Are Significantly Different between Sites, and Metal Contaminants

Parameter	Rank order of correlating liver metals with corresponding correlation coefficients (R)
WBC	Arsenic (−0.71), zinc (−0.59), selenium (−0.56), copper (−0.56)
Lym	Chromium (−0.39)
Neu	Chromium (0.38)
CF	Zinc (−0.47), cadmium (−0.38), chromium (−0.33), arsenic (−0.31), copper (−0.31)
LSI	Copper (−0.34), chromium (−0.29)

Note. Metals and R values given. R values near +1 or −1 indicate strong relationships; those near zero indicate weak relationships. There is less than a 5% probability ($P < 0.05$) of being wrong in concluding that there is a true relationship between the fish parameters and corresponding liver metals.

to ash pond metals (Fig. 3). Interspecies differences in hematology were not tested and seasonal differences were not apparent.

Condition Indices

The mean condition factor of fish from Little Scary Creek was significantly lower ($P < 0.05$) than that of fish from Campaign Creek, Ohio River, in 1997, and Stingy Run in 1993–1994, but the same as that of fish from the Ohio River and Stingy Run in 1995 (Table 7). Condition factors for fish from Stingy Run in 1995 were also lower than those from Stingy Run in 1993–1994. Condition factor values were negatively correlated ($P < 0.05$) with liver tissue levels of arsenic, cadmium, chromium, copper, and, in particular, zinc, but were not correlated with liver tissue levels of lead or selenium. Condition factor values were only weakly correlated ($R = 0.4$) with percent monocytes in an inverse relationship.

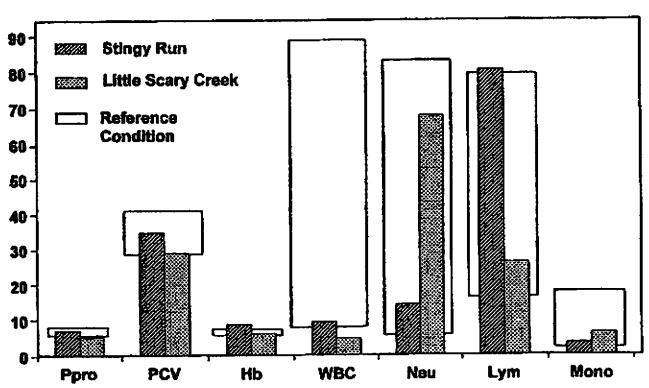

FIG. 3. Comparison between sunfish hematology biomarkers measured at two power plant sites and range of biomarkers from two reference sites. Plasma protein (Ppro) and hemoglobin (Hb) measured as gm/dL; white blood cell count (WBC) measured as 10E9 cells/L; packed cell volume (PVC), neutrophils (Neu), lymphocytes (Lym), and monocytes (Mono) all measured as percentage.

There were no significant differences ($P < 0.05$) in mean liver somatic index (LSI) for fish collected from Stingy Run, Little Scary Creek, Campaign Creek, and the Ohio River. For all species combined, LSI values were very similar despite the large differences in water chemistry and liver metal concentrations (Table 7). Despite having significantly lower condition factors, Little Scary Creek bluegill had comparable liver weight and LSI values, relative to the Campaign Creek reference population. Sunfish from Stingy Run also had LSI values statistically similar to those of fish from Campaign Creek. Although mean LSI values between the sampled sites were not significantly different, there was a significant ($P < 0.05$), but weak ($R = 0.34$), negative correlation between LSI values and liver tissue levels of copper and chromium. LSI values were not correlated with liver selenium levels or any of the hematology measurements.

Fish Growth

Length–weight regressions revealed significant ($P < 0.001$) relationships between length and weight for fish from Stingy Run, Little Scary Creek, Campaign Creek, and the Ohio River (Table 7). There was no evidence that this relationship differed between the four sites, although fish taken from Campaign Creek were generally smaller. Sunfish collected from Little Scary Creek were also smaller, having significantly smaller length and weight (t test; $P < 0.05$) than bluegill from the Ohio River (Reash *et al.*, 1999).

Age–length regressions also revealed significant ($P < 0.05$) relationships between age and length for fish from all four locations (Table 7); however, Stingy Run R^2 values for this relationship in 1993/1994 were low ($R^2 = 0.2$). Growth (length) was used as an indicator of a population-level effect in fish from the effluent receiving streams. For each of the major age classes of sunfish (2+ to 7+), the mean lengths of fish from Stingy Run and Little Scary Creek were statistically the same as those of fish taken from Campaign Creek or the Ohio River (Table 7). So few age 1+ and 8+ fish were collected that these age classes were not included in the analysis. Growth appears to continue for fish from all sites from year to year (Fig. 4). The decrease in the mean length of fish from the Ohio River after age 6+ may have been an artifact of the small sample size of age 7+ fish ($n = 1$).

The distribution of age groups was confirmed by scale analysis and revealed similar age-class representation among the study sites (Fig. 5). The sunfish population in Stingy Run had a continuous year-class representation.

TABLE 7
Length–Weight Regression (LWR), Age–Length Regression (ALR), Mean Condition Factor (CF), and Mean Liver Somatic Index (LSI) for Sunfish from Campaign Creek (CC), Ohio River (OR), Stingy Run (SR), and Little Scary Creek (LSC)

Location	LWR	R^2	n	ALR	R^2	n	CF	LSI
CC 1994	$\log W = 3.04 \log L - 1.49$	0.92	18	SL = 0.66(age) + 8.55	0.80	7	3.61 ± 0.48 (18)BC	0.99 ± 0.19 (4)
OR 1995	$\log W = 3.04 \log L - 1.50$	0.96	14	SL = 1.43(age) + 6.55	0.64	13	3.59 ± 0.42 (14)ABC	1.13 ± 0.31 (14)
OR 1997	$\log W = 2.52 \log L - 0.89$	0.92	8				3.73 ± 0.45 (8)BC	—
SR 1993–1994	$\log W = 3.35 \log L - 1.84$	0.92	26	SL = 0.48(age) + 11.2	0.20	23	3.66 ± 0.40 (26)B	1.01 ± 0.23 (12)
SR 1995	$\log W = 2.91 \log L - 1.40$	0.99	30	SL = 1.16(age) + 6.5	0.81	24	3.32 ± 0.35 (30)AC	1.34 ± 0.42 (20)
LSC 1996[a]	$\log W = 3.32 \log L - 1.84$	0.97	13	SL = 1.17(age) + 6.89	0.64	13	3.15 ± 0.35 (13)A	1.00 ± 0.39 (12)

Note. Mean ± SD is given; (n) = number of fish analyzed. Significant differences between LWR and ALR values were not determined. Significant differences between mean condition factors are indicated by different letters. There were no significant differences between mean liver somatic index values.
[a]From Reash *et al.* (1999).

Bluegill in age classes 2+ through 7+ were sampled from the stream during collection events. Young-of-year (YOY) bluegills and green sunfish were also collected and noted during sampling in 1994 and 1995. The frequency of age-class representation differed somewhat among the populations in Little Scary Creek and the Ohio River. Bluegill in age-classes 2+ to 7+ were collected from both streams; however, no YOY fish were collected from either stream (Fig. 5). Fish from the Ohio River were generally older, with most of these fish being in year-classes 5+ or 6+. In contrast, most sunfish collected from Little Scary Creek were age 2+, 3+, or 4+ fish (Reash *et al.*, 1999).

DISCUSSION

Hematology

Despite exposure to elevated concentrations of trace metals and the accumulation of arsenic, copper, and selenium in liver tissues, plasma protein levels of Stingy Run sunfish were not significantly different from those of reference fish; however, those in Little Scary Creek fish were significantly lower (Table 4, Fig. 3). Plasma protein can vary with sex, size, and maturity and is influenced by temperature and food availability. Low plasma protein can indicate starvation, which is typical of temperate zone fish in the winter and early spring (Goede and Barten, 1990). Reduced food intake and food aversion are also symptoms of fish fed selenium-contaminated food (Finley, 1985; Woock *et al.*, 1987) which theoretically could lead to reduced plasma protein. The plasma protein data suggest that the Stingy Run sunfish were not suffering adverse effects due

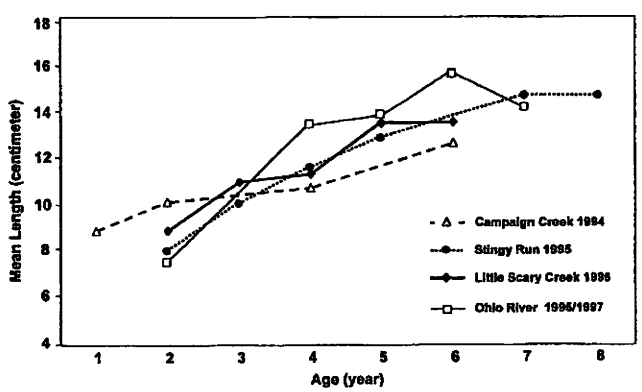

FIG. 4. Mean length for the major age classes of sunfish collected from Stingy Run, Little Scary Creek and reference streams.

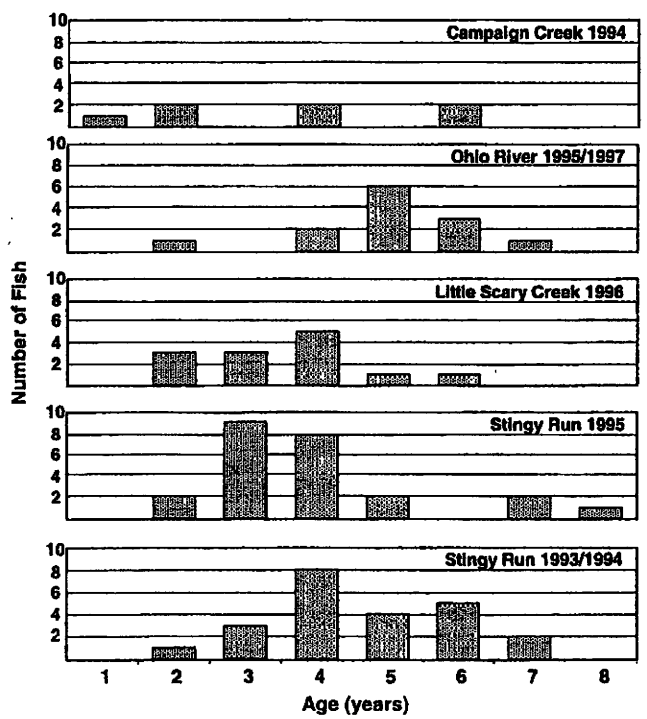

FIG. 5. Frequency of age-class representation for sunfish collected from Stingy Run, Little Scary Creek, and reference streams.

to aquatic metal exposures or a contaminated food supply; however, those from Little Scary Creek may have had a reduced food supply. The Little Scary Creek sampling site was small and could have had a limited food supply.

Evaluations of packed cell volume and hemoglobin allow a determination of possible anemia. Reduced PCV or hematocrits (volume of RBCs per unit volume of whole blood; hematocrit is synonymous with PCV, although a small portion of PCV includes WBCs and platelets) in fish exposed to high selenium- and metal-contaminated effluents have been reported in a number of studies (Sorenson *et al.*, 1982, 1984; Sorensen and Bauer, 1983; Sjobeck *et al.*, 1984; Gill and Pant, 1987). A low hematocrit in fish may indicate disease (Goede and Barton, 1990). Reduced hematocrits and decreased hemoglobin concentrations have been observed in ducks (Hoffman *et al.*, 1991) and in rats (Goehring *et al.*, 1984) fed high selenium diets. The PCV results for this study indicate that Stingy Run and Little Scary Creek sunfish are not anemic.

Juvenile erythrocytes (polychromasia) were found in fish from Campaign Creek, the Ohio River in 1997, and Little Scary Creek, but were not found in Stingy Run or Ohio River fish in 1995. Polychromasia is typically found in young animals or in regenerating anemias. Sunfish from Campaign Creek were younger than those from Stingy Run or the Ohio River; therefore, evidence of polychromasia in these fish was normal. The absence of immature ertyhtocytes in Stingy Run fish could have been the result of high selenium exposures. In a study of sunfish from a lake which received selenium-laden effluent from a power plant in Texas, Sorenson and Bauer (1983) noted a reduction in the number of erythroblasts or immature erythrocytes. A reduction in the number of immature erythrocytes could be indicative of a reduced rate of erythropoiesis, which could lead to reduced oxygen availability to tissues. This erythrocytic fragility or hemolytic action could inhibit the synthesis of new hemoglobin or erythrocytes, thus explaining the low PCV and hematocrits seen in selenium-exposed fish. Finley (1985) noted a similar effect in bluegill sunfish fed selenium-contaminated *Hexagenia* nymphs collected from Belews Lake, North Carolina, as did Lemly (1993), who exposed bluegill sunfish to waterborne (5 μg/L) and dietary (5 μg/g dry weight) selenium for a period of 180 days.

Leukopenia (reduced WBC counts) was associated with increasing liver metal concentrations in fish from Stingy Run and Little Scary Creek (Table 6). The livers of these fish had an average selenium concentration of 57.3 and 53.8 μg/g dry weight, respectively. Sorenson *et al.* (1984) and Sorenson and Bauer (1983) also reported leukopenia in feral fish exposed to elevated aqueous selenium concentrations. The fish in the referenced studies had selenium hepatopancreas concentrations as high as 21–40 μg/g (wet weight) compared to an estimated average liver selenium concentration of 14.3 μg/g (wet weight) in the current study. Both leukopenia and, conversely, leukocytosis have been reported in fish populations exposed to heavy metals (Mishra and Srivastava, 1980; Gill and Pant, 1987; Singh and Reddy, 1990). WBC abundance provides an indication of fish health and a high WBC count may indicate a subclinical infection. An extremely low WBC count indicates either suppression of circulating lymphocytes, a characteristic acute stress response, or that an active bacterial infection has induced leukocytolysis (Goede and Barten, 1990). Fish from Stingy Run may have been expressing the former, since there were no signs of bacterial infection (e.g., lesions, extensive fin erosion) in these fish. White blood cell counts as low as 0.2 cells $\times 10^9$/L have been reported in feral bluegill sunfish that had been held in aquaria for 180 days (Lemly, 1993).

Fish from Stingy Run and Campaign Creek appeared to exhibit lymphocytosis (high lymphocyte percentages) and neutropenia (low neutrophil percentages) when compared to fish from the Ohio River and Little Scary Creek. Changes in leukocyte subpopulations have been reported in fish exposed to heavy metals (Sjobeck and Larsson, 1978; Sorensen and Bauer, 1983; Sjobeck *et al.*, 1984; Gill and Pant, 1987). The proportion of lymphocytes in the fish was positively correlated with liver selenium concentrations, indicating that selenium may induce such a response. Increased numbers of lymphocytes are indicative of infection and/or abnormal hematopoiesis. Such a condition may reflect a bacterial or viral infection, metal-induced cell or tissue damage, or direct stimulation of the immune defense by the presence of the foreign substance metals (Ellis, 1976). The fish from Campaign Creek also exhibited lymphocytosis; however, these fish were not exposed to elevated selenium concentrations. In reference redear sunfish (*L. microlophus*) from Lake Martin, Sorenson and Bauer (1983) found that lymphocytes composed an average of 20% of the leukocyte population and Lemly (1993) found that percent lymphocyte values in control bluegill sunfish (*L. macrochirus*) ranged from 16 to 23%. It appears that the Stingy Run and Campaign Creek lymphocyte percentages are high in relation to other studies and that those of the Ohio River and Little Scary Creek fish are normal (Table 4). It may be that the Stingy Run and Campaign Creek fish were experiencing different, unrelated stresses, such as a bacterial infection or a metal-induced immune response, that resulted in a similar lymphocyte response.

Suppression of neutrophil response has been shown in studies with fish exposed to selenium and other metals (Sorenson and Bauer, 1983; Weeks *et al.*, 1986, 1990; Faisal and Huggett, 1993). Reduced neutrophil numbers are possibly indicative of reduced or disrupted phagocytotic capacity and reduced disease resistance. However, it is not clear why fish from Campaign Creek would express neutropenia or those from Little Scary Creek would express neutrophilia, but increased neutrophil activity has also been observed in fish exposed to other pollutants (Stasiak and

Bauman, 1996). Most investigators have reported that neutrophils make up 2–25% of the fish leukocyte population (Houston, 1990). Based on this, neutrophil counts in Stingy Run and Campaign Creek fish are normal, whereas those in Ohio River and Little Scary Creek fish are elevated. It is possible that the Ohio River and Little Scary Creek fish were expressing neutrophilia in response to an unknown stress. Dohle bodies and cytoplasmic basophilia were also noted in blood smears from Ohio River fish, but not in fish from Stingy Run or Campaign Creek. Cytoplasmic basophilia has been noted in other studies involving the exposure of fish to heavy metals (Gill and Pant, 1987). Cytoplasmic basophilia and dohle bodies are indicative of disease (Jain, 1986) and this is a possible indication that Ohio River and Little Scary Creek fish were suffering from an unknown stress which manifested itself through neutrophilia, basophilia, and the presence of dohle bodies.

Condition Indices

Hematology parameters were significantly altered; however, changes in condition factor and liver somatic index values were not related. Apparently, other factors were affecting condition indices. The condition factor is supposed to reflect the overall well-being of fish and is often used to compare growth against established empirical standards or to evaluate stressed fish populations. Condition factor can be affected by numerous factors including fish density (Fagerlund *et al.*, 1981), acidification (Schindler *et al.*, 1985), and other adverse environmental conditions (Barnes *et al.*, 1984; Adams *et al.*, 1985). Goede and Barton (1990) noted that a decline in condition factor is usually interpreted as depletion of energy resources, such as stored liver glycogen or body fat. However, there was no correlation between condition factor and selenium, the primary contaminant and stressor of ash pond effluents. It is possible that the reduced condition factor was the result of factors other than the metals in the discharge.

A decline in condition factor may also reflect a change in feeding patterns (Goede and Barton, 1990), behavioral responses to certain stressors (Brown *et al.*, 1987), or an increase in metabolic rate (Barton and Schreck, 1987) and need not be strictly due to stress or starvation. Condition factor can also fluctuate seasonally, with physiological development, sexual maturation, and geographic location (Goede and Barton, 1990). The reduced condition factor values in Little Scary Creek fish could have been due to exposure to trace metals in the ash pond discharge, but was more likely due to reduced food availability in the creek. Condition factors and LSI values are typically elevated in fish exposed to selenium (Sorensen *et al.*, 1984). In Belews Lake, North Carolina, green sunfish had significantly higher condition factors (as well as histopathological and hematological effects) compared to reference fish. In addition, these same fish had higher relative weights of hepatopancreas tissue as a result of edema (Sorensen and Bauer, 1984). In a lake receiving fly ash effluent from a coal-fired power plant (Lake Martin, Texas), redear sunfish (*L. microlophus*) showed decreased condition factor and hepatopancreas relative weight with increasing selenium concentration in various organs. Nakamoto and Hassler (1992) found that female bluegills from a selenium-contaminated river had a higher condition factor, whereas males showed no spatial differences.

As further evidence of a lack of impact due to the trace metals, the LSI values of fish collected for the present study did not vary significantly among the four fish populations in Stingy Run, Little Scary Creek, Campaign Creek, and the Ohio River. Condition factor, relative weight data, and liver somatic index appear to be unpredictable indicators of chronic selenium exposure. Selenium exposure may, in fact, effect growth rate and cause various biological manifestations at a given site (Sorensen *et al.*, 1984); however, waterbody-specific factors unrelated to selenium exposure, such as productivity and food availability, may be more important.

Growth Response

Although hematology was affected, there was apparently no concurrent effect on the growth of the fish. There was some evidence, however, based on age–length regressions, that the fish from Stingy Run and Campaign Creek were growing more slowly than fish from the Ohio River. Portions of Campaign Creek have intermittent flows which could interrupt food availability to the fish and explain their slower growth. It is also possible that a smaller food base in Stingy Run affected fish growth in that stream; however, there were no noticeable differences in length–weight regressions between the sites. In addition, for each of the major age classes, there was no significant difference in the mean length of fish from all four sites. It is apparent that the sunfish in the effluent-receiving streams are growing at a rate similar to that of sunfish in the reference streams.

Adams *et al.* (1992) hypothesized that higher growth rates downstream of industrial discharges may be caused by general reproductive failure of the population leading to decreased recruitment, reduced population abundance, decreased competition, increased resource availability, and therefore faster growth of survivors. Evidence for such a situation would include reduced abundance of young (age 0+ and 1+). This hypothesis could be valid for Stingy Run and Little Scary Creek where fish age data indicate a lower frequency of younger individuals (Fig. 5). However, the lack of YOY fish does not prove conclusively that YOY fish are not present in the stream. Factors unrelated to water quality (e.g., fish were collected after the spawning season, all available habitats were not sampled, electrofishing is

more selective for juvenile and adult fish) may, at least partially, explain the lack of YOY fish from both sites.

Ecological Assessment

The finding of persistent populations of bluegill and green sunfish in streams with elevated levels of selenium and other metals contradicts previous studies that found significant adverse effects at lower environmental selenium levels (Olmsted *et al.*, 1986; Coughlan and Velte, 1989; Lemly, 1996). Based on the liver selenium levels of this and other studies (Belews Lake, Lake Martin), the fish from the coal fly ash-receiving streams should be adversely affected. The fish collected in these studies had elevated liver concentrations of arsenic, copper, and selenium and significant changes in hematology; however, it appears that the observed changes were not severe enough to affect the overall health of the fish. Condition factors (with the exception of Little Scary Creek fish), liver indices, and growth responses all indicated that the fish in Stingy Run and Little Scary Creek were surviving and growing within the same bounds as fish in reference streams. There is evidence that high levels of selenium and other metals are not always associated with adverse population-level effects. Several investigators have reported the presence of fish populations exposed to selenium-laden effluents (Loeffler *et al.*, 1981; Lemly, 1985; Reash *et al.*, 1988; Besser *et al.*, 1996). The levels of selenium in these water bodies often exceeded water quality criteria for the protection of aquatic life (Loeffler *et al.*, 1981; Besser *et al.*, 1996).

There are several possible explanations for the apparent lack of selenium toxicity. Among them is that selenium may not be sufficiently bioavailable, either in the external environment, or in the fish themselves. Selenium can be present as selenate (Se^{+6}), selenite (Se^{+4}), elemental selenium (Se^{0}), and inorganic and organic selenides (Se^{-2}). Elemental selenium is stable, insoluble, and poorly assimilated by aquatic organisms, providing relatively little toxic threat (Maier *et al.*, 1993). Selenate and selenite are often the dominant forms in aerobic waters and are potentially toxic to aquatic organisms (Maier *et al.*, 1993), with selenite generally considered to be the more toxic form due to greater bioavailability (USEPA, 1998). Selenides can occur as inorganic or organic forms. Inorganic selenides are formed under anaerobic conditions as insoluble complex precipitates that pose minimal potential toxicity (Hemphill, 1976). Organic selenides are the result of inorganic selenium uptake by primary producers and synthesis of organic compounds in which selenium replaces sulfur (Maier *et al.*, 1993). Organic selenides can pose a disproportionately higher threat of direct toxicity and reproductive effects than selenite or selenate (Masscheleyn and Patrick, 1993); however, the primary form of selenium in the Stingy Run and Little Scary Creek discharges is selenite, which is much less toxic.

There is also evidence that other metals can antagonize the toxicity of selenium. Selenium forms complexes with copper (Amdur *et al.*, 1991), arsenic (Levander, 1977), cadmium (Van Puymbroeck *et al.*, 1982), and mercury (Southworth *et al.*, 1994) that can reduce the toxicity of selenium. Antagonism has also been observed between aqueous selenium (as selenite) and mercury (+2) in northern creek chubs (Kim *et al.*, 1977) and in other fish species (Turner and Swick, 1983; Cuvin and Furness, 1988). Stingy Run and Little Scary Creek had elevated water levels of arsenic, chromium, nickel, and selenium and fish livers had elevated levels of arsenic, copper, and selenium. It is possible that these other metals interfered with the toxicity of selenium in the fish. There is also evidence that sulfate may interfere with the acute toxicity of selenium (Maier *et al.*, 1993; Ogle and Knight, 1996). This is a plausible explanation for the lack of selenium toxicity in Stingy Run and Little Scary Creek, as sulfate levels were elevated in both (Table 1).

Another explanation for the lack of apparent toxicity is that the sunfish in Stingy Run and Little Scary Creek may have a protective physiological mechanism that mediates metal toxicity. Natural populations of aquatic organisms can develop increased tolerances to certain metals and it is possible that fish in Stingy Run and Little Scary Creek have developed a similar tolerance. Metallothionein and other metalloproteins are known to be involved in the metabolism and detoxification of certain trace metals in aquatic organisms (Benson and Birge, 1985; Dyer *et al.*, 1993; Roesijadi, 1994) and it is possible that such a mechanism was involved here.

CONCLUSION

Relative to reference sites, fish from Stingy Run and Little Scary Creek had lowered condition factors and WBC counts. These findings are consistent with previous studies of sunfish collected from fly ash pond reservoirs; however, no evidence was found that indicated that the bluegill in Stingy Run or Little Scary Creek were experiencing significant impairment or mortality. Five age-classes were represented in single sampling events and the condition factor of these fish was similar to those of fish from the Ohio River and Campaign Creek. Although there is evidence that the selenium levels encountered in this study may not have been detrimental to the exposed fish populations, several hematological indicators were found to be significantly different from reference conditions. Despite these changes, it is important to consider the population health of the affected populations. There must be significant correlation between the biological markers and population effects if the parameters are to be useful as indicators of toxicity or adverse impact. Based on this study, changes in hematology were not sufficient to be ecologically detrimental to the sunfish populations in Stingy Run or Little Scary Creek.

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Assessment of Tolerant Sunfish Populations (Lepomis sp.) Inhabiting Selenium-Laden Coal Ash Effluents

2. Tissue Biochemistry Evaluation

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Sunfish were collected from a fly ash pond-receiving stream and an Ohio River reference site to assess biochemical responses to coal ash effluent exposure. Selenium levels in sunfish from the receiving stream were higher than toxic thresholds associated with adverse population effects and reproductive impairment. Tissue biochemistry was found to be indicative of metal exposure and effect, but varied widely. Liver glycogen was positively correlated with increased liver metal levels, indicating no adverse effect upon stored carbohydrate levels. Lipid levels decreased with increasing metals, indicating possible nutritional stress. Protein levels increased with increasing metal levels, possibly due to the synthesis of proteins to sequester the metals. ATPase, dUTPase, and alkaline phosphatase activity generally decreased with exposure to ash pond metals, but remained within normal physiological ranges. Fish condition factors and liver somatic indices were correlated with liver lipid levels, dUTPase activity, and gill ATPase and alkaline phosphatase activity. Exposure to coal ash effluents produced biochemical markers of exposure that were associated with fish condition indicators; however, the indices themselves were not significantly affected by effluent exposure. © 2001 Elsevier Science

Key Words: **coal ash; bluegill; selenium; biomarkers; biochemistry.**

INTRODUCTION

Elevated levels of metals and metalloids are known to be released from wet coal ash disposal treatment systems. These metals, considered to be the most likely causative agent for coal ash toxicity, and known to disrupt the integrity of biochemical and physiological processes in exposed fish. Gill and Pant (1983) noted hypoglycemia and diminished cholesterol levels and Dubale and Shah (1981) found decreased liver glycogen and protein in fish chronically exposed to cadmium. Sastry and Sunita (1983) noted similar changes in fish chronically exposed to chromium. Histopathological alterations of gill, liver, and spleen tissue have also been documented in fish exposed to a variety of metals and other pollutants (Theodorakis *et al.*, 1992; Teh *et al.*, 1997). Tissue biochemical and pathological changes have also been documented in fish following exposure to selenium, the primary contaminant of coal ash effluents (Sorenson *et al.*, 1982, 1984; Finley, 1985; Lemly, 1993).

Tissue biochemical changes can be used as indicators of fish physiological stress and health. Fish store energy as either glycogen or lipids and during times of stress, these energy stores are mobilized. Protein can also be used as an energy source during severe stress (Mayer *et al.*, 1992). The analysis of these three types of energy reserves can be used as a general indicator of fish health. Changes in these systems are generally indicative of long-term sublethal exposure to a stressor (Mayer *et al.*, 1992). Analysis of additional biochemical or molecular changes can also be indicative of pollutant exposure and effect. Studies of mammalian cell morphology and histogenesis have utilized enzymatic and histochemical markers for foci of cellular alteration (Moore and Myers, 1994). In fish, the more commonly assessed markers include enzymes such as adenosine triphosphatase (ATPase), glucose-6-phosphatase, and alkaline phosphatase (AP) (Moore and Myers, 1994).

Although sensitive, changes in tissue biochemistry and enzyme activity are not always associated with adverse effects on fish health at the population level (Niimi, 1990). Biochemical responses can be affected by other environmental factors, such as water temperature, age, disease, nutritional status, and seasonal changes. Therefore, the objectives of this study were to measure tissue biochemical and histochemical changes in fish collected from fly ash pond-receiving streams, determine whether these changes were related to fish health indices, and evaluate their use as indicators of coal ash toxicity.

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METHODS

Study site location, fish collection and sampling, water quality monitoring and metal analysis procedures are described elsewhere (Reash *et al.*, 1999; Lohner *et al.*, 2001a).

Tissue Chemistry

After capture, fish were examined externally and internally for evidence of lesions or other abnormalities. Gill tissue, spleens, and livers of fish were then removed using acid-rinsed, stainles-steel instruments, placed in small polyethylene bags, and kept on ice. Organ samples were frozen and kept at −70°C until they were analyzed. For protein, lipid, and glycogen analysis, liver tissues were divided into pieces, weighed, and then ground in 4 ml of 50 mM of phosphate buffer (pH 7.2), 1 mM EDTA, 0.5 mM PMSF with a motor-driven homogenizer. Protein, lipid, and glycogen assays were conducted using the methods of Bradford (1976), Van Handel (1985a), and Van Handel (1985b), respectively.

For the analysis of DNA synthesis and repair enzymes, liver, gill, and spleen samples were extracted in 1.0 ml of extraction buffer which contained 10 mM Tris–HCl, pH 8.0, 20% (vol/vol) glycerol, 2 mM β-mercaptoethanol, and 1 mM $MgCl_2$. Samples were doused 10 times, sonicated for 15 pulses, and centrifuged. The supernatant was used for the enzyme assays. The activity of deoxyuridine triphosphate nucleotidohydrolase (dUTPase) was determined using the procedure described by Williams and Parris (1987). The reaction mixture contained in a total volume of 100 µl: 50 mM Tris–HCl, pH 8.0, 2 mM β-mercaptoethanol, 1 mM $MgCl_2$, 0.1% (w/v) bovine serum albumin, 2 mM *p*-nitrophenyl phosphate, 5 mM ATP, 0.1 mM [5-^{3}H]dUTP (50 µCi/µmol), and the enzyme. Reactions were terminated and processed as described previously.

Uracil-DNA-glycosylase (glycosylase) activity was determined using a modification of the procedure described by Winters and Williams (1993). The reaction mixture contained in a total volume of 0.2 ml: 50 mM Tris–HCl, pH 7.5, 2 mM β-mercaptoethanol, 10 mM EDTA, 20 µg heat-inactivated bovine serum albumin, 4 µg of [^{3}H] uracil-labeled double-stranded calf thymus DNA, and the enzyme. Reactions were terminated and processed as described previously.

Alkaline phosphatase reactions were performed using a reaction mixture that was contained in a total volume of 1.1 ml: 100 mM 2-amino-2-methyl-1-propanol HCl, pH 10.6, 10 mM *p*-nitrophenyl phosphate, 0.1 mM $MgCl_2$, 1 µM zinc sulfate, and the enzyme. Reactions were terminated by the addition of 2.5 ml of 1 M NaOH and the absorbance was read at a wavelength of 420 nm.

ATPase reactions were performed using a modification of the dUTPase reaction mixture. The reaction mixture was contained in a total volume of 100 µl: 50 mM Tris–HCl, pH 7.5, 2.5 mM KCl, 2.5 mM NaCl, 2.5 mM $MgCl_2$, 0.1% (w/v) bovine serum albumin, 2.5 mM ATP (specific activity 75 µCi/µmol), and the enzyme. Reactions were terminated and processed as described for the dUTPase reaction.

Data Analysis

Statistical analyses were carried out using SigmaStat statistical software (Jandel Scientific, 1995). All data were tested for normality. Spearman rank order or Pearson product moment correlation analyses were used to test for significant associations between fish morphologic, tissue chemistry, and liver metal data. Condition factors, liver somatic indices, and fish growth data were evaluated as previously described (Lohner *et al.*, 2001a). Possible statistical differences between tissue biochemistry parameters, liver metals, and condition indices versus location were tested using a one-way ANOVA (when assumptions of data normality and equal variance were confirmed) or a Kruskal–Wallis test (nonparametric analog of one-way ANOVA). Tukey's (parametric) or Dunn's (nonparametric) test for pair-wise comparison of means was used if the ANOVA test was significant ($P < 0.05$).

RESULTS

Summaries of water quality monitoring, metal analyses, condition indice response, fish growth, and reproductive status as related to these studies are presented in Lohner *et al.* (2001a) and Reash *et al.* (1999).

Tissue Chemistry

Liver tissue biochemistry was performed twice on fish from Stingy Run and once on fish from the Ohio River. Results varied widely, but were significantly correlated with liver metal levels for several parameters. Liver glycogen was highest in fish collected from Stingy Run in September 1995, lowest in fish collected from Stingy Run in May 1995, and intermediate in fish from the Ohio River (Table 1). However, liver glycogen was strongly correlated with liver levels of cadmium, selenium, nickel, and arsenic, increasing with increasing metal levels (Table 2). Liver lipid levels were significantly lower in Stingy Run fish than in Ohio River fish; however, protein levels were significantly higher in Stingy Run fish (Table 1). Lipid and protein levels were also significantly correlated with liver metal levels; however, lipid levels decreased with increasing metals and protein levels increased with increasing metal levels (Table 2 and Fig. 1).

In general, ATPase and dUTPase activity was significantly higher in fish from Stingy Run than in fish from the Ohio River. This pattern was consistent for liver, gill, and

TABLE 1
Terminal Tissue Parameters for Sunfish from the Ohio River (Reference) and Stingy Run (Effluent-Receiving Stream)

	Ohio River 1995	Stingy Run May 1995	Stingy Run Sep 1995
Liver			
Glycogen (μg/g)	1949.3±3106.8 (5)A	856.2±951.0 (5)A	11466.2±2431.0 (5)B
Lipid (mg/g)	120.9±46.1 (5)A	9.6±2.8(5)B	36.7±4.6 (5)B
Protein (mg/g)	52.8±8.8 (5)A	100.4±10.0 (5)B	76.1±15.4 (5) C
ATPase (μm/m/mgp)	17.4±1.3 (4)A	29.5±7.2 (5)B	8.63±6.00 (5)A
dUTPase (μm/m/mgp)	0.50±0.071 (4)	1.62±0.32 (5)A	0.38±0.15 (5)B
Glycosylase (μm/m/mgp)	0.092±0.012 (4)A	0.035±0.028 (5)B	0.047±0.020 (5)B
AP (μm/m/mgp)	1.36±0.086 (4)A	0.58±0.096 (5)B	1.19±0.41 (4)
Gill			
ATPase (μm/m/mgp)	11.7±7.1 (14)A	48.6±12.8 (9)B	21.2±5.2 (10)A
dUTPase (μm/m/mgp)	0.60±0.33 (14)A	1.61±0.28 (9)B	0.44±0.16 (10)A
Glycosylase (μm/m/mgp)	0.090±0.044 (14)	0.11±0.011 (9)	0.12±0.053 (10)
AP (μm/m/mgp)	1.14±0.52 (14)A	0.35±0.10 (9)B	1.29±0.47 (10)A
Spleen			
ATPase (μm/m/mgp)	17.1±7.02 (14)A	41.8±7.6 (8)B	24.0±13.4 (10)A
dUTPase (μm/m/mgp)	0.54±0.21 (14)A	1.37±0.46 (8)B	0.34±0.15 (10)A
Glycosylase (μm/m/mgp)	0.105±0.067 (14)	0.059±0.029 (8)	0.12±0.079 (10)
AP (μm/m/mgp)	1.70±1.41 (13)	0.52±0.36 (7)A	2.0±0.64 (9)B

Note. Mean±SD is given; (n) = number of fish analyzed; values with different letters are significantly different ($P < 0.05$).

spleen tissues. The activity levels of these two enzymes was strongly correlated with liver metals, but varied depending on the metal. With the exception of selenium, ATPase and dUTPase activity generally decreased with exposure to fly ash metals (Table 2 and Fig. 2–4).

Glycosylase activity in gill and spleen tissue did not vary between sites; however, liver glycosylase activity was significantly lower in Stingy Run fish than in fish from the Ohio River (Table 1). However, this activity was not significantly correlated with metal concentrations in the liver (Table 2), indicating that some other factor(s) may be affecting glycoslayse activity.

TABLE 2
Correlations between Biomarkers That Are Significantly Different between Sites, and Metal Contaminants

Tissue	Parameter	Rank order of correlating liver metals with corresponding correlation coefficients (R)
Liver	Glycogen	Cadmium (0.80), selenium (0.70), nickel (0.70), arsenic (0.68)
	Lipid	Cadmium (−0.77), selenium (−0.77)
	Protein	Nickel (0.90), selenium (0.85), cadmium (0.77), chromium (0.70)
	ATPase	Arsenic (−0.74), chromium (−0.71), cadmium (−0.68), copper (−0.58), selenium (0.56)
	dUTPase	Selenium (0.78), chromium (−0.73), arsenic (−0.70), cadmium (−0.69)
	AP	Nickel (0.63), arsenic (0.59), chromium (0.62)
Gill	ATPase	Selenium (0.49)
	dUTPase	Copper (−0.50), selenium (0.43)
	AP	Chromium (0.41), copper (0.39)
Spleen	ATPase	Selenium (0.54)
	dUTPase	Cadmium (−0.57), copper (−0.50), chromium (−0.48), arsenic (−0.46)
	AP	Copper (0.58)

Note. Metals and R values given. R values near +1 or −1 indicate strong relationships; those near zero indicate weak relationships. There is less than a 5% probability ($P < 0.05$) of being wrong in concluding that there is a true relationship between the fish parameters and corresponding liver metals.

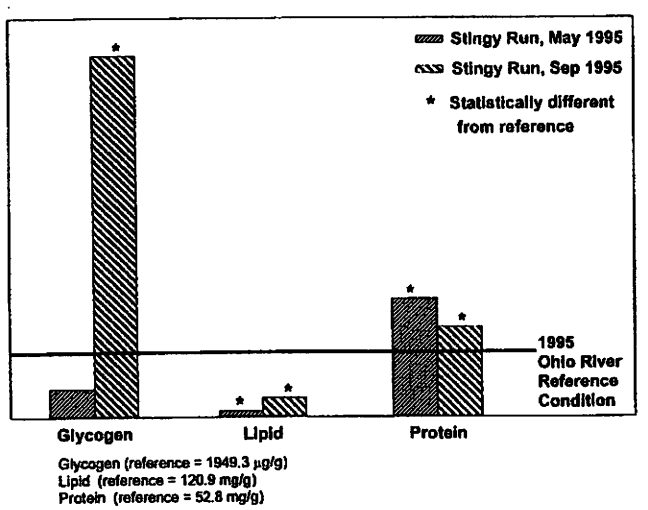

FIG. 1. Liver tissue chemistry for sunfish normalized to Ohio River reference site.

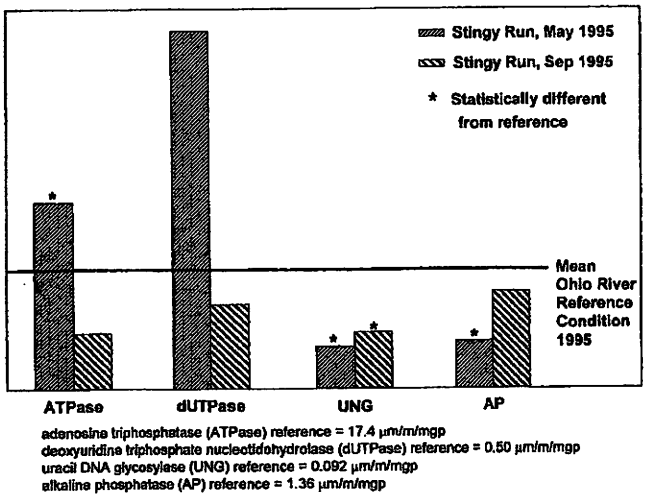

FIG. 2. Liver biochemistry for sunfish normalized to Ohio River reference site.

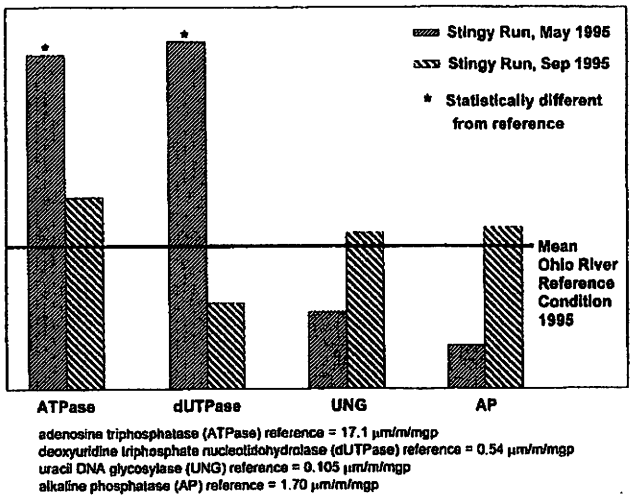

FIG. 4. Spleen biochemistry for sunfish normalized to Ohio River reference site.

AP activity was also variable. These levels were lowest in liver tissue, but either lower or higher in gill or spleen tissue in fish from Stingy Run relative to fish collected from the Ohio River (Table 1). AP activity increased significantly with increasing metal concentrations in all three tissues (Table 2), yet overall, activity levels were lower in fish from ash pond-receiving streams (Figs. 2–4).

Relationship between Tissue Chemistry and Condition Indicies

Liver lipid levels and dUTPase activity, as well as gill ATPase and AP activity, were the only tissue biochemical parameters significantly correlated with fish condition factors or liver somatic indices (Table 3). Liver lipid levels were positively correlated with condition factor ($R = 0.55$) but negatively ($R = -0.75$) correlated with liver somatic indices (Table 3). Liver dUTPase was positively correlated with liver somatic indices. Two gill enzymes, ATPase and AP, were negatively correlated with condition factor and liver somatic indices, respectively.

Condition factors for fish from Stingy Run in 1995 were lower than those from Stingy Run in 1993–1994, but neither were different from Ohio River fish. Condition factor values were negatively correlated ($P < 0.05$) with liver tissue levels of arsenic, cadmium, copper, and, in particular, zinc, but were not correlated with liver tissue levels of lead or selenium (Lohner *et al.*, 2001a). There were no significant differences ($P < 0.05$) in mean liver somatic index (LSI) for

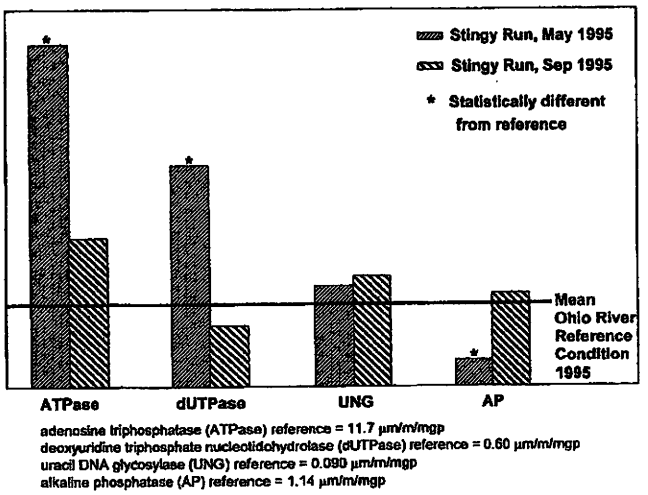

FIG. 3. Gill biochemistry for sunfish normalized to Ohio River reference site.

TABLE 3
Correlations between Biomarkers That Are Significantly Different between Sites and Fish Condition Factors

Tissue	Parameter	Rank order of correlating condition factors with corresponding correlation coefficients (R)
Liver	Lipid	CF (0.55), LSI (−0.75)
	dUTPase	LSI (0.53)
Gill	ATPase	CF (−0.41)
	AP	LSI (−0.52)

Note. CF, condition factor; LSI, liver somatic index. Condition factors and R values given. R values near +1 or −1 indicate strong relationships; those near zero indicate weak relationships. There is less than a 5% probability ($P < 0.05$) of being wrong in concluding that there is a true relationship between the fish parameters and corresponding condition factors.

fish collected from Stingy Run or the Ohio River (Lohner *et al.*, 2001a). Although mean LSI values between the sampled sites were not significantly different, there was a significant ($P < 0.05$), but weak, negative correlation between LSI values and liver tissue levels of copper ($R = -0.34$) and chromium ($R = -0.29$) (Lohner *et al.*, 2001a).

DISCUSSION

Tissue Biochemistry

Liver glycogen and protein levels were found to increase with increasing metal concentrations; however, liver lipid levels decreased with increasing liver metal concentrations (Table 1). Decreasing tissue glycogen levels may reflect long-term stress caused by increased glycogen mobilization or decreased glycogen synthesis. Chronic exposure to metals generally causes a decrease in liver glycogen concentrations indicating the possibility of poor nutritional status (Versteeg *et al.*, 1988; Adams *et al.*, 1999). A depletion of liver glycogen with an increase of blood glucose (hyperglycemia), as occurred in fish collected from Stingy Run in May 1995 (Lohner *et al.*, 2001b), is the normal physiological stress response in fish reacting to handling and noxious chemicals (Hontela *et al.*, 1995; Bleau *et al.*, 1996). However, fish collected from Stingy Run in September 1995 had increased glycogen and decreased serum glucose levels compared to those found in Ohio River fish (Lohner *et al.*, 2001b). These fish may have experienced less stress as sampling techniques improved and the time to blood sampling decreased. Bleau *et al.* (1996) found that liver glycogen levels in control fish increased after 1 week indicating a positive energy balance, probably resulting from effortless feeding.

Liver protein levels were significantly higher in fish from the ash pond discharges than in fish from the Ohio River and these levels were positively correlated with liver metal levels (Tables 1 and 2). It is known that metals can be sequestered in tissues and be partially bound to metal-binding proteins such as metallothionein (MT) (Benson and Birge, 1985). Metallothionein and other metalloproteins are also known to be involved in the metabolism and detoxification of certain trace metals in aquatic organisms (Roesijadi, 1994). It is believed that with both essential and nonessential metals, binding to metallothioneins or similar proteins limits metal availability at susceptible sites and confers protection against toxicity (Roesijadi, 1994).

The amount of MT in fish tissues has been found to be proportional to the level of metal exposure (Benson and Birge, 1985; Dyer *et al.*, 1993). Benson and Birge (1985) found that minnows taken from a metal-contaminated fly ash pond were significantly more tolerant of cadmium and copper than were hatchery minnows. They also determined that gill metallothionein concentrations were significantly higher in the metal-tolerant fish than in the susceptible fish. Dyer *et al.* (1993) measured increased levels of arsenite-induced proteins in gill and muscle tissue after exposing fathead minnows to sublethal concentrations of sodium arsenite. Hilmy *et al.* (1987) observed increases in liver total protein levels in catfish (*Clarias lazera*) and bolti (*Tilapia zilli*) exposed to zinc. Thus, it appears that the increased level of liver protein observed in fish from the ash pond-receiving streams could be due to the synthesis of MT or similar proteins.

If metalloproteins were limiting the toxicity of metals in the fish from Stingy Run, it would seem likely that these same proteins would provide protection to other fish populations that are similarly exposed. Metallothioneins are ubiquitous in their distribution and have been found in virtually all types of organisms including mammals (Probst *et al.*, 1977), fish (Benson. and Birge, 1985), molluscs (Roesijadi, 1994), and blue-green algae (Maclean *et al.*, 1972); however, fish in Belews Lake and Lake Martin were apparently susceptible to the ash pond metals and did not benefit from the action of such proteins (Sorenson *et al.*, 1982, 1984). Although such proteins may have been present in these susceptible fish populations, not all circumstances will allow them to be protective. Natural populations of fish can develop elevated tolerances to certain metals, but exposure must be at tolerable concentrations of metals in order for this phenomenon to be triggered. In addition, the tolerance is lost when exposure to the metals is removed (Benson and Birge, 1985). Fish in Stingy Run have historically been exposed to acid mine drainage which is typically high in metals such as iron and manganese. These metals could have induced metallothioneins in the fish, thereby increasing their tolerance prior to exposure to the ash pond effluents. The fish in Belews Lake and Lake Martin may not have had the benefit of such previous exposures to tolerable metal exposures that would have allowed them to develop resistance to subsequent metal exposures.

Lipid levels in fish from both Stingy Run sampling efforts were significantly lower than those in fish from the Ohio River indicating possible nutritional stress (Table 1). The tissue-specific lipid content of fish can be influenced by a variety of factors, including diet (Fletcher, 1984), reproductive condition (Love, 1970), and temperature (Hansen and Abraham, 1983); however, in most cases of toxicant-induced stress, the lipid content of fish decreases (Mayer *et al.*, 1992). If nutritional stress was occurring in the Stingy Run fish, then these results would be consistent with those of reduced serum protein and cholesterol levels also found in fish from the fly ash pond-receiving streams (Lohner *et al.*, 2001b).

Biochemistry

The enzymes (ATPase, dUTPase, AP, and glycosylase), which were measured in this study, are commonly used as

markers of cellular alterations. The activity of these types of enzymes is used as a biomarker, due to their involvement in the adaptive cellular response to the potential cytotoxicity/genotoxicity of pollutants such as heavy metals. Many metals are genotoxic and have the capacity to cause various types of DNA damage. Metals can also inhibit DNA repair. For example, mercury inhibits dUTPhase, which prevents the incorporation of dUTP into DNA by DNA polymerases. (Williams, 1986). The cellular metabolism of genotoxic chemicals can be relatively complex and often results in structural alterations to the DNA molecule. Cellular responses can lead to repair of the damage or death of the cells containing the damaged DNA. Tumors may result from those cellular lesions that are not repaired. Studies of mammalian genotoxicity have utilized enzymatic and histochemical markers to detect hepatocellular alterations and tumors and similar studies have been done with fish.

In this study, liver ATPase and dUTPase activity was significantly higher in fish that were collected in May 1995 from Stingy Run than in fish collected from Stingy Run in September 1995 or from the Ohio River, indicating possible cellular alterations (Table 1, Fig. 2). Other studies, however, have found that ATPase was generally inhibited by heavy metal or pollutant exposure (Versteeg *et al.*, 1988; Moore and Myers, 1994). Many laboratory studies have documented the inhibitory effects of various metals on fish gill ATPases; however, many of these studies involved lethal or near-lethal metal concentrations (Jagoe *et al.*, 1996). The fish from Stingy Run and the Ohio River were not exposed to lethal metal levels and the enzyme activity levels could have also been affected by diet, season, and water chemistry. Jagoe *et al.* (1996) did not detect any differences in gill Na^+K^+-ATPase activity in bass collected from three reservoirs with different levels of mercury contamination. Lemaire-Gony *et al.* (1995) also found no effects on gill Na^+K^+-ATPase activity in sea bass following long-term exposure to cadmium. They speculated that the expected decrease in activity due to cadmium exposure could have been hidden by an increase in enzyme quantity.

The enzyme activity in the Stingy Run and Ohio River fish was positively correlated with selenium levels, but negatively correlated with liver levels of arsenic, cadmium, chromium, and copper (Table 2). This response was also noted in spleen and gill tissue. It is possible that the enzymes were responding to metals other than selenium (especially after September 1995, when the ash pond discharge ceased and selenium levels began to decline and other metal levels began to increase), becoming more available to inhibit the enzymes. It is also possible that the measured ATPase and dUTPase activity levels were within the normal physiological range of the collected sunfish.

Glycosylase activity in liver, gill, and spleen tissues was inconsistent, but AP activity was found to be significantly lower in fish from Stingy Run in May 1995 than in fish from Stingy Run in September 1995 or from the Ohio River (Table 1). This may indicate a lack of deleterious cellular alterations since alkaline phosphatase is generally positive in fish neoplasia (Moore and Myers, 1994). AP activity in the Stingy Run and Ohio River sunfish was positively correlated with nickel, arsenic, copper, and chromium, but not correlated with selenium levels, indicating that other metals may have been responsible for the inhibition of enzyme activity in the May 1995 Stingy Run fish. It is also possible that the enzyme response was equivocal or that the AP activity levels were within the normal physiological range of the collected fish.

Ecological Assessment and Relationship to Tissue Biochemistry

Liver glycogen and protein levels were significantly higher in fish from the ash pond-receiving streams indicating no nutritional stress on the fish; however, liver lipid levels decreased with exposure to metals, indicating a possible toxicant-induced stress. Liver lipid levels were correlated with condition factors and liver somatic indices, indicating that lipid levels could be used as an early indicator of potential adverse impact. But neither the condition factors nor the liver somatic indices of fish from the ash pond-receiving streams were significantly different from those of fish from the Ohio River reference site.

Goede and Barton (1990) noted that a decline in condition factor is usually interpreted as a depletion of energy resources such as stored liver glycogen and body fat. In the present study, there was a positive correlation between liver lipid levels and condition factors and both were negatively correlated with liver metal levels. As metal exposure increased, liver lipid levels decreased significantly, but condition factors did not, indicating a possible stress that may not have directly impacted the health of individual fish.

The liver somatic index can reflect both metabolic energy demand and short-term nutritional status and can be considered a general health indicator, sensitive to environmental contaminants (Everaarts *et al.*, 1993). Martin and Black (1998) determined increased liver somatic indices from catfish exposed to heavy metals from an abandoned strip mine and Sorenson *et al.* (1984) noted increased LSI values in fish exposed to elevated selenium. Increased liver size can be caused by hyperplasia (cell multiplication) or hypertrophy (cell enlargement) and may increase its capacity to biotransform xenobiotics (Martin and Black, 1998). Selenium is also known to cause liver edema and subsequent increases in LSI values (Sorenson *et al.*, 1984). Decreases in liver lipid levels in the fish from Stingy Run may have been due to nutritional or toxicant-induced stress, but the corresponding LSI values did not vary significantly between the sample sites. This indicates again a possible

stress that may not have directly impacted the health of the individual fish.

CONCLUSION

The ecological significance of changes in ATPase and other enzyme activity is difficult to assess due to the large reserve capacity of ATPase (Versteeg *et al.*, 1998) and the physiological range of enzyme activity in feral fish populations. The results also show that the effects of the ash pond metals on wild fish population enzyme levels may not be predictable based on data derived in laboratory settings. In addition, enzyme activity may either increase or decrease in response to environmental stress and separating normal variation from toxicant-induced alterations may be difficult. Some biochemical indicators in this study were different between sites and these differences were related to condition indices, suggesting the possibility of their use as early indicators of coal ash exposure and toxicity, prior to the manifestation of any adverse health effects. However, in these studies, the biochemical changes were not sufficient to significantly affect fish health indices.

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Assessment of Tolerant Sunfish Populations (*Lepomis* sp.) Inhabiting Selenium-Laden Coal Ash Effluents

3. Serum Chemistry and Fish Health Indicators

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Sunfish were collected from fly ash discharge-receiving streams to assess the possible effects of exposure to elevated selenium. Concentrations of selenium, copper, and arsenic were statistically higher in fish tissue (liver) samples from effluent-exposed fish than in reference fish. Several biomarkers were indicative of metal exposure and effect. Plasma protein levels and cholesterol levels were significantly lower in exposed fish, indicating nutritional stress. Ion levels (i.e., K) increased with exposure to ash pond metals, indicating possible gill damage. Fish from the receiving streams also had increased serum glucose and osmolality indicating possible acute stress due to sampling. Fish health assessments revealed a lower incidence of fin erosion, kidney discoloration, urolithiasis or nephrocalcinosis, liver discoloration, and parasites in exposed fish and a higher incidence of skin, eye, and gill aberrations. Condition factors of exposed fish were correlated with biomarker response and were the same as or lower than those of reference fish, but not related to selenium levels. Although several serum biochemical indicators differed between the ash pond-receiving stream and reference sites, pollutant exposure was apparently not sufficient to cause functional damage to critical organ systems. © 2001 Elsevier Science

Key Words: **coal ash; bluegill; selenium; serum chemistry; biomarkers.**

INTRODUCTION

Exposure to coal fly ash effluents has been associated with sublethal developmental, physiological, biochemical, and behavioral changes in fish and aquatic wildlife collected from waters receiving treated coal ash discharges (Sorenson *et al.*, 1982, 1984; Lemly, 1993; Rowe *et al.*, 1996; Hopkins *et al.*, 2000). Swollen and vacuolated gill lamellae, liver edema, uremia-induced pericarditis, and necrotic and ruptured egg follicles were noted in green sunfish collected from Belews Lake, North Carolina, which received fly ash sluice water from a coal-fired power plant (Sorenson *et al.*, 1984). Increased incidence of axial and oral malformations and altered swimming performance were documented in bullfrog larvae collected from sites contaminated with coal combustion wastes in South Carolina (Rowe *et al.*, 1996; Hopkins *et al.*, 2000).

Elevated levels of metals and metalloids, in particular, copper, lead, selenium, and zinc, which are present in wet ash disposal effluents, are considered to be the most likely causative agent of coal ash toxicity. These metals can disrupt the integrity of biochemical and physiological processes in fish. Folmar *et al.* (1993) observed histopathological abnormalities and significant increases in serum blood urea nitrogen (BUN), uric acid, triglycerides, inorganic phosphorus, alanine aminotransferase (ALT), lactate dehydrogenase (LDL), calcium, and iron in fish from the Buffalo and Niagara Rivers. Both rivers are contaminated with a variety of organic and metal pollutants. Fish from the Black River in Ohio, which received steel plant and coking facility effluents, showed significantly greater serum ALT, aspartate aminotransferase (AST), LDL, total protein, BUN, triglycerides, and calcium, and significantly less serum phosphorus than reference fish (Folmar *et al.*, 1995).

Serum chemistry and fish health indicators, such as condition factors and organo-somatic indices, are often used as indicators of pollutant exposure and effect (Kloepper-Sams *et al.*, 1994; Adams *et al.*, 1996). Condition factors, based on the analysis of length–weight data, and organo-somatic indices are believed to be good indicators of the general well-being or fitness of fish poulations (Bolger and Connolly, 1989). The prevalence of fish with visible pathological disorders has also been used as a convenient and easy indicator of environmental quality (Goede and Barton, 1990; Adams *et al.*, 1993). Visible lesions generally include fish erosion, skin ulcers, eye disorders, visible tumors, and

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skeletal deformities. Serum biochemical parameters, such as creatinine for kidney and ALT for liver, can be evaluated as indicators of organ dysfunction (Adams *et al.*, 1996).

Despite the potential usefulness of serum and autopsy-based indicators to evaluate fish health, the significance of such results is often unclear. Redear sunfish from Martin Lake, Texas, did not vary significantly from reference redears with respect to condition factors, hematocrits, and percentage hepatopancreas weight to body weight, despite increased selenium levels in the exposed fish (Sorenson *et al.*, 1982). Rowe *et al.* (1996) found that despite exposure to coal ash sluice water and altered oral morphology, bullfrog tadpoles were abundant and recently metamorphosed juveniles indicated that conditions were not severe enough to cause mortality. Kloepper-Sams *et al.* (1994) noted that increased liver size and apparent differences in sex steroid profiles in longnose suckers exposed to bleached-kraft effluent did not translate to other health effects or population-level effects. Differences in serum biochemistry and organ response can be due to changes in exposure or habitat, other chemicals, or changes in water chemistry. A variety of other contaminant sources and environmental stressors may also affect a system. It is often difficult to assign cause and effect under such conditions.

The relationship between exposure to coal ash effluent, biochemical response, and fish health indicators is not clear. Therefore, the objective of this study was to assess changes in serum biochemistry relative to health indicators in fish exposed to coal ash effluents at two sites. Historically, these sites, the Gavin and Amos Plant fly ash pond-receiving streams (Stingy Run and Little Scary Creek), have had high selenium levels in water and sediments (Reash *et al.*, 1988, 1999). Biological monitoring studies have shown, however, that viable sunfish populations are maintained despite elevated concentrations of some metals in the water column. This article provides an overview of the serum biochemical responses as related to gross organ damage, as well as a perspective on the relevance of these endpoints in the environmental assessment of coal ash waste waters. This work was part of a larger effort to evaluate metal transport, bioaccumulation, biomarker response, and fish health in fly ash-receiving streams. The results of these concurrent studies are provided in accompanying articles (Lohner *et al.*, 2001a,b) and Reash *et al.* (1999) and are used to examine the significance of serum biochemical changes in exposed fish.

METHODS

Study site location, fish collection and sampling, water quality monitoring, and metal analysis procedures are described elsewhere (Reash *et al.*, 1999; Lohner *et al.*, 2001a).

Seum Chemistry Analysis

Blood samples were drawn from the caudal vein using serum nonheparized (red top) 3-ml Vacutainers with 21G × 1″ needles (inserted ventrally, midline, posterior to the anal fin) or collected via pericardial puncture or dorsal gill incision (Watson *et al.*, 1989) into 250-μL capillary tubes and preserved on ice. For determination of serum chemistry parameters, separate blood samples were spun at 3000 rpm for 10 min in a Sorvall T6000D centrifuge. Serum was removed following centrifugation and chemical analysis was performed using a Boehringer Mannheim Hitachi 911 chemistry analyzer.

Cytology

Fish livers from Little Scary Creek were evaluated at the Ohio State University Veterinary Medicine Clinical Laboratory for impression smears and a cytological description. Livers were removed from fish and cleanly cut in half with a razor blade. The face of the exposed liver cut was then pressed lightly against a glass slide for an "impression." This impression was allowed to dry and then submitted to the Ohio State Veterinary Laboratory for analysis by a pathologist.

Health Assessments

The health assessment index (HAI) is a qualitative indicator of general fish health where individual metrics within the index are assigned numerical values on the basis of the degree of severity or damage incurred by an organ or tissue from environmental stress factors. This study used a modified version of the field necropsy system originally developed by Goede and Barton (1990). The modified version includes a more quantitative estimate of fish health based on assigning index values for nine individual health indicator variables (Adams *et al.*, 1993). These nine variables consist of the percentage of fish with normal and abnormal eyes, gills, spleens, livers, and kidneys, and index values of damage to skin, fins, and hindgut, and the presence of parasites. After blood removal, fish were examined externally and internally for evidence of lesions or other abnormalities. A gross analysis of the fins, spleen, hindgut, kidney, skin, liver, eyes, and gills was made to determine fish health metrics. The gills, liver, and spleen were removed using acid-rinsed, stainless-steel instruments for additional analysis. The organs were placed in polyethylene bags and stored at −70°C until analysis.

Data Analysis

Statistical analyses were carried out using SigmaStat statistical software (Jandel Scientific, 1995). Liver metal

concentrations were $\log_{10}$-transformed. All data were tested for normality. Spearman rank order or Pearson product moment correlation analyses were used to test for significant associations between fish morphologic, serum chemistry, and liver metal data.

Condition factors, liver somatic indices, and fish growth data were evaluated as previously described (Lohner *et al.*, 2001a). Possible statistical differences between serum parameters, liver metals, and condition indices versus location were tested using a one-way ANOVA (when assumptions of data normality and equal variance were confirmed) or the Kruskal–Wallis test (nonparametric analog of one-way ANOVA). Tukey's (parametric) or Dunn's (nonparametric) test for pair-wise comparison of means was used if the ANOVA test was significant ($P < 0.05$). A t test was used to test for differences in fish health metrics.

RESULTS

Summaries of water quality monitoring, metal analyses, condition index response, fish growth, and reproductive status as related to these studies are presented in Lohner *et al.* (2001a) and Reash *et al.* (1999).

Serum Chemistry

Serum chemistry results varied widely with few consistent patterns becoming apparent (Figs. 1–3). Plasma glucose, a metabolic stress indicator, was significantly higher in fish collected from Stingy Run in May 1995 than in fish collected from that same stream in September 1995; however, glucose levels in these fish were not significantly different from levels measured in fish from the Ohio River or Little Scary Creek (Table 1). Plasma protein levels were significantly lower in Little Scary Creek fish than in fish from in the Ohio River in 1997 and BUN, an indicator of kidney function, was significantly lower in Stingy Run fish than in fish from the Ohio River in 1995; however, only BUN was significantly correlated with the liver concentration of any ash pond metals (Table 2). Cholesterol levels varied significantly, being lower in fish from Stingy Run and Little Scary Creek than in those collected from the Ohio River in 1997 (Table 1, Fig. 2). Cholesterol was also found to be significantly correlated with liver lead levels (Table 2).

Plasma ion levels varied significantly; however, no consistent pattern was noted (Fig. 1). Sodium levels were lower in fish from Stingy Run and the Ohio River in 1995 than in fish from the Ohio River in 1997, whereas potassium levels were higher in Little Scary Creek fish than in fish from the Ohio River in 1997. Chloride levels varied considerably, with levels in Stingy Run fish being significantly higher than those in fish from the Ohio River in 1995 or 1997, but were the same as those in fish from Little Scary Creek. Chloride levels in Little Scary Creek fish were also higher than in fish from the Ohio River in 1995. Only sodium and chloride were significantly correlated with any liver metals, increasing significantly with increasing levels of selenium (Table 2). In general, ion levels tended to be higher in fish from the fly

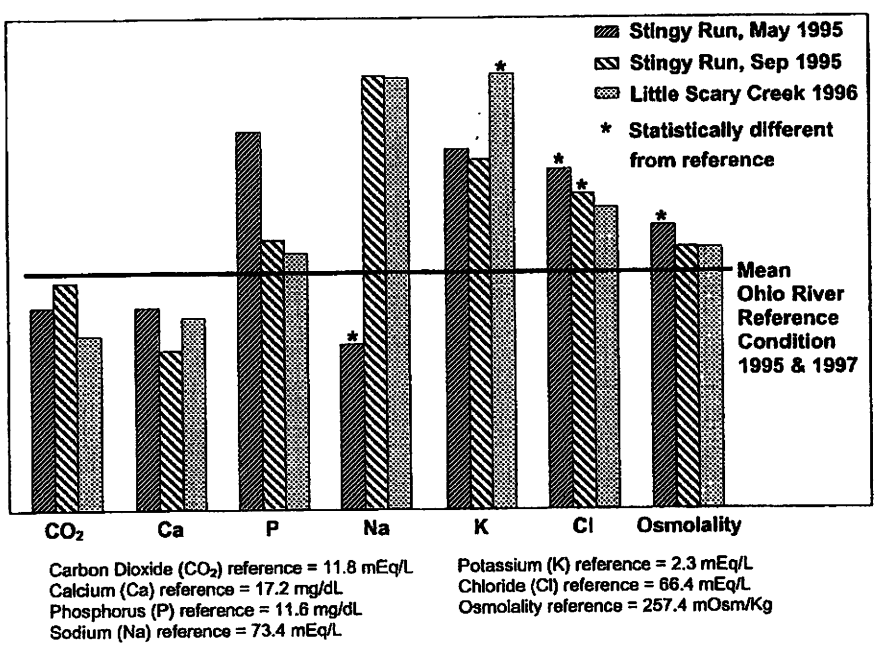

FIG. 1. Terminal serum indicators for sunfish normalized to Ohio River reference site.

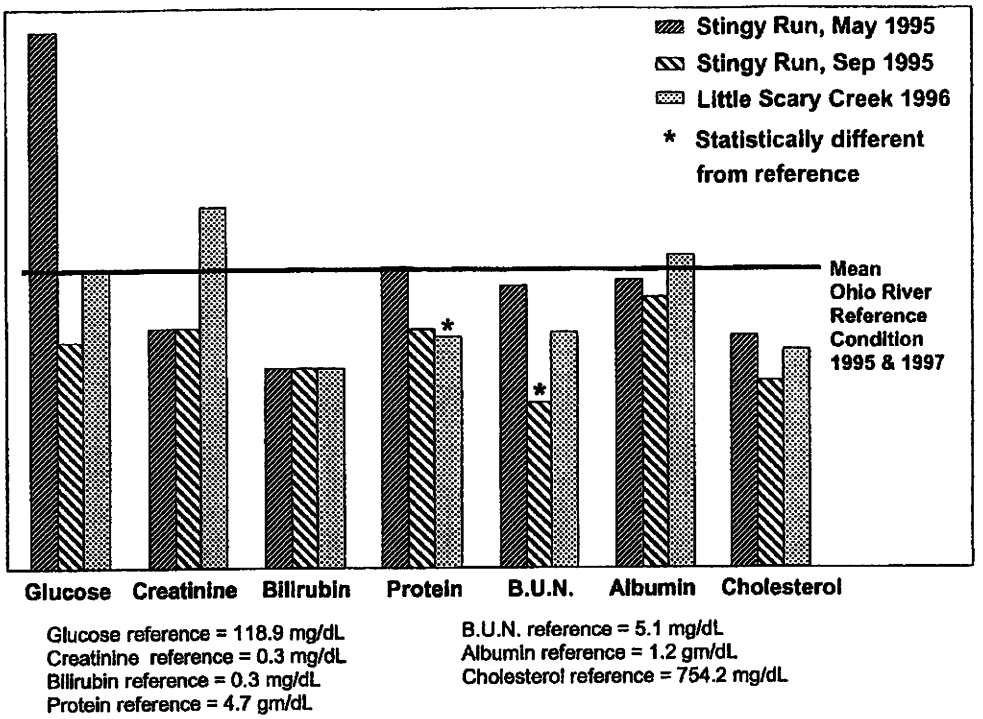

FIG. 2. Terminal serum indicators for sunfish normalized to Ohio River reference site.

ash pond-receiving streams (Fig. 1). Osmolality, an indicator of osmotic balance which is related to serum ion concentrations, also varied in a pattern similar to that noted in the individual ion concentrations. Osmolality levels were generally higher in Stingy Run and Little Scary Creek fish than in fish from the Ohio River in 1995 and 1997 (Table 1). Similarly, osmolality levels were significantly correlated with liver selenium levels (Table 2).

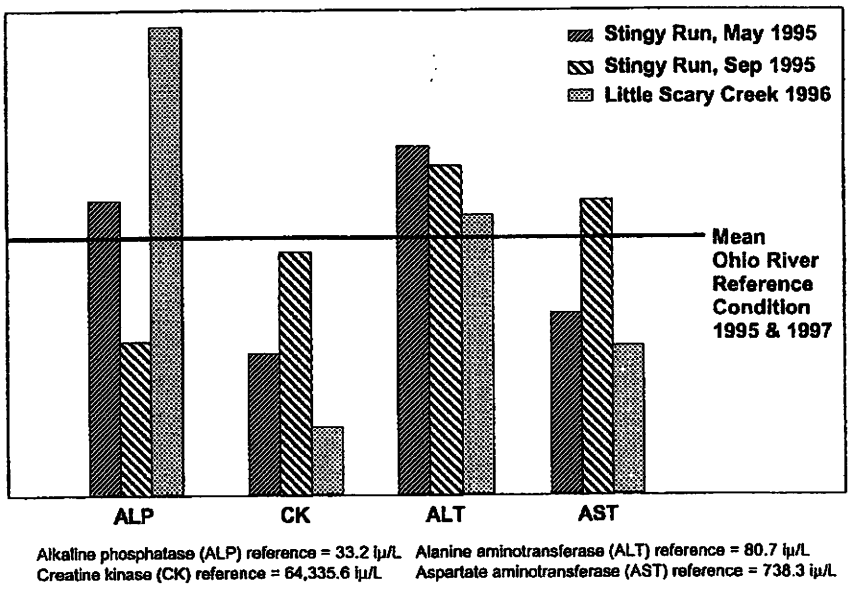

FIG. 3. Terminal serum indicators for sunfish normalized to Ohio River reference site.

TABLE 1
Terminal Serum Parameters for Sunfish from the Ohio River (Reference), Stingy Run (Effluent-Receiving Stream), and Little Scary Creek (Effluent-Receiving Stream)

	Ohio River 1995 ($n = 5$)	Ohio River 1997 ($n = 4$)	Stingy Run May 1995 ($n = 4$)	Stingy Run September 1995 ($n = 4$)	Little Scary Creek 1996 ($n = 5$)
CO_2 (mEq/L)	11.8 ± 2.5	11.8 ± 1.5	10.2 ± 0.5	11.5 ± 1.5	8.8 ± 1.8
Ca (mg/dL)	11.6 ± 1.5	24.1 ± 21.3	15.4 ± 4.5	12.1 ± 1.1	14.6 ± 3.6
Phosphorus[a] (mg/dL)	11.8 ± 3.0	11.4 ± 5.8	18.8 ± 0.4	13.4 ± 3.2	12.7 ± 3.2
Glucose (mg/dL)	130.2 ± 54.4	104.8 ± 36.3	209.5 ± 72.0A	88.5 ± 20.4B	116.2 ± 61.2
Creatinine (mg/dL)	0.3 ± 0.1	0.2 ± 0.0	0.2 ± 0.0	0.2 ± 0.0	0.3 ± 0.1
Bilirubin (T) (mg/dL)	0.3 ± 0.04	0.3 ± 0.08	0.2 ± 0.0	0.2 ± 0.1	0.2 ± 0.1
Na (mEq/L)	25.8 ± 15.2A	133.0 ± 7.3A	56.2 ± 2.2B	147.5 ± 1.7	147.0 ± 9.9
K (mEq/L)	2.7 ± 0.8	1.8 ± 0.5A	3.4 ± 0.5	3.3 ± 1.0	4.1 ± 1.7B
Cl (mEq/L)	64.4 ± 13.6A	69.0 ± 5.9AC	97.2 ± 3.4B	89.8 ± 2.4B	86.0 ± 9.0BC
Total protein (gm/dL)	4.0 ± 0.9	5.5 ± 1.3A	4.8 ± 0.7	3.8 ± 0.2	3.7 ± 0.4B
BUN (mg/dL)	5.4 ± 1.1A	4.8 ± 1.0	4.8 ± 1.0	2.8 ± 0.5B	4.0 ± 1.0
Albumin (gm/dL)	1.1 ± 0.2	1.4 ± 0.4	1.2 ± 0.2	1.0 ± 0.1	1.3 ± 0.4
Cholesterol (mg/dL)	552.0 ± 184.5B	1007.0 ± 104.2A	603.8 ± 60.0B	485.8 ± 75.8B	564.4 ± 177.9B
ALP (iμ/L)	39.0 ± 13.4	26.0 ± 9.5	37.2 ± 6.7	19.5 ± 10.0	59.2 ± 68.8
CK (iμ/L)	59,104.0 ± 27,095.9	70,875.0 ± 44,117.8	36,169.8 ± 14,513.3	62,706.2 ± 32,502.1	16,987,0 ± 13,028.8
ALT (iμ/L)	86.2 ± 34.2	73.8 ± 19.9	121.0 ± 72.4	114.8 ± 80.9	97.4 ± 59.1
AST (iμ/L)	871.8 ± 148.8	571.5 ± 206.3	516.5 ± 231.5	843.2 ± 666.1	421.8 ± 214.4
Osmolality S - calculated (mOsm/kg)	252.2 ± 26.9A	264.0 ± 13.9AC	313.0 ± 2.2B	289.2 ± 3.1BC	287.2 ± 16.0BC

Note. Mean ± SD is given; (n) = number of fish analyzed; values with different letters are significantly different ($P < 0.05$).
[a]ANOVA indicates a significant difference ($P < 0.05$) but pair-wise comparisons are not significantly different.

Fish Health Indices

Fish health assessments were conducted on fish from Little Scary Creek in 1996 and the Ohio River in 1997. Less fin erosion, kidney discoloration, urolithiasis and nephrocalcinosis, liver discoloration, and parasites were observed in fish from Little Scary Creek than in those from the Ohio River (Table 3). Fish from Little Scary Creek did exhibit a higher incidence of skin, eye, and gill aberrations. Cytological analysis of fish livers from Little Scary Creek revealed mild hepatocellular vacuolar degeneration (liver cell damage). No etiologic (disease) agents or abnormal cells were detected and no infiltrates (abnormal substances, such as blood cells, cancer cells, fat, starch, or calcium and mag-

TABLE 2
Correlations between Serum Biomarkers That Are Significantly Different between Sites and Metal Contaminants

Serum	Rank order of correlating liver metals with corresponding correlation coefficients (R)
Sodium	Selenium (0.58), cadmium (0.45)
Chloride	Selenium (0.53)
BUN	Cadmium (−0.53), chromium (−0.45)
Cholesterol	Lead (−0.45)
CK	Copper (−0.61), arsenic (−0.52), cadmium (−0.47)
Osmolality	Selenium (0.57)

Note. Metals and R values given. R values near +1 or −1 indicate strong relationships; those near zero indicate weak relationships. There is less than a 5% probability ($P < 0.05$) of being wrong in concluding that there is a true relationship between the fish parameters and corresponding liver metals.

TABLE 3
Mean Health Assessment Index (HAI) Values for Measured Features and Populations of Fish Sampled from the Ohio River and Little Scary Creek

Measured feature	Ohio River 1997 $n = 8$	Little Scary Creek 1996, $n = 13$
Fins	11.2	5.4
Spleen	0	0
Hindgut	1.2	0.8
Kidney	22.5	9.2
Skin	0	0.8
Liver	26.2	16.1
Eyes	0	2.3
Gills	0	4.6
Parasites	7.5	2.3
Population HAI[a]	68.8[a]	41.5[a]

[a]Significant difference between sites (M-N rank sum test, $P < 0.05$); lower score represents better overall health.

TABLE 4
Significant Correlations between Serum Biomarkers and Fish Condition Factors

Serum parameter	Rank order of correlating condition factors with corresponding correlation coefficients (R)
Calcium	LSI (0.47)
Potassium	CF (− 0.56)
Protein	CF (0.54)
Cholesterol	CF (0.49)
ALT	CF (− 0.47)

Note. CF, condition factor; LSI, liver somatic index. Condition factors and R values given. R values near +1 or −1 indicate strong relationships; those near zero indicate weak relationships. There is less than a 5% probability ($P < 0.05$) of being wrong in concluding that there is a true relationship between the fish parameters and corresponding condition factors.

nesium salts, in a cell) were detected. When considering the composite health index, fish from Little Scary Creek were in better "health" than those from the Ohio River (lower HAI scores indicate less departure from the normal condition). The differences in the mean health assessment index values were significantly different (Table 3).

Serum Chemistry and Condition Index Relationships

Serum potassium, cholesterol, protein, and ALT were significantly correlated with fish condition factors (Table 4). Serum cholesterol and protein were positively correlated, while potassium and ALT were negatively correlated. Serum calcium was the only parameter significantly correlated with liver somatic indices (Table 4), with calcium levels increasing with increasing liver index values. Condition factors of fish collected from Stingy Run in 1995 and from Little Scary Creek did not differ significantly from Ohio River fish collected in 1995; however, Little Scary Creek values were lower than those of Ohio River fish collected in 1997. Mean liver somatic index values from all sites and years were statistically the same.

DISCUSSION

Serum Biochemistry

For fish from the ash pond-receiving streams, indications of biochemical dysfunction included differences in serum glucose, plasma protein, BUN, cholesterol, Na, K, Cl, and osmolality levels, which were elevated or reduced relative to those from Ohio River fish (Table 1, Figs. 1–3). Similar biochemical changes have been noted in fish exposed to industrial discharges contaminated with heavy metals. Folmar *et al.* (1993) noted significantly lower serum glucose, albumin, cholesterol, and creatinine levels, and significantly higher levels of serum BUN, sodium, potassium, calcium, ALT, and uric acid in brown bullheads from the Buffalo and Niagara Rivers. These changes were thought to be associated with the chronic stress of being in an environment contaminated with chlorinated pesticides, PCBs, polynuclear aromatic hydrocarbons, and heavy metals. Folmar *et al.* (1995) found that fish from the Black River, which has received effluents from steel and coking plants, had significantly higher serum ALT, AST, LDL, total protein, BUN, triglycerides, and calcium and significantly less serum phosphorus than fish from a reference site.

The increased serum glucose levels observed in May 1995 Stingy Run fish may have been due to acute sampling stress. Martin and Black (1998) found that caged catfish, exposed to abandoned coal mine drainage, had increased plasma glucose levels, possibly due to glucose mobilization in response to environmental stress, that eventually decreased and then returned to normal levels after 28 days of exposure. Many studies have reported significant increases in serum glucose associated with exposure to pollutants; however, short-term changes in measurements such as glucose levels can also be induced by handling stress, changes in temperature, pH, water velocity, hypoxia, or other seasonal variations (Wedemeyer and Yasutake, 1977; Folmar, 1993). Increased serum glucose levels have been associated with increases in serum osmolality and this was also noted in the fish from the ash pond discharges, which had elevated osmolality levels relative to those from Ohio River fish (Fig. 1). High plasma osmolality levels can indicate possible stress-induced diuresis (Wedemeyer and Yasutake, 1977). The plasma glucose levels found in the Stingy Run and Little Scary Creek fish were probably within the normal physiological stress range for these fish.

Plasma protein levels were generally lower in the exposed fish indicating a condition of possible nutritional imbalance, infectious disease, kidney damage, or inanition (condition of exhaustion caused by a lack of nutrients in the blood) (Wedemeyer and Yasutake, 1977). High protein concentrations would have indicated possible increases in liver enzymes, potential tumor-specific proteins (Denslow *et al.*, 1994), hemoconcentration, or impaired water balance (Wedemeyer and Yasutake, 1977). The lower BUN levels in fish from the ash pond discharges indicated no renal or gill dysfunction, which is generally associated with increased BUN levels. However, histopathological evaluations of the organs were not done to confirm this condition. Cholesterol levels, like the plasma protein levels, can be used as an indicator of feeding and nutritional status. Lower than normal plasma cholesterol levels may indicate impaired lipid metabolism due to chronic stress. The lower cholesterol levels in fish from Stingy Run and Little Scary Creek appear to confirm the results of plasma protein analyses and age–length analyses, which indicated that the fish from these streams were possibly experiencing nutritional imbalances.

The higher serum ion concentrations (Na, K, Cl), which are indicators of potential gill and other organ damage,

were significantly correlated with increasing liver metal concentrations. Christenson *et al.* (1977) found significant increases in plasma sodium and chloride levels in brook trout exposed to lead, cadmium, and methylmercury. Versteeg *et al.* (1988) noted that metal exposure can cause alterations in internal ion concentrations through a number of physiological mechanisms such as hormonally mediated responses, gill damage, and effects on the ion-transporting enzyme Na^+/K^+-ATPase. The values for Na and K reported in this study are within the ranges for normal or unexposed fish (Folmar, 1993) and could be related to normal temporal variability or differences in diet quality. Zinc and other heavy metals can disrupt the branchial respiratory epithelium of the gills, influencing aspects of osmotic and ionic regulation in fish (Skidmore and Tovell, 1972). High concentrations of metals can result in the loss of chloride ions through the gills. The chloride levels in fish from both streams appear low when compared to literature values for normal fish (Folmar, 1993), but serum chloride levels in the fish were consistently above those from the Ohio River, indicating possible gill damage.

In summary, increased glucose and osmolality levels indicated that, on some occasions, the fish may have been under acute stress, possibly due to sampling. Reduced protein and cholesterol levels indicated that the fish from the ash pond-receiving streams may have been nutritionally stressed due to a restricted food supply. Increased serum ion levels also indicated the potential for gill damage possibly due to metal exposure in the effluents. Other serum physiological indicators of organ dysfunction, including ALT (liver), albumin (liver), and creatinine (kidney), were not significantly different between fish collected from the ash pond discharges and the Ohio River reference site (Table 1, Figs. 1–3). Although several serum biochemical indicators differed between the ash pond and reference sites, pollutant exposure was apparently not sufficient to cause functional damage to critical organs such as the kidney or liver.

Fish Health Indices

The lower HAI values for fish from Little Scary Creek provide evidence that the overall health status of these fish is greater than that of fish from the Ohio River. Changes in liver and kidney were the main anomalies observed in fish from the Ohio River. The livers and kidneys of Ohio River fish were characterized by focal discoloration, nodules or cysts, and gray discoloration and granular appearance, respectively. Focal discoloration can be caused by various factors including focal necrosis caused by bacterial infections (Adams *et al.*, 1993). Although the white blood cell counts of Ohio River fish did not indicate the presence of a bacterial infection, the presence of basophilia, dohle bodies, and a low neutrophil count in these fish did suggest a diseased condition (Lohner *et al.*, 2001a).

The HAI is a more integrative index of fish health than most individual measures of fish condition, providing an overall health profile of the population (Adams *et al.*, 1992); however, the HAI is not diagnostic. The index indicates only that the health and condition of fish in Little Scary Creek is at least as good as, or better than, those in the Ohio River, overriding the concerns of lower condition factors in these fish. The occurrence of elevated selenium levels in sunfish from Little Scary Creek was apparently not sufficient to affect health assessment indices beyond those observed in reference populations.

Relationship between Serum Chemistry and Fish Health Indices

Serum protein and cholesterol levels indicated the possibility of poor nutrition and disease in fish collected from the fly ash effluent-receiving streams. These biochemicals were significantly correlated with fish condition factors indicating that they could be used as early indicators of potential adverse impact. Goede and Barton (1990) noted that a decline in condition factor is usually interpreted as a depletion of energy resources. In the present study, serum protein and cholesterol levels were associated with decreased condition factors; however, neither were significantly related to liver selenium levels, or any other metal with the exception of lead. Serum cholesterol was inversely correlated with lead levels, decreasing with increasing liver lead concentrations. Folmar *et al.* (1993) noted similar decreases in serum cholesterol associated with metal exposures.

Serum ion concentrations were typically elevated in fly ash-exposed fish and potassium levels were found to be inversely related to condition factor. Increasing potassium levels are indicative of potential gill injury and the corresponding decrease in condition factor values suggests that ion levels could also be used as an early indicator of biochemical stress. However, while sodium and chloride levels were significantly correlated with liver selenium concentrations, potassium levels were not related to any of the measured metals. This implies that changes in serum potassium were not related to coal ash effluent exposure.

ALT levels, an indicator of liver impairment, were inversely related to condition factor, suggesting that ALT levels are also an early indicator of fish health. However, despite increased ALT levels and possible liver injury, fish from Little Scary Creek had a better health index (Table 4). Also, ALT levels did not vary significantly between sites. Calcium levels were associated with liver somatic indice values, but, again, neither parameter varied significantly between sites.

CONCLUSION

Despite the possibility that serum protein, cholesterol, and potassium levels are early indicators of organismal

condition, only cholesterol was related to metal exposure. The condition factors of Little Scary Creek fish were significantly lower than those of reference fish, but the changes were not related to selenium levels, the primary contaminant of coal ash pond effluents. Fish health assessments also revealed that fish from Little Scary Creek were "healthier" than those from the Ohio River, suggesting that significant organ dysfunction had not occurred.

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COAL AND DEODORIZER RESIDUES IN MARINE SEDIMENTS—CONTAMINANTS OR POLLUTANTS?

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Abstract—Sediment studies around the diffuser of a relatively untreated major marine municipal sewage discharge indicated that 1,4-dichlorobenzene (1,4-DCB) and polycyclic aromatic hydrocarbons (PAHs) were among the contaminants of concern. Subsequent investigations revealed that elevated PAH concentrations were due to the shipwreck of a collier in the 1890s and were apparently not bioavailable. Coal is a common contaminant in marine and freshwater sediments and may be responsible, in some cases, for high PAH contaminant concentrations not resulting in pollution (i.e., biological effects) and can also affect total organic carbon measurements and normalizations. Little information exists regarding 1,4-DCB, whose main source to sewage appears to be toilet block deodorizers and which appears to be a useful marker of the extent of contamination for untreated sewage discharges. Correlative analyses suggest it is a pollutant, but this remains to be confirmed by experimental testing.

Keywords—Coal Polycyclic aromatic hydrocarbons 1,4-Dichlorobenzene Sewage Sediments

INTRODUCTION

In 1992 detailed investigations were conducted of the effects of the Macaulay Point marine outfall (Victoria, BC, Canada) on the sediments [1–3]. Three contaminants were detected at concentrations above sediment quality guidelines: polycyclic aromatic hydrocarbons (PAHs, total and a variety of individual compounds), mercury, and 1,4-dichlorobenzene (1,4-DCB). Mercury and 1,4-DCB showed a concentration gradient which peaked at the outfall and decreased with distance. In contrast, PAH concentrations peaked at one station 400 m away from the outfall. Sediment toxicity tests and benthic community structure studies indicated biological effects commensurate with concentrations of mercury and 1,4-DCB in excess of sediment guideline concentrations (i.e., 0 to 100 m from the outfall). The PAHs exceeded sediment guidelines at only one station 400 m from the outfall. This did not match any pattern of toxicity and benthos alteration, and the PAH contamination was eventually found to be due to coal from the shipwreck of a collier in the 1890s [1].

The purpose of this paper is twofold: first, to discuss the implications of PAHs related to coal in sediments, in terms of bioavailability, implications to total organic carbon (TOC) analyses (and normalizations), and to the reliability of chemical measures; and second, to detail information on 1,4-DCB, a little studied contaminant whose primary source to sewage appears to be toilet block deodorizers and which may be a useful marker of the extent of untreated sewage discharges.

METHODS

Detailed methodology including quality assurance/quality control (QA/QC) has been previously published [1,3]. Briefly, sediment samples were collected with a 0.1-m² stainless steel van Veen grab, appropriately cleaned between samples and stations. Sediment chemistry (three field replicates) and toxicity samples (five field replicates) were synoptically collected (first three grabs used for both) using appropriate techniques that properly controlled cross-contamination. Benthic infaunal samples for community structure analyses (three field replicates) were collected coincidentally, at the same time but from different grabs.

Analyses of PAH, 1,4-DCB, and TOC (CHN analyzer) followed methods recommended by the U.S. Environmental Protection Agency (EPA) [4]; particle size analyses followed procedures of the Association of Official Analytical Chemists [5] (sieve and hydrometer). Further details, including a full list of analytes, are provided by Chapman et al. [1,3]. Toxicity testing (*Rhepoxynius abronius*, 10-d survival; *Neanthes arenaceodentata*, 20-d survival and growth; *Mytilus edulis*, 48-h development) followed EPA procedures [6]. Benthic infauna were sieved through 1.0- and 0.5-mm screens, sorted, and identified to the lowest possible taxonomic level (generally to species).

Data analyses included analysis of variance (ANOVA) and principal components analysis (PCA) [7] at a significance level of $p = 0.05$ for individual components (i.e., chemistry, toxicity, benthos). Mantel's test [8] and Spearman rank correlations were used to evaluate correspondence among components (chemistry, toxicity, benthos).

RESULTS

Major differences in grain size occurred due to the presence of "gravel" at some stations. At these stations variability between PAH analyses for the three field replicates was generally an order of magnitude or more (Table 1). Quality assurance/quality control analyses indicated unacceptable variation between replicates, and selected reanalysis confirmed high variability. A subsequent visual examination of the sediments found that some of the gravel consisted of coal and coke, which was confirmed by subsequent petrographic analyses. Air drying, grinding, and blending of the samples in a mortar and pestle reduced variability because the coal and coke particles were

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Table 1. Results of PAH analyses to determine the influence of coal or coke in sediment samples on analytical variability

	M1600E-1 Original analysis (μg/dry kg)			M1600E-1 Re-analysis[a] (μg/dry kg)			Coal or coke particle (μg/dry kg)
	Rep. 1	Rep. 2	Rep. 3	Rep. 1	Rep. 2	Rep. 3	
Naphthalene	510	76	120	430	410	430	2,740
Acenaphthylene	42	83	1,200	98	95	110	400
Acenaphthene	12	22	49	19	16	20	510
Fluorene	54	41	200	79	70	91	1,530
Phenanthrene	160	270	1,350	340	310	370	4,940
Anthracene	59	97	1,020	150	130	170	1,430
Fluoranthene	85	350	1,790	390	360	430	1,620
Pyrene	76	330	4,470	310	280	330	1,650
Benzo(a)anthracene	43	220	3,320	170	160	210	1,460
Chrysene	54	240	3,010	180	160	210	1,530
Benzo(b)fluoranthene	50	310	2,910	180	160	200	1,320
Benzo(k)fluoranthene	21	88	1,460	74	63	84	330
Benzo(a)pyrene	34	310	2,960	150	130	160	1,270
Indeno(1,2,3-cd)pyrene	28	200	1,800	430	410	430	620
Dibenzo(a,h)anthracene	<20	28	550	27	22	36	260
Benzo(g,h,i)perylene	27	140	1,360	84	69	88	830

M1600E = Macaulay, 1,600 m east of outfall; Rep. = replicate.
[a]After air drying, grinding, and blending.

pulverized, allowing representative subsampling (Table 1). A large, but not necessarily representative, piece of the recovered coal or coke was also air-dried and hand-blended, and had elevated PAH concentrations (Table 1).

Peak TOC concentrations (4.28%) occurred at the outfall and also in sediments away from the outfall which contained coal and coke (to 4.35%). These analyses included the organic content associated with the coal and coke.

Concentrations of 1,4-DCB ranged from below detection (after subtracting blanks) to 1,700 mg/kg dry weight. Highest concentrations occurred near the outfall.

Metals and 1,4-DCB showed very different distributional trends than did PAHs. The former compounds had highest concentrations around the outfall (see Fig. 1). In contrast, PAHs were highest at stations to the east of the outfall (peak concentrations occurred 400 m to the east). Both PCA and ANOVA indicated that east-west directional effects were strong for PAHs compared to metals and 1,4- DCB; PAH exhibited the strongest distance–distance interaction and weakest relationship with the outfall. Comparison to regional sediment quality guidelines (Table 2 [9]) clearly indicates the differences between PAHs and the other two compounds which exceed guidelines (mercury and 1,4-DCB), but, based on the guidelines, toxicity would still be expected at stations up to 400 m from the outfall.

However, elevated sediment toxicity and major alterations in benthic community structure were restricted to stations 0 and 100 m from the outfall [1–3]. Moderate alterations in benthic community structure also occurred at stations with gravel (i.e., coal containing PAHs), but are most probably related to grain-size differences (i.e., the presence of gravel-like material) [3]. The PAHs showed low correspondence with toxicity but high correspondence with benthic community structure, which was reduced when PAHs were normalized to TOC. The 1,4-DCB showed high correspondence with both toxicity and benthic community structure, and the correspondence with toxicity increased when 1,4-DCB concentrations were normalized to TOC.

DISCUSSION

Mercury distributions and their significance are discussed in Chapman et al. [1,3]. The focus of this article is coal and 1,4-DCB.

Coal

Research into marine shipping files indicated that the S.S. San Pedro, a collier carrying 4,000 tons of bituminous coal, ran aground in this area November 23, 1891. During attempts to refloat the vessel, coal was dumped overboard; not all the coal had been salvaged when, in 1896, the ship's hulk was dynamited [10]. Analyses of coal fragments in the sediments indicated the presence of bituminous coal, which matched the historical profile of the San Pedro's cargo.

Unburned coal is a significant source of hydrocarbons in marine coastal sediments (e.g., in Europe [11], the eastern Atlantic [12], and the western Pacific [13]) and in freshwater bodies such as the Great Lakes [14]. The available literature indicates that coal and coal leachates are not acutely or chronically toxic to aquatic life, i.e., that these PAHs are not readily bioavailable. Bender et al. [15] found that 28 d of exposure to as much as 10 mg/L of coal dust did not affect survival or shell growth of Eastern oysters (*Crassostrea virginica*), nor did significant bioaccumulation of PAHs occur. Similarly, Hillaby [16] found no effect on survival, gill ventilation, or respiration in Dungeness crabs (*Cancer magister*) living on a surface composed primarily of coal dust (up to 75% coal to sand by volume) for 21 d. Carlson et al. [17] found that fathead minnows and *Daphnia pulicara* exposed to coal leachates showed no acute effects; fatheads exposed for 24 weeks showed no growth effect, and rainbow trout exposed for 28 d showed no change in mixed function oxidase (MFO) enzyme activity compared to control fish. Fedinger et al. [18] found that leaching of PAHs from coal was minimal even under highly acidic conditions. Photo-induced toxicity, though not tested for, is unlikely since, for this to occur, PAH compounds must be water soluble enough to be photo-oxidized to lead to toxic effects [19].

Barrick et al. [13] conducted studies which indicated the usefulness of molecular markers in discriminating between PAHs from coal and PAHs from other sources. However, sampling, analysis, and interpretation of PAHs in sediments from such sources as coal remains problematic [20].

Moreover, a major analytical problem with samples collected from sediments containing coal or coke is the overestimation

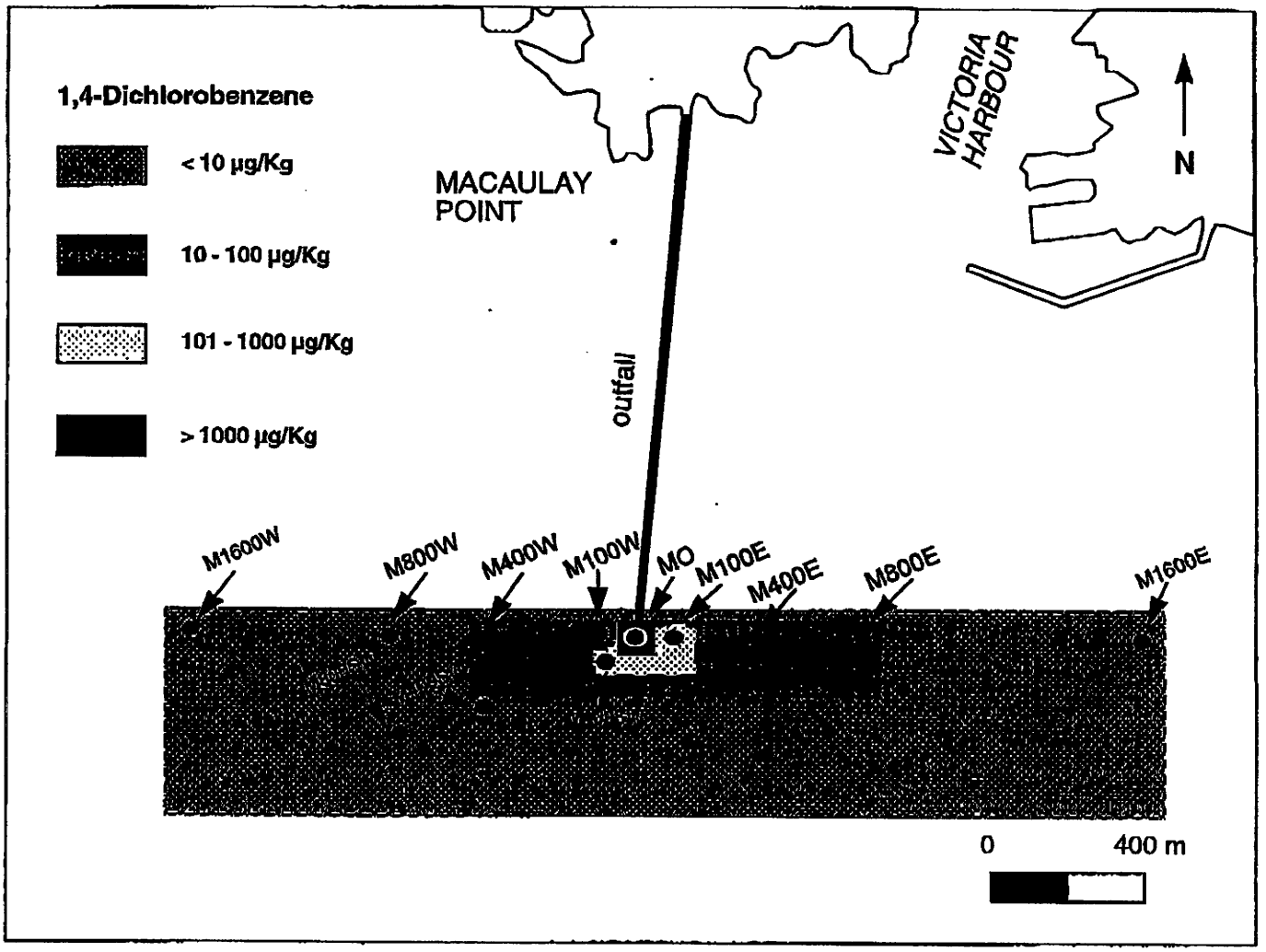

Fig. 1. Sediment 1,4-dichlorobenzene concentrations around the Macaulay Point outfall. Similar patterns were observed for metals. Station designations provide distance (m) and compass direction from the outfall, MO = Macaulay, 0 m (at the mouth of the outfall); M100E = Macaulay, 100 m east.

of TOC caused by these materials being included in the combustion process (i.e., the analytical method used to determine CHN). Clearly in these cases, normalization of organic contaminants to TOC will result in questionable results not directly applicable to equilibrium partitioning theory.

Furthermore, it is important to note that the presence of coal was discovered only because this study collected replicate samples for chemical analyses. Most studies collect only single samples for sediment chemistry, and thus may mistakenly accept PAH data that meet QA/QC requirements but which may be

Table 2. Sediment quality guideline exceedance values

Chemical	Guidelines[a]		Outfall stations[b]		
	Standard	Limit	M0	M100	M400
Hg (mg/dry kg)	0.41	0.59	0.98		
Total LPAHs (µg/dry kg)	5,200	5,200			13,679
Total HPAHs (µg/dry kg)	12,000	17,000			12,818
1,4-DCB (µg/dry kg)	110	110	1,710	277	
Total LPAHs (mg/kg oc)	370	780			
Total HPAHs (mg/kg oc)	960	5,300			
1,4-DCB (mg/kg oc)	3.1	9	40	10	

HPAH = high-molecular-weight polycyclic aromatic hydrocarbons.
LPAH = low-molecular-weight polycyclic aromatic hydrocarbons.
1,4-DCB = 1,4-dichlorobenzene.
[a]Standards and limits from the Washington Department of Ecology, Olympia, Washington, USA [9].
[b]Mean (n = 3) values for each station; highest exceedance value is shown. MO = one station at outfall; M100 and M400 = three stations each, 100 m and 400 m from the outfall. Double underlined values exceed limits; underlined values exceed standards.

due to coal or coke in the sediments. In these cases there will be no correspondence between any observed biological effects and sediment PAH concentrations, and sediment quality guidelines will not be applicable.

1,4-Dichlorobenzene

The principal direct uses of 1,4-DCB are as a moth repellant (moth balls), as an air freshener, and as a toilet block deodorant [21]. Removal from the water column, at least in freshwater, appears to be a minor transport mechanism [22]; once associated with sediments, 1,4-DCB is persistent [23,24]. Rogers et al. [25] could not determine a safe level for 1,4-DCB in sewage sludge and noted the need for investigations to determine any environmental impact in sewage discharges.

1,4-Dichlorobenzene is considered to be a concern in the aquatic environment [26] and has a moderate risk rating in the Great Lakes [27], but there is little information on which to base such a judgment [25,28]; studies to date have been observational and correlational (e.g., the present study, [9]). There is a need to determine, through direct experimentation, whether this compound is in fact a pollutant (i.e., causes adverse biological effects) in sediments rather than simply a contaminant. If it is a pollutant, then source control is relatively easily accomplished by removal of toilet block deodorizers. This has been done in San Diego, California, USA, where 1,4-DCB was considered a hazard in sludge. It has also been considered a hazard in sludge in England [25].

At relatively untreated sewage discharges such as Macaulay Point, 1,4-DCB serves as a useful marker of the extent of outfall-related sediment contamination. Primary and particularly secondary treatments probably remove this material quite effectively (hence the sludge problems noted above). For instance, 1,4-DCB has only rarely been recorded in effluent from secondary-treatment outfalls in southern California or in the surrounding sediments [29–31]. However, it is possible that methods of analyses and detection limits are not appropriate. Hence, sewage dischargers may want to examine this compound more closely, both as a marker and as a possible sediment contaminant.

CONCLUSIONS

Coal appears to be a contaminant rather than a pollutant in aquatic sediments; that is, constituents such as PAHs do not readily leach, are not bioavailable, and do not adversely affect exposed biota. However, the presence of coal can, if undetected, result in highly variable PAH measurements in sediments and in unrealistically high TOC concentrations.

1,4-Dichlorobenzene appears to be a pollutant in aquatic sediments based on correlative analyses. If this is confirmed with experimental testing, 1,4-DCB should be subject to strict source control measures, in particular the removal of toilet block deodorizers containing this material. It is also, at least for sewage discharged without higher levels of treatment, a marker of the extent of outfall contamination of sediments.

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LIMITED BIOAVAILABILITY OF SEDIMENT PAH NEAR AN ALUMINUM SMELTER: CONTAMINATION DOES NOT EQUAL EFFECTS

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Abstract—A Sediment Quality Triad study involving synoptic measures of polycyclic aromatic hydrocarbon (PAH) contamination, toxicity, and resident community (benthic infauna, crab) alteration was conducted to assess impacts from an aluminum smelter discharge. No sediment toxicity was observed, despite extensive testing since 1988 on four test species. Evidence of effects on resident communities was minimal. Effects were not expected in areas >1 km from the smelter, because PAH concentrations have decreased with recent effluent improvements to below levels associated with effects in other studies. However, concentrations within 1 km of the smelter were high (maximum concentration was 10,000 mg/kg total PAH, although most were <150 mg/kg). Based on the literature, those concentrations should have had significant effects on toxicity test responses and benthic communities. Because they did not, we conclude that availability of sediment PAH was limited. Concentrations of parent PAH and metabolites in Dungeness crab (*Cancer magister*) were also low, supporting the hypothesis of limited bioavailability. Bioavailability may be limited because much of the PAH is present as pitch or coal particles. This study indicates that high contaminant concentrations may not be associated with effects, if availability is limited.

Keywords—Sediment Quality Triad Polycyclic aromatic hydrocarbons Sediment Toxicity Benthos

INTRODUCTION

This article details chemical and biological components of a Sediment Quality Triad study [1–3] conducted in Kitimat Arm and a reference area, Kildala Arm, BC, Canada to assess the significance of contamination of sediment by polycyclic aromatic hydrocarbons (PAHs). Biological components included two different sediment toxicity tests and assessment of resident community alteration (crab and benthic infauna).

This extensive study results from an agreement between Alcan Aluminum and the provincial government to evaluate the impact of PAHs on the biota of Kitimat Arm (Fig. 1). The Alcan aluminum smelter has been operating since 1954. A significant portion of the PAHs originated from wet scrubbers designed to clean air emissions from smelter potlines. Since the 1970s, wet scrubbers have been replaced with dry scrubbers, which have virtually eliminated water-borne PAH discharges from this source, except during infrequent maintenance periods. Alcan is eliminating wet scrubber use during maintenance and is in the process of reducing PAH discharges from other areas such as wharf unloading operations and a settling lagoon.

The overall objective of this triad study was to assess the extent and significance of any adverse effects on biota related to PAH contamination from the smelter. The findings of this study may be relevant to aluminum smelter discharges in general [4].

METHODS

Sediment chemistry and toxicity

Five field replicate sediment samples were collected between May 11 and 20, 1994, from each of 10 subtidal sampling areas (Fig. 1) using a modified 0.1-m² Smith–McIntyre sampler. Sediment from IH-I and DLF-I, which are intertidal, was collected at low tide using a stainless-steel bowl and spoon. The top 2 to 5 cm of sediment was pooled in a precleaned stainless-steel basin until sufficient material had been collected for analysis, then thoroughly mixed and apportioned to different analyses using clean techniques. A field blank consisted of the control sediment used for toxicity testing. With the exception of site IH, each sampling area was divided by a grid containing six to 13 units. One field replicate was collected in each of five randomly selected units. For site IH, provincial environmental agency personnel specified the locations for replicate sampling. Sediments collected in Kildala Arm were used as the reference for chemical and toxicity testing.

Chemical analyses. Chemical analyses were performed on sediment samples collected at all 12 sampling areas (Fig. 1). Individual field replicates were analyzed for areas IH-I, IH, and DLF-I, which are nearest the smelter. Composite samples were analyzed for the other areas. Polycyclic aromatic hydrocarbon analysis was carried out using a procedure adapted from U.S. Enviromental Protection Agency (EPA) Methods 3540, 3630, and 8270 [5]. The procedure involved a Soxhlet extraction with dichloromethane and cleanup using silica gel column chromatography. This cleanup procedure effectively removes aliphatic and heterocyclic hydrocarbons, which could potentially interfere with the analysis. The final extract was analyzed by capillary column gas chromatography with mass spectrometric detection. Measurement of sediment total organic carbon (TOC) was carried out according to U.S. EPA Method 9060A [5]. The procedure involved a carbonate analysis (Leco gasometer) and a total carbon analysis (Leco induction furnace). The difference in carbon values was reported as the TOC concentration. Grain size analysis was conducted by oven-drying the sample, then using standard sieves to de-

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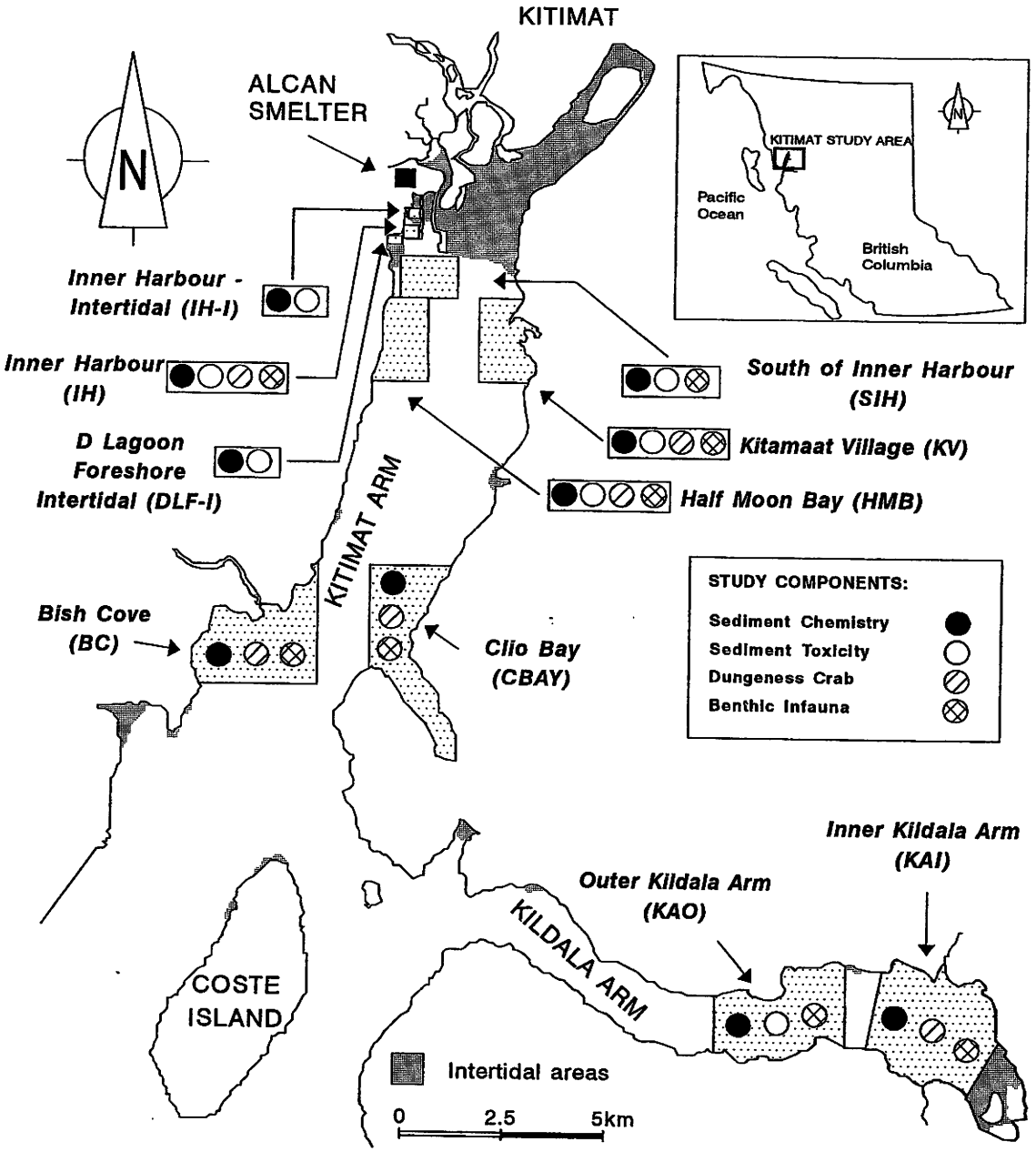

Fig. 1. Study and sampling areas.

termine the sand and silt fractions and using the pipette method for the clay fraction. Quality assurance/quality control (QA/QC) procedures followed standard protocols and included analyses of method blanks, travel blanks, laboratory replicates, and certified reference material.

Toxicity testing. Toxicity testing was performed on five individual field replicates (i.e., not composites) from seven of the 12 sampling areas (Fig. 1). Sediment toxicity tests involved assessing echinoderm (sand dollar, *Dendraster excentricus*) development from fertilized egg to the 48-h echinopluteus stage [6] and 10-d survival of the amphipod *Rhepoxynius abronius* [6,7]. Quality assurance/quality control procedures included positive (i.e., reference toxicants) and negative controls and other measures detailed in the procedures for these tests.

Resident communities: Benthic infauna

Sample collection and processing. Benthic infauna samples were collected between May 11 and 20, 1994, from eight subtidal sampling areas in Kitimat and Kildala Arms (Fig. 1). Because the Inner Harbour was considerably shallower than other Kitimat Arm areas, the areas were subdivided into deep (SIH, HMB, KV, BC, CBAY, KAO) and shallow (IH, KAI) areas, and both deep and shallow reference areas were sampled in Kildala Arm. The benthos replicates were collected at the same point locations as samples for sediment chemistry and toxicity testing so that results for all three components could be directly compared.

Benthos samples were also collected using a modified 0.1-m^2 Smith–McIntyre grab sampler. The overlying water in the grab was removed using a siphon, sediments were washed with seawater using a 1.0-mm mesh screen, and the material remaining on the screen was preserved in 10% buffered formalin.

In the laboratory, all organisms were counted and identified to the lowest practical taxonomic level, generally to species. If animal fragments were present, only anterior portions were counted. Identifications were performed by regional taxonomic

experts. Quality assurance/quality control procedures for both sorting and taxonomy were rigorously followed. Ten percent of the processed samples were resorted by someone other than the original sorter to check sorting efficiency and accuracy. Taxonomic QA/QC involved sending samples from each major taxonomic group out for independent reidentification by a qualified regional expert.

Statistical analyses. The objective of the cluster analyses was to summarize benthic infaunal community patterns and differences among areas. Cluster analyses were performed on abundances of the 10 most abundant taxa using Euclidean distance and the average linkage method [8]. Abundances were transformed using $\log(X + 1)$. Shallow and deep sampling areas were analyzed separately in all cluster and statistical analyses.

One sample from the Inner Harbour subtidal area (IH-C, Fig. 1) had unusually low richness and abundance and was a statistical outlier for analyses. Because IH-C was the least contaminated of the Inner Harbour subtidal sample locations (total PAH = 1.3 mg/kg), the low abundance and richness were presumably not a function of PAH contamination. The outlier was therefore deleted from all analyses. Although removing the outlier reduced differences between IH and KAI, power generally increased because variances were also reduced [9].

Variables analyzed were abundance and richness of all major taxa and of Polychaeta and Bivalvia. Log–log regressions of total richness on total abundance were also examined. In general, there will be a positive relationship between richness and abundance similar to species-area curves [10]. These regressions provide an indication of richness for any given abundance and have some similarity to evenness and diversity indices. Abundance and richness variables were compared among areas using analysis of variance (ANOVA); regressions of richness on abundance were compared among areas using analysis of covariance (ANCOVA). For deep areas, orthogonal contrasts were used to further examine differences among areas [11,12]. The first, a single-degree-of-freedom contrast, compared the five Kitimat Arm areas (BC, CBAY, KV, HMB, SIH) with Outer Kildala Arm (i.e., contaminated versus reference). The second, a multiple degree-of-freedom contrast, compared the five Kitimat Arm areas. These two contrasts accounted for all the variance among areas. If an effect existed, the first contrast would be significant and account for most of the variance. The among-Kitimat contrast could not be broken down to further test for effects along a contaminant gradient. The strong contaminant (PAH) gradient which previously existed among these areas [13,14] had apparently disappeared by 1994.

Observed differences between contaminated and reference areas (i.e., IH vs. KAI, Kitimat vs. Kildala contrast) and their 95% confidence limits (CLs) are provided as an indication of statistical power. All differences and CLs were based on log-transformed data, back-transformed to express the percent difference between contaminated and reference areas. Formulae for calculating CLs for contrasts and for differences in intercepts or adjusted means from ANCOVA are provided in Snedecor and Cochran [15] and in Appendix C of Allard et al. [9]. Cluster analyses, ANOVA, and ANCOVA were conducted using SYSTAT statistical software [8].

Resident communities: Crab

Sample collection and processing. Adult Dungeness crab (*Cancer magister*) were trapped between June 10 and August 12, 1994, from six sampling areas in Kitimat and Kildala Arms (Fig. 1). The sampling areas matched those used for the sediment chemistry, toxicity, and benthic infaunal surveys. However, crab sampling units within each area were not randomly selected and were located in shallower water and nearer shore than sampling units for other surveys because trapping was most successful at depths <15 m. Most traps were retrieved either within 2 to 4 h or on the following day, depending on scheduling and distance from the smelter. A few traps were left for more than 24 h when rough water or other complications prevented earlier retrieval.

Carapace width of all captured crab was measured immediately after trap retrieval. Widths were spine-to-spine (i.e., they included the 10th anterolateral spine). The study objective was to collect 10 to 15 crab of each sex from each sampling area, and crab were released once those targets had been reached. Sampled crab were kept alive and held on ice, at ambient temperature, or in seawater until they were dissected in the laboratory 30 min to 4 h after capture.

In the laboratory, hemolymph for PAH metabolite analyses was collected by amputating the distal portion of one of the smaller legs and allowing the hemolymph to drip into a vial. The hepatopancreas was removed for analyses of parent PAH. Ovaries were removed for determination of ovary weight, ovum weight, and fecundity. Testes were not easy to differentiate and separate from other tissues and consequently were not removed from males.

Chemical analyses. Hepatopancreas samples were frozen prior to analysis. Most samples were composites, except for eight individual males from IH and one male from KAO. Not enough tissue was available to conduct lipid analyses on the samples and to achieve low detection limits. Because achieving lower detection limits was considered more important, lipid analyses were not conducted. Tissues were thawed for approx. 2 h prior to homogenization and subsequent subsampling for extraction and analysis. Parent PAH analyses were carried out in accordance with U.S. EPA methods [5]. The procedure involved a Soxhlet extraction with methylene chloride followed by analysis using capillary column gas chromatography with mass spectrometric detection.

Hemolymph samples were stored frozen in dark vials. Concentrations of the metabolite 1-OH pyrene (1-OHP) were analyzed by Curtis Eickhoff (Simon Fraser University, Burnaby, BC, Canada), who adapted a fluorescence method developed for analyses of 1-OHP in fish bile [16]. Appendix B of Allard et al. [9] provides detailed methods. Briefly, samples were thawed, alcohol was added, and then the mixture was centrifuged. The supernatant was decanted and scanned in a fluorometric spectrometer. Concentrations of 1-OHP were determined by comparison with standard curves and the known peak fluorescence of 1-OHP. This study comprises one of the first applications of the fluorescence method to analyses of crab hemolymph. The method holds promise as a nondestructive PAH assay, assuming that crab can be released after amputation and sample collection and that loss of the distal portion of one of the smaller legs will not affect survival before the limb is regenerated.

Effects variables. In most cases, the number of crab of each sex caught in each trap was recorded. However, in a few cases, only the combined catch from two or more traps was recorded. Therefore, the basic unit of replication was a "set," which usually consisted of one trap but occasionally included two or three traps. Catch-per-unit-effort (CPUE) for each trap set was defined as the number of crab caught per trap (i.e., number crab caught/number traps in set).

Table 1. Polycyclic aromatic hydrocarbon (PAH) concentrations, grain size, and total organic carbon in Kitimat and Kildala Arm sediments, with exceedances of sediment quality values[a]

Sampling area	IH-1[b]	IH[b]	DLF-I[b]	SIH	HMB	KV	CBAY	BC	KAO	KAI
Sample type[c]	I	I	I	C	C	C	C	C	C	C
n	5	5	5	5	5	5	5	5	5	5
Total low molecular weight PAHs	<0.20–4.33	0.098–1,000	0.508–37.8	0.386	0.084	0.058	0.278	0.274	0.03	<0.020
Benzo[*a*]pyrene	<0.020–5.97[d]	<0.135–1,100[d]	0.343–64[d]	0.247	0.094	0.065	0.228	0.23	<0.020	<0.020
Total high molecular weight PAHs	0.085–54	1.21–8,890	3.05–495	2.46	0.829	0.602	2.05	2.16	0.027	<0.020
Total PAHs	0.085–58.3[d]	1.31–9,890[d]	3.56–533[d]	2.85	0.913	0.66	2.33	2.44	0.057	<0.020
Total organic carbon (%)	0.1–2.6	1.3–25.2	1.0–8.7	1.5	1.4	1.4	1.9	2.25	2.55	1.5

[a] Results are expressed as milligrams per kilogram (dry weight) except where noted.
[b] Range for five individual field replicates.
[c] C = composite; I = individual(s).
[d] Underline indicates exceedances of the Effects Range Median for benzo[*a*]pyrene (1.6 mg/kg) and total PAHs (44.792 mg/kg) [20].
Abbreviations refer to the areas on the map in Fig. 1.

Carapace width was the primary measure of size and was recorded for every crab. Weights were taken from most sampled crab. Condition (K) was calculated using the formula traditionally used for fish:

$$K = 100(\text{weight})/(\text{width})^3$$

with weight in grams and width in centimeters. Length is the standard one-dimensional measure used for fish, but width is the standard used for crab. In crab, weight and K will be strongly influenced by the degree of hardening of the exoskeleton, as well as by the weight of muscle and other soft tissue.

Ovaries were shipped frozen for analyses, then thawed and weighed to provide whole ovary weight. A subsample of the ovary was weighed, and ova in the subsample counted. Subsample weight divided by the number of ova in the subsample provided ovum weight. Total ovary weight divided by ovum weight provided fecundity (number of ova).

Field sampling and field measurements followed standard procedures, including marking, labeling, and separating individuals from separate areas. Quality assurance/quality control for the analysis of parent PAH in hepatopancreas included analyses of method blanks, laboratory replicates, surrogate compounds, and spiked samples. The Synchronous Fluorescence Scan analysis for the hemolymph samples was calibrated using 1-OHP standards following procedures given by Ariese et al. [16]. The detection limit for this assay was 3.2 ng/ml 1-OHP conjugates in hemolymph.

Statistical analyses. Nonparametric Kruskal–Wallis (KW) tests were used to compare catch (CPUE) among areas because distributions were decidedly nonnormal. Analysis of variance or ANCOVA was used for analyses of life history variables. Log transformations were used in all cases. The general approach was to begin with a model incorporating area and sex as factors, all covariates, and all interactions. If the sex–area interaction was significant at $p \leq 0.20$, sexes were analyzed separately. Otherwise, the interaction term was dropped. In ANCOVA, sexes were also analyzed separately if slopes differed significantly at $p \leq 0.01$. The p value used as the criterion for dropping slope terms was lower than that used for dropping the sex–area interaction because comparisons of intercepts or adjusted means in ANCOVA are reasonably robust even when slopes differ [17]. If covariates were not significant at $p \leq 0.20$, they were also dropped.

Julian date (untransformed) was used as a covariate for analyses of carapace width (all crab) because the crab were expected to grow over the sampling interval. Variance among sampling areas was partitioned further using three contrasts [11,12]. The "IH versus all other areas" contrast compared IH with the other five sampling areas. The "Kitimat versus Kildala" contrast compared the four Kitimat Arm sampling areas outside IH with KAO. The "Among Kitimat" contrast compared the four Kitimat Arm sampling areas outside IH.

The first two contrasts tested for differences between areas which differed in exposure (i.e., contaminant concentrations). The third contrast tested for other differences among areas which did not differ substantially in exposure. This third contrast provided an estimate of the background (i.e., natural variance among areas). These contrasts were also used for analyses of other size, condition, and reproduction variables.

Condition (sampled crab only) was analyzed by comparing log weight–log width regressions between sexes and among areas. Ovary weight, ovum weight, and fecundity were analyzed in ANCOVA with width as the covariate.

RESULTS

Sediment chemistry and toxicity

Chemical analyses. Concentrations of PAHs were highest in areas immediately adjacent to the Alcan Inner Harbour (IH-I, IH, DLF-I), no PAHs were detected in KAI, and there was no gradient outside IH (Table 1). Benzo[*b*]fluoranthene and phenanthrene were the only PAHs detected in KAO sediments, at concentrations very close to detection limits. Total PAH concentrations ranged from 1.31 to 9,890 mg/kg in IH, from 3.56 to 533 mg/kg in DLF-I, and from 0.085 to 58.3 mg/kg in IH-I. Sampling areas not directly adjacent to Alcan Inner Harbour had low total PAH concentrations (<3 mg/kg). High molecular weight PAHs (HPAHs) were dominant in contaminated sediments, with the HPAH:LPAH (low molecular weight PAH) ratio ≈10:1.

Total organic carbon concentrations ranged from 0.1% for one IH-I sample to 25.2% for one IH sample. Anomalously high TOC concentrations (possibly those >2% and certainly those >4%) probably reflect carbon associated with pitch/coke particulates. Sediment in areas near the Alcan Inner Harbour (i.e., IH-I, IH, DLF-I) contained higher proportions of sand than sediment from other sampling areas in Kitimat Arm and Kildala Arm. The latter were mostly comprised of silt and clay.

Toxicity testing. Abnormality and mortality for echinoderm larvae tests in all control, test (IH, SIH, HMB, KV, DLF-I, IH-I), and reference (KAI) sediments were within specified control criteria [6] of ≤10% abnormality, ≤30% mortality, and ≤50% combined mortality and abnormality [18]. Therefore, no statistical analyses were performed.

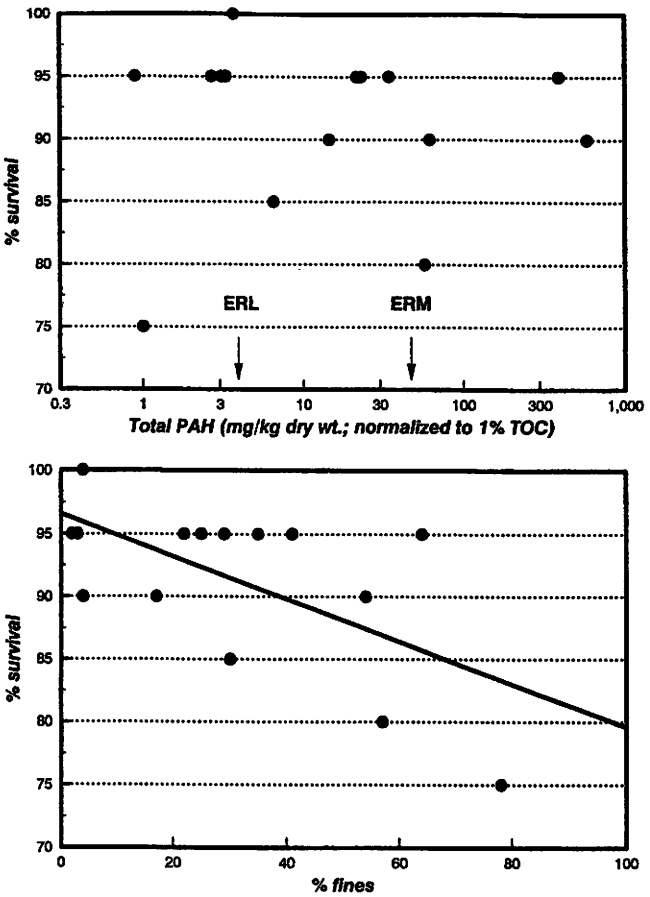

Fig. 2. Relationship between amphipod (*Rhepoxynius abronius*) survival and polycyclic aromatic hydrocarbons (PAHs) (**top**) ($r^2 = 0.00$, $p > 0.05$) and grain size (**bottom**) ($r^2 = 0.37$, $p < 0.05$). Data are from replicates from sample areas nearest the smelter (IH-I, IH, DLF-I). Concentrations of PAHs were normalized to 1% total organic carbon (TOC), approximately the average for marine and estuarine sediments used to derive Effects Range Low (ERL) and Effects Range Median (ERM) values [20].

Amphipod test survival in control sediments met the criterion specified by the American Society for Testing and Materials [7] (≥90%), but some test sediments exceeded this criterion. Survival in test, reference, and control sediments ranged from 83 to 97%. No significant differences (one-tailed t tests, all $p > 0.05$) were observed between test and reference sediments. No relationship was observed between amphipod survival and sediment PAH concentrations for individual replicates from IH, IH-I, and DLF-I (Fig. 2). However, there was an inverse relationship between survival and grain size (Fig. 2). A significant inverse relationship was also noted between survival and grain size for area means for both the 1993 and 1994 tests.

Resident communities: Benthic infauna

Re-sorts indicated that 99 to 100% of the invertebrates had been removed on the original sort. An independent expert agreed with original identifications for 76 of 77 individual organisms submitted for verification. The expert questioned whether one immature polychaete could be confidently assigned to the Cirratulidae as it was in the original identification.

General community description. A total of 10,027 individuals were collected in 40 samples (mean = 251/sample). There were 157 taxa identified, most at the genus or species level. The communities were dominated by polychaete worms, bivalve molluscs (clams and mussels), and crustaceans. Nematoda (not identified to lower levels) were abundant in some samples and accounted for 10% of total abundance. Table 2 provides a list of the 10 most abundant taxa collected. Although polychaetes dominated the community, the two most abundant taxa were the clam *Axinopsida serricata* and Nematoda. The remaining eight taxa were all polychaete worms. Nematoda were either very abundant or not present in most samples. These are small organisms, and recovery by the 1.0-mm sieves used was inefficient and variable. Nematoda were excluded from analyses of total abundance.

Table 2. Dominant benthic invertebrate taxa

Taxon	Abundance: No. collected	Abundance: % Of total	Occurrence: No. samples	Occurrence: % Occurrence
Axinopsida serricata[a]	2,211	22.1	24	60
Nematoda	1,028	10.3	13	33
Leitoscoloplos pugettensis	858	8.6	10	25
Aricidea spp.	725	7.2	26	65
Lumbrineridae	656	6.5	38	95
Scalibregma inflatum	388	3.8	10	25
Ophelina spp.	298	3.0	8	20
Levinsenia gracilis	272	2.7	24	60
Cossura spp.	251	2.5	18	45
Nephtys cornuta	186	1.9	27	68

[a] Bivalvia; remainder (except Nematoda) are Polychaeta.

Statistical analyses—Shallow areas. Figure 3 provides cluster diagrams of replicate samples from the shallow areas. Sample C from IH was an obvious outlier, clustering separately from all other samples. The other four IH samples were similar in community composition, clustering together before clustering with any of the KAI samples. The KAI samples were more heterogeneous and did not form a cluster or group distinct from the IH samples.

Table 3 provides abundance of all taxa and of several major

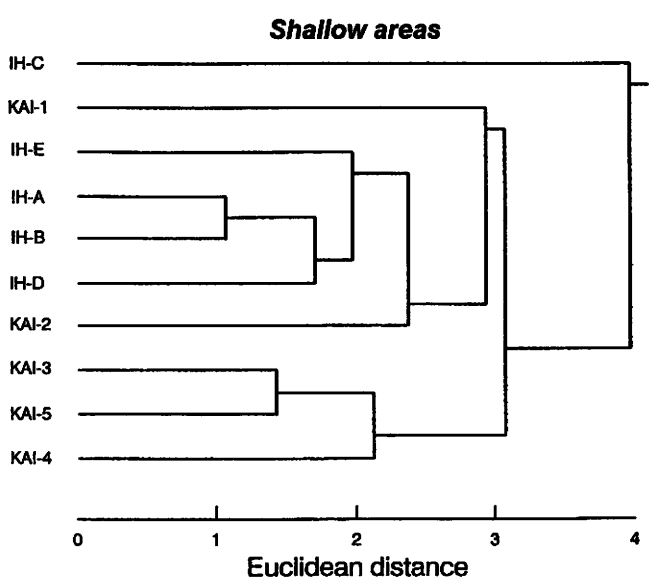

Fig. 3. Cluster analyses of benthic infaunal communities from shallow areas. Analyses were based on log-transformed abundances of the 10 most abundant taxa (see Table 2 for list of taxa). Site locations and abbreviations for this and for subsequent figures are provided in Figure 1.

Table 3. Total and major benthic invertebrate taxon abundances

Sampling area	No. of organisms per sample (mean ± SD)			
	Total (minus Nematoda)	Polychaeta	Bivalvia	Nematoda
Shallow sampling areas				
IH[a]	411 ± 258 (511 ± 149)	250 ± 136 (310 ± 26)	135 ± 140 (169 ± 136)	26 ± 15 (24 ± 16)
KAI	783 ± 231	439 ± 112	338 ± 188	170 ± 224
Deep sampling areas				
SIH	144 ± 123	101 ± 93	34 ± 31	0
HMB	61 ± 67	52 ± 67	2 ± 3	0
KV	166 ± 76	134 ± 69	18 ± 12	0
BC	95 ± 72	48 ± 53	16 ± 12	7 ± 15
CBAY	57 ± 27	25 ± 14	9 ± 6	<1
KAO	81 ± 49	64 ± 45	7 ± 4	2 ± 5

[a] Values in parentheses are with outlier (replicate C) deleted.

taxa for the two shallow areas. Total abundance and abundances of polychaetes and bivalves were greater in KAI than in IH. Total (minus Nematoda) and polychaete abundances were ~30% lower in IH than in KAI, and differences were significant or nearly so (Table 4). Differences in polychaete abundance were associated with differences in community composition. *Leitoscoloplos pugettensis* and *Ophelina* spp. dominated KAI samples; Lumbrineridae and *Scalibregma inflatum* dominated IH samples. Differences in bivalve abundance could not be analyzed statistically because deletion of the one outlier from IH generated new outliers from both areas. The dominant bivalve, *A. serricata,* was more abundant in KAI than in IH (Fig. 4). Furthermore, abundance of *A. serricata* in IH increased with decreasing PAH. Abundances of other bivalves were *higher* in IH than in KAI, with no strong relationship with PAH (Fig. 4).

Despite limited sample sizes, comparisons of abundance between the two shallow areas were remarkably powerful because variances were low. Given the 95% CL in Table 4, there was little chance that real abundances were elevated in IH relative to KAI and that any reductions in abundances in IH were greater than twofold.

Although both total and major taxon richness were greater in IH than in KAI (Table 5), only the difference in bivalve richness was significant (Table 4). The KAI samples were almost completely dominated by *A. serricata,* with only one to five other taxa present (Fig. 4). In contrast, IH samples contained five to nine other taxa. Within IH, bivalve (and total, although not shown) richness was negatively correlated with sediment PAH (Fig. 4). When log–log regressions of total richness on total abundance were compared between areas, differences in intercepts were highly significant (Table 4). For any given abundance, richness in IH was approximately double richness in KAI.

Given the 95% CL for richness variables in Table 4, large

Table 4. Shallow sampling areas: results of statistical tests comparing areas, and observed differences (δ) in abundance (*N*) and richness (*S*) variables and their confidence limits (CLs)[a]

Variable	*p*	δ (%)	95% CL Upper	95% CL Lower
Total *N*[b]	0.08	−34	+8	−60
Polychaete *N*	0.05	−28	0	−48
Total *S*	0.07	+44	+114	−4
Polychaete *S*	0.21	+29	+98	−17
Bivalve *S*	0.005	+109	+228	+34
Total *S* (adjusted for *N*)	<0.001	+99	+144	+62

[a] Differences and CLs are expressed in terms of IH values as percent decrease (−) or increase (+) relative to KAI values.
[b] Total *N* excludes Nematoda.

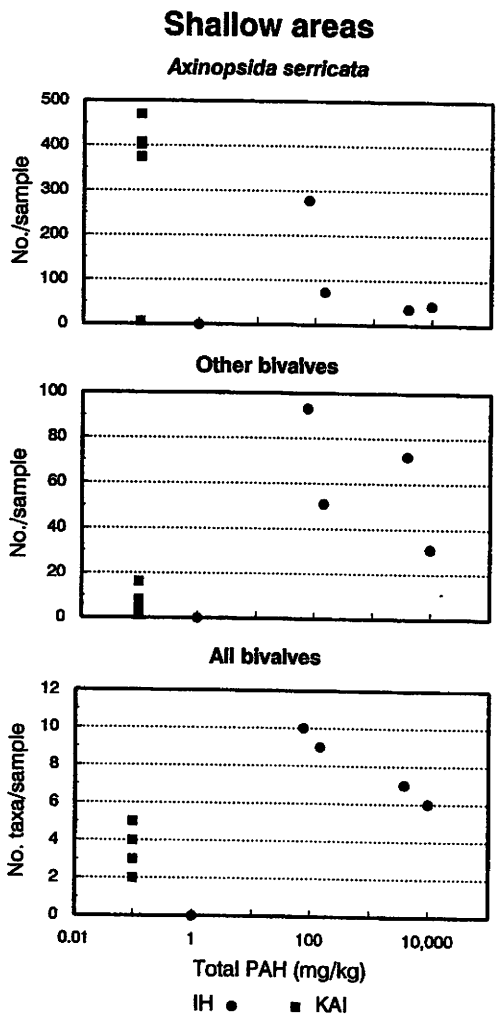

Fig. 4. Shallow areas: relationship between abundance and richness of bivalves and polycyclic aromatic hydrocarbons (PAHs) in sediments.

Table 5. Total and major benthic invertebrate taxon richness

Sampling area	No. taxa per sample (mean ± SD)		
	Total	Polychaeta	Bivalvia
Shallow sampling areas			
IH[a]	32 ± 16	20 ± 10	6.4 ± 3.9
	(38 ± 8)	(24 ± 3)	(8.0 ± 1.8)
KAI	27 ± 6	19 ± 6	3.2 ± 1.3
Deep sampling areas			
SIH	25 ± 2	15 ± 3	4.0 ± 1.2
HMB	14 ± 5	10 ± 5	1.0 ± 1.4
KV	23 ± 4	14 ± 3	3.2 ± 1.3
BC	24 ± 9	12 ± 7	3.6 ± 1.4
CBAY	20 ± 6	10 ± 3	2.4 ± 1.1
KAO	22 ± 4	14 ± 3	2.4 ± 0.9

[a] Values in parentheses are with outlier (replicate C) deleted.

(i.e., >25%) reductions in total and polychaete richness in IH relative to KAI were unlikely.

Statistical analyses—Deep areas. Figure 5 provides cluster diagrams for the deep areas based on area mean abundances of dominant taxa in Table 2. Areas were separated largely by depth. The two shallowest areas, SIH and KV, clustered separately from the remaining four areas. Within those other four areas, the two deepest areas, BC and CBAY, clustered separately. HMB was clustered with the two deep Kitimat Arm areas rather than with KAO, which was similar in depth. Thus, within the middepth range (150 to 200 m), there may have been some community differences between Kildala and Kitimat Arms. However, depth was the dominant factor affecting community composition and most variables analyzed (see below).

Table 3 provides abundance data for deep sampling areas. Abundances were much lower than in shallow sampling areas. Abundances also decreased with depth within the deep areas (Fig. 6). The deep sampling areas were dominated by polychaetes and bivalves. Abundances in Kildala Arm (KAO), which was intermediate in depth, were generally in the midrange of values from the Kitimat Arm areas. Differences in abundance variables among deep areas varied from marginally (total abundance) to highly significant (bivalves) (Table 6). The contrasts indicated that most differences occurred among Kitimat Arm sites, rather than between Kitimat Arm and Kildala Arm. Differences within Kitimat Arm were largely related to depth differences.

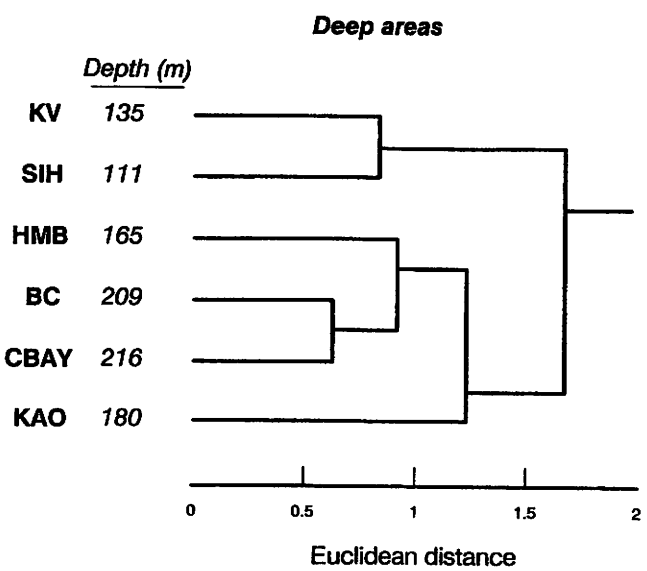

Fig. 5. Cluster analyses of benthic infaunal communities from deep areas. Analyses were based on log-transformed abundances of the 10 most abundant taxa (see Table 2 for list of taxa) and on area means.

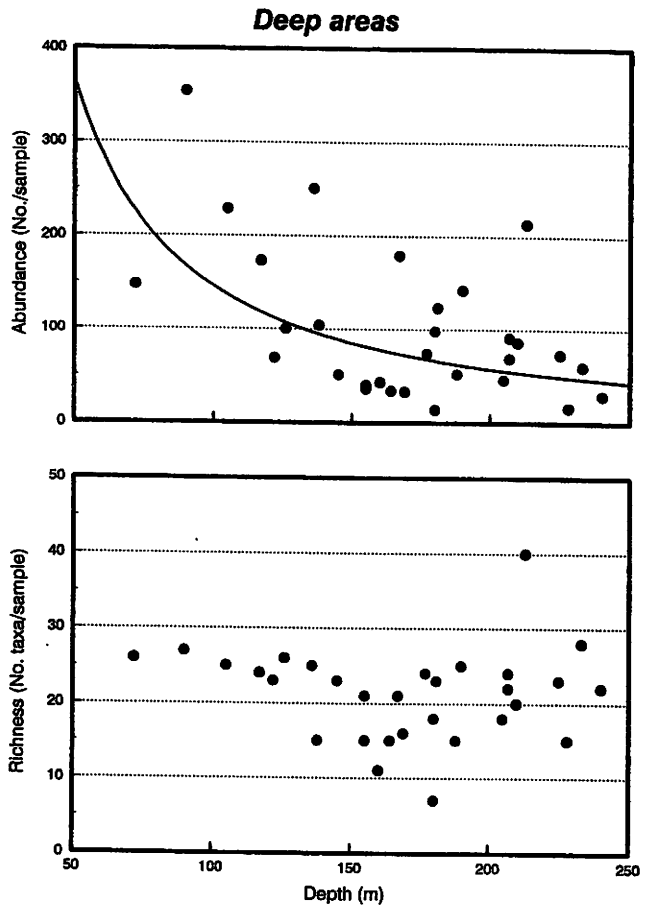

Fig. 6. Deep areas: relationship between total abundance (N, minus Nematoda) and total richness (S) of benthic invertebrates and depth (D). For N, $N = 67{,}000D^{-1.33}$, $r^2 = 0.24$, $p < 0.05$. For S, $r^2 = 0.02$, $p > 0.05$.

Within deep sampling areas, there was no relationship between richness and depth (Fig. 6). Richness was lower in deep areas than in shallow sampling areas largely because there were fewer polychaete taxa (Table 5).

Total and bivalve richness differed significantly among deep areas; polychaete richness did not (Table 6). Differences in total and bivalve richness occurred among Kitimat Arm areas rather than between Kitimat and Kildala Arm areas. Total and bivalve richness were low in HMB and high in SIH; there were only minor differences among the other four areas. These differences in richness were reduced when regressions of richness on abundance were analyzed; nevertheless, differences in intercepts or adjusted means were still significant. Even after adjustment for abundance, richness was low in HMB. Differences between HMB and other areas were 25 to 50%; differences among other areas were <25%.

Observed differences in abundance and richness variables between Kitimat and Kildala Arms were relatively small (all ≤25% in either direction) and split evenly between positive and negative (Table 6). Confidence limits for abundances were wide, and twofold or greater positive or negative differences (i.e., −50 to +100%) could have existed despite the small observed dif-

Table 6. Deep sampling areas: results of tests comparing areas, and observed differences (δ) in abundance (*N*) and richness (*S*) variables and their confidence limits (CLs)[a]

Variable	*p*			Kitimat vs. Kidalda Arm		
	Among areas	Among Kitimat areas	Kitimat vs. Kildala Arm	δ (%)	Upper 95% CL	Lower 95% CL
Total *N*[b]	0.09	0.05	0.77	+11	+130	−46
Polychaete *N*	0.04	0.02	0.77	−11	+106	−62
Bivalve *N*	0.005	0.003	0.61	+25	+205	−49
Total *S*	0.01	0.007	0.59	−7	+22	−29
Polychaete *S*	0.22	0.19	0.37	−15	+21	−40
Bivalve *S*	0.004	0.002	0.86	+4	+56	−31
Total *S* (adjusted for *N*)	0.03	0.02	0.47	−10	+11	−26

[a] Differences and CLs are expressed in terms of Kitimat Arm values as percent decrease (−) or increase (+) relative to Kildala Arm values.
[b] Total *N* excludes Nematoda.

ferences. Real differences for richness (total and major taxa) are likely to be much smaller (within ±50%). Real differences in diversity or evenness, if defined as differences between intercepts from richness–abundance regressions, were likely to be ≤25%.

Resident communities: Crab

No parent PAHs measured in hepatopancreas were detected in method blanks. Laboratory replicate results agreed to within ±30% of the mean. All sample spike recovery results were acceptable (between 60% and 140%), with the exception of naphthalene, which due to its volatility can often be just outside the acceptability ranges without compromising the data. Surrogate recoveries (25 to 96%) for all samples met U.S. EPA limits for the analyses used.

Catches and catch-per-unit effort. A total of 403 crab were caught in 97 traps (92 sets), with males ($N = 237$) outnumbering females ($N = 166$). Mean (±SD) CPUE was 4.2 ± 6.2 crab/trap. Figure 7 provides CPUE data for each area. The CPUE was lowest in KAO. Within Kitimat Arm, CPUE was lower near the smelter (IH, HMB) than in BC or CBAY.

When CPUEs for all areas were compared using KW tests, differences among areas were significant ($p = 0.001$). Those results reflect lower catches in KAO. When CPUEs were compared among Kitimat Arm areas, *p* values were the same (=0.02) whether IH was included or excluded. Those results indicate that differences within Kitimat Arm were smaller than differences between Kitimat Arm and Kildala Arm and that any differences present were among areas outside IH rather than between IH and other areas.

The power of the nonparametric tests used to analyze CPUE data cannot be estimated except by simulation. These data, like most other fish or shellfish catch data, had high variances relative to means, and we were frankly surprised that any differences were detected.

Tissue chemistry. Tables 7 and 8 provide data on PAHs in crab hepatopancreas for males and females, respectively. Only eight of the 16 compounds analyzed were detected, mostly in samples of crab from near the smelter. All measured concentrations were between 5 and 20 μg/kg, barely above detection limits. Although sediments were dominated by HPAHs (Table 1), the crab hepatopancreas were dominated by LPAHs. There were no differences between males and females that could not be accounted for by different sample sizes or detection limits for different batches of crab [9].

Figure 8 provides mean concentrations of 1-OHP in crab hemolymph. Concentrations in females were approximately double those in males for all sampling areas where both sexes were sampled. The highest concentrations in females were measured in IH. The IH average was skewed by one female with a concentration of 40.4 ng/ml; other detectable concentrations ranged from 3.6 to 15.5 ng/ml. Concentrations in female crab from the other sampling areas were approximately half those for IH females.

Concentrations of 1-OHP in male crab were elevated in IH, the only sampling area where most concentrations were above detection limits. Concentrations outside IH may also have been slightly higher than those in Kildala Arm, as 1-OHP was occasionally detected in the Kitimat Arm males but was not detected in any KAO males.

Effects measures. Table 9 provides mean widths for all crab and mean widths, weights, and condition factors (*K*) for weighed crab. Eight male crab from BC were not weighed. Otherwise, summary statistics in Table 9 apply to crab used for parent PAH analyses. Although there must have been several age classes present for each sex, frequency histograms were near-normal and apparently unimodal. The histograms could not be used to distinguish age classes or instars. Therefore, all sizes were pooled for analyses, and any differences in size could have been the result of differences in age as well as size-at-age (i.e., growth). Males were larger than females, which is characteristic of Dungeness and other crab species [19].

Table 10 provides differences in size and condition and their confidence limits. Although it was expected that crab would grow over the study period (June–August 1994), there was no significant effect of sample date on width ($p > 0.20$). Also, no interaction was observed between sex and area ($p > 0.20$). Widths differed significantly between the sexes ($p < 0.001$), reflecting the sexual size dimorphism in this species. Differences among areas were highly significant, because crab from KAO were 5 to 10% wider than those from Kitimat Arm (Table 9). The largest crab from Kitimat Arm were collected from IH. As a result, the KAO versus Kitimat Arm (except IH) contrast accounted for most of the differences among areas.

Table 9 shows that sampled (i.e., weighed) crab were a biased sample of captured crab. In general, widths for weighed crab were greater than widths for all crab. Because of this bias, and because of smaller sample sizes, differences in weights were less significant than differences in widths for all crab (Table 10). Differences in weights between the sexes were, of course,

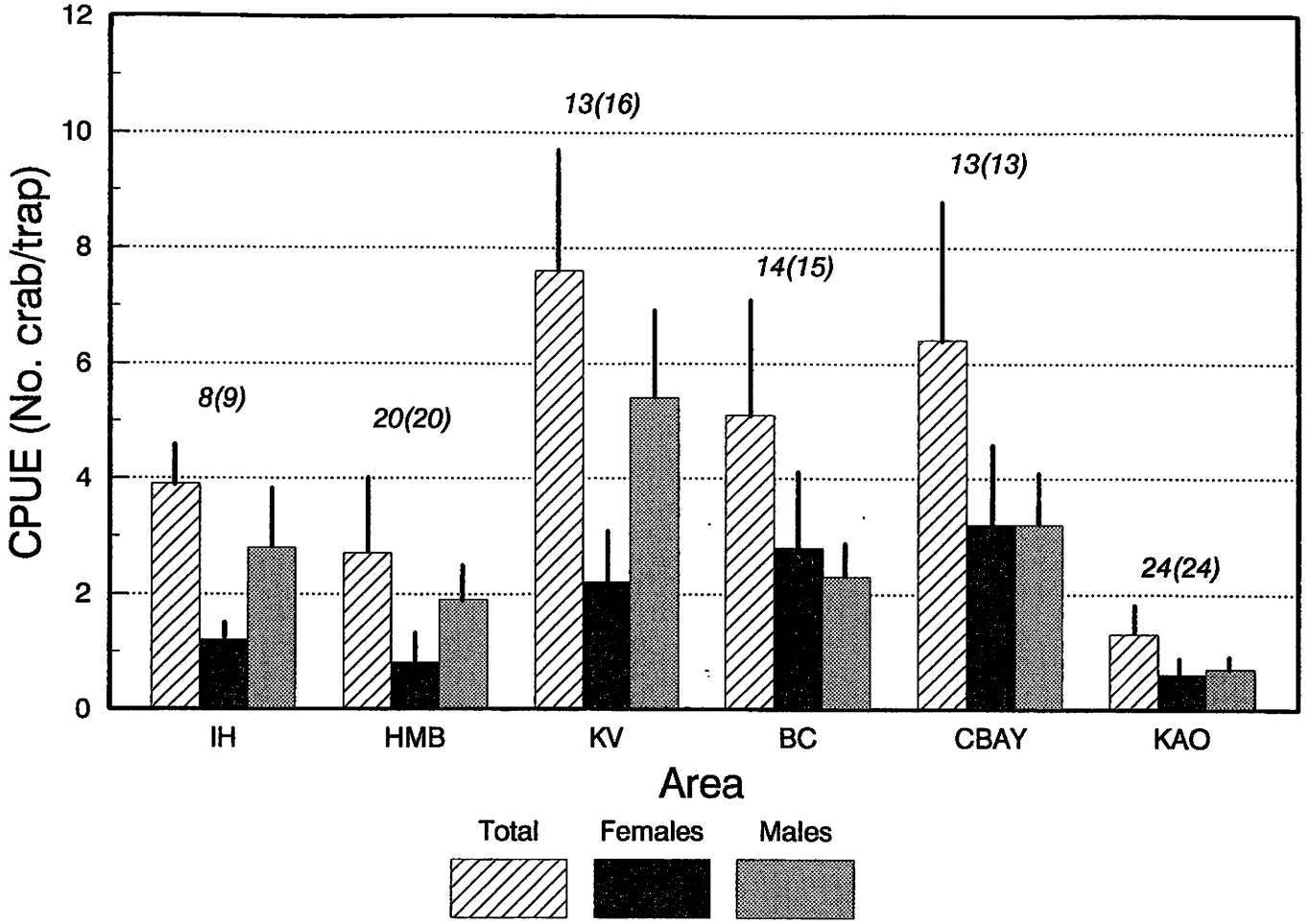

Fig. 7. Catch-per-unit-effort (CPUE) for all months. Vertical lines above bars are 1 SE. Numbers above bars are the number of sets, with the number of traps set in parentheses.

significant ($p < 0.001$). Differences among sampling areas were also significant but were associated with differences among KAO and the Kitimat Arm areas outside IH (last two contrasts). Weights of IH crab were intermediate; crab from KAO weighed more than those from other areas.

Interactions among sex, sampling area, and width for regressions of log weight on log width were significant ($p < 0.01$). Therefore, sexes were analyzed separately. Slopes did not differ among areas within each sex ($p > 0.10$). Slopes of log–log relationships were ~3 (2.8 for females, 2.9 for males), indi-

Table 7. Polycyclic aromatic hydrocarbon (PAH) concentrations (μg/kg) in male crab hepatopancreas

Sampling area	IH[a]		HMB		KV	BC		CBAY		KAO	
Sample type[b]	I	C	C		C	C		C		C	I
n	8	2	8	8	14	8	9	5	12	9	1
Batch	1	2	1	2	1	1	2	1	2	1	2
Low molecular weight PAHs											
Naphthalene	<5–*6* (4)	<20	*6*	<20	<5	*5*	<20	<5	<20	<5	<20
Acenaphthene	<5–*20* (7)	<5	*17*	<5	<5	<5	<5	<5	<5	<5	<5
Fluorene	<5 (0)	<5	*6*	<5	<5	<5	<5	<5	<5	<5	<5
Phenanthrene	<5–*10* (7)	<5	*9*	*5*	<5	*7*	<5	<5	<5	<5	*9*
High molecular weight PAHs											
Fluoranthene	<5–*9* (2)	<10	<5	<10	<5	<5	<10	<5	<10	<5	<10
Pyrene	<5–*12* (2)	<10	<5	<10	<5	<5	<10	<5	<10	*6*	*13*
Benzo[*a*]anthracene	<5–*9* (2)	<10	<5	<10	<5	<5	<10	<5	<10	<5	<10
Chrysene	<5–*7* (3)	<10	<5	<10	<5	<5	<10	<5	<10	<5	<10

[a] Range. The number of values greater than detection limits is given in parentheses. Concentrations above detection limits are italicized.
[b] C = composite; I = individual(s).
Other PAH analyzed but not detected (detection limits in parentheses; two different batches analyzed): acenaphthylene and anthracene (5); and benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenzo[*a,h*]anthracene, benzo[*ghi*]perylene, and indeno[1,2,3-*cd*]pyrene (5,20).

Table 8. Polycyclic aromatic hydrocarbon (PAH) concentrations (μg/kg) in composites of female crab hepatopancreas

	Sampling area					
Compound	IH[a] (*n* = 10)	HMB (*n* = 14)	KV (*n* = 9)	BC (*n* = 14)	CBAY (*n* = 17)	KAO (*n* = 11)
Low molecular weight PAHs						
Phenanthrene	*8*	<5	<5	<5	<5	<5
High molecular weight PAHs						
Fluoranthene	*12*	<10	<10	<10	<10	<10
Chrysene	*12*	<10	<10	<10	<10	<10

[a] Concentrations above detection limits are italicized.
For other PAHs analyzed but not detected, see Table 7.

cating that weight was approximately proportional to the cube of width. Since calculation of K in Table 9 assumes a cubic relationship, comparison of K values is roughly equivalent to comparison of the regression intercepts or adjusted means. Differences in adjusted means among areas were significant or nearly so (Table 10). The contrasts indicated that most differences among areas were associated with differences among Kitimat Arm areas outside IH.

Confidence limits for differences in size and condition were narrow (Table 10), reflecting the low variance of variables analyzed and the relatively large sample sizes, especially for width. Observed differences between IH and other areas and between Kildala Arm and Kitimat Arm (excluding IH) were small (all but one <10%). In four cases, CLs also excluded differences >10%, and all CLs excluded differences >20%. Thus, analyses had sufficient power to detect small differences or effects (and did so) and to indicate that real differences were probably <20% and in some cases <10%.

Table 11 provides mean ovary weights, ovum weights, and fecundities for female crab from each sampling area. Sample sizes were reduced for ovum weight and fecundity because some ovaries contained ova which were too small to differentiate and count. Eleven crab had undifferentiated ova; five of these crab came from BC. Elimination of crab with undifferentiated ova positively biased estimates of ovum weight, especially for BC. Sample sizes were also reduced when reproductive parameters were regressed on width. Identification codes were incomplete for three ovary samples from CBAY, and reproductive data from these samples could not be matched with size data recorded in the field. Finally, one outlier was deleted from the analyses of log–log regressions of ovary weight on width.

Crab from KAO had the largest ovaries. However, differences in ovary weight were affected by differences in width. Analyses of log ovary weight–log width regressions indicated that there was a significant relationship between width and ovary weight

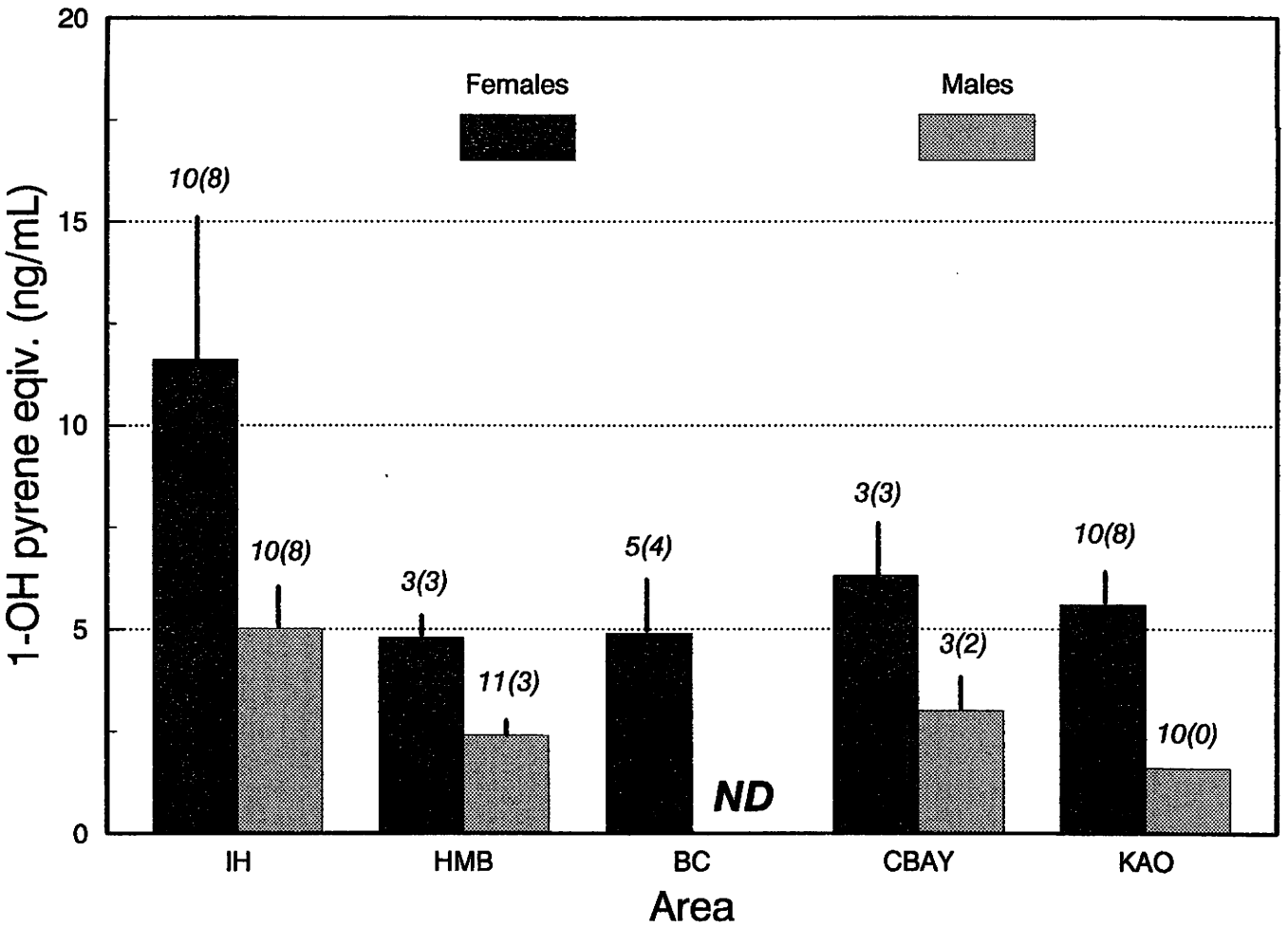

Fig. 8. Polycyclic aromatic hydrocarbon (PAH) metabolite concentrations in hemolymph of male and female crab. Vertical lines above bars are 1 SE. Values below detection limits were assumed to be one-half the detection limits for calculation of the mean and SE. Numbers above bars are sample sizes, with the number of values above the detection limit of 3.2 ng/ml given in parentheses. ND = No data.

Table 9. Mean (±SD) size and condition of crab captured from Kitimat and Kildala Arms

Sampling area	Sex[a]	All crab		Weighed crab			
		n	Width (cm)	*n*	Width (cm)	Weight (g)	*K*[b]
IH	F	11	14.8 ± 1.4	10	14.8 ± 1.5	423 ± 118	12.8 ± 0.8
	M	24	16.8 ± 2.1	10	17.8 ± 1.0	732 ± 161	12.9 ± 0.9
HMB	F	16	14.0 ± 1.7	14	14.0 ± 1.8	420 ± 153	14.7 ± 1.9
	M	38	15.6 ± 2.3	16	17.8 ± 1.0	693 ± 122	12.1 ± 1.1
KV	F	29	14.3 ± 1.2	9	15.4 ± 0.9	484 ± 76	13.2 ± 0.8
	M	77	16.1 ± 1.8	14	17.7 ± 0.7	755 ± 130	13.5 ± 0.8
BC	F	54	14.4 ± 1.0	14	15.1 ± 0.8	441 ± 70	12.8 ± 1.2
	M	40	16.3 ± 1.9	9	17.5 ± 0.6	710 ± 73	13.2 ± 1.4
CBAY	F	41	13.7 ± 1.2	17	14.3 ± 1.1	413 ± 97	13.9 ± 1.5
	M	42	15.7 ± 1.3	17	16.8 ± 1.0	628 ± 128	13.2 ± 1.4
KAO	F	15	15.3 ± 1.4	12	15.1 ± 1.4	476 ± 138	13.7 ± 1.3
	M	16	17.5 ± 2.3	10	18.5 ± 1.5	827 ± 184	12.9 ± 1.6

[a] F = female; M = male.
[b] *K* = condition factor (i.e., weight relative to width; see text for details).

(p = 0.02) but no significant differences in intercepts among areas (Table 10).

CBAY females had the largest ova; IH females had ova of intermediate weight (Table 11). Ovum weight was also significantly correlated with width (p = 0.05). Differences in intercepts of log ovum weight–log width regressions among sampling areas were not quite significant, but differences among Kitimat Arm areas outside IH were significant (Table 10). Ranks based on ovum weights adjusted for width were similar to those based on raw ovum weights.

Fecundities were much lower in CBAY than in other sampling areas and were greatest in BC, HMB, and KAO (Table 11). Thus, there was a trade-off between ovum size and ovum number, with females from CBAY having fewer but larger ova and females from HMB and BC having more, but smaller, ova. No relationship was observed between fecundity and width (p > 0.20). Fecundities differed significantly among areas and between offshore Kitimat Arm areas and KAO (Table 10). These differences were due to low fecundities for CBAY females and disappeared when data were reanalyzed with CBAY samples deleted.

Table 10 shows that 95% CLs for reproductive variables were broad. Sample sizes were smaller than for analyses of size and condition, and variances were much greater. Thus, although the differences observed, especially between IH and other areas, were small, real differences could be much larger and represent significant positive or negative contaminant effects.

Table 12 also provides ranks for the effects categories. Crab from IH, the most contaminated site, were intermediate or average (average rank = 3.5) for all three effects categories and overall. Correlations were observed among ranks for the different categories. Specifically, KAO ranked low in terms of catch but high in terms of size and reproductive investment, suggesting density-dependent effects on growth (or survival/longevity, since size is also a function of age) and reproduction. No evidence was found of these density-dependent effects among Kitimat Arm areas. Instead, there was a strong negative correlation (Spearman rank, r = −0.97) between size and reproductive investment, suggesting trade-offs between growth or survival and reproduction.

DISCUSSION

Sediment chemistry

Outside the Inner Harbour/D Lagoon Foreshore (DLF-I), concentrations of PAHs in Kitimat Arm sediment have decreased

Table 10. Results of tests comparing areas, and observed differences (δ) and confidence limits (CLs) for crab life history variables

			Contrast									
			Among all areas	IH vs. all other areas[a]				Kitimat vs. Kildala[b]				Among Kitimat[c]
						95% CL (%)				95% CL (%)		
Y	*X*	*N*	*p*	*p*	δ (%)	Upper	Lower	*p*	δ (%)	Upper	Lower	*p*
Size and condition												
Width		403	<0.001	0.07	+4	+8	0	<0.001	−9	−5	−12	0.02
Weight		152	0.02	0.63	−3	+8	−12	0.03	−11	−1	−20	0.03
Weight (females)	Width	76	0.03	0.07	−6	+1	−12	0.87	0	+6	−6	0.02
Weight (males)	Width	76	0.06	0.93	0	+7	−7	0.90	0	+7	−6	0.02
Reproduction												
Ovary weight	Width	69	0.33	0.69	−5	+77	−49	0.34	−40	+7	−67	0.26
Ovum weight	Width	60	0.08	0.96	−1	+70	−43	0.58	−14	+47	−49	0.03
Fecundity		63	0.001	0.64	−10	+43	−43	0.22	−24	+18	−51	<0.001

[a] δ and CL (U = upper; L = lower) are back-transformed from log-transformed values and are expressed as IH minus the average of the other five areas.
[b] δ and CL are back-transformed from log-transformed values and are expressed as the average of the Kitimat Arm areas (excluding IH) minus Kildala Arm (KAO).
[c] Compares all Kitimat Arm areas except IH.

Table 11. Means (±SD) for female crab reproductive variables[a]

Sampling area	*n* (ovaries)	Ovary weight (g)	*n* (ovum weight, fecundity)	Ovum weight (μg)	Fecundity (1,000s)
IH	10	10.0 ± 8.1	8	71 ± 49	169 ± 95
HMB	14	10.9 ± 6.7	14	52 ± 41	239 ± 125
KV	8	11.1 ± 8.6	8	63 ± 46	168 ± 63
BC	14	8.4 ± 6.9	9	59 ± 46	250 ± 171
CBAY	17	9.0 ± 9.9	15	92 ± 65	113 ± 80
KAO	11	15.6 ± 8.5	9	79 ± 53	230 ± 110

[a] Sample sizes for ovum weight and fecundity are lower than those for ovary weight because ova in some ovaries were too small to differentiate and weigh.

Table 12. Summary of sample area ranks for Dungeness crab effects categories (catch, size, and reproduction)

Sampling area	Effects category: Catch[a]	Size[b]	Reproduction[c]
IH	3	3	3.5
HMB	2	1	5
KV	6	4.5	1.5
BC	4	4.5	1.5
CBAY	5	2	3.5
KAO	1	6	6

[a] Ranks for mean catch-per-unit-effort.
[b] Ranks for female and male width (all crab) and female and male condition (sampled crab; adjusted means from regressions of weight on width) were averaged, then those averages were ranked.
[c] Ranks for ovary and ovum width (both adjusted for width) and fecundity were averaged, then those averages were ranked.

since the 1980s (Fig. 9). The most dramatic decreases have occurred in HMB and SIH. Decreases have also occurred elsewhere, especially KV, but these changes could be within the range expected given spatial heterogeneity and the change in chemical analysts between 1987–1989 and 1993–1994.

Sediment chemistry results were compared to effects-based criteria developed by Long et al. [20] using an empirical approach based on a sediment chemistry and biological effects database. In 1994, all sediment samples from outside the Alcan Inner Harbour area and DLF-I had benzo[*a*]pyrene (B*a*P) and total PAH levels less than Long et al.'s [20] "Effects Range Low" (ERL) for those compounds. Effects Range Low values are concentrations below which effects are rarely observed. Concentrations of total and most individual PAHs in Kitimat Arm remain above concentrations in Kildala Arm. One con-

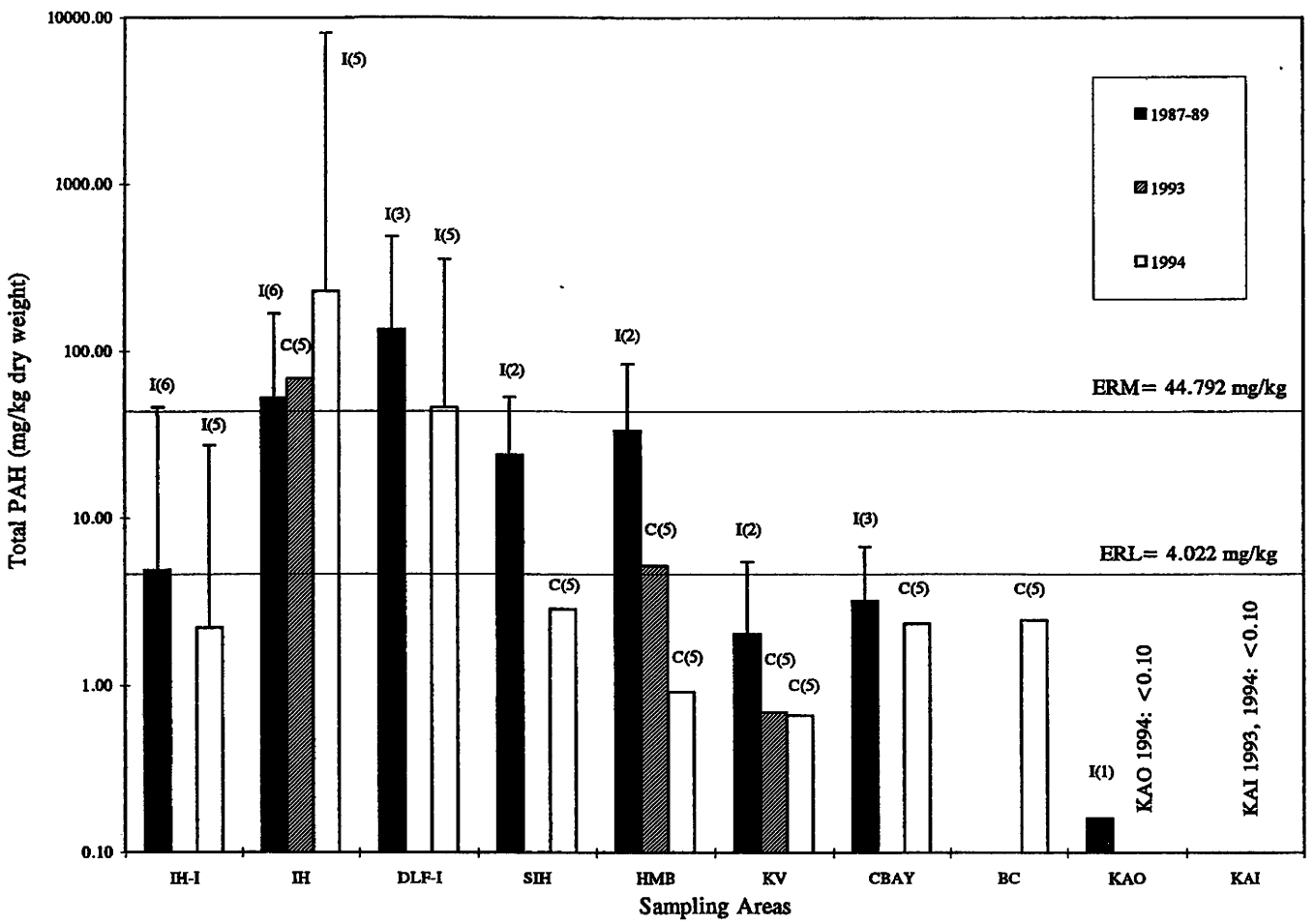

Fig. 9. Total polycyclic aromatic hydrocarbon (PAH) concentrations (mg/dry kg) in sediment of Outer Kitimat Arm and Kildala Arm sampling areas for 1987–1989, 1993, and 1994. Data for 1987–1989 are provided in Paine [13]; for 1993, in Chapman et al. [14]; and for 1994, in this study. The Effects Range Low (ERL) is based on Long et al. [20]. The number of samples (*I* = individual; *C* = composite) is provided for each sampling area. Vertical lines above bars are 1 SD. Means and SDs are back-transformed from log-transformed values, and 0.5 DL was used for values below the detection limit (DL).

sequence of the dramatic decreases in sediment PAHs along the west shore of Kitimat Arm is that the strong contaminant gradient which existed in 1987–1989 and even in 1993 has disappeared.

Concentrations of PAHs near the smelter (IH-I, IH, DLF-I) remain high, generally above ERL and even "Effects Range Median" (ERM) values (Table 1 and Fig. 9) and also above other sediment criteria or objectives [9]. Effects Range Median values are concentrations above which effects are usually observed. Concentrations of PAHs near the smelter have not decreased since 1987–1989, although spatial heterogeneity would probably obscure most temporal changes. Concentrations are lower in IH-I, nearest the B Lagoon discharge, than in IH and DLF-I, suggesting that other sources such as the wharf may also be important. Also, contaminated sediment may be removed from IH-I by wave and tidal action.

The conversion to dry scrubbers beginning in the mid-1970s reduced PAH emissions from the smelter, and previously highly contaminated sediments appear to have been naturally capped by cleaner sediment. Interconnection of dry scrubbers has further reduced PAHs in smelter effluent. Similar rapid reductions in sediment dioxin and furan concentrations have been documented around pulp mills after dioxin and furan concentrations in effluent were reduced [21]. Sediment capping is the most probable process to account for these decreases in dioxin and furan and for decreases in PAHs in Kitimat Arm, as we would expect other processes such as desorption and biodegradation to be much slower due to low temperatures and lack of light.

Sediment toxicity

No sediment toxicity was found. Because PAH concentrations outside the Inner Harbour were low (i.e., <ERL for total PAH and BaP), there was no strong reason to expect effects. However, many PAH concentrations in the Inner Harbour and D Lagoon Foreshore sediments exceeded ERL and even ERM values, and effects would be expected if PAHs were bioavailable (Figs. 2 and 9).

The results of these toxicity tests extend and strengthen conclusions from past studies. Since 1988, four species have been tested over a broad range of sediment PAH concentrations (~0 to 10,000 mg/kg total PAH, although most concentrations were <100 mg/kg). The amphipod *Rhepoxynius abronius* has been tested since 1988 and was the only organism to show significant negative effects (reduced survival) in Kitimat Arm sediments relative to reference (Kildala Arm) sediments in 1993 [14]. These effects were generally minor, as mean survival for any site has never been <75%. Furthermore, these negative effects were apparently grain size effects rather than PAH effects [14]; grain size effects appear to be the dominant factor controlling amphipod survival in these sediments (Fig. 2) [9]. A similar negative relationship between amphipod survival and grain size has also been observed in Puget Sound sediments [22].

The absence of effects in previous (1988, 1993) and present (1994) sediment toxicity tests indicates that bioavailability of sediment PAHs in Kitimat Arm was and is limited. Bioavailability may be limited because much of the PAH is present as pitch and/or coke particles or globules, which are visibly obvious in the most contaminated samples. The organic carbon content of many samples with high PAH concentrations was also elevated, which supports the hypothesis that significant quantities of pitch and/or coke are present (there is no other obvious source of organic carbon).

The toxicity tests provide the strongest evidence in support of the hypothesis of limited bioavailability of sediment PAHs. Test sensitivity is not an issue. The tests used have provided abundant evidence of effects at concentrations above ERL, and especially above ERM, values in other studies [20]. If sediment PAHs were available, there would have been a strong correlation between survival and PAH concentration in Figure 2, and low survival (down to 0%) would have been observed at the higher concentrations.

Resident communities: Benthic infauna

Two types of evidence were used for PAH (and other contaminant) effects on benthic infauna in the shallow sampling areas: correlations between variables and PAH concentrations within IH and differences between IH and KAI. Within IH, abundance of *A. serricata* and bivalve and total richness were negatively correlated with PAH concentration (Fig. 4). Abundance of *A. serricata* was also greater in KAI than in IH. These apparent effects within IH will be the focus of future monitoring [9].

Abundance was generally higher, and richness lower, in KAI than in IH. In IH, abundances of dominant taxa (e.g., *A. serricata*) were lower than in KAI, and abundances and richness of subdominant taxa greater. The differences in abundance and richness are the opposite of enrichment and contaminant effects generally observed as richness is generally reduced in contaminated sites [23–25]. Therefore, the differences between IH and KAI were probably not contaminant effects. Instead, the differences may be the result of differences in wave exposure. Kildala Arm lies perpendicular to, whereas Kitimat Arm lies along, prevailing wind directions [26].

Evidence from the benthic infaunal survey of the shallow areas is not adequate to make definitive conclusions about the presence or absence of PAH effects. Sample sizes were limited, outliers were present, and natural factors such as differences in wave exposure may confound interpretation [9]. However, the data provided strong support for the hypothesis of limited availability of PAHs as large effects were not observed. Effects have generally been observed in other benthic community studies at PAH concentrations similar to, and lower than, those in IH [20]. Concentrations in IH were within the range where decreases in abundance of all or most taxa would be expected. Because the benthic infauna survey incorporated the effects of dietary uptake, as well as uptake from interstitial water, availability of PAHs from food also appears to be limited.

For the deep areas, no differences in abundance and richness between Kitimat and Kildala Arms were >25% or statistically significant. The only issue is whether it can be concluded that there were no effects. The answer is no. Confidence limits for differences in abundance included large (greater than twofold) differences. Confidence limits for differences in richness excluded the possibility that reductions of >50% existed but not the possibility that reductions >25% existed. The results from the deep areas provide no evidence for or against the hypothesis of limited bioavailability of PAHs. Even if the PAHs were available, concentrations were below those at which effects have been observed in other studies [20].

Resident communities: Crab

The survey of adult Dungeness crab related exposure measures (tissue chemistry) to effects measures (catch, life history traits). Crab were selected for the survey because they are abundant and ecologically and economically important in the study

area. Concerns have also been raised about potential risks to human health from PAHs in crab tissue.

Tissue chemistry. Tissue chemistry analyses indicated that PAH concentrations were elevated only in crab from areas near the smelter. Contamination was largely restricted to the Inner Harbour (IH). Parent PAH and 1-OHP levels in some crab and/or samples from Kitimat Arm areas outside IH were greater than those in the Kildala Arm reference area. However, there was no consistent spatial gradient evident among these sporadic elevated PAH and 1-OHP concentrations. These conclusions are consistent with results from 1993 tissue analyses of a smaller set of crab samples [14]. In 1992, the Department of Fisheries and Oceans [27] collected samples of crab hepatopancreas from Kildala and Kitimat Arms and concluded that PAH levels in crab were low and not of concern.

The 1994 crab tissue chemistry results were also consistent with sediment chemistry results. Sediment PAH levels were highest in IH, and there was no apparent spatial gradient among the above-background levels measured in Kitimat Arm outside the Inner Harbour. This study indicated that analyses of 1-OHP in tissue were effective and inexpensive contaminant monitoring tools. The more expensive parent PAH analyses revealed little that was not evident from the 1-OHP analyses.

Tissue chemistry results also indicated that crab were resident in the areas where they were captured long enough to accumulate contaminants. However, 1-OHP concentrations can measure residency only over the short term (weeks). More persistent compounds such as parent PAH may reflect residency and exposure over months (i.e., the duration of our sampling period).

Effects measures. Differences between the most contaminated area, IH, and the other areas could reflect contaminant effects from short-term exposure (i.e., over the summer) but probably not effects from long-term exposures (years). Dungeness crab move offshore in the fall and back inshore in spring [19]. There is no evidence that crab return to the same inshore areas year after year, although females may show some fidelity to offshore areas [28]. Differences among the other Kitimat Arm areas probably cannot be used to assess the effects of either short-term or long-term exposures. Minimal differences in tissue concentrations were observed among these areas, indicating that short-term exposures did not differ greatly. The difference between Kitimat Arm and Kildala Arm crab is probably the only difference which may reflect effects of long-term exposure. The Kildala Arm sampling area was ≥20 km from the Kitimat Arm areas and separated from them by deep (and steep) habitat.

Catch was obviously lower in Kildala Arm than in Kitimat Arm. Reduced catches in Kildala Arm were not an exploitation effect, as harvest is greater in Kitimat Arm [9]. Low catches in Kildala Arm were probably related to limited availability of suitable habitat. Sampled areas in KAO were mostly steep-sloped with rock bottoms. Crab prefer sand or sand/mud flat bottoms [19]. Also, catches were highest at depths <20 m, and the benthos survey clearly indicated that productivity decreased with depth.

Statistical power was not an issue for the assessment of effects on size and condition. Some small differences among areas were detected, and the possibility that there were large differences was rejected. Crab from the most contaminated sampling area, IH, were larger than crab from other Kitimat Arm areas. There is a limit to the magnitude of size effects expected from short-term exposures of fish and shellfish. Intermoult or annual width increments for adult legal-size male crab along the Pacific coast are 2 to 3 cm (i.e., 10 to 20% per year) [29,30]; increments for adult females would be smaller or nonexistent.

Short-term exposures should affect reproduction more than size, because reproductive tissue is turned over annually. Thus, the reproductive variables measured recent, not lifetime, investment. Female reproductive investment in IH was not lower than in other sampling areas, suggesting no effects from short-term exposures. However, statistical power for analyses of reproduction was poor, which prevented us from concluding that effects, even from short-term exposure, were improbable. Reproductive investment was greater in Kildala Arm than in Kitimat Arm, which could be evidence of effects of exposure on reproduction as well as growth. However, density-dependent effects on reproduction could also account for the difference. Apparent trade-offs between growth/survival and reproduction among the offshore Kitimat Arm areas would probably account for the differences in both size and reproduction among those areas.

In summary, effects of short-term exposures, derived from comparisons of crab from IH with those from other areas, were apparently minimal. Table 9 indicates that IH crab were stunningly average. The ability of the crab survey to detect effects was limited to some extent. However, the survey, and the species chosen, were adequate to detect some significant differences among the Kitimat Arm areas outside IH, which were entirely consistent with an expected trade-off between reproduction and growth/survival.

Finally, the crab survey provided only indirect evidence that availability of PAHs was limited. Tissue PAH concentrations, even in the Inner Harbour, were low despite the high concentrations in sediment. However, there are few or no comparable data available from other areas, so the possibility that the crab simply do not take up PAHs readily cannot be excluded. The dominance of LPAHs in the crab tissue may indicate that it is HPAHs, and not all PAHs, which are unavailable.

CONCLUSIONS

The results of this integrated (triad) study, when considered together (e.g., per Chapman [3] and Chapman et al. [31]), clearly indicate a general absence of adverse effects on the ecology of Kitimat Arm related to sediment PAHs from the Alcan aluminum smelter (Table 13). More specifically, outside the Inner Harbour there is no evidence of pollution-induced degradation. This is in accord with the decreases in sediment PAHs along the west shore of Kitimat Arm, where the strong contamination gradient which existed in 1987–1989 and even in 1993 has largely disappeared. Inside the Inner Harbour, PAHs appear to have limited bioavailability in the most contaminated area (IH). The presence of adverse effects near the smelter cannot be ruled out based on the evidence presented in this study. However, IH would not be characterized as suffering from pollution-induced degradation. These results clearly demonstrate a fact more honored in the breach than in the observance: the presence of a contaminant, even at highly elevated concentrations (compare Fig. 9 and Table 13), is not necessarily synonymous with adverse effects (i.e., contamination is not pollution). Pitch or coke globules (this study) or coal [32] may result in highly elevated levels of PAH sediment but limited or no bioavailability. Norwegian studies [33] suggest that the present study's findings of limited PAH bioavailability may be applicable to sediments around other smelters.

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Table 13. Conclusions derived from the Sediment Quality Triad with responses shown as present (Yes) or not (No), indicating whether measurable differences from reference conditions were determined

Sites	Sediment chemical contamination[a]			Laboratory toxicity			Resident communities			Pollution-induced degradation?
							Benthos alteration	Bioaccumulation[c]	Effects	
	1994	1993	1989–1987	1994	1993	1989–1987	1994	1994	1994	
Inner Kitimat Arm										
Inner Harbour (IH-I, IH, DLF-I)	Yes	Yes	Yes	No	No	No	(No)[b]	(Yes)[d]	(No)[e]	Probably not; limited bioavailability
Central, east, and west (SIH, HMB, KV)	No	Yes	Yes	No	No	NA[f]	No	Minimal	No	No
Outer Kitimat Arm (BC, CBAY)	No	NA[f]	No	No	NA[f]	NA[f]	No	No	No	No
Kildala Arm (KAO, KAI)	No	No	No	No	No	No	No	No	No	No

[a] Relative to Effects Range Low value (Fig. 9).
[b] No evidence of effects; decreased abundance but increased richness at IH not considered alteration due to polycyclic aromatic hydrocarbons, but subtle effects possible (see text).
[c] Crab hepatopancreas, hemolymph.
[d] Largely restricted to IH. Polycyclic aromatic hydrocarbon metabolites found in crab hepatopancreas and English sole bile in 1993 but do not themselves constitute adverse effects [14].
[e] Minor histopathological abnormalities noted in 2 of 11 English sole from IH [14].
[f] NA = not analyzed.

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Particle-Scale Understanding of the Bioavailability of PAHs in Sediment

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This study reports results of sediment bioslurry treatment and earthworm bioaccumulation for polycyclic aromatic hydrocarbon (PAH) contaminants found in sediment dredged from Milwaukee Harbor. A significant finding was that bioslurry treatment reduced PAHs on the sediment clay/silt fraction but not on the sediment coal-derived fraction and that PAH reduction in the clay/silt fraction correlated with substantial reduction in earthworm PAH bioaccumulation. These findings are used to infer PAH bioavailability from characterization of particle-scale PAH distribution, association, and binding among the principal particle fractions in the sediment. The results are consistent with work showing that the sediment comprised two principal particle classes for PAHs, coal-derived and clay/silt, each having much different PAH levels, release rates, and desorption activation energies. PAH sorption on coal-derived particles is associated with minimal biodegradation, slow release rates, and high desorption activation energies, while PAH sorption on clay/silt particles is associated with significant potential biodegradability, relatively fast release rates, and lower desorption activation energies. These characteristics are attributed to fundamental differences in the organic matter to which the PAHs are sorbed. Although the majority of the PAHs are found preferentially on coal-derived particles, the PAHs on the clay/silt sediment fraction are more mobile and available, and thus potentially of greater concern. This study demonstrates that a suite of tests comprising both bioassays and particle-scale investigations provide a basis to assess larger-scale phenomena of biotreatment of PAH-impacted sediments and bioavailability and potential toxicity of PAH contaminants in sediments. Improved understanding of contaminant bioavailability aids decision-making on the effectiveness of biotreatment of PAH-impacted sediments and the likelihood for possible reuse of dredged sediments as reclaimed soil or fill.

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Introduction

Approximately 400 million cubic yards of sediment are dredged from United States ports, harbors, and waterways each year to maintain the nation's navigation system. It is estimated that approximately 10% of these dredged materials are impacted by organic and inorganic contaminants (*1*). Contaminated dredged materials are generally discharged into diked, confined disposal facilities (CDFs). Many CDFs are filled or reaching their design capacity, and economic treatments are sought to extend the life of CDFs by reclaiming dredged material for reuse as fill or soil.

The reuse of dredged material as reclaimed soil will extend the operational life of CDFs while benefiting the environment through reclamation of topsoil and fill material. However, dredged harbor sediments contaminated with polycyclic aromatic hydrocarbons (PAHs) face very stringent cleanup standards prior to reuse. The reuse of contaminant-impacted dredged material is restricted to terrestrial application; therefore, the material generally must meet either state soil or solid waste cleanup criteria. This is a serious impediment for reuse of dredged materials. In Wisconsin, for example, the use of contaminated dredged material for topsoil is governed by suggested generic soil cleanup levels (*2*). If the contaminated dredged material is reused as fill material, it falls under Wisconsin's regulation for the beneficial use of industrial byproducts (*3*). As shown in Table 1, for use in nonindustrial (topsoil) or residential (fill material) applications, certain PAH contaminants such as benzo[*a*]pyrene and dibenz[*a*,*h*]anthracene must be cleaned up to as low as 8.8 ppb (*2*, *4*). These levels are practically unachievable using bioreclamation technologies. Thus, relatively low-cost, natural cleanup processes such as composting may not meet cleanup standards. These low-level cleanup standards assume that the PAHs are readily available and may result in environmental exposure. While there is growing awareness that contaminant availability and risk should determine cleanup levels, adequate tools to evaluate and understand contaminant availability in dredged materials are lacking. As is the case with contaminated soils (*5*), conservative, low-level cleanup standards are invoked, wherein sediment cleanup is driven by total contaminant mass removal not bioavialability (*6*). Consequently, the adherence and slow release of PAHs from geosorbents is both an obstacle to remediation (*7*, *8*) and a challenge to concepts about cleanup standards and risks (*5*, *9*).

Bioremediation of PAH-contaminated sediments often results in high residual concentrations that do not satisfy the minimum standards for reuse as soil (*10*). It is believed that residual PAH concentrations are caused by the limited bioavailability of PAHs. Operational, physicochemical tests are being developed to assess contaminant bioavailability and to evaluate the potential feasibility of biological treatments to meet cleanup objectives. Often such tests are based on the determination of readily available PAHs as measured by release into the water phase. These tests may involve long-term, batch rate of release experiments with the uptake of dissolved PAHs onto a solid sorbent (*11*, *12*) and the data evaluated using an empirical first-order or a two-site model consisting of two first-order expressions (*13*). Thermal techniques may be useful in conjunction with aqueous desorption tests to characterize the available fraction (*14*).

Study Objectives. The primary question addressed in this work was whether the macroscopic bioavailability behavior of PAHs in dredged sediment could be explained by particle-scale characterizations of PAH distribution, association, and

TABLE 1. Comparison of PAH Concentrations (mg/kg) in Untreated Milwaukee CDF Sediment and Wisconsin Required Cleanup Levels (mg/kg) for Reuse of Dredged Material

		WI generic soil cleanup levels			WI solid waste cleanup levels	
compd	concn	GW pathway	nonindustrial	industrial	unrestricted	restricted
naphthalene[a]	1.2	0.4	20	110	600	6000
2-methylnaphthalene	2.1	20	600	40000	na	na
acenaphthylene	0.1	0.7	18	360	8.8	88
acenaphthene	1.9	38	900	60000	900	9000
fluorene	2.3	100	600	40000	600	6000
phenanthrene[a]	15.4	1.8	18	390	0.88	8.8
anthracene	3.1	3000	5000	300000	5000	50000
fluoranthene	21.8	500	600	40000	600	6000
pyrene	17.7	8700	500	30000	500	5000
chrysene[a]	9.8	37	8.8	390	8.8	88
benzo[*a*]anthracene[a]	8.9	17	0.088	3.9	0.088	0.88
benzo[*b*]fluoranthrene[a]	7.6	360	0.088	3.9	0.088	0.88
benzo[*k*]fluoranthrene[a]	6.3	870	0.88	39	0.88	8.8
benzo[*a*]pyrene[a]	7.0	48	0.0088	0.39	0.0088	0.08
indeno[1,2,3-*c,d*]pyrene[a]	5.6	680	0.088	3.9	0.088	0.88
dibenz[*a,h*]anthracene[a]	1.1	38	0.0088	0.39	0.0088	0.088
benzo[*g,h,i*]perylene[a]	5.1	6800	1.8	39	0.88	8.8

[a] Denotes PAHs that exceed at least one of the cleanup levels required for reuse of dredged materials. Generic soil cleanup levels are for reuse as topsoil or near-surface soil. Nonindustrial and industrial soil cleanup levels are based on direct contact pathways. Groundwater (GW) pathway cleanup levels assume reuse will be in areas where the material will come into contact with groundwater. Restricted solid waste cleanup levels limit the reuse to capped, readfill, or nonresidential applications. Unrestricted solid waste cleanup levels are based on unrestricted reuse as fill material. Compiled from refs *2* and *3*.

binding with sediment. To this end, the research comprised aerobic bioslurry testing and earthworm PAH uptake studies before and after bioslurry treatment. These data were interpreted in view of recent reporting (*14, 15*) of particle-scale measurements of PAH distribution, organic matter association, release rates, and desorption binding energies for this sediment.

Milwaukee Confined Disposal Facility (CDF). The sediment used in this study was obtained from the Jones Island Confined Disposal Facility (CDF), commonly known as the Milwaukee CDF and operated by the Milwaukee Harbor Port Authority. Shown in Figure 1 is the 44-acre CDF located in the South Milwaukee Harbor. Constructed in 1975 with a maximum thickness of 10 m, it serves as a disposal facility for maintenance-dredged materials unsuitable for open-lake disposal. The majority of the CDF was filled via hydraulic dredging and consists of consolidated, fine-grained material. Borings from the Milwaukee CDF indicate 50 mg/kg total PAH near the surface (within 2 m), 275 mg/kg at 5 m, and 100 mg/kg at 7 m (*16*). Samples for this work were collected in fall 1996 by backhoe at a depth of 4 m, placed in a 55-gal drum and sealed on site, shipped via refrigerated truck to the Environmental Laboratory, U.S. Army Engineer Research and Development Center, and stored at 4 °C for 2 yr prior to use.

Experimental Methods

Homogenization of Dredged Materials. Drummed sediment was placed in an aluminum trough and homogenized for 6 h using a heavy-duty mixer. Wet sieving removed material larger than 2 mm. Sievings were poured into a 55-gal drum and allowed to settle for 1 month at 4 °C, and then the overlying water layer was removed using a peristaltic pump. The sediment was homogenized again prior to sampling and loading the bioslurry reactors.

Bioslurry Reactor System. The bioslurry reactor system comprised six 5-L reactors. Two reactors were controls (anaerobic and poisoned), and four were active (aerobic) reactors. Each bioreactor received 5.3 kg (wet weight) of dredged material, which consisted of 56.5% solids. To produce a 30% (by volume) slurry, 3.5 L of modified Stanier's basal media (*17*) was added to each reactor. The media did not

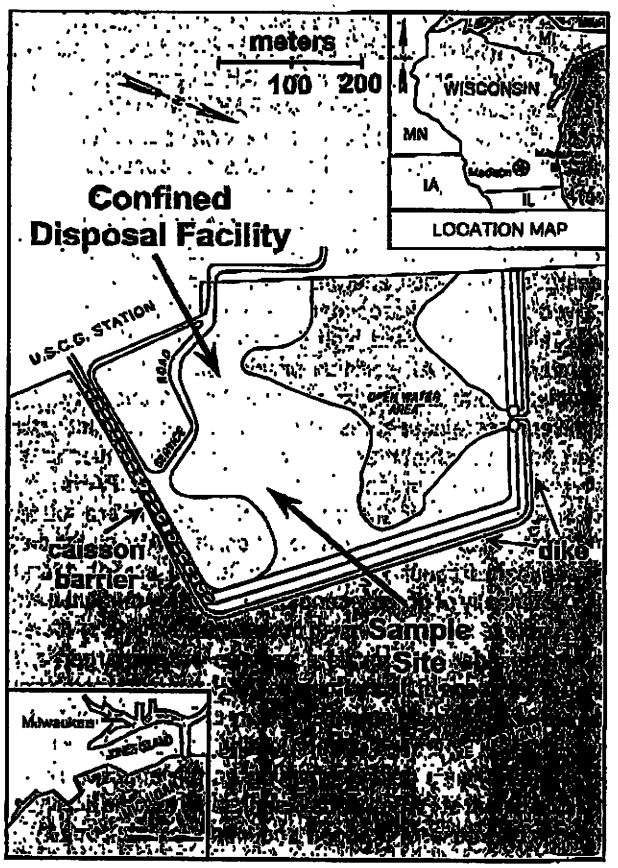

FIGURE 1. Site map of Milwaukee Confined Disposal Facility and sample site. The sample was collected at a depth of 4 m.

contain any carbon source. The reactors had two 3.8-in impellers mounted to a mixing shaft. The lower impeller was positioned about 1 in. from the bottom of the reactor, and the upper impeller was mounted about 3 in. above the lower impeller. Each reactor had three diffuser stones in the bottom that bubbled either argon (control reactors) or air (aerobic

reactors). The gas was fed from compressed gas cylinders and passed through double charcoal filters before entering the bioreactors. The reactors were continuously stirred at 350 rpm. The reactors were vented to a fume hood. Off-gas monitoring in related tests showed no significant loss of PAHs by volatilization.

The anaerobic reactors were poisoned with 500 ppm each of sodium azide and mercuric chloride. Initial biomass analyses indicated that the poisoning was not effective in killing the microbial community for longer than a few days. Thus another 500 ppm of both compounds was added 18 d into the experiment, 1000 ppm 1 week later, and 750 ppm every 3 weeks thereafter. This maintained poisoned, anaerobic controls, as shown by streaking the slurry onto nutrient agar plates and incubating for 72 h. The bioreactors were tested daily for pH, dissolved oxygen, oxidation–reduction potential, and temperature and for nitrate and phosphate initially every 2 days and then weekly after the first month. Carbon, nitrogen, and phosphorus ratios were maintained at 100:10:1, with the carbon content based on the sediment total organic carbon content. Dissolved oxygen was maintained in the range of 8–9 mg/L for the aerobic reactors with pH 7.0.

Each month sediment was sampled using 50-mL pipets after allowing the reactors to settle for 1 h. Samples were collected from five different locations and at three different depths (top, middle, and bottom) within each reactor. The collected slurry was placed in sterile screw-top containers and centrifuged at 8000 rpm for 20 min, and the supernatant was decanted; the solids were placed in a pan lined with sterile aluminum foil and mixed thoroughly and placed into sample vials. At the end of the test, the reactor was emptied, and a composite sample was collected. All sampling tools were autoclaved prior to use.

Physical Separation. The whole sediment was separated into four size fractions (>1000, 1000–250, 250–63, and <63 μm) for purposes of determining PAH presence and availability among sediment fractions. The larger size fractions (>63 μm) comprised primarily sandy grains, coal-derived particles, and woody material. It was possible to wash off the lighter fractions (coal and wood) from the heavier sand by swirling with water in a beaker and draining off the entrained lighter particles. Materials in the fine fraction (<63 μm) were density separated using a cesium chloride solution having a specific gravity of 1.8 (*15*). Five grams of wet sediment and 40 mL of cesium chloride solution were centrifuged at 200 rpm for 10 min in 50-mL glass centrifuge tubes. The fine coal-derived and wood particles floated, were decanted, and were collected on filter paper and rinsed with water several times. The heavy clay and silt fractions were similarly washed several times to remove cesium chloride. Each of these density-separated fractions was placed in cold storage.

Desorption Analyses. Room temperature, batch, desorption kinetic studies evaluated the mass transfer of the PAHs from the whole and separated fractions of sediment to Tenax beads (*15*). Duplicate rate of release tests followed procedures reported previously by Ghosh et al. (*15*) and others (*18, 19*). Contaminated sediment (2.0 g) and Tenax beads (0.5 g, 40–60 mesh, Suppelco, PA) were added to 15-mL glass vials containing 10 mL of deionized water and continuously mixed on a rotator. Mercuric chloride (1.0 mg) was added to the mixture to prevent biological growth. At sampling times, the Tenax beads were harvested by allowing the sediment to settle, and the Tenax beads to float up. The Tenax beads were removed from the glass vials, and fresh Tenax beads were added. PAHs were extracted from the Tenax beads by agitating the beads in 10 mL of hexane and acetone (50:50 mixture) for 12 h and repeating twice. The extracts were then combined and concentrated, cleaned using silica gel, and analyzed by GC-FID.

Thermal program desorption (TPD) measurements employed a gas chromatograph quadrupole mass spectrometer (GCQ-MS) with a direct insertion probe manufactured by Thermoquest. These tests evaluated binding activation energies, as interpreted from TPD rate responses, for PAHs from untreated and bioslurry treated sediment. TPD tests followed procedures described by Talley (*20*), which showed that the release of PAHs is dependent both on PAH molecular weight and the character of the sorbent material. Milligram-level samples of whole sediment and separated fractions were placed into the mass spectrometer via a 1 mm diameter glass vial inserted in the probe. The temperature of the probe containing the sample glass vial was then increased at 10 °C/min from 30 to 400 °C. As the probe heated, the volatilized compounds were ionized, selectively filtered in the quadrupole, and detected in the mass spectrometer. The high sensitivity of the GCQ-MS enabled sample size down to the particle level. The thermogram data reduction techniques are described in Ghosh et al. (*14*).

Chemical Analyses. PAH concentrations were determined by analysis of four replicate samples from the sieved and mixed sediment prior to placing in the bioslurry reactors. After the bioslurry reactors were loaded, samples were collected monthly from each reactor and analyzed for PAHs by Soxhlet extraction and GC/MS analysis for PAHs using EPA Method 3540. GC-FID was used for PAH analyses on whole sediment and separated size fractions to determine PAH distribution by particle size and density. These analyses followed EPA Method 3550B with ultrasonic extraction and silica gel cleanup by EPA Method 3630C (*15*). Samples were analyzed for the 16 PAHs on the EPA Priority Pollutant List as well as for methyl naphthalene. Transmission FTIR analysis was performed with a Mattson ATI FTIR–NIR spectrometer using sediment particles ground and formed into KBr pellets.

Microbial Analyses. Microcosm studies used radiolabeled phenanthrene, pyrene, chrysene, and benzo(*a*)pyrene to confirm that viable PAH-degrading microorganisms were present in the sediment. The aerobic systems were evaluated for acetate, phenanthrene, pyrene, chrysene, and benzo(*a*)-pyrene mineralization. Anaerobic systems were tested for acetate and phenanthrene mineralization. Microcosm studies were conducted on sediment collected from each bioslurry reactor after 18 h of mixing and then monthly thereafter. One gram (wet weight) of slurry material was placed into 15-mL Teflon-lined screw-cap test tubes to which was added 2.7 mL of the modified Stanier's basal media (*17*) and 20 000 DPM amount of ^{14}C-labeled substrate in triplicate for each substrate. A modified version of the method described by Fulthorpe et al. (*21*) assessed microbial activity in which glass fiber filters (Whatman, Maidstone, U.K.), 10 mm diameter and saturated in 1 M barium hydroxide, were placed into the caps of screw-top test tubes to trap evolved $^{14}CO_2$ (*31*). The filters were placed in 15-mL scintillation cocktail (Ultima Gold, Packard Instruments Co., Downers Grove, IL) and counted twice with a top count microplate scintillation counter (Packard Instrument Co., Downers Grove, IL). Counts were corrected for background and counting efficiency using the external standard method described by the manufacturer.

Polar lipid fatty acid analyses (PLFA), as described by White and Ringelberg (*22*), identified the level of biomass present in the sediment and provided information about the microbial community structure. The total lipid extractant was separated into neutral, glyco-, and polar lipid fractions (*23*) and prepared for gas chromatography/mass spectrometry (GC/MS) by mild alkaline methanolic transesterification (*31*). Peak identities were confirmed using a gas chromatograph-mass selective detector (Hewlett-Packard GC6890-5973 MSD) with electron impact ionization at 70 eV. DNA analysis targeted the presence of select genes known to be present during active PAH degradation. Total DNA was isolated from

triplicate 500-mg slurry samples using a mini-bead beater system as described by Borneomeman et al. (*24*) and purified using Fast DNA SPIN Kit (FastPrep7 Instrument FP120; BIO 101, Vista, CA). Total DNA was suspended in 50 μL of molecular biology grade H_2O (Five prime-Three prime, WI) and stored at −20 °C (*31*).

Earthworm Bioassays. Earthworm acute toxicity and bioaccumulation bioassays evaluated the adverse effects of the sediment PAHs to *Eisenia fetida*. In as much as dredged sediment for the Milwaukee CDF was disposed on land and reuse of dredged sediment would involve terrestrial application, earthworm bioassays were determined to be most appropriate test for toxicity end point assessments. The use of these organisms as indicators of environmental pollution is well-documented (*25, 26*). Acute toxicity was assessed by earthworm survival in 14-day tests following EPA procedures (*27, 28*). Earthworms were exposed in a static system of the untreated sediment mixtures and artificial soil (70% sand, 20% kaolin, and 10% peat). Ten concentrations of sediment (100%, 75%, 50%, 25%, 12.5%, 6.25%, 3.125%, 1.56%, 0.78%, and 0%) were prepared in triplicate, where the percent concentration refers to the amount of contaminated sediment present in the test with 100 g dry weight total in covered 250-mL flasks with air holes. The 0% concentration (100% artificial soil) served as the control. After being mixed, the test sediment was hydrated to 75% of water-holding capacity with deionized water. Ten earthworms were placed into each jar on the surface of the sediment. The jars were capped and stored in a humidity-controlled room at 25 °C. Test results were based on earthworm survival.

Earthworm bioaccumulation tests followed a modified ASTM method E1676-97 (*29*) where 500 g of sediment was collected from each reactor at the conclusion of the bioslurry tests. After the sample was homogenized, three test containers were filled with 160 g each. Sixteen earthworms were added to each test container. The sediment and artificial soil were hydrated to 75% of water-holding capacity, covered with cotton muslin cloth to allow the passage of air, and stored in a humidity-controlled room for 28 d. A few flakes of powdered oatmeal were added to the surface of each test container to attract the earthworms to the surface, resulting in greater earthworm mobility and activity. At the end of the 28 d, the earthworms were rinsed with dechlorinated water and placed in glass vials lined with filter paper. The worms remained in the vials (2 per vial) for 1 d in order to allow their gullet to cleanse. The worms were then placed in a −70 °C freezer. On the day of chemical analysis, the worms were removed from the freezer and freeze-dried in a lyophilizer, producing a dry earthworm powdery material for Soxhlet extraction (EPA Method 3540) and analysis by GC/MS. Bioaccumulation tests were performed on untreated and final biotreated sediment.

Results and Discussion

Sediment Composition. Composite sediment samples were separated into two density fractions: (i) specific gravity <1.8 comprising mainly coal-derived material with some plant and woody matter and (ii) specific gravity >1.8 comprising clay, silt, and sand. Elemental analyses using SEM with wavelength dispersive X-ray showed silica the most abundant material in the heavier, >63 μm size fraction, and clays dominant in the heavier, <63 μm size fraction (*15*). The second most abundant particle class within all size fractions comprised high-carbon content black particles, principally coal-derived with some coal as determined by petrography microanalysis under reflected light of polished particles (ASTM standard methods for coal analysis: D2797, D2798, D2799). Historic coal coking, coal gasification, and coal shipping operations are believed to be the source of this material (*30*). The sediment mass distribution by size and

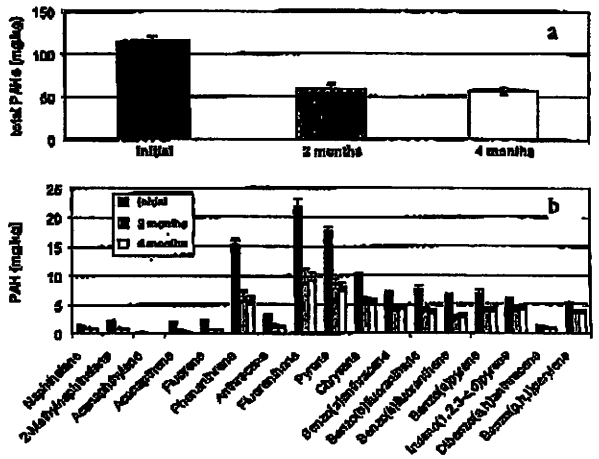

FIGURE 2. Bioslurry treatment results: (a) total PAH concentrations for initial sample, second and fourth month; (b) individual PAH concentrations for initial sample, second and fourth month. There was a 49% reduction of total PAHs by month 2 and a 50% reduction by month 4. Error bars indicate ± 1 SD.

density showed clay and silt comprised about 60% of the sediment by weight and sand particles greater than 63 μm about 35% of the sediment. Thus, the heavy sediment fraction constituted 95% of the sediment by weight, while the light fraction, comprising coal-derived, wood material, and plant debris constituted the remaining 5% of the sediment weight.

Distribution of PAHs in Sediment. Total PAHs were 115 ± 5.7 mg/kg as determined by Soxhlet extraction and GC/MS analysis of composite samples prior to bioslurry treatment. The distribution of PAHs in whole sediment is shown in Figure 2, among which fluoranthene had the highest concentration at 21.8 mg/kg. Ten of the 17 PAH compounds exceeded either the Wisconsin suggested generic soil cleanup levels (*2*) or the solid waste cleanup levels for the beneficial use of industrial byproducts (*3, 4*), as indicated in Table 1.

The coal-derived/wood material and debris contained 62% of the total PAHs, with 38% of the total PAHs associated with the sand, clay, and silt in the sediment (*15*). Although the clays and silt were the most abundant component in the sediment at about 60 wt %, this size fraction accounted for only about one-third of the total PAHs. A significant observation is that the coal-derived/wood material and debris comprised only 5% of the sediment mass but contained more than three-fifths of the total PAHs. The clay/silt fraction contained about 52 mg/kg total PAHs as compared to as much as several thousand mg/kg total PAHs in the light <63 μm size fraction. Additional analysis involving separation of wood-derived particles from coal in the lighter density fraction showed more than 95% of PAHs in the lighter fraction were associated with coal-derived particles. Thus, we refer to this lighter density fraction as coal-derived in the rest of the paper.

Reduction of PAHs by Bioslurry Treatment. Bioslurry treatment was conducted for 4 months with one reactor sacrificed after 2 months. There was a small amount of reduction of PAHs for the control reactors in which samplings at 2 and 3 months showed average PAH levels of 100 mg/kg as compared to 115 mg/kg initially. This slight decrease in total PAH concentration was judged not significant and was most likely a consequence of the difficulty of sampling representatively from the reactors versus sampling from the initial whole sediment composite prior to filling the reactors.

Average concentrations of total and individual PAHs for the active bioreactors for the initial sample before biotreatment and at months 2 and 4 after biotreatment are shown in Figure 2. No significant change in PAH concentrations occurred between 2 and 4 months of treatment, and thus the

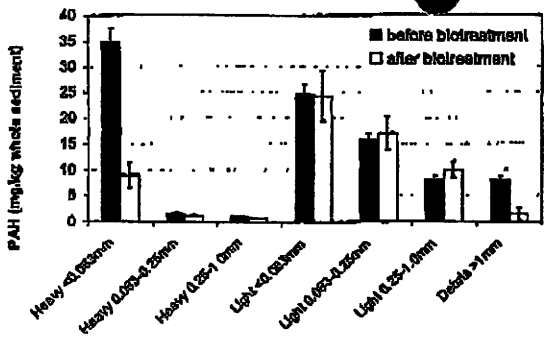

FIGURE 3. PAH reduction in sediment fractions before and after bioslurry treatment. These values are based on the contribution of each fraction to the total PAH concentration of 90 mg/kg as measured by GC-FID. Error bars indicate ± 1 SD based on analysis of four reactors.

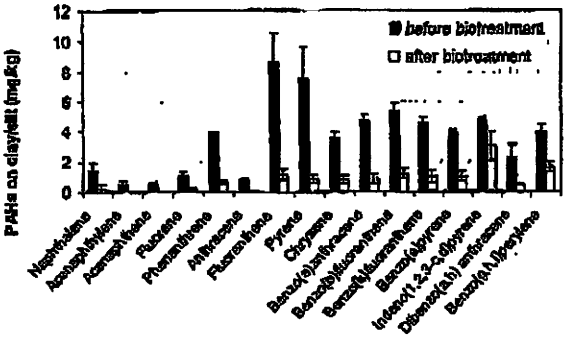

FIGURE 4. PAH concentrations for the Milwaukee CDF clay/silt fraction (heavy, <63 μm) before and after bioslurry treatment. Error bars indicate ± 1 SD based on analysis of four reactors.

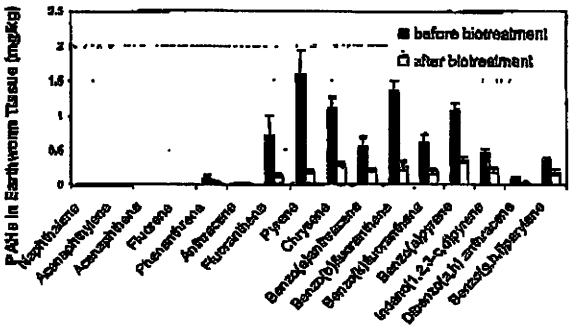

FIGURE 5. Measurement of the bioaccumulation of PAHs by earthworms (*Eisenia fetida*) from Milwaukee CDF sediment before and after biotreatment. Error bars indicate ± 1 SD.

2-month reactor data were included in an overall average for determining final PAH reduction.

The aerobic bioreactors showed a net reduction in total extractable PAH of approximately 50% over the 4-month study from an average of 115 mg/kg to 57 mg/kg. As shown in Figure 2b, all PAH compounds decreased in concentration. The greatest decrease was 64% that occurred for PAHs in the 128–178 MW range, followed by 51% reduction in the 202–228 MW range. The higher molecular mass compounds in the 252–278 MW range showed an average 38% decrease.

A total of 500 g of sediment samples was collected from each of the four bioslurry reactors after 2 or 4 months of treatment to assess PAH biodegradation by examination of sediment particle size and type. Average PAH reductions by size fraction for all reactors are shown in Figure 3, and these data reveal a significant difference in the extent of PAH biodegradation among the sediment particle types. A marked distinction in the biotreatability of PAHs among the heavy and light density fractions was evident. PAH biodegradation was achieved mainly within the <63 μm heavy fraction comprising the clays and silt, for which there was 75% reduction in PAHs. The coal-derived material, which was the principal PAH-containing component in >63 μm to 1 mm size fractions, showed no reduction in PAH concentrations. The apparent reduction in the PAHs in the >1 mm light fraction, which included more friable woody material and debris, is believed to be due attrition rather than biodegradation because the particle mass decreased in this size fraction during bioslurry treatment.

The data in Figure 3 suggest that the PAHs on the <63 μm clay/silt fractions are largely available for biodegradation and that the PAHs on the coal-derived <63 μm to 1 mm size fractions are not available to the microorganisms during bioslurry treatment. The lack of change of PAHs in the coal-derived fraction clearly indicates that the PAHs on this fraction are not bioavailable to the microorganisms. In contrast, data in Figure 4 show for the <63 μm clay/silt fraction that all PAHs monitored in this study were reduced as a result of biotreatment of the sediment. The largest percent reduction (>85%) was achieved for fluoranthene and pyrene, which were the most prominent PAHs in the clay/silt fraction.

Biodegradation Capability of Indigenous Microorganisms. Radiolabeled microcosm studies were performed with material from bioslurry bioreactors to assess whether Milwaukee CDF sediment contained indigenous microorganisms capable of degrading PAHs. These results showed that viable PAH-degrading organisms were present in the sediment throughout the study and that mineralization rates for each of the PAHs examined was greatest at 1 and 2 months.

PLFA analyses revealed that microbial biomass was relatively low in the control reactors averaging less than 8000 total pmol of PLFA g^{-1} through 3 months. Biomass in the active reactors ranged from slightly less than 10 000 total pmol of PLFA g^{-1} initially to almost 50000 total pmol of PLFA g^{-1} at 2 months, decreasing to about 30 000 total pmol of PLFA g^{-1} by 4 months (*31*). Biomass increased during the first 2 months of the study during the time that the total PAH concentration showed a concomitant decrease in concentration. These data provide supporting evidence of a microbial link to the PAH degradation and that the aerobic reactors contained viable PAH-degrading microorganisms.

The DNA analyses of the sediment at the start of the study showed gene encoding enzymes associated with aromatic degradation (naphthalene dioxygenase, biphenyl dioxygenase, catechol 2,3-dioxygenase, toluene monooxygenase, and alkane hydroxylase) were present in copy numbers below the detection limit of the assay (<1 gene copy per gram). By the first and second month of bioslurry treatment, the copy numbers for each of the genes assayed increased to the maximum detectable number—10 000 copies g^{-1}. This correlates strongly to the microbial biomass increase and to the decrease in PAH concentrations. The increase in the copies of these genes and increase in microbial biomass is consistent with observed mineralization response for phenanthrene, pyrene, and chrysene detected in the microcosm studies.

Earthworm Toxicity and Bioaccumulation. Earthworm acute toxicity tests with sediment prior to biotreatment showed a 100% survival rate, indicating that the PAHs present initially in the sediment were not toxic to induce death. Earthworm bioaccumulation tests were performed on sediment before bioslurry treatment and after 4 months of bioslurry treatment. The bioaccumulation results for individual PAHs are shown in Figure 5. These data comprise an average of the results from 192 earthworms exposed to sediment before treatment and 144 earthworms exposed to sediment after 4 months of bioslurry treatment. Each reactor was evaluated in triplicate with 16 earthworms per subsample for extraction and analyses. The uptake of total PAHs in

earthworm tissue from the untreated sediment was 8.1 mg/kg. Earthworm uptake after bioslurry treatment was reduced to 2.0 mg/kg. This represents a 75% reduction in total PAH uptake. Seven PAHs (naphthalene, 2-methylnaphthalene, acenaphthene, fluorene, fluoranthene, pyrene, and benzo-[*b*]fluoranthene) showed reductions in bioaccumulation over 80% as a result of bioslurry treatment. Every PAH showed at least 56% reduction in uptake in the earthworm tissue.

When comparing Figures 4 and 5, a similar trend is apparent. Both the clay/silt fraction (Figure 4) and the earthworm uptake (Figure 5) showed 75% PAH reduction as a result of bioslurry treatment, while the coal-derived fraction showed no reduction in PAHs. Thus, a strong correlation exists between the individual PAHs biodegraded and a beneficial effect on lowered bioaccumulation as measured by earthworm tissue uptake. This observation suggests that only the PAHs in the clay/silt fraction comprise the readily available fraction to both microorganisms and earthworms.

PAH Rate of Release and Availability. The binding and association of PAHs with the silt/clay and coal-derived particles were assessed by PAH rate of release experiments at room temperature, PAH binding activation energy assessments using thermal programmed desorption, and sorbent organic matter characterizations using infrared microspectroscopy.

Desorption kinetic studies were conducted with the whole sediment and separated fractions to investigate the availability of PAHs (*15*). The 100-d desorption kinetic tests with whole sediment showed that approximately 40% of the PAHs were released quickly within about 1 month, while the remaining approximately 60% were strongly bound and not released over 100 d. Thus, approximately 40% of the PAHs in the whole sediment may constitute a readily available fraction. An important finding from tests with separated particles was that the clay/silt and coal-derived fractions showed much different PAH release rates. The PAHs associated with the coal-derived fraction appear strongly bound, as only about 8% of the PAHs in the 63–250 μm coal-derived fraction were released in 100 d. In contrast, desorption data from the clay/silt fraction indicate a higher availability with nearly 80% of the PAHs in this fraction readily desorbing within two months. These trends mirror the results from the bioslurry tests, wherein the majority of the PAHs in the clay/silt fraction apparently are bioavailable and degraded in comparison to the coal-derived material. The majority of the PAHs in the coal-derived material apparently are not bioavailable during bioslurry treatment nor desorbed in long-term tests. Thus, a supposition from these data is that the majority of the PAHs associated with the coal-derived particles may not be bioavailable for degradation nor exhibit a highly toxic response as inferred from the bioslurry and bioaccumulation tests.

Thermal Programmed Desorption Analysis of PAH Release from Untreated Sediment. The thermodynamics of the desorption process for the <63 μm clay/silt fraction and the 63–250 μm coal-derived fraction was investigated by the effect of temperature on PAH desorption, as measured by thermal programmed desorption MS. Room temperature desorption data for individual PAH mass homologues was used to determine the fast and slow desorbing PAH fraction and the respective apparent first-order or effective diffusive rate for four PAH mass homologues in each particle class (*14*). The effect of temperature on the desorption rate was modeled as an activated first-order or diffusion process with the activation energy determined by fitting the thermal programmed desorption data. These results showed that the coal-derived and clay/silt particles had much different PAH desorption activation energies. PAH binding with the coal-derived particles was associated with high activation energies, i.e., in the range of 115–139 kJ/mol. Activation energy values

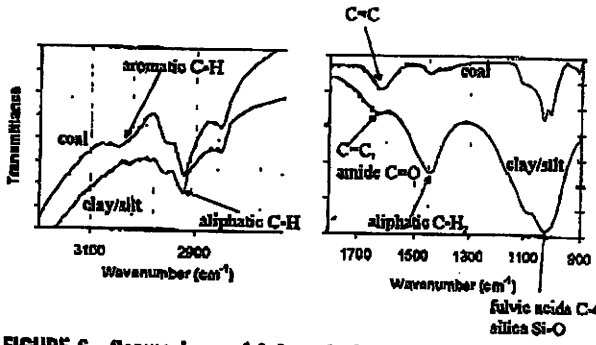

FIGURE 6. Comparison of infrared absorbance spectra of coal-derived particles in sediment and clay/silt particles. The coal-derived particles show higher absorbance of aromatic C–H stretch and a higher absorbance for C=C indicating a much more aromatic nature of the coal–carbon as compared to the organic matter associated with the sediment clay/silt matrix. The clay/silt material also showed higher absorbance for oxygen-containing groups.

greater than 60 kJ/mol may be associated with diffusion through polymeric materials (*32, 33*). In contrast, PAHs associated with the clay/silt material had much lower desorption activation energies, i.e., in the range of 37–41 kJ/mol. Low values of desorption activation energies in the range of 10–50 kJ/mol have been reported for pore diffusion (*33, 34*). TPD analysis of coal-derived particles after bioslurry treatment showed little or no change in response, while TPD analysis of clay/silt particles showed marked decrease in mass ions, consistent with PAH reduction in this fraction.

Infrared Analysis of Sorbent Organic Matter. Infrared (IR) absorption analysis investigated the differences in organic matter character between the two primary classes of sediment particle types in the Milwaukee Harbor sediment. Separated clay/silt particles and coal-derived particles from the sediment were ground and mixed with KBr to form a pellet for transmission IR analysis. As shown in Figure 6, the IR absorption spectra of the coal-derived particles and the clay/silt particles have marked differences. The coal-derived particles show a higher absorbance of aromatic C–H stretching vibrations and C=C stretching vibrations indicating a much more aromatic nature of the coal–carbon as compared to the organic matter associated with the sediment clay/silt matrix. The clay/silt material also showed higher IR absorbance associated with oxygen-containing groups and aliphatic $C-H_2$ bending vibrations. Thus, the coal-derived particles are more aromatic and nonpolar and provide a substrate that is more conducive to the binding of the highly aromatic PAH molecules. For example, it has been shown that carbon-normalized partition coefficients (K_{oc}) of phenanthrene and TCE for highly aromatic sorbents such as soot and coal are 2–3 orders of magnitude higher as compared to that for natural organic matter (*35–37*). The differences in release rates and desorption activation energies of PAHs may thus be attributed to fundamental differences in the organic matter to which the PAHs are bound. These characteristics are then manifested in larger-scale phenomena of PAH biodegradability and bioaccumulation.

Relevance to Sediment Management. We show in this work that the PAHs associated with the fine clay/silt fraction are potentially the PAH contaminants of greatest concern. PAHs associated with the clay/silt fraction comprise about one-third of the total PAHs in this sediment, and this is the PAH fraction that is much more mobile and biodegradable, and if reduced in total mass results in substantial improvement with respect to earthworm bioaccumulation. In contrast, PAHs associated with coal-derived materials are much less available, not biotreatable, and apparently are not significant with respect to bioaccumulation by earthworms. Thus, an hypothesis from our work is that PAHs in the coal-

derived fraction are potentially much less of a concern for protection of the environment, even though the PAHs in this fraction comprise the majority of the PAHs in the sediment. Consequently, decisions about dredged sediment quality criteria and treatment and material reuse should focus on the PAHs associated with the available fraction, which in this case comprises those PAHs in clays and silt. Determining which sediments pose greatest risk and which do not is of greatest concern in deciding whether sediments need active management. The work presented here provides support for the hypothesis that total concentrations of a particular hydrophobic organic contaminant in sediment does not translate directly to risk.

The approach presented in this work, which included both particle-scale mechanistic characterizations and larger-scale bioassay tests, provides a framework to improve decision-making regarding the management and treatment of PAH-impacted sediments. We demonstrate that PAH behavior at the particle-scale is relevant to understanding larger-scale phenomena of PAH contaminant availability and bioaccumulation. By recognizing that both labile and residual fractions of PAH contamination may exist and that these fractions are associated with identifiable sediment components, it is possible to justify treatments that focus on the fraction of concern. This will increase the likelihood for reuse of dredged and deposited sediment and suggest alternatives for in situ management, while being protective of the environment.

Some suggestions on how the new knowledge in this study might be applied include the following. Biotreatment to a low bioavailability end point may be a reasonable objective. An intensive treatment process to separate the high- and low-risk sediment fractions might be economical in some instances. Addition of coal-derived carbon to sediments as a treatment approach may promote in situ stabilization of organic contaminants. More broadly, using information from this work to understand and explain low bioavailability of PAHs and other hydrophobic organic contaminants in sediments and perhaps to justify low-intensity management approaches will be an important benefit.

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TECHNICAL BASIS FOR NARCOTIC CHEMICALS AND POLYCYCLIC AROMATIC HYDROCARBON CRITERIA. II. MIXTURES AND SEDIMENTS

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Abstract—A method is presented for developing sediment quality guidelines (SQG) for narcotic chemicals in general and polycyclic aromatic hydrocarbons (PAHs) in particular. The guidelines can be applied to any individual or mixture of narcotic chemicals including PAHs using only the chemical's octanol/water partition coefficient. They are derived using the final chronic values for type I narcotics developed from a database consisting of LC50s for 145 chemicals and 33 species, including fish, amphibians, arthropods, mollusks, polychaetes, coelenterates, and protozoans. The target lipid model is used that accounts for the variations in toxicity due to differing species sensitivities as well as chemical differences. The SQGs are derived using the equilibrium partitioning model (EqP), and the results are compared to other sediment quality guidelines. The criterion for a mixture of PAHs is based on the known additivity of narcotic chemicals. The toxic unit concentration corrected for solubility is calculated for each chemical in the mixture and then summed. A total toxic unit greater than one indicates a toxic mixture. The prediction is compared to the results from an experiment using sediment spiked singly and with a mixture of PAHs. The toxicity and amphipod abundance of field-collected sediments are also examined.

Keywords—Critical body burden Target lipid model Equilibrium partitioning Sediment quality Amphipod abundance

INTRODUCTION

The model used below to develop sediment quality guidelines (SQGs) is presented in the companion paper [1]. Equilibrium partitioning (EqP) [2] is used to convert water quality criteria (WQC) into the equivalent SQG. The model is similar to an amphipod toxicity model for a mixture of 13 polycyclic aromatic hydrocarbons (PAHs) presented by Swartz et al. [3] that relies on additivity, a QSAR that relates toxicity to the octanol/water partition coefficient, and EqP. The model is parameterized using data from amphipod sediment toxicity tests.

For narcotic chemicals as a class, there exist data for many more chemicals and many other species. Thus, a model that can describe the toxicity for type I narcotics including PAHs and that considers the species sensitivity explicitly can be used to develop more robust WQCs following the U.S. Environmental Protection Agency (U.S. EPA) technical guidelines [4] and sediment quality guidelines using EqP [2]. The water quality and tissue criteria are presented in the companion paper [1]. The application to sediments, PAHs, and mixtures is presented below.

PRELIMINARIES

Mixtures and additivity

Narcotic chemicals occur as mixtures in the water column, tissues, and sediments. Therefore, criteria and guidelines need to be formulated appropriately. The toxicity of mixtures is assessed using the concept of toxic units [5]. A toxic unit (TU) is defined as the ratio of the concentration in a medium to the effect concentration in that medium. Thus, water (W), tissue (T), and sediment (S) toxic units are defined as

$$TU_{Wi} = \frac{C_{Wi}}{C_{WQCi}} \quad (1)$$

$$TU_{Ti} = \frac{C_{Ti}}{C_{TQCi}} \quad (2)$$

$$TU_{Si} = \frac{C_{S,OCi}}{C_{SQGi}} \quad (3)$$

respectively, where the subscript i denotes the individual chemicals and the denominators are the guideline values. The guideline values for water and tissues are provided in Tables 5 and 6 in Di Toro et al. [1]. The toxicity of the mixture is the sum of the individuals TUs, i.e.,

$$TU = \sum_i TU_i \quad (4)$$

The additivity of the toxicity of narcotic chemicals has been demonstrated by a number of investigators. Figure 1, adopted from Hermens [6], presents the results of mixture experiments that employed a large enough number of narcotic chemicals so that nonadditive behavior would be easily detected. Three of the four experiments demonstrated essentially additive behavior, and the fourth, a chronic exposure, was almost additive. Thus, the correct use of the water and sediment quality guidelines for narcotic chemicals in general, and PAHs in particular, is as a mixture guideline.

Aqueous solubility constraint

The highest dissolved concentration in water that can be achieved by a chemical is its aqueous solubility S. Therefore, the maximum lipid concentration that can be achieved is limited as well. It is for this reason that the acute LC50 database that was used to generate the water quality criteria for narcotic chemicals was screened initially for LC50s $< S$ [1]. This is

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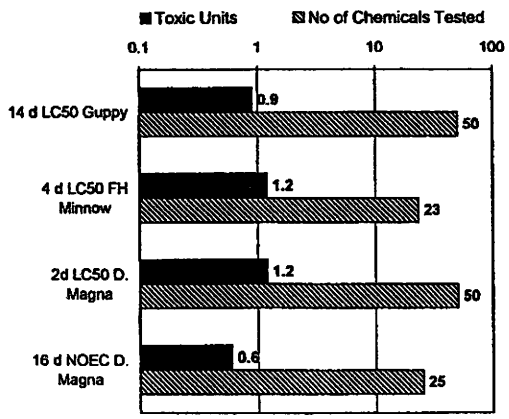

Fig. 1. Additivity of type I narcosis toxicity (adopted from Hermens [6]). Comparison of the observed toxic unit (TU) concentration to the predicted TU = 1. Number of chemicals in the tested mixture is as indicated.

also the reason that the LC50 database is limited to chemicals with $\log(K_{OW}) \leq 5.3$. It appears that, for chemicals with higher K_{OW}s, the aqueous solubilities are too low to result in the lipid concentration necessary to cause mortality of even the most sensitive species. The existence of a solubility cutoff was suggested by Veith et al. [7] based on data for fathead minnows and guppies.

For sediments, this principle should apply as well. Thus, a solubility constraint is applied to sediment concentrations when computing the toxic unit concentrations. This is readily done using the relationship between pore water and organic carbon normalized sediment concentration given by Equation 6 discussed below. Since the pore-water concentration is limited by the aqueous solubility S, the sediment concentration $C_{s,OC}$ should be limited by the concentration in sediment organic carbon that is in equilibrium with the pore water at the aqueous solubility. Therefore, observed sediment concentrations are limited by the condition

$$C_{s,OC} \leq C_{s,OC,max} = K_{OC}S \tag{5}$$

before they are used in Equation 3 to compute toxic units.

The question of whether highly insoluble chemicals, e.g., heavy PAHs, contribute to toxicity when present as mixtures is currently being examined experimentally [8]. Narcosis theory suggests that they, in fact, should contribute fractional toxic units, limited by the solubility constraint (Eqn. 5). This observation points out the importance of knowing the aqueous solubility S of these chemicals so that Equation 5 can be applied reliably.

SEDIMENT QUALITY GUIDELINES

The EqP model can be used to predict sediment toxicity by applying water-only effects concentrations to pore-water concentrations [9]. For chemicals for which the pore-water–sediment partitioning is understood, a sediment effects concentration can also be derived [2]. For nonionic chemicals, partitioning is primarily determined by the organic carbon concentration of the sediment. Although there are some known exceptions, e.g., if the organic carbon fraction $f_{OC} < 0.1$ to 0.2% or if equilibrium between pore water and the solid phase is not achieved, it is possible to predict the sediment effect concentrations from the effects concentration in water-only exposures. Since the target lipid model provides the water effects concentration, it can be used to establish sediment quality guidelines for narcosis chemicals in general and PAHs in particular.

The partitioning equation between organic carbon (OC) normalized sediment concentration $C_{s,OC}$ (μmol/g OC = mmol/kg OC) and the pore-water concentration C_W (mmol/L) is

$$C_{s,OC} = K_{OC}C_W \tag{6}$$

where K_{OC} (L/kg) is the sediment organic carbon partition coefficient that can be calculated from K_{OW} using the following equation [10]:

$$\log(K_{OC}) = 0.00028 + 0.983 \log(K_{OW}) \tag{7}$$

Sediment quality guidelines are calculated using Equation 6 with the final chronic value (FCV) as the water effects concentration, i.e.,

$$C_{SQG} = K_{OC}\text{FCV} \quad \text{or} \tag{8}$$

$$\log(C_{SQG}) = \log(K_{OC}) + \log(\text{FCV}) \tag{9}$$

The final chronic value can be calculated from the target lipid model using the equation

$$\log(\text{FCV}) = \log(C_L^*) - 0.945 \log(K_{OW}) \tag{10}$$

where C_L^* is the critical body burden corresponding to the FCV [1]. Using Equation 10 for the final chronic value and substituting Equation 7 for K_{OC} yields

$$\log(C_{SQG}) = 0.00028 + 0.983 \log(K_{OW}) + \log(C_L^*) - 0.945 \log(K_{OW}) \quad \text{or} \tag{11}$$

$$\log(C_{SQG}) = 0.00028 + \log(C_L^*) + 0.038 \log(K_{OW}) \tag{12}$$

This is the desired equation. For baseline narcotic chemicals, the critical body burden corresponding to the FCV is C_L^* = 6.94 μmol/g octanol and C_{SQG} ranges from 6.94 to 10.8 μmol/g OC over a range of log K_{OW} of 0 to 5. For PAHs, C_L^* = 3.79 μmol/g octanol and C_{SQG} ranges from 4.9 to 5.9 μmol/g OC over a range of log K_{OW} of 3 to 5. These results are listed in Table 1. Table 2 presents SQGs for the 23 PAHs that are quantified in the EMAP [11,12] and NOAA National Status and Trends [13] data sets. Table 3 presents SQGs for type I narcotic chemicals that are reported to be found in sediments in the EPA STORET database. These are based on Equation 12 and the critical body burdens and chemical class corrections discussed above and in the companion paper [1].

It should be pointed out that, for the PAHs in Table 2 with $\log(K_{OW}) \gtrsim 5$, these criteria are an extrapolation beyond the limits of the data set used to validate the target lipid model. Their validity will be examined below by comparison to laboratory and field data sets.

Multiple phase equilibrium

The explanation of the relationships between the concentrations in organic carbon and lipid (Table 1) can be understood by considering the phase partitioning. Although the derivation of Equation 12 is straightforward, it is instructive to examine the equilibrium concentration relationships between water, octanol, lipid, and organic carbon. The partition coefficients between octanol (K_{OW}), organic carbon (K_{OC}), lipid (K_{LW}), and water can be used to compute the concentrations in these phases. The concentrations in water (C_W), octanol ($C_{Octanol}$), organic carbon (C_{OC}), and lipid (C_L) are

Table 1. Polycyclic aromatic hydrocarbon (PAH) equilibrium partitioning (EqP) sediment quality guidelines

Octanol/water partition coefficient		K_{OW}	10^0	10^3	10^5
Baseline narcotics	Tissue	C_L^* (μmol/g octanol)[a]	6.94	6.94	6.94
	Sediment	C_{SQG} (μmol/g OC)	6.94	9.03	10.8
PAHs	Tissue	C_L^* (μmol/g octanol)	3.79	3.79	3.79
	Sediment	C_{SQG} (μmol/g OC)	3.79	4.93	5.87

[a] The units μmol/g octanol reflect the fact that these concentrations are obtained from the y-intercept of the LC50–K_{OW} relationship. The experimental finding that measured tissue lipid concentrations (μmol/g lipid) are equal to the predicted C_L^* supports their use as tissue criteria.

$$C_L = K_{LW} C_W \quad (13)$$

$$C_{Octanol} = K_{OW} C_W \quad (14)$$

$$C_{OC} = K_{OC} C_W \quad (15)$$

Dividing the appropriate Equations 13 through 15 yields

$$\frac{C_L}{C_{Octanol}} = K_{Lipid,Octanol} = \frac{K_{LW}}{K_{OW}} \quad (16)$$

$$\frac{C_{OC}}{C_{Octanol}} = K_{Organic\ carbon,Octanol} = \frac{K_{OC}}{K_{OW}} \quad (17)$$

$$\frac{C_L}{C_{OC}} = K_{Lipid,Organic\ carbon} = \frac{K_{LW}}{K_{OC}} \quad (18)$$

The partition coefficients are given by Equation 10 for lipid-water,

$$\log(K_{LW}) = 0.945 \log(K_{OW}) \quad (19)$$

and Equation 7 for organic carbon-water, K_{OC}. For a range of K_{OW}s, the concentration ratios in the phases are listed in Table 4. For a chemical with $\log(K_{OW}) = 0$ so that $K_{OW} = 10^0 = 1$, the concentrations are all equal. For lipid, this is the consequence of the lack of a constant term in Equation 19, which, in turn, is due to the experimental finding that the predicted LC50 concentration in octanol is equal to the measured concentration in extracted lipid [1]. For organic carbon, it is due to the very small constant term in Equation 7 so that it is approximately true that

$$\log(K_{OC}) \cong 0.983 \log(K_{OW}) \quad (20)$$

For $K_{OW} > 1$, narcotic chemical concentrations are lower in lipid than they are in octanol and the ratio decreases as the K_{OW} increases (Table 4, line (a)). For organic carbon, the concentration is also lower than in octanol but less so than in lipid (Table 4, line (b)). As a consequence, the concentration in organic carbon is slightly higher than in lipid (Table 4, line (c)). Hence, a slightly larger concentration of chemical in organic carbon is necessary to achieve a prescribed concentration

Table 2. Polycyclic aromatic hydrocarbon (PAH) equilibrium partitioning (EqP) sediment quality guidelines[a]

Chemical	CAS number	MW (g/mol)	$\log(K_{OW})$	$\log(S)$[b] (mol/L)	$C_{s,OC}$ (μmol/g OC)	$C_{s,OC,max}$ (μmol/g OC)
Acenaphthylene[c]	208968	152.2	3.22	−3.97	5.03	158
Naphthalene[c]	91203	128.19	3.36	−3.62	5.09	482
1-Methylnaphthalene	90120	142.2	3.84	−3.71	5.31	1,160
2-Methylnaphthalene	91576	142.2	3.86	−3.75	5.32	1,088
Acenaphthene[c]	83329	154.21	4.01	−4.61	5.39	217
Fluorene[c]	86737	166.2	4.21	−4.94	5.48	157
2,6-Dimethylnaphthalene	581420	156.23	4.37	−4.96	5.56	217
Anthracene[c]	120127	178.2	4.53	−6.60	5.64	7.25
Phenanthrene[c]	85018	178.2	4.57	−5.21	5.66	192
2,3,5-Trimethylnaphthalene	2245387	170.26	4.86	−4.43[d]	5.80	2,230
Pyrene[c]	129000	202.26	4.92	−6.19	5.83	45.0
1-Methylphenanthrene	832699	192.26	5.04	−5.85	5.89	127
Fluoranthene[c]	206440	202.26	5.08	−5.93	5.92	118
Benzo[*a*]anthracene[c]	56553	228.29	5.67	−7.32	6.23	18.2
Chrysene[c]	218019	228.29	5.71	−8.06	6.25	3.62
Benzo[*a*]pyrene[c]	50328	252.31	6.11	−7.82	6.47	15.2
Perylene	198550	252.31	6.14	−8.80	6.49	1.71
Benzo[*e*]pyrene	192972	252.32	6.14	−7.80	6.49	17.1
Benzo[*b*]fluoranthene[c]	205992	252.32	6.27	−8.23	6.56	8.60
Benzo[*k*]fluoranthene[c]	207089	252.32	6.29	−8.50	6.58	4.85
Benzo[*ghi*]perylene	191242	276.34	6.51	−9.03	6.70	2.35
Dibenz[*a,h*]anthracene	53703	278.35	6.71	−8.67	6.82	8.58
Indeno[1,2,3-*cd*]pyrene	193395	276.34	6.72	−8.37[d]	6.83	17.2

[a] CAS = chemical abstract number; MW = molecular weight.
[b] [33].
[c] The 13 PAHs measured for the data presented in Figure 4.
[d] Computed using SPARC [34].

Table 3. Equilibrium partioning (EqP) sediment quality guidelines for selected narcotic chemicals[a]

Chemical	Rank[b]	CAS number	MW (g/mol)	$\log(K_{OW})$	$\log(S)$ (mol/L)	$C_{s,OC}$ (μmol/gOC)
Acetone	175	67641	58.08	−0.16	1.14	3.90
2-Butanone	188	78933	72.11	0.32	0.45	4.06
Chloromethane	132	74873	50.49	0.68	−1.18	4.20
4-Methyl-2-pentanone	186	108101	100.16	1.17	−0.06	4.38
Methylene chloride	107	75092	84.93	1.18	−0.68	4.39
Benzyl alcohol	147	100516	108.14	1.20	−0.73	7.71
2-Hexanone	182	591786	100.16	1.29	−0.22	4.42
1,2-Dichloroethane	115	107062	98.96	1.40	−0.94	4.48
Chloroethane	111	75003	64.52	1.42	−1.07	4.48
1,1-Dichloroethane	121	75343	98.96	1.82	−1.30	4.64
1,3-Dichloropropane	165	142289	112.99	1.84	−1.44	4.65
1,2-Dichloropropane	124	78875	112.99	1.86	−1.47	4.66
Chloroform	100	67663	119.38	1.91	−1.50	4.68
1,1,2-Trichloroethane	109	79005	133.40	1.91	−1.43	4.68
Bis(chloromethyl) ether	145	542881	114.96	1.92	−4.63	4.68
Bromodichloromethane	123	75274	163.83	1.97	−1.51	4.70
Benzene	42	71432	78.11	2.00	−1.59	8.27
trans-1,2-Dichloroethylene	119	156605	96.94	2.10	−1.69	4.76
Chlorodibromomethane	120	124481	208.29	2.12		4.77
Bromoform	110	75252	252.73	2.25	−2.19	4.82
1,1,2,2-Tetrachloroethane	108	79345	167.85	2.31	−1.74	4.85
Dichlorodifluoromethane	154	75718	120.91	2.31	−2.67	4.85
1,1,1-Trichloroethane	99	71556	133.40	2.38	−2.18	4.88
Trichlorofluoromethane	129	75694	137.37	2.53	−2.12	4.94
Chlorobenzene	112	108907	112.56	2.58	−2.49	4.96
Toluene	103	108883	92.14	2.62	−2.22	8.73
Styrene	178	100425	104.15	2.72	−2.26	8.81
Carbontetrachloride	116	56235	153.82	2.73	−2.61	5.03
Trichloroethylene	98	79016	131.39	2.81	−2.44	5.06
Ethylbenzene	106	100414	106.17	3.06	−2.66	9.08
Xylene	166		106.17	3.20	−2.79	9.19
1,4-Dichlorobenzene	72	106467	147.00	3.24	−3.24	5.26
1,2-Dichlorobenzene	73	95501	147.00	3.31	−3.29	5.29
1,3-Dichlorobenzene	77	541731	147.00	3.31	−3.28	5.29
Tetrachloroethylene	105	127184	165.83	3.38	−3.15	5.31
Hexachloroethane	82	67721	236.74	3.58	−4.85	5.42
2-Chloronaphthalene	91	91587	162.62	3.88	−4.00	3.03
Dibenzofuran	138	132649	168.20	3.95	−4.63	9.81
1,2,4-Trichlorobenzene	78	120821	181.45	4.00	−4.05	5.62
4-Chloro diphenyl ether	96	7005723	204.66	4.77	−5.01	6.01
4-Bromo diphenyl ether	93	101553	249.11	5.06	−5.39	6.17

[a] CAS = chemical abstract number; MW = molecular weight.
[b] Ranking is based on the number of times the chemical is reported to be found in sediments in the STORET database.

in lipid. This is the reason that the organic carbon normalized guidelines for PAHs in sediments are slightly higher than the critical body burden. The C_{SQG} ranges from 4.9 to 5.9 μmol/g OC over a range of log K_{OW} of 3 to 5 for a critical body burden of $C_L^* = 3.79$ μmol/g lipid.

It may be that these small differences (Table 4) are due to kinetic effects, i.e., are the result of incomplete equilibration, and that it is actually the case that lipid = organic carbon = octanol. However, regression analyses restricted to $\log(K_{OW}) < 3.5$, 4.0, etc., gave essentially the same slopes, indicating that the slope in Equation 19 is not determined by the more hydrophobic chemicals [1]. Furthermore, for applications where the exposure time is similar to that for which the data were generated, e.g., analyzing 96-h tests, these differences are real and need to be considered.

Table 4. Partition coefficients between water, octanol, lipid, and organic carbon

$K_{Octanol,\ Water}$	K_{OW}	10^0	10^1	10^3	10^5	10^7	
$K_{Lipid,\ Octanol}$	$K_{OW}^{-0.055}$	1.00	0.881	0.684	0.531	0.412	(a)
$K_{Organic\ carbon,\ Octanol}$	$K_{OW}^{-0.017}$	1.00	0.962	0.890	0.823	0.761	(b)
$K_{Lipid,\ Organic\ carbon}$	$K_{OW}^{-0.038}$	1.00	0.916	0.769	0.645	0.542	(c)

Biota sediment accumulation factor and metabolism

The target lipid model can be used to compute the biota sediment accumulation factor (BSAF), which is the ratio of the chemical concentration in organism lipid and sediment organic carbon,

$$\mathrm{BSAF} = K_{\mathrm{Lipid,Organic\ carbon}} = \frac{C_L}{C_{OC}} \tag{21}$$

The results in Table 4 indicate that, for narcotic chemicals in general and PAHs in particular, the BSAF is predicted to be less than one. It should decrease from 1.0 to ~0.5 as log K_{OW} increases (Table 4, line (c)). Observed BSAFs for PAHs average 0.34 for benthic organisms [14], although there are other organisms with much lower BSAFs (see Parkerton et al. [15] for a compilation).

The reason for this wide range of BSAFs is that PAHs are

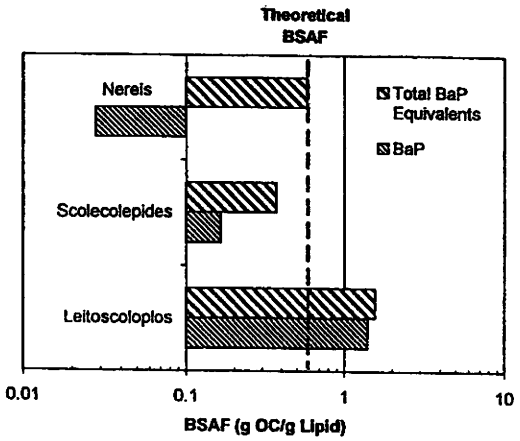

Fig. 2. Measured biota sediment accumulation factor (BSAF) for three polychaetes for B*a*P only and for total B*a*P equivalents estimated from total radioactivity [17]. Dashed line is the theoretical BSAF estimate (Table 4, line (c)).

metabolized by certain organisms [16]. Since the data upon which the target lipid model narcotic criteria are based come from both short- and long-term exposures—the acute and chronic databases—the effect of metabolism is implicitly included. The question is why the target lipid model, which ignores metabolism entirely, appears to describe narcosis toxicity. The only plausible explanation is that a large portion of the metabolic end products remain in the organism. Since narcosis toxicity is additive (Fig. 1), these metabolites exert an equivalent toxicity. The decrease in the parent compound is compensated for by an increase in metabolites. The BSAF for the parent compound reflects the reduction due to metabolism, but the toxicity is much less affected.

Polychaete bioaccumulation experiments by Driscoll and McElroy [17] utilizing radiolabeled benzo[*a*]pyrene (B*a*P) for a 9-d exposure clearly demonstrate this effect (Fig. 2). The B*a*P BSAFs for three polychaetes range from 0.028 to 1.40, which illustrates the wide variation in metabolism that can occur. However, if total B*a*P equivalents based on the radioactivity are used, then the BSAFs range from 0.58 to 1.56, a much smaller variation [17]. Figure 2 also includes the theoretical BSAF for B*a*P (Table 4, line (c)) that is similar to the observed total B*a*P data. Some reduction in toxicity due to metabolic activity and excretion of the metabolites must occur, but it appears to be of secondary importance, although it may be a reason for the observed range in species sensitivity and the occasional outlier in the toxicity data [1].

APPLICATION TO POLYAROMATIC HYDROCARBONS

The motivation for the development of the target lipid model was to apply it to mixtures of PAHs and other persistent narcotic chemicals in sediments. The narcosis database used to determine the universal narcosis slope and the critical body burdens consists of 145 chemicals, of which 10 are unsubstituted and substituted PAHs [1]. A comparison of the LC50 data for just these chemicals and the target lipid model is shown in Figure 3. The solid log(LC50)–log(K_{ow}) lines are computed using the universal narcosis slope and the appropriate body burdens for PAHs for each organism listed. The dotted lines apply to the chloronaphthalenes that have a slightly lower critical body burden due to the halogen substitution [1]. The lines are an adequate fit of the data, although the scatter in the *Daphnia* data is larger than some of the other species with multiple sources of data and there is a clear outlier for *Mysidopsis*. The 10-d *Rhepoxynius* data are discussed below.

It is clear from this plot that fitting a narcosis model to just the PAH data would yield less certain estimates for the slopes and critical body burdens. In contrast to this, the target lipid model is fit to the entire narcosis data set that produces more reliable estimates of the universal slope, critical body burdens, and chemical class corrections.

Mixture experiment

The additivity of mixtures of narcotic chemicals in water exposures is well established (Fig. 1). An experimental test of the additivity of mixtures of PAHs using sediment exposures has been reported by Swartz et al. [18]. *Rhepoxynius abronius* was exposed for 10 d to sediments spiked with acenaphthene, phenanthrene, fluoranthene, and pyrene alone and then with an equitoxic mixture of the four chemicals. An analysis of this experiment within the context of the narcosis target lipid model is presented below. A similar analysis was presented by Swartz et al. [18] using their ΣPAH mixture model. In their analysis, slightly less than additive behavior was found. Since the *Rhepoxynius* sediment test duration is 10 d, similar duration water-only test data would be required in order to make an independent estimate of the critical body burden. These data are not available. However, pore-water concentrations are available from another set of spiked sediment tests reported by Ozretich et al. [19]. These data will be used in lieu of water-only exposure data. The critical body burden is computed by fitting the narcosis model [1],

$$\log(\mathrm{LC50}) = \log(C_L^*) - 0.945 \log(K_{ow}) \qquad (22)$$

to the pore-water LC50 concentrations. The resulting critical body burden is $C_L^* = 12.2$ μmol/g octanol. This relationship is shown in Figure 3 (lower right-hand side). With the exception of the one data point at $\log(K_{ow}) = 3.3$, the narcosis slope appears to be representative. Due to its deviation from the universal narcosis slope, this data point is considered an outlier and has been excluded from the analysis.

In order to analyze the sediment data spiked with single PAHs and a mixture of PAHs, the organic carbon normalized LC50s for each PAH are required. These are computed using the critical body burden $C_L^* = 12.2$ μmol/g octanol replacing the criteria value in Equation 12.

$$\log(C_{s,oc}^*) = 0.00028 + \log(C_L^*) + 0.038 \log(K_{ow}) \qquad (23)$$

$$= 0.00028 + \log(12.2) + 0.038 \log(K_{ow}) \qquad (24)$$

The resulting $C_{s,oc}^*$ are the predicted organic carbon normalized LC50s. For acenaphthene, phenanthrene, fluoranthene, and pyrene, they range from 17.3 to 19.0 μmol/g OC, with an average of 18.3 μmol/g OC.

For the case of PAHs, the toxic unit computation can be simplified considerably. Since the predicted LC50s are almost equal for the four PAHs (17.3–19.0 μmol/g OC), the total measured concentrations can be compared to the average predicted LC50, bypassing the toxic unit calculation. This can be seen from the defining equations,

$$\mathrm{TU}_i = \frac{C_{s,oc,i}}{C_{s,oc,i}^*} \quad \text{and} \qquad (25)$$

$$\mathrm{TU} = \sum_i \mathrm{TU}_i = \sum_i \frac{C_{s,oc,i}}{C_{s,oc,i}^*} \cong \frac{1}{C_{s,oc}^*} \sum_i C_{s,oc,i} \qquad (26)$$

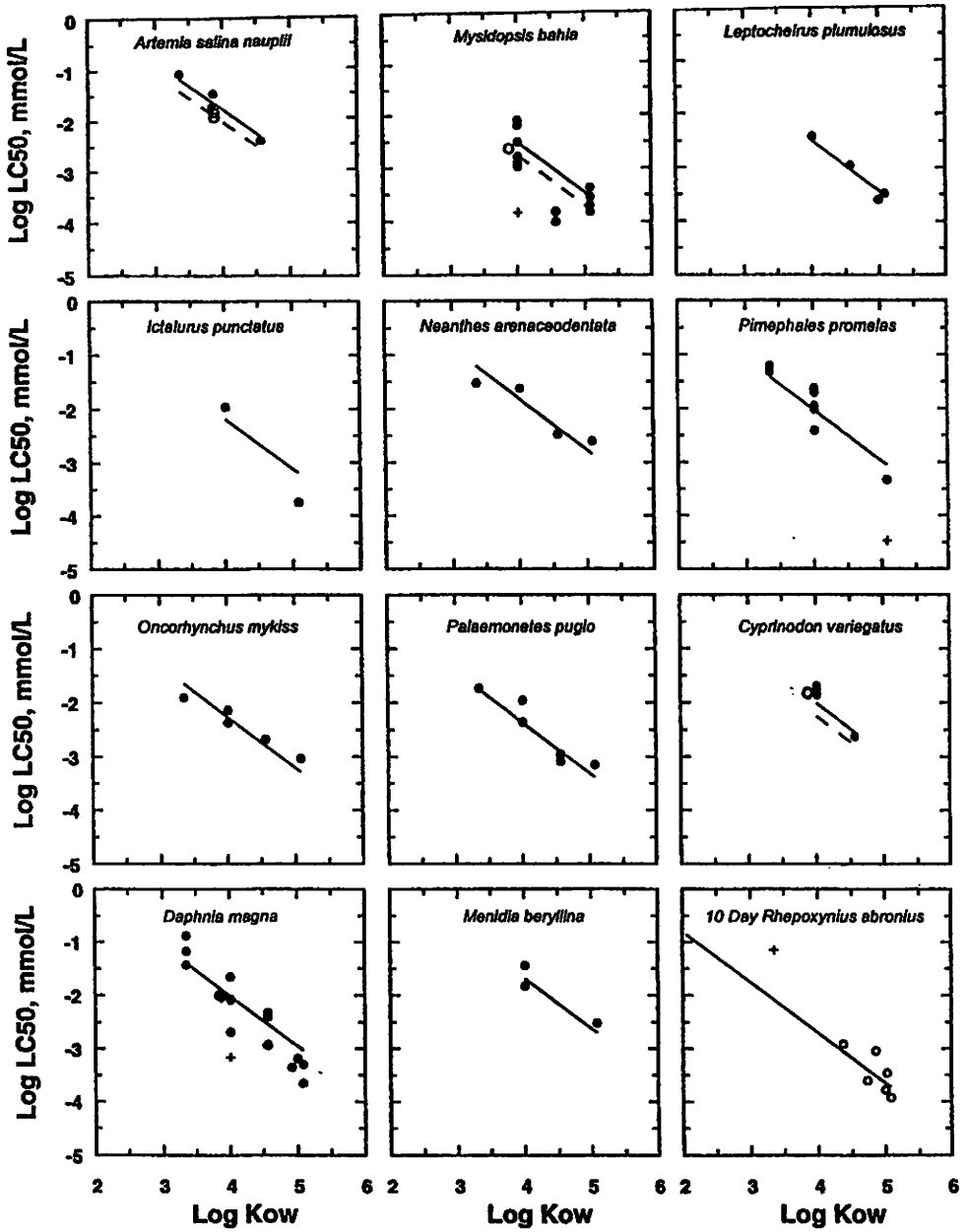

Fig. 3. Comparison of target lipid model fit and observed LC50 data for polycyclic aromatic hydrocarbons (PAHs) and the indicated species. The PAHs included are naphthalene (3.36), 1-methylnaphthalene (3.84), 2-methylnaphthalene (3.86), 2-chloronaphthalene (3.88), 1-chloronaphthalene (3.88), acenaphthene (4.01), phenanthrene (4.57), pyrene (4.92), 9-methylanthracene (5.01), fluoranthene (5.08). Number in parentheses is $\log(K_{ow})$. Solid line and filled symbols for nonhalogenated PAHs. Dotted line and unfilled symbols for the halogenated (i.e., chlorinated) PAHs: + denotes outliers (see [1] for criteria).

where $C^*_{s,oc}$ = 18.3 μmol/g OC. A toxic unit of one occurs when

$$1 = \frac{1}{C^*_{s,oc}} \sum_i C_{s,oc,i} \quad \text{or} \tag{27}$$

$$\sum_i C_{s,oc,i} = C^*_{s,oc} \tag{28}$$

Thus, a comparison of the total PAH concentration $\Sigma_i C_{s,oc,i}$ to the average LC50 = $C^*_{s,oc}$ is equivalent to the toxic unit analysis. This procedure retains the concentration units, which facilitates the comparison to field data and other sediment guidelines.

This comparison is made in Figure 4A. The line is the predicted LC50. The two parallel lines represent ± a factor of two, which is the approximate uncertainty of EqP-derived sediment organic carbon normalized LC50s. As can be seen, the model reproduces the observed dose–response for both the single chemical and mixture spiked sediment data.

PAHs with log(K_{ow}) > 5

The PAHs employed in the mixture tested in the experiment analyzed above all have $\log(K_{ow}) < 5$. The remaining question is whether the highly insoluble PAHs with $\log(K_{ow}) > 5$ (and, by implication, all the other insoluble chemicals) contribute to narcotic toxicity, each limited by their aqueous solubility. Narcosis theory suggests that all the organic chemicals in a sediment should contribute additively to the toxicity exhibited by that sediment. This conclusion follows from the additivity

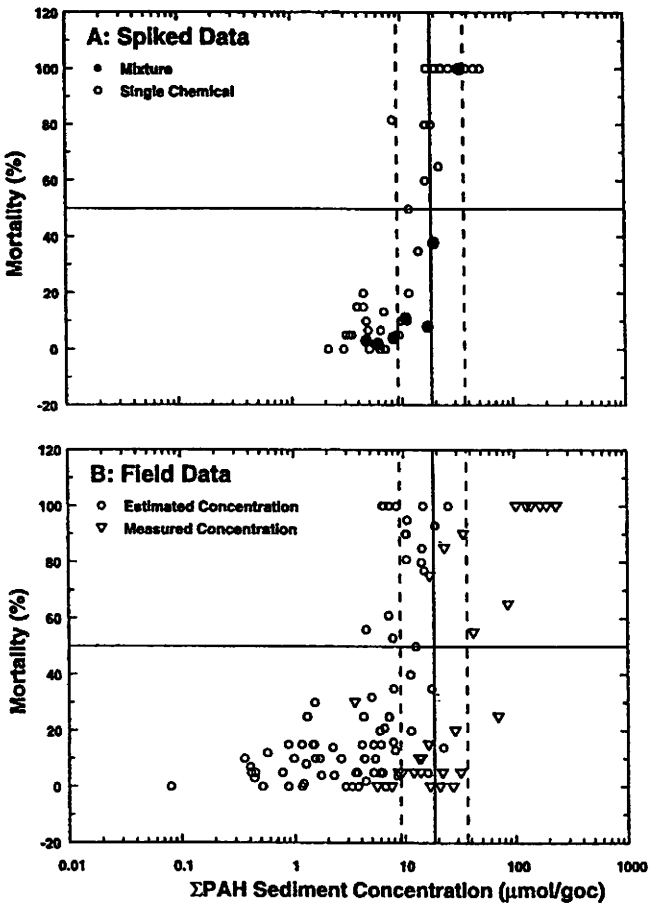

Fig. 4. Comparison of observed morality in *Rhepoxynius abronius* 10-d sediment toxicity tests. (A) Data from the spiked mixture experiment of Swartz et al. [18] for either the individual PAHs (○) or the sum of the PAH concentrations (●). (B) Data from Swartz et al. [3] using the estimated total of 34 PAHs from the measured 13 PAHs (○) or the measured 34 PAHs from the Ozretich et al. [19] Elliot Bay data set (▽).

of narcotic chemicals. However, the bioavailability of chemicals is constrained by their aqueous solubility. This is the explanation for the lack of any reported toxicity for single chemicals with $\log(K_{OW}) \gtrsim 5$.

An experiment has been performed by Spehar et al. [8] that directly addresses this issue. A mixture of 13 PAHs was employed, with each $\log(K_{OW})$ ranging from 5.36 to 6.76, of which seven had $\log(K_{OW}) > 6$. The concentration of each chemical was limited either to 0.5 TUs or less if limited by its solubility. The TUs were computed from an estimate of the critical body burden for *Hyalella azteca*, the test animal employed. The test duration was 28 and 10 d for flow-through and static exposures, respectively, with survival, growth, and reproduction measured. In addition, *Leptocheirus plumulosus* were also tested using the same mixture of PAHs. Significant mortality and growth effects occurred at a total PAH tissue concentration of 20 to 35 μmol/g lipid. This experiment clearly shows that high K_{OW} PAHs can collectively cause toxicity by additive narcosis at tissue concentrations predicted from the target lipid model.

Thus, the available experimental information supports the extension of the narcosis model beyond the limit of $\log(K_{OW}) \lesssim 5$, which is the limit of the single chemical data employed in its derivation.

FIELD DATA

The ultimate test of validity of sediment guidelines is their predictive ability, i.e., can they be used to predict effects seen in field-collected samples. Unfortunately, the problem of validation using field-collected samples has no straightforward solution. It is extremely difficult to separate actual cause and effect from simple correlation. The primary reason is the presence of covariation of many chemical contaminants in field-collected sediments, some of which may be unmeasured. Therefore, it cannot be presumed that the response is due to only the chemical(s) being investigated.

However, one fact is unequivocal. If the guideline predicts an effect, e.g., 50% mortality of a test organism, at a certain chemical concentration and the organism survives exposures above that concentration, then the criterion is invalidated. No other comparison is definitive. Mortality at concentrations below the predicted effects concentration may be due to other causes and provides no evidence for the validity or invalidity of the prediction.

Toxicity tests

A set of toxicity data has been assembled by Swartz et al. [3] from locations for which PAHs are suspected to be the primary cause of toxicity. In addition, a set of data obtained by Ozretich et al. [19] from Elliott Bay is also available. For these data sets, the number of PAHs included in the total PAH concentration depends on (1) the number that were explicitly measured and (2) the number that would be expected to be present.

This issue is discussed at some length in the U.S. EPA's ESG (Equilibrium Partitioning Sediment Guidelines) [20]. The most complete data sets comprise 34 PAHs that include the commonly measured parent, i.e., unsubstituted, PAHs as well as some alkylated homologous series that are less frequently measured. It is shown that the toxicity of sediment-associated PAHs can be severely underestimated if these alkylated PAHs are not considered. A method for estimating the total of the 34 PAH concentrations using either a subset of 13 or 23 commonly measured PAHs is provided in the document. The median ratio of the concentration of 34 PAHs to the concentration of the 13 PAHs is 2.75.

The Ozretich et al. [19] Elliott Bay data set had measurements for 33 PAHs that included some alkylated homologous series. The alkylated PAHs were well represented. Thus, the reported total concentrations were used without any correction factor. The Swartz et al. [3] data set had measurements for only 13 PAHs. The estimated total concentration of the 34 PAHs is obtained by multiplying the reported total concentration of the 13 PAHs by 2.75 [20].

Figure 4B is a comparison of observed mortality of *Rhepoxynius abronius* in the standard 10-d sediment test to the total PAH concentration for both data sets. The line is the predicted LC50 = 18.3 μmol/g OC obtained from the pore-water data [19] analyzed above. The measured and estimated data refer to the Elliott Bay and the Swartz et al. [3] data sets, respectively.

Consider first the data for which the total PAH concentration is measured. There is only one point below 50% mortality. All the rest exhibited >50% mortality, consistent with the prediction. Strictly speaking, that one observation below 50% mortality invalidates the guideline since less than 50% of the test organisms died. However, since it is only one test, we regard it as a statistical fluctuation. However, if many of the

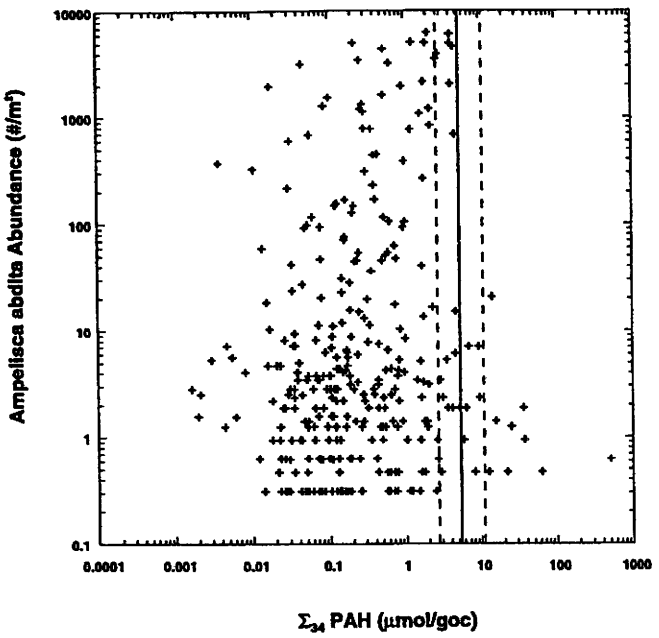

Fig. 5. *Ampelisca abdita* abundance versus estimated total of the 34 PAHs using the measured 23 PAHs. Data from Virginian and Louisianian province EMAP [11,12] and the New York/New Jersey Harbor REMAP [13]. Vertical lines are average final chronic value (FCV) sediment quality guideline ± a factor of two.

tests exhibited that behavior—surviving when the observed total PAH concentration exceeded the predicted LC50—then these observations would invalidate the guideline.

For the remaining data, the total PAH concentrations are estimated from the 13 measured PAHs. A number of sediments exceeded 50% mortality at concentrations below ~10 µmol/g OC, the lower bound of the predicted LC50 in Figure 4B. The total PAH concentration is estimated using the median ratio of the observed total of 34 PAHs to the total of 13 PAHs. This ratio has 90% confidence limits of 1.57 to 16.9 [20]. Thus, the deviations are well within the probable error of this estimate.

Organism abundance

Another test of the guidelines is observations of the organism density of sensitive animals in field-collected samples. Figure 5 presents the observed *Ampelisca abdita* abundance versus estimated total PAH. The data are from sediments collected as part of the Virginian and Louisianian province EMAP [11,12] and the New York/New Jersey Harbor REMAP [13] sediment sampling programs. The total PAH estimate is obtained using the sum of the 23 measured PAHs and the median ratio of 1.64 (90% confidence limits: 1.12–4.14) [20] between the 23 PAHs and the 34 PAHs found in the EMAP data sets. The identity of the measured PAHs are listed in Table 2. The vertical lines are the averages of the FCV sediment quality guidelines listed in Table 2. The results are very encouraging. All the sediments that exceed the FCV guideline have significantly lower amphipod abundance, consistent with the narcosis prediction.

It is tempting to conclude from the coincidence of the predicted effect concentration and the drop in amphipod abundance that in fact these data support the validity of the guidelines. However, it should be pointed out again that these data can only be used to demonstrate that the guidelines are not in conflict with observations. They cannot be used to validate the guidelines. For example, a very much larger effects concentration would also fail to be invalidated. However, these data would invalidate a much lower concentration since an effect would be predicted and none would be observed. We return to this observation later.

The validation procedure requires sediments for which the nature of all the biologically active chemicals are known and quantified. This is only satisfied with laboratory-spiked sediments where the identity of the toxic components is certain, hence, the importance of the experimental demonstration of the validity of the narcosis mixture guidelines (Fig. 4A).

Resistant PAH phases and soot carbon sorption

The comparison of the target lipid model narcotic SQG using field-contaminated sediments rather than laboratory-spiked sediments is important because there is concern that solid phase PAHs might be present in field-contaminated sediments that are not in equilibrium with the pore water, thereby invalidating Equation 8 and, presumably, the sediment quality guidelines. Both chemical [21,22] and biological [23] data have been used to suggest that this may be occurring in certain situations. The idea is that particles of coal or tar-like materials may be present. They would be measured as part of the sediment PAH concentration, but if they are kinetically inhibited from dissolving, then Equation 8 would not apply.

The toxicological data presented by Paine et al. [23] for *Rhepoxynius abronius* 10-d mortality tests indicates 75% survival at total PAH concentrations greater than the 10-d LC50 of 18.3 µmol/g OC ≈ 3,200 µg/g OC ≈ 32.0 µg/g for a sediment with f_{OC} = 1% OC. The sediments are reported to contain visible pitch and/or coke particles or globules. The organic carbon content of many samples with high PAH concentrations was also elevated, suggesting significant quantities of pitch and/or coke [23].

A second problem is the failure of the partitioning model, not from a lack of equilibrium but because the partitioning phases are incompletely specified. It has been suggested that PAHs partition to soot carbon in addition to natural organic carbon and that the partitioning model for PAHs be expanded to include this phase explicitly,

$$K_d = f_{OC}K_{OC} + f_{SC}K_{SC} \tag{29}$$

where K_d is the sediment–pore-water partition coefficient (L/kg dry wt), f_{SC} is the fraction of soot carbon in the sediment, and K_{SC} is the partition coefficient to soot carbon [24]. An extraction method has been developed to determine f_{SC}, and a relationship between K_{SC} and K_{OW} has been presented. Thus, this additional phase can be incorporated into the proposed criteria. The modification to the sediment quality guideline Equation 8 that includes this complication is

$$C_{SQG} = \left(K_{OC} + \frac{f_{SC}}{f_{OC}}K_{SC}\right)\text{FCV} \tag{30}$$

where Equation 29 is used for the partition coefficient. The existence of these observations suggests that the SQGs listed in Table 2 should be used with care when the presence of these resistant phases or when a significant soot partitioning is suspected or observed.

It is important to note that both of these phenomena, the lack of equilibrium and the presence of a more highly sorptive phase, would result in higher sediment quality guideline concentrations. Thus, at a minimum, the proposed criteria without

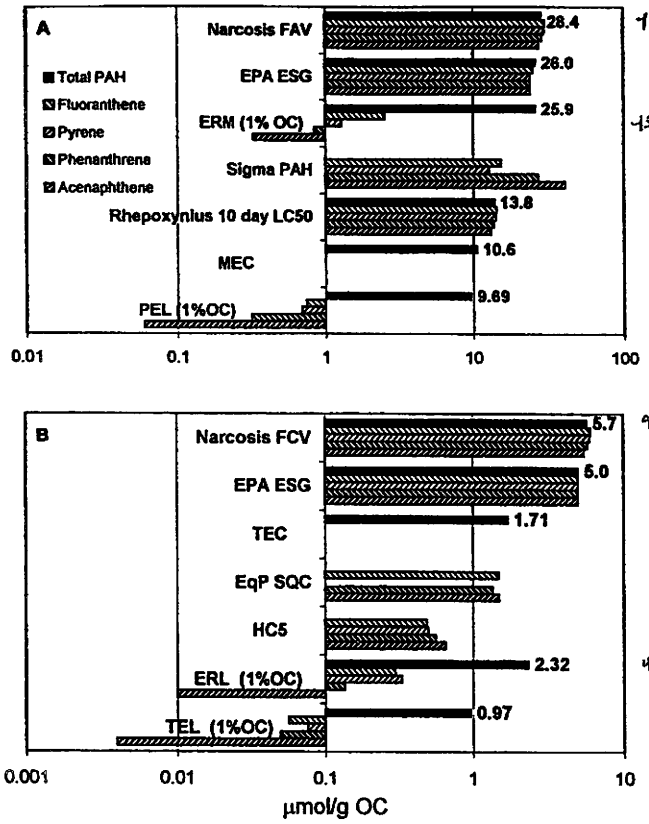

Fig. 6. Comparison of various estimates of sediment effects concentrations. The effects range low (ERLs) and effects range median (ERMs) from Long and Morgan [25]; threshold effects level (TELs) and probable effects level (PELs) from MacDonald et al. [26]; HC_5 from Van Leeuwen et al. [27]; ΣPAH from Swartz et al. [3]: EPA SQC from [28–30]; threshold effects concentration (TEC) and median effects concentration (MEC) from Swartz [31]; *Rhepoxynius* 10-d LC50 from Swartz et al. [18]; EPA ESG from [20]; narcosis final acute value (FAV) and final chronic value (FCV) from this work.

the modification in Equation 30 or a method to quantify lack of equilibrium can still be used reliably to assess sediments for the lack of toxicity. If the guideline is exceeded, then the other tenet of the EqP model, that pore-water concentrations can be used to predict the toxicity of sediments [2], can be used together with the FCVs (Table 6 in [1]) to make an assessment.

However, the comparisons presented in Figures 5 and 6 suggest that this problem may not be a common occurrence since there are no sediments in these comparisons with predicted but not observed effects, which would be the consequence of significant soot carbon partitioning and lack of pore-water equilibrium.

Other PAH effects

The basis for the sediment quality guidelines presented in this paper are the acute and chronic toxicity data included in the analysis. The endpoints considered are mortality, growth, and reproduction. Other endpoints associated with PAHs, e.g., tumors and immunological and endocrine disruption, are not specifically addressed. To the extent that these affect the ability of organisms to survive and reproduce, which are the endpoints that are considered, their effects are implicitly included in the guidelines. A more detailed analysis of these effects is available as part of the U.S. EPA Equilibrium Partitioning Sediment Guidelines (ESG) for PAHs [20].

COMPARISON TO OTHER APPROACHES

There are many other sediment criteria and guidelines that have been suggested for individual and for total PAHs as mixtures. Table 5 lists a representative sample. The effects range low and effects range median [25] and the threshold effects level and probable effects level [26] are estimates of threshold and definite effects levels derived from an analysis of field data sets. They are based on dry weight concentrations and therefore ignore the effect of organic carbon on bioavailability of nonionic hydrophobic organic chemicals in sediments [2].

The HC_5 concentrations [27] are based on an analysis similar to the multilinear regression analysis used in the target lipid model [1]. The QSARs for the effects of narcotic chemicals and K_{OW}s were developed for 19 species where species-specific slopes and *y*-intercepts were computed. The QSARs represent chronic toxicity and were expressed on a NOEC (no-observed-effect concentration) basis. If the data were acute, an acute-to-chronic ratio (ACR) was applied to convert the data to chronic values. From the individual QSARs, concentrations were extrapolated to a level that protects 95% of the aquatic community. These levels were denoted as HC_5, the hazardous concentration for 5% of the species.

The EqP SQG estimates are derived from the final chronic values computed from aquatic toxicological data for the individual chemicals [28–30] following the U.S. EPA technical guidelines [4]. Equilibrium partitioning is used to derive the sediment quality guidelines.

The ΣPAH model [3] is similar to the narcosis model. The 10-d LC50 predicted pore-water concentrations C^*_{PW} (µmol/L) are related to the octanol/water partition coefficient via

$$\log(C^*_{PW}) = 5.92 - 1.33 \log(K_{OW}) \qquad (31)$$

The principle difference is the slope (−1.33) employed relative to the narcosis slope (−0.945). Equation 31 is based on data for three PAHs and four different species without individual sensitivities considered, totaling six data points. Thus, the slope and intercept estimates have considerable statistical uncertainty.

The threshold effects concentration and median effects concentration are threshold and median consensus values derived by Swartz [31] from an analysis of various suggested guidelines, including the results of the ΣPAH model [3].

The U.S. EPA's ESG (Equilibrium Partitioning Sediment Guidelines) [20] are derived following the National Water Quality Criteria Guidelines [4]. The acute toxicity data base included 104 (77) freshwater (saltwater) water-only tests employing 12 (8) different PAHs and 24 (30) species from 20 (29) genera. The narcosis model was used to translate these water-only LC50s to critical body burdens using the universal narcosis slope (Eqn. 22). This is a much larger database than the PAHs included in the narcosis database (see Fig. 3).

A comparison of these guidelines is facilitated by a graphical presentation (Fig. 6). The guidelines that are expressed on a dry weight basis are converted to molar concentrations using the molecular weight (mol wt) for each chemical, or an average mol wt = 173 g/mol for total PAH, and an assumed organic carbon fraction of one percent, i.e., f_{OC} = 0.01. For criteria that apply to individual PAHs only, the total PAH criteria are computed from the average of five PAHs as indicated.

It should be pointed out that there are substantial variations in sediment organic carbon. For the EMAP data sets, the median f_{OC} is 1% but the 68% range (the log mean ± 1 log

Table 5. Comparison of sediment quality guidelines[a,b]

	Acenaphthene	Phenanthrene	Pyrene	Fluoranthene	Total PAH
	(μmol/g OC)				
TEL (a)[c]	0.004	0.049	0.076	0.056	0.97[d]
ERL (b)[c]	0.010	0.135	0.329	0.297	2.32[d]
HC5 (c)	0.65	0.56	0.50	0.49	
EqP SQC (d)	1.49	1.35		1.48	
TEC (e)					1.71
U.S. EPA ESG (f)	3.17	3.33	3.43	3.48	3.35[e]
Narcosis FCV (i)	5.39	5.66	5.83	5.92	5.70[e]
PEL (a)[c]	0.06	0.31	0.69	0.74	9.69[d]
MEC (c)					10.6
Rhepoxynius					
10-d LC50 (g)	13.1	13.7	14.1	14.3	13.8
EPA ESG (f)	13.2	13.8	14.3	14.5	13.9[e]
Σ PAH (h)	40.6	27.0	12.8	15.3	
ERM (b)[c]	0.32	0.84	1.29	2.52	25.9[d]
Narcosis FAV (i)	27.4	28.8	29.7	30.1	29.0[e]

[a] TEL = threshold effects level; ERL = effects range low; HC5 = hazardous concentration for 5% of species; EqP SQC = equilibrium partitioning sediment quality criteria; TEC = threshold effects concentration; U.S. EPA ESG = U.S Environmental Protection Agency equilibrium partitioning sediment guidelines; FCV = final chronic value; PEL = probable effects level; MEC = median effects concentration; ERM = effects range median.

[b] In the first column, (a) = MacDonald et al. [26]; (b) = Long et al. [35]; (c) = Van Leeuwen et al. [27]; (d) = U.S. EPA [28–30]; (e) = Swartz [31]; (f) = U.S. EPA [20]; (g) = Swartz et al. [18]; (h) = Swartz et al. [3]; (i) = this work.

[c] Computed assuming f_{OC} = 1.0%.

[d] Computed using average molecular weight, MW = 173.

[e] Average of acenaphthene, anthracene, phenanthrene, pyrene, and fluoranthene.

standard deviation) is from 0.3 to 3% organic carbon, an order of magnitude. Therefore, the dry weight normalized guidelines have a one order of magnitude uncertainty when the bioavailable chemical concentration is considered. Therefore, the dry weight guidelines will be denoted as median effects range median, etc.

For total PAHs, the acute guidelines based on the narcosis final acute value (FAV) is the largest of the suggested concentrations (Fig. 6A). The U.S. EPA ESG is essentially the same. The median effects range median is remarkably close, and the median effects concentration and median probable effects level are approximately a factor of three lower. The narcosis FAV concentrations for each individual PAH are also essentially constant at 27 to 30 μmol/g OC. This is in sharp contrast to the median effects range median and probable effects level, which are a factor of 10 to 100 smaller for the individual PAHs. Since PAHs are all narcotic chemicals, it is virtually impossible that these low concentrations would, by themselves, produce mortality, growth, or reproduction effects. The *Rhepoxynius abronius* 10-d LC50s (Table 5) are included to support this observation. These median effects range median and probable effects level concentrations are more a reflection of the composition of PAHs in toxic sediments, since they are derived by analyzing the chemical concentrations in toxic sediments [32], rather than a reflection of the toxicity of the individual chemicals. Swartz [31] has examined these relationships more closely. The SQGs derived from the ΣPAH model have an inverse relationship to K_{OW} due to the large negative slope (Eqn. 31).

The final chronic value (FCV) narcotic guidelines for total PAH are also the largest concentrations of the threshold values (Fig. 6B). Again, the U.S. EPA ESG is essentially the same. The other total PAH concentrations are a factor of three lower. The individual PAH concentrations for the median effects range low and threshold effects level are one to two orders of magnitude lower. The explanation is the same as given above.

The HC_5 values (~0.5 μmol/g OC) [27] are approximately an order of magnitude lower than the FCV narcotic estimate (5.70 μmol/g OC). The reason is that the extrapolation used to compute the fifth percentiles for these guidelines considers not only the variation in the intercepts of the regressions but is also sensitive to the variations in the species-specific slopes. The target lipid model considers only the variations in the intercepts. The statistical test applied to the slopes of the narcosis database failed to reject the hypothesis of a single universal narcosis slope [1]. Therefore, the variations in slopes, which are amplified as the lines are extrapolated beyond the range of data for each line, are more a reflection of the statistical uncertainty of the slope estimate rather than a measure of species sensitivity. Nevertheless, these variations contribute variability, which produces a lower fifth percentile. Note that the resulting HC_5 concentration of ~0.5 μmol/g OC is considerably lower than the ~3.0 μmol/g OC threshold limit above which *Ampelisca* abundance declines (Fig. 5). Assuming that this is a measure of the threshold of effects that the HC_5 is protective of, the coexistence of apparently abundant populations and the HC_5 concentration suggests that this concentration is too low.

Therefore, it appears that the SQGs, which are based on the target lipid model of narcosis toxicity, should be preferred over the other sediment guidelines. They properly account for mixtures of PAHs, which is always the situation encountered in contaminated sediments. They are based on a very large narcotic chemical database that results in more reliable estimates of the universal narcosis slope and the critical body burdens from which the criteria are derived. They are based on direct experimental determinations of acute and chronic effects of narcotic chemicals and PAHs, so causality is not in

question. They do not predict effects when none are observed except as discussed above where the partitioning model breaks down. For these cases, the guidelines are conservative.

In contrast, the empirically based guidelines are based on dry weight normalized concentrations so that they make no correction for bioavailability. And since they are derived from tests and observations using field collected sediments, which contain many covarying chemicals, they have no cause and effect basis. This is the reason that the empirical guidelines for individual PAHs are unrealistically low.

CONCLUSIONS

The target lipid narcosis model has been used to derive sediment quality guidelines for narcotic chemicals in general and PAHs in particular. Guideline concentrations corresponding to the FAV and FCV levels of protection are almost constant over the range of K_{ow}s characteristic of PAHs until solubility lowers the applicable concentrations. The total PAH guideline is evaluated using strict additivity. The predictions of the target lipid model are verified using the results of a spiked sediment mixture experiment.

The predictions are compared to the results of *Rhepoxynius* toxicity tests using field-collected sediments from locations where PAHs are suspected to be the primary cause of toxicity. The results are consistent with the predictions when 31 PAHs were measured. For the data when only 13 PAHs and no alkylated PAHs were quantified, the results are comparable if an estimate of the total PAH concentration is used.

Observations of *Ampelisca* abundance in field-collected sediments is consistent with the prediction of benthic effects when the narcosis FCV guideline is exceeded. The lower effects levels suggested by others are inconsistent with these data.

A situation has been reported where *Rhepoxynius* toxicity is predicted but not observed. This is attributed to the presence of visible pitch and/or coke particles or globules that are not in equilibrium with the pore water.

Empirically derived guidelines for total PAH are roughly equal to, or a factor of three lower, for a 1% organic carbon sediment. However, there is a one order of magnitude uncertainty due to the variation in organic carbon concentrations in sediments that they do not account for. The individual PAH empirical guidelines are one to two orders of magnitude smaller than the narcotic concentrations that are known to cause mortality, growth, or reproduction effects and therefore are not reflective of actual effects concentrations for these endpoints.

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Increased CYP1A1 and ribosomal protein L5 gene expression in a teleost: The response of juvenile chinook salmon to coal dust exposure

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Abstract

Molecular studies on the sublethal physiological effects of coal dust exposure in vertebrates are sparse. Coal dust contamination of the marine environment occurs, for example, around coal loading and storage terminals. To determine the potential impact of coal dust exposure on juvenile chinook salmon, fish were exposed for an 8 day period to 60 mg L^{-1}, 200 mg L^{-1} or 500 mg L^{-1} of coal dust in sea water and the levels of CYP1A1 mRNA quantitated using RT-cPCR. Two control groups were utilized; one 'negative' control group was maintained in sea water only, whilst the second 'positive' control group was i.p. injected with β-naphthoflavone (BNF: 50 mg kg^{-1}). There was a significant increase in CYP1A1 expression in fish exposed to coal dust (ANOVA; $P < 0.001$), and in fish injected with BNF (*t*-test; $P < 0.001$), relative to controls. In addition, RT-PCR analysis indicated increased expression of a second gene in the fish exposed to coal dust. Sequence analysis identified the second coal-dust-inducible gene as ribosomal protein L5. Both of these genes, CYP1A1 and L5, encode proteins vital in cellular metabolism. The enzyme encoded by CYP1A1 (P4501A1) plays an important role in the metabolic activation of PAHs to carcinogenic and mutagenic metabolites. L5 plays a crucial role in ribosome biogenesis. At present, the significance of the increased hepatic expression of L5 in coal dust exposed fish is unclear and warrants further investigation.

Keywords: CYP1A1; Ribosomal protein L5; Coal dust; Chinook salmon; RT-cPCR; Liver; Gene expression

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1. Introduction

Molecular physiological studies on the sublethal effects of coal dust exposure in vertebrates are sparse. There are, however, a few indications in the literature, based almost exclusively on lung pathophysiological studies, that coal dust exposure causes changes in cellular metabolism that can ultimately be manifest as tissue damage and reduced health (Kuhn et al., 1990; Heederik et al., 1994; Lee et al., 1994). However, despite the fact that coal dust contains planar PAHs capable of inducing CYP1A1 (a gene encoding the xenobiotic-metabolizing enzyme P4501A1), previous studies on the response of mammals to coal dust exposure indicated no effect on P4501A1-associated enzyme activities in either liver or lung microsomes (Rabovsky et al., 1984).

The potential impact of coal dust exposure on species living in environs immediately surrounding sources of coal dust contamination have received little attention. Coal dust can enter the marine environment around coal ports through storm water discharge, coal pile drainage run-off, and when coal dust from storage piles, transfer conveyer belts and rail cars becomes airborne and is deposited in the surrounding environment (i.e. fugitive coal dust)(Xuan and Robins, 1994). The practice of using additives, such as surfactants, in the water being used for surface wetting of coal piles can increase the solubility of hydrophobic compounds and thus their mobility in the aquatic environment (Enzminger and Ahlert, 1987).

Coal dust contamination of estuarine habitat can occur around coal loading and storage terminals and hence may impinge on vital habitat for juvenile chinook salmon (*Oncorhynchus tshawytscha*)(Levings and Riddell, 1992; Macdonald et al., 1988). Previous studies have shown that low tide use of habitats immediately surrounding coal ports on the British Columbia coast by juvenile Pacific salmon is extensive (Levings, 1985). Chinook salmon may be exposed to coal-dust-derived PAHs through contaminated water and via their food since chironomid larvae, a significant food source for juvenile salmon, have been shown to bioaccumulate PAHs in estuaries contaminated with coal byproducts (Dickmann et al., 1992). The construction and expansion of coal terminals has already exerted some pressure on the survival of some stocks of Pacific salmon since this activity has reduced the amount of suitable estuarine habitat available for juvenile salmonids (Levings, 1985; Levings and Riddell, 1992). The exposure of Pacific salmon to pollution is of some concern since it is one of the contributing factors implicated in the depletion of some chinook salmon stocks on the West Coast of Canada over the past decade (Rogers et al., 1988 and Rogers et al., 1989; Birtwell and Kruzynski, 1989; Servizi et al., 1993; Kruzynski et al., 1994).

The P450 system in vertebrates is responsible for the metabolism of a wide range of endogenous and xenobiotic compounds and consequently plays vital roles in the toxicology, metabolism, activation and excretion of drugs, pollutants and potentially carcinogenic compounds. Unlike mammals, in which two forms of CYP1A (P4501A) are found (CYP1A1 and CYP1A2) only one form, CYP1A1, is known in teleosts (Heilmann et al., 1988; Stegeman and Hahn, 1994), although this gene is duplicated in salmonids (Berndston and Chen, 1994). The induction of CYP1A1 has

been used as a sensitive marker for the exposure, and the responsiveness, of animals to organic pollutants including PAHs. In this study, hepatic CYP1A1 mRNA levels were quantitated using a recently developed, sensitive RT-cPCR assay (Campbell and Devlin, 1996) to determine the response of chinook salmon to coal dust exposure. In addition, it was noted that coal dust exposure caused increased hepatic expression of a second gene which was subsequently identified as ribosomal protein L5.

2. Materials and methods

2.1. Materials

Lab chemicals were purchased from commercial suppliers (Sigma Chemicals, St. Louis, MO). Enzymes were purchased from Gibco BRL (Burlington, Ont.) and Perkin Elmer Cetus (Norwalk, CT). Deoxynucleotides were purchased from Pharmacia Canada (Baie d'Urfe, Qué.). Sequenase PCR product sequencing kits were purchased from Amersham Life Sciences Inc., (IL, USA).

2.2. Experimental animals

Juvenile chinook salmon (mean weight (g) 23.49 ± 4.19, $n = 50$) were maintained outdoors in large (1500 L), circular, fibreglass tanks each supplied with an independent, constant flow of sea water (8.7 ± 0.5°C) until required for experiments. At the start of the experiment the fish were transferred to 200 L indoor fibreglass aquaria, also supplied with a constant flow of sea water. The fish were allowed to acclimate in the indoor aquaria with sea water flow-through for 6 days. Fish were fed once daily with extruded dry pellets (Moore-Clark, La Connor, WA). Fish were not fed 24 h before, or during, the exposure period.

2.3. Treatment and sampling method

For the 8 day exposure period a static system was utilized: the tanks were filled with sea water only or sea water containing either 60 mg L^{-1}, 200 mg L^{-1} or 500 mg L^{-1} coal dust. These concentrations were chosen since present regulations in British Columbia (Environment Canada) limit levels of suspended solids in coal terminal effluent to 60 mg L^{-1} however, consideration is presently being given to a request that allowable levels of suspended solids in coal terminal effluent be raised to 200 mg l^{-1}. The use of submersible pumps ensured that the water in each tank was constantly recirculated, and in-tank cooling coils equilibrated the temperature to 12°C. The tanks were covered to exclude light during the exposure period. The sea water, or sea water containing the appropriate concentration of coal dust, was replaced in each tank every 2 days. In addition, two control groups of fish were utilized: A 'negative' control group which were held in sea water only, and a 'positive' control group which were held in sea water only but were also anaesthe-

tized with MS-222 (100 mg L^{-1}, buffered with 100 mg L^{-1} sodium bicarbonate) and intraperitoneally injected at the start of the 8-day experiment with 50 mg kg^{-1} body weight β-naphthflavone (BNF) dissolved by sonication in corn oil (5 mg ml^{-1}). At the end of the exposure period eight fish were sampled from each treatment group. Fish were rapidly removed from the tanks and anaesthetized in water containing MS-222, weights and lengths were recorded, and the fish were then killed instantly with a sharp blow to the head. Livers were rapidly removed, cut into 8–10 pieces using fine scissors, and immediately placed in tubes containing 10 ml 95% ethanol. The alcohol-fixed livers were stored at room temperature prior to analysis. This method of sampling tissue (as an alternative to freezing of tissue) prior to mRNA analysis by RT-cPCR has been validated previously (see Campbell et al., 1996).

2.4. RNA isolation and RT-cPCR

Total RNA was isolated using the single step method of Chomczynski and Sacchi (1987), and the RT-cPCR analysis carried out using the method of Campbell and Devlin (1996).

2.5. Sequence analysis

The RT-PCR products obtained from coal dust exposed fish were electrophoretically separated in a 1% TAE agarose gel (Ultrapure, Gibco BRL), the 270 bp and 300 bp bands excised, and purified using the freeze/thaw method of Qian and Wilkinson (1991). The purified fragments were then amplified by PCR in 100 μl reaction volumes containing purified cDNA, PCR premix [50 mM KCl, 10 mM Tris (pH 8.3), 1.5 mM $MgCl_2$, 100 μg ml^{-1} gelatin; Gibco BRL), dNTPs (0.2 mM each)], 3′ primer 1A1-2 (50 pmol) and 5′ primer 1A1-3 (50 pmol) and Taq DNA polymerase (0.05 u μl^{-1}). After an initial denaturation of 95°C for 3 min, reactions were run for 30 cycles with a 60°C annealing cycle (1 min), 72°C extension cycle (2 min), and a 95°C denaturing cycle (1 min) in a Perkin Elmer Cetus DNA thermal cycler followed by a final incubation at 72°C for 10 min. Both purified fragments, the 270 bp CYP1A1 fragment, and the 300 bp second gene product (subsequently identified as rp L5) were then sequenced using a Sequenase PCR product sequencing kit (Amersham Life Science Inc., IL, USA).

2.6. Particle size and PAH analysis

Coal-dust contaminated sea water samples were collected from the coal-pile run-off collecting lagoon of a major coal terminal. Particle size analysis was accomplished by the Elzone 280PC method, i.e. electronic size analysis using a particle size counter following preparation of the sample in 1% sodium chloride, with a drop of Triton X-100 added as a dispersant, and subsequent sonication for 15 min and filtration through a 0.45 μm filter. The presence of coal dust derived PAHs in sea water were analyzed by GC/MS. The contaminated sea water from the collecting lagoon was analyzed for PAH content. The sea water contaminated with coal dust

which contained 100 mg L^{-1}total suspended solids (90% of coal particles <8 μm diameter) was allowed to settle for 24 h. The supernatant, which contained 36 mg L^{-1} of non-settleable solids, was solvent extracted for 16 h with 15% acetone in dichloromethane using a separatory funnel technique. The extracts were then concentrated on a rotary evaporator at 35°C, and the final sample held in 2.0 ml of toluene for analysis at 4°C. Samples were analyzed on a Hewlett-Packard Model 5988A gas chromatograph/mass spectrophotometer (GC/MS) operated in selected ion mode. The GC/MS was equipped with a 30 mm×0.25 mm fused silica DB-5 capillary column and a split/splitless injection port. The method used was based on the EPA Method 8270 SW-846 (BCRI, 1995). Coal dust was obtained from the same coal terminal for the exposure experiments—a subsample of this coal was added to sea water (100 mg L^{-1}) and analyzed for the presence of PAHs to ensure that the coal dust suspensions used in the exposure experiments, and the relative amounts of PAHs leached from these suspensions, were representative of the coal-contaminated sea water present in coal-terminal collecting lagoons.

2.7. Statistical analysis

The levels of CYP1A1 mRNA in the livers of the juvenile chinook were analysed by one-way analysis of variance (ANOVA; Sigmastat, Jandel Scientific, San Rafael, CA). Pairwise comparisons were conducted using Student-Newman-Keuls multiple comparison test or *t*-test. Where appropriate, log transformations were selected to improve the homogeniety of variance. The level of significance was derived from these analyses, although data are presented as arithmetic means ± SEM.

3. Results

3.1. Detection of CYP1A1 expression: RT-PCR

CYP1A1 mRNA isolated from the livers of juvenile chinook was converted to cDNA using primer 1A1-3, and the CYP1A1 mRNA levels were detected using RT-PCR. The 1A1-1/1A1-3 primer pair amplifies a 270 bp fragment from CYP1A1 mRNA—this band is strongly evident in the samples obtained from the BNF-treated fish (see Fig. 1, Lanes 3 and 4), but barely detectable in the samples from the negative control fish (Fig. 1, Lanes 1 and 2). This 270 bp band is also evident in the samples from the coal dust exposed fish, with the intensity of the band increasing between the samples taken from fish exposed to 200 mg L^{-1} (Fig. 1, Lanes 5 and 6) and 500 mg L^{-1} (Fig. 1, Lanes 7 and 8) of coal dust. In addition, a second gene product was amplified from the samples obtained from coal-dust-exposed fish, this is evidenced by the second band at 300 bp obtained following RT-PCR (Fig. 1, Lanes 5–8). The 300 bp band was faint in the 60 mg L^{-1} group but increasingly evident in the 200 mg L^{-1} and 500 mg L^{-1} group. This 300 bp fragment is not seen in either of the control groups (Fig. 1, Lanes 1–4).

Fig. 1. Photograph of an agarose gel showing an example of RT-PCR results using RNA isolated from the livers of two fish from each of the following treatment groups: Controls held in sea water only (Lanes 1 and 2); Positive controls injected with 50 mg kg^{-1} BNF (Lanes 3 and 4); Fish exposed to 200 mg L^{-1} coal dust (Lanes 5 and 6) and fish exposed to 500 mg L^{-1} coal dust (Lanes 7 and 8). The band at 270 bp indicates amplification from CYP1A1 mRNA whereas the band at 300 bp indicates amplification from ribosomal protein L5.

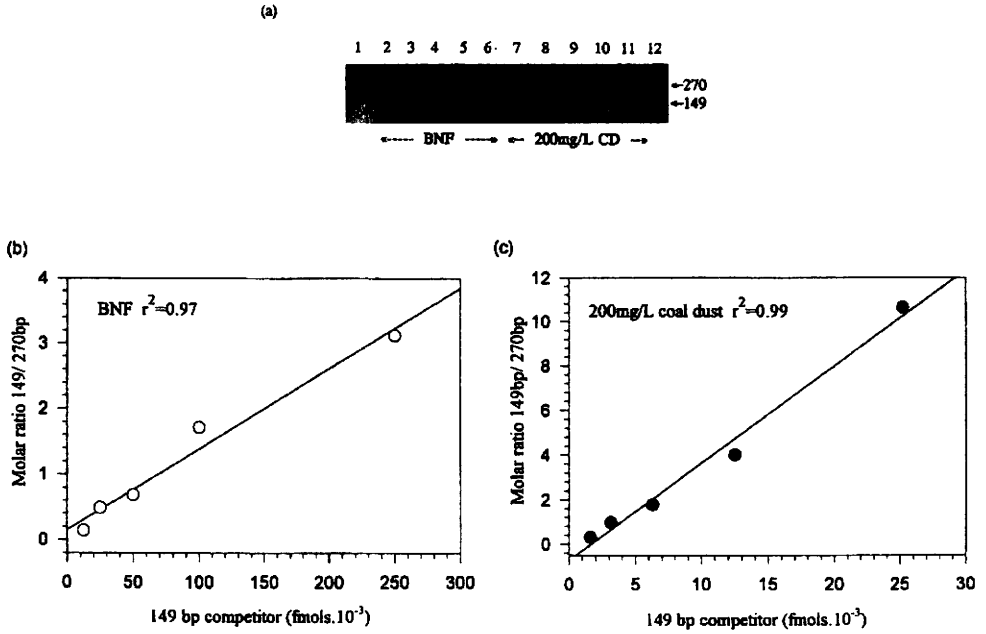

Fig. 2. Quantitation of CYP1A1 expression in liver samples from juvenile chinook salmon using RT-cPCR. An agarose gel (a) shows examples of RT-cPCR results obtained from a positive control fish injected with BNF (Lanes 2–6) and a fish exposed to 200 mg L^{-1} coal dust (Lanes 7–11). Following densitometric scanning of these RT-cPCR results the appropriate regressions were obtained for the BNF-treated fish (b) and the coal-dust exposed fish (c) and the CYP1A1 mRNA levels quantitated. Amplification from CYP1A1 cDNA results in the production of a 270 bp band, whereas amplification from the competitor results in the production of a 149 bp band.

3.2. Quantitation of CYP1A1 expression using RT-cPCR

The CYP1A1 mRNA levels in the liver samples were quantitated using the method of Campbell and Devlin (1996). Fig. 2 shows the results of two such RT-cPCR analyses; Lanes 2–6 of the gel shown in Fig. 2(a) show the results obtained using RNA from the liver of a BNF-treated fish, whereas Lanes 7–11 show the results obtained using RNA isolated from the liver of a fish exposed to 200 mg L^{-1} coal dust. For each analysis, five equal aliquots of RNA were prepared and the CYP1A1 mRNA within these samples was converted to cDNA. Two-fold dilutions of the 149 bp competitor DNA were added to each tube. The two fragments, the 270 bp fragment from the CYP1A1 cDNA and the control 149 bp fragment, then competed for amplification within the PCR. Fig. 2 shows that as the amount of competitor increases, the amount of CYP1A1 cDNA being amplified decreases; hence the ratio of the two bands changes between Lanes 2–6 and between Lanes 7–11. After densitometric scanning, the molar ratio of the competitive DNA to CYP1A1 cDNA products was regressed against the amount of competitor added. The results for the BNF-treated fish are shown in Fig. 2(b), and the results for the 200 mg L^{-1} coal dust exposed fish in Fig. 2(c). In these examples, the amount of CYP1A1 cDNA in the sample from the BNF-treated fish was 69.0 attomols μg^{-1} RNA (Fig. 2(b)) compared with 3.94 attomols μg^{-1} RNA Fig. 2(c)) for the sample from the coal dust (200 mg l^{-1}) exposed fish.

The 300 bp band seen in the results from RT-PCR analysis of RNA from coal dust exposed fish was found to be barely detectable or undetectable in the results of RT-cPCR analysis of the same samples (compare Fig. 1, Lanes 5–6 and Fig. 2, Lanes 7–11) suggesting it does not amplify effectively within the highly competitive conditions within the RT-cPCR.

The RT-cPCR assay was used to quantify CYP1A1 mRNA levels in the livers of juvenile chinook following the 8 day exposure period (Fig. 3). The mean levels of CYP1A1 mRNA in the livers of the control fish maintained in sea water only were

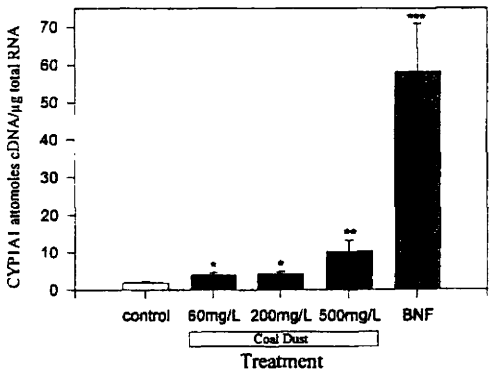

Fig. 3. Hepatic CYP1A1 mRNA levels in juvenile chinook salmon quantitated by RT-cPCR, asterisks indicate mean CYP1A1 levels which are significantly (*$P<0.05$, **$P<0.01$, ***$P<0.001$) different from control values.

```
(a)

PR1 TTC ACC ATC CCI CAC AGC AC→ --- --- --- --- --- --- --- --- ---
RAT TTA TCT ATC CCC CAT AGT ACC AAA CGA TTC CCT GGC TAT GAC TCT GAA
XEN TTA TCT ATT CCA CAC AGT ACC AAG CGT TTC CCT GGC TAT GAC TCT GAA
CHK --- --- --- --- --- --- --C AAA CGT TTC CCT GGG TAT GAT GCT GAG
    **. .*. **. **. **. **. *** **. **. *** *** **. *** **. .** **.

RAT AGC AAG GAA TTC AAT GCA GAG GTG CAC CGG AAG CAC ATC ATG GGT CAG
XEN AGC AAA GAA TTC AAT CCT GAG GTC CAC CGC AAG CAC ATC TTT GCC CAG
CHK AGC AAA GAA TTC AAT GCG GAG GTC CAC CGC AAG CAC ATC ATG GGC CAG
    *** **. *** *** *** .*. *** **. *** **. *** *** *** .*. *.. ***

RAT AAT GTG GCA GAC TAC ATG CGC TAC CTG ATG GAG GAG GAT GAG GAT GCG
XEN AAC GTT GCA GAG TAC ATG CGT CTT CTG ATG GAA GAA GAT GAA GAT GCG
CHK AAC GTT GCA GAG TAC ATG CGT TAC CTG ATG GAG GAA GAT GAA GAT GCA
    **. **. *** **. *** *** **. ... *** *** **. **. *** **. *** **.

RAT TAT AAG AAA CAG TTC TCT CAG TAC ATC AAG AAC AAC GTG ACT CCA GAC
XEN TAT AAA AAG CAG TTC TCT CAA TAC ATA AAG AAT GGT GTG ACT GCA GAC
CHK TAC AAA AAG CAG TTC TCC CGC TTC ATC AAG AAT GGC GTG GTT CCT GAC
    **. **. **. *** *** **. *.. *.* **. *** **. ... *** ..* .*. ***

RAT --- ATG GAG GAG ATG TAT AAG AAA GCT CAT GCT GCT ATC CGA GAG AAT
XEN CAG GTG GAA GAC CTG TAC AAA AAG GCT CAT GCA GGT ATT CGG GAG AAT
CHK AAG GTG GAA GAA ATG TAC AAA AAG GCT CAC GCT GGC ATT CGG GAG AAT
    ... .** **. **. .** **. **. **. *** **. **. *.. **. **. *** ***

RAT CCA GTC TAC GAG AAG AAG CCC AAG AGA GAA GTG AAG AAG AAG AGG TGG
XEN CCA GTG CAC GAA AAG AAA CCC AAG AAG GAA GTC AAA AAG AAG AGG TGG
CHK CCA CTG CAC GAA AAG AAA CCC AAG AAG GAA GTC AAG AAG AA- --- ---
PR2 --- --- --- --- --- --- --- --- --- --- --- --- --- ←G AGG TCT
    *** .*. .** **. *** **. *** *** *.. *** **. **. *** *** *** *..

RAT AAT CGT CCC AAA
XEN AAC CGT GCC AAA
CHK --- --- --- ---
PR2 TCC TCT TCC TGG
    ... ..*  ** ...

(b)
        180                     200                     220
RAT   KRFPGYDSESKEFNAEVHRKHIMGQNVADYMRYLMEEDEDAYKKQFSQYIKNNVTPD
XEN   KRFPGYDSESKEFNPEVHRKHIFAQNVAEYMRLLMEEDEDAYKKQFSQYIKNGVTAD
CHK   KRFPGYDAESKEFNAEVHRKHIFAQNVAEYMRYLMEEDEDAYKKQFSRFIKNGVVPD
      *******.******.*******..****.***.***************.****.*..*

          240                     260
RAT   -MEEMYKKAHAAIRENPVYEKKPKREVKK
XEN   QVEDLYKKAHAGIRENPVHEKKPKKEVKK
CHK   KVEEMYKKAHAGIRENPLHEKKPKKEVKK
       .*..******.*****..*****.****
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Fig. 4. A comparison of the (a) nucleotide sequences of a portion (between nucleotides 594 and 888) of rat L5 cDNA (Chan et al., 1987), Xenopus L5a cDNA (Wormington, 1989), and the 300 bp fragment isolated from coal dust exposed fish. The corresponding amino acid sequence alignment is also shown (b). The oligonucleotide primers 1A1-1 (PR1) and 1A1-3 (PR2) are also shown. Asterisks (*) show that a position in the alignment has been perfectly conserved, a period (.) shows that a position is well conserved (2/3 of sites). Dashes indicate spaces inserted for alignment purposes.

1.83 attomols μg^{-1} RNA. The mean CYP1A1 mRNA levels in the coal dust exposed fish were significantly elevated above control values (ANOVA; $P<0.001$) with RT-cPCR analysis revealing mean CYP1A1 mRNA levels of 3.9 attomols μg^{-1} RNA (Student-Newman-Keuls; $P<0.05$), 4.23 attomols μg^{-1} RNA (Student-Newman-Keuls; $P<0.05$) and 10.28 attomols μg^{-1} RNA (Student-Newman-Keuls; $P<0.01$) for the 60 mg L^{-1}, 200 mg L^{-1} and 500 mg L^{-1} coal dust

```
1A1-1 --------------------->
TROUT TTCACCATCC CACACTGCAC AGTCAAGGAT ACATCGCTCA ATGGCTACTT
CHK                         AGTCAAGGAT ACATCTCCTC ATGGCTGCTT
                            ********** ***** *    ****** ***

TROUT CATTCCCAAG GACACCTGTG TCTTCATCAA CCAGTGGCAG GTCAACCATG
CHK   CATTCCCAAG GACACCTGTT TCTTCATCAA CCAGTGGCAG GTCAACCATG
      ********** *********  ********** ********** **********

TROUT ACCCGGAGCT GTGGAAGGAG CCTTCTTCAT TCAACCCTGA CCGTTTCCTG
CHK   ACCCGGAGCT GTGGAAGGAG CCTTCTTTAT TCAACCCTGA CCGTTTCCTG
      ********** ********** ******* ** ********** **********

TROUT AGTGCTGATG GCACAGAACT CAACAAATTG GAGGGGGAGA AGGTGCTCGT
CHK   AGTGCTGATG GTACAGAACT CAACAAGCTG GAGGGGGAGA AAGTGCTCGT
      ********** * ******** ******  ** ********** * ********

TROUT ATTTGGCATG GGCAAGCGCC GCTGCATAGG TGAGGCCATC GGACGCAATG
CHK   ATTCGGGATG GGCAAGCGCC GCAGCATCGG TGAGGCCATC GGACGCAAC
      *** ** *** ********** ** **** ** ********** ********
                                                          <-1A1-3
                                                          (cont.)
TROUT AGGTCTACCT CTTCTTGG
CHK
      <------------------1A1-3
```

Fig. 5. Comparison of the nucleotide sequence of a portion (between nucleotides 1164 and 1432) of trout CYP1A1 cDNA (Heilmann et al., 1988) and the 270 bp fragment isolated from coal dust exposed fish. Asterisks (*) show that a position in the alignment has been perfectly conserved.

exposures, respectively. The mean levels of CYP1A1 mRNA in the BNF-treated fish were 58.1 attomols μg^{-1} RNA and hence were very significantly elevated above control values (t-test; $P < 0.001$).

3.3. Sequence analysis

The additional 300 bp fragment obtained by RT-PCR analysis of RNA from coal-dust-exposed fish was sequenced. A Genbank search revealed that the nucleotide sequence of the 300 bp fragment had very high homology with the nucleotide sequences of ribosomal protein L5 from other vertebrates including rat rp L5 (Accession # M17419), *Xenopus laevis* (both L5a, Accession # M29032 and L5b, Accession # M29033), chicken rp L5 (Accession # X57016) and human rp L5 (Accession # U14966). A comparison of the nucleotide sequences, specifically the region containing the putative RNA binding domain, of rat L5, *Xenopus* ribosomal protein L5a and the 300 bp fragment isolated from coal dust exposed fish is shown in Fig. 4(a). This figure illustrates an 87% similarity between the 300 bp fragment (excluding primer sequences) and *Xenopus* L5a, and an 80% similarity with rat L5. Comparison of the deduced amino acid sequence for the 300 bp fragment with the protein sequences of rat L5 (85% similar) and *Xenopus* L5a (91% similar) is shown in Fig. 4(b) and provides further evidence that the 300 bp fragment is indeed amplification of a region of chinook salmon L5 mRNA, and indicates that this region of the protein has been very well conserved throughout evolution. The 270 bp fragment amplified from coal dust exposed fish was also sequenced and confirmed to be amplification from chinook salmon CYP1A1 cDNA with 94% similarity with rainbow trout CYP1A1 (Heilmann et al., 1988) (see Fig. 5).

Table 1
Polynuclear aromatic hydrocarbons (PAHs) present in coal dust contaminated sea water. The coal dust sample analyzed was obtained from the coal pile run-off collecting lagoon of a major coal terminal and contained 100 mg L^{-1} total suspended solids, 36 mg L^{-1} non-settleable solids (NSS) and 5577 ng L^{-1} total PAHs. Coal dust obtained from the same terminal was used in the exposure experiments and, for comparative purposes, 100 mg L^{-1} of this sample was placed in sea water and was found to yield 51 mg L^{-1} of non-settleable solids and 4906 ng L^{-1} total PAHs

Compound	Limit of quantitation (ng L^{-1})	Blank (ng L^{-1})	Coal dust leachate (ng L^{-1})
Low molecular weight PHAs			
Naphthalene	1.0	nd	408
Acenaphthylene	1.0	nd	nd
Acenaphthene	1.0	nd	nd
Fluorene	1.0	nd	280
Phenanthrene	1.0	nd	2037
Anthracene	1.01	nd	143
Total LMW PAHs			2868
High molecular weight PAHs			
Fluoranthrene	1.0	nd	353
Pyrene	1.0	nd	373
Benzo(a)anthracene	1.0	nd	285
Chrysene/Triphenylene	1.0	nd	466
Benzo(b/k)fluoranthrene	1.0	nd	417
Benzo(a)pyrene	1.0	nd	233
Indeno(1,2,3-cd)pyrene	1.0	nd	134
Benzo(g,h,i)perylene	1.0	nd	292
Dibenzo(a,h)anthracene	1.0	nd	156
Total HMW PAHS			2709
Total PAHS			*5577*

nd: not detected.

3.4. PAH analysis

The analysis of total PAHs leached from coal dust into sea water, in a sample collected from a coal terminal collecting lagoon which had been allowed to settle for 24 h (100 mg L^{-1} total suspended solids; 36 mg L^{-1} non-settleable solids), revealed the presence of 5577 ng L^{-1} total PAHs with 2868 ng L^{-1} total low molecular weight PAHs and 2709 ng L^{-1} total high molecular weight PAHs. The PAH analysis is presented in detail in Table 1 and indicates that procarcinogens including benzo(a)pyrene, dibenzo(a,h)anthracene, indeno(1,2,3-*cd*)pyrene and benzo(g,h,i)-perylene are present in coal dust contaminated sea water that is eventually released in coal terminal effluent. To ensure that the method used to prepare the coal dust suspensions for the exposures resulted in suspensions that were representative of the coal-dust contaminated sea water found in coal terminal collecting lagoons, the coal used in the exposure experiments was added to sea water at 100 mg L^{-1} and

analyzed for total PAHs. It was found that 100 mg L^{-1} of the coal dust used in the exposure experiments yielded 51 mg L^{-1} non-settleable solids and 4706 mg L^{-1} total PAHs when added to sea water and allowed a 24 h settling period. Hence the coal dust samples suspended in sea water and used to expose the fish were similar to the coal suspensions found in the coal terminal collecting lagoon, i.e. for the same level of coal dust, a similar level of non-settleable solids and total PAHs was found in both types of sample.

4. Discussion

The results of this study directly demonstrate that juvenile chinook salmon exposed to coal dust exhibit increased hepatic expression of both L5 and CYP1A1, genes which encode proteins which play crucial roles in cellular metabolism. This is the first study, to our knowledge, to partially characterize L5 from a teleost and to show that L5 expression can be altered by contaminant exposure.

In this study, mean hepatic CYP1A1 mRNA levels increased up to 6-fold following the 8-day exposure of juvenile salmon to the highest concentration of coal dust (500 mg L^{-1}). Previous studies have indicated similar fold increases (3-fold to 8-fold) in CYP1A1-associated enzyme activity in fish exposed to refinery effluent containing PAHs (Imber et al., 1995), and in fish sampled from a coal tar contaminated estuary (Vignier et al., 1994). Hence the level of CYP1A1 induction observed in this study corresponds well with the levels of induction noted previously in fish exposed to environmentally relevant doses of PAHs derived from coal byproducts. Chemical analysis of the PAHs which leach from coal dust into sea water revealed the presence of procarcinogens e.g. benzo(*a*)pyrene and dibenzo(a,h)anthracene which can be converted by P4501A1 into active carcinogens (Varanasi et al., 1986, 1987; Stegeman and Hahn, 1994). The induction of hepatic CYP1A1 in juvenile chinook living in coal-contaminated estuaries could therefore result in the production of mutagenic metabolites and hence have profound physiological consequences (Varanasi et al., 1989; Stein et al., 1990). These results are, however, in contrast to the information available on mammals in which coal dust exposure has not been shown to induce CYP1A1 in either liver or lung despite prolonged exposure (Rabovsky et al., 1984). This discrepancy could arise from the fact that teleosts may be more sensitive than mammals to some CYP1A1 inducers, e.g. 2,3,7,8-tetrachlorodibenzofuran, (Hahn and Stegeman, 1994) and this may also be true for some of the CYP1A1-inducing components in coal dust. It is also possible that CYP1A1-inducing components were extracted from the coal dust by the sea water and hence were more bioavailable in the present study.

The results of this study also indicated that coal dust exposure caused an increase in hepatic L5 gene expression, although the physiological consequences of this are presently unclear. It is well established in other vertebrate species, including mammals and *Xenopus laevis*, that L5 plays a vital role in ribosome biogenesis (Mager, 1988; Steitz et al., 1988; Wormington, 1989).

The region of L5 amplified by RT-PCR from coal dust exposed fish contained the

sequence encoding the putative RNA binding domain of this protein (Wormington, 1989). It is interesting to note that L5 does not share any sequence similarities to the highly conserved RNA recognition motif (RRM), which has been identified in a large number of RNA-binding proteins (Bandziulis et al., 1989; Kenan et al., 1991), indicating that alternative structures contribute to its specific interaction with 5S rRNA.

Ribosomal constituents, 3–4 rRNAs and 60–80 ribosomal proteins, are assembled in a precise and efficient manner, and the rate of ribosome formation is accurately tuned to the cellular need for protein biosyntheic capacity (Mager, 1988). Not only must the appearance of various ribosomal components be coordinated on the transcriptional level, but those that are not synthesized in the nucleolus (5S and ribosomal proteins) must become specifically concentrated there. There is much evidence that L5 specifically binds 5S rRNA and acts as a nuclear shuttling protein (Guddat et al., 1990). It is interesting to note that a direct inhibitory effect of coal dust on protein synthesis was noted by Lee et al. (1994) however, despite continued exposure, this inhibitory effect gradually disappeared. In this study, an upregulation of L5 expression following exposure to coal dust may indicate a compensatory response to these inhibitory effects on protein synthesis, since increased L5 expression may indicate enhanced or restored cellular protein biosynthesizing capacity.

The expression of ribosomal proteins, including L5, has also been shown in mammals to be senescence-regulated (Seshadri et al., 1993) and this down-regulation in senescent cells, coupled with the fact that increased expression of ribosomal proteins is observed in hepatocellular carcinomas (Frigerio et al., 1995), is thought to reflect an altered state of differentiation (Seshadri et al., 1993). These observations suggest that overexpression of a subset of ribosomal proteins is associated with cell growth and proliferation.

The mechanisms underlying the increased expression of L5 in coal dust exposed fish remains to be established. In fact, relatively little is known of the mechanisms that control vertebrate L5 gene expression. In contrast, the mechanisms by which CYP1A1 expression is controlled have been studied extensively. CYP1A1 gene expression can be induced by PAHs through both the well defined Ah receptor-dependent pathway (Whitlock, 1990; Okey, 1990) and the more recently elucidated and much less well defined AhR-independent pathway (Raha et al., 1995). The AhR-dependent pathway involves the binding of certain organic compounds (e.g. dioxin) to the Ah receptor complex (Whitlock, 1990; Neuhold et al., 1989; Okey, 1990; Wen et al., 1990; Reyes et al., 1992). The AhR-independent mechanisms are thought to involve the activation of a 33-kDal protein, recently identified as glycine *N*-methyltransferase (GNMT) (Raha et al., 1995). A nuclear protein of approximately the same size has also been shown to bind to the promotor regions of L5 and is thought to play a role in transcriptional regulation of this gene (Kenmochi and Tanaka, 1993). Whether a PAH-binding protein, such as the AhR or GNMT, could simultaneously influence the expression of both CYP1A1 and L5 remains to be established.

It is clear that coal dust has effects on the expression of several genes in juvenile chinook salmon. It is also possible that these sublethal effects may become manifest

at higher levels of biological organization. Coal byproducts and specific components found in coal dust leachate have been shown to reduce the growth rate of trout (Herbert and Richards, 1963), cause oocyte atresia and reduced ovarian growth in crayfish (Sarojini et al., 1995) and to promote DNA adduct formation and hepatocellular carcinoma in fish (Hendricks et al., 1985; Varanasi et al., 1986; Stein et al., 1990). It is known that CYP1A1 plays a role in the activation of procarcinogens and the formation of DNA adducts (Varanasi et al., 1986, 1989; Okey, 1990). However, to a large extent the mechanisms underlying the physiological disruptions observed in animals living in polluted environments is unknown. It is likely that these physiological effects are mediated through a number of mechanisms including the altered expression of several genes, only one of which is CYP1A1 (Gaido and Maness, 1994). Since L5 plays such a crucial role in ribosome biogenesis and cellular metabolism it is certainly plausible that the altered expression of this gene by contaminant exposure may ultimately have physiological consequences. The results of this study also indicate that alterations in the expression of L5 may potentially be used as a biomarker of specific PAH exposure in teleosts.

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Aspects of the Exxon Valdez oil spill—a forensic study and a toxics controversy

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ABSTRACT

After the *Exxon Valdez* oil spill in Prince William Sound in March, 1989, much work has been done to track the spilled oil and study its fate and its affect on the environment. Our studies involved developing and applying methods to identify and track the spilled *Exxon Valdez* oil (EVO) as it weathered, as well as to differentiate it from other petrogenic hydrocarbon input sources in PWS. Application of these methods to the study area has yielded two important findings. First, it was discovered that not all the oil or tar on the beaches was EVO. Instead, tarry residues of oil from the Monterey Formation, Southern California, also were prominent on some of the Prince William Sound beaches along with EVO. Monterey Formation oil was used in the early development of Alaska, before the discovery of North Slope Crude, and most likely was disbursed throughout the Sound from the port of Old Valdez in the Great Alaskan Earthquake of 1964. The second study also involves differentiating petrogenic sources. A third petroleum input source to PWS, namely natural oil seeps in the Gulf of Alaska, has been claimed by others to contribute a substantial, and potentially toxic, polycyclic aromatic hydrocarbon (PAH) background to the Prince William Sound benthic sediments. If this claim is true, it would have the effect of mitigating the long-term effects of the oil spill. Our studies and cooperative work with NOAA provide evidence that it is coal and not oil that contributes this PAH background. Unlike the case with oil, PAHs in coal would not be bioavailable and thus would be considered contaminants but not pollutants capable of causing adverse effects on exposed biota. Resolution of the source of the PAHs is, therefore, an important environmental issue.

This work in identifying petroleum sources, both natural and anthropogenic, has a great deal of transfer value to other estuarine systems. The geochemical information obtained in Prince William Sound can be extrapolated and applied to the study of oil residues on the California coastline and in San Francisco Bay. Current studies are attempting to correlate or differentiate spills in these two areas and sort out the origin of the petroleum input sources.

INTRODUCTION

On 24 March 1989, the T/V *Exxon Valdez* grounded on Bligh Reef in Prince William Sound (PWS), Alaska (Fig. 1), causing the largest oil spill in U.S. history. About 41 million liters (11 million gals = 258,000 bbls) of North Slope crude oil spilled into the water and eventually reached about 16% (500 km) of the shorelines of the sound. The oil spill was an environmental and visual disaster as crude oil spread throughout the sound and washed up on the pristine beaches. Massive efforts were undertaken to clean up the oil-contaminated beaches and remove oil from the water. Over the years many studies have been undertaken to document the effects of the spill. Some studies analyzed the biological effects (for example, Maki, 1991, and Rice and others, 1996); others focused on tracking the spilled oil and studying its distribution and fate in the environment (for example, Page and others, 1995; Bence and others, 1996; O'Clair and others, 1996; Short and others, 1996; Short and Heintz, 1997). Starting two months after the spill and continuing through 1997, the U.S. Geological Survey conducted a series of investigations to look at the geological fate of the spilled oil (Kvenvolden and others, 1993; Hostettler and Kvenvolden, 1994; Carlson and others, 1997). Various aspects of the oil spill aftermath have been pursued, with the focus particularly on two areas: a forensic study to determine the source of

oil(s) present on the PWS beaches, and a study to help determine the source of background hydrocarbons, particularly polycyclic aromatic hydrocarbons (PAHs), many

PAH constituents, PAHs from oil are bioavailable and capable of causing adverse effects to exposed biota, whereas PAHs from coal are very tightly bound within the coal matrix and generally not bioavailable (Chapman and others, 1996). If oil from natural seeps were a chronic PAH source to PWS, then biota in the marine ecosystem would have already adapted to these hydrocarbons. Long-term effects of an oil spill would, therefore, be mitigated, and once the catastrophic impacts immediately after the spill had passed, there would be no further impact attributable to the spill oil. On the other hand, if the PAH are derived from coal, there is no adaptive benefit to biota with respect to PAH input from anthropogenic sources, and long-term environmental effects of the oil spill can be more readily evaluated.

In both of these studies, the identification and differentiation of sources of hydrocarbons in a sedimentary environment is critical. A variety of molecular and isotopic techniques can be applied. For individual oils from a single source, carbon isotopic analysis of the whole oil can be a defining characteristic, even when the oil is in a weathered state. Another analytical approach is individual component analysis. Oils, tars, and sediments are very complex mixtures that may contain a wide variety of organic constituents. This paper will focus on petrogenic hydrocarbons. In sediments these organic compounds can derive from very diverse sources, both natural and anthropogenic. In addition, there is broad overlap among specific compounds that might originate from any of these sources. Finally, the sedimentary system is generally dynamic, in that its components are subject to change through the processes of diagenesis and weathering.

Weathering adds a further dimension to the problem of identifying hydrocarbon input in the environment. Weathering can involve water-washing, chemical degradation (e.g., photo-oxidation), microbial degradation, solubilization, evaporation, mechanical redistribution, and other such processes (Hunt, 1996). Thus, in addition to the high degree of complexity of sedimentary constituents, the system is in a constant state of flux because these components are continually exposed to weathering. Furthermore, weathering effects can vary. Petroleum PAHs, for example, have been noted to be more subject to weathering than those in coal (Short and others, 1999) and those from pyrogenic sources (Bouloubassi and Saliot, 1993) due to differences in matrix effects and particle associations. Weathering of PAH in petroleum has been shown to follow a progression in the number of rings, in which compounds like naphthalene with two fused aromatic rings are degraded faster than three-ring compounds such as phenanthrene, with the rate of degradation being 2>3>4>5 aromatic rings. In addition, parent PAHs degrade faster than their alkylated homologs, and C1>C2>C3>C4 (Volkman and others, 1984).

There are several approaches to identifying sources of hydrocarbons that are subject to weathering. The first approach, referred to here as *weathering invariant*, involves identifying a specific analyte or group of analytes, either not subject to weathering or not yet weathered, which is known to come from a given source. The use of ratios of aliphatic hopane and sterane biomarkers to differentiate specific crude oils in PWS, Alaska, is one example of this approach (Kvenvolden and others, 1995). Biomarkers, which are molecular fossils, are highly refractory and have been shown to resist postdepositional alteration in the environment until extreme weathering has occurred (Volkman and others, 1984). A second approach, *weathering variant*, considers the weathered system and mathematically extrapolates backward from the current levels of constituents to the original concentrations of the pure source material at the time of deposition. This approach was used by Short and Heintz (1997) in their work in following EVO as it weathered in the environment. A third approach, *weathering covariant*, utilizes ratios of analytes assumed to weather at the same rate. This approach has been used by Page and others (1995) and Douglas and others (1996) who utilized ratios of alkyl dibenzothiophenes to alkyl phenanthrenes in tracking EVO in PWS and differentiating it from background aromatic hydrocarbons. All three approaches provide powerful tools for establishing hydrocarbon sources. However, of the three approaches, *weathering invariant* may be the most robust, because it utilizes constituents that have not yet been altered in the environment and hence carry the chemical signature of the original source most reliably.

Our study also introduced a new parameter, the PAH refractory index (RI), to apply to correlations of petrogenic systems. The RI is a ratio of specific members of two classes of the most refractory PAH compounds present in crude oils, namely triaromatic steranes (T) and monomethyl chrysenes (C) (T/C, see Fig. 2 and Table 1). Triaromatic steranes are perhaps the most refractory components of oil; they are present even when almost no traces of other PAHs are resolvable through analysis by gas chromatography-mass spectrometry (GC/MS) (for example, Hostettler and Kvenvolden, 1994). They also persist in sediments as some of the last of the resolvable PAH components of weathered petroleum contamination (Killops and Howell, 1988; Hostettler and others, 1992). In general, however, triaromatic steranes are either absent or less common in coal than in oil, (Lu and Kaplan, 1992) due to differences in formation pathways between crude oil and coal. Chrysene and its alkylated homologs are also highly refractory. As the highest molecular weight PAH family typically present in an analytical profile of petroleum (for example, Page and others, 1995), the chrysenes are, therefore, among the most refractory of the regular PAHs. Alkylated chrysenes are common in both crude oils and coals (Barrick and others, 1984). Monomethyl chrysene, rather than chrysene, was chosen for the refractory index because chrysene can have a combustion as well as a petroleum source. The refractory index, then, falls into the *weathering invariant* category, like hopane and sterane biomarkers, and, as such, should be a useful parameter for source correlation. It has been shown to work well in differentiating specific oil families in PWS, specifically EVO, California (Monterey) oil, and Katalla seep oil, but to give values close to 0 for several Alaska coals (Hostettler and others, 1999).

METHODS

Sample collection. Samples and sampling procedures are described in Carlson and others (1997) and Short and others (1999). Samples for this study include EVO and other oils and tars from PWS beaches, a composite sample of unweathered Katalla oil, a surface seep sample of exposed Katalla oil, offshore sediments from the northern Gulf of Alaska and PWS, and terrestrial riparian sediment samples from the Duktoth, Copper, and Bering Rivers. Coal samples were collected from outcrops in the Bering River coal field and from the beach at Katalla.

Sample analysis. Bulk carbon isotopic analysis was done on the tars and oils from the beaches as described in Carlson and others (1997). Individual component analysis on all samples also is described in the same reference. Briefly, this analysis consisted of air drying the sediment samples and grinding to pass a 32 mesh screen, or, in the case of the tars, weighing out an aliquot, extracting with or dissolving in dichloromethane, treating with HCl-activated copper to remove sulfur, and fractionating by alumina/silica gel column chromatography into a hexane fraction, containing aliphatic hydrocarbons, and a 30% benzene- or dichloromethane-in-hexane fraction containing PAHs and other aromatic compounds. These fractions were then analyzed by GC/MS in the full-scan and selected-ion-monitoring (SIM) modes. Biomarker parameters used in the identification of the various petrogenic sources were calculated and are discussed elsewhere (Kvenvolden and others, 1993, 1995; Carlson and others, 1997). Full-scan GC/MS analysis of the aromatic fraction was used for calculation of the refractory index and a semi-quantitative comparison of naphthalenes, phenanthrenes, dibenzothiophenes, chrysenes, and triaromatic steranes. The refractory index was calculated

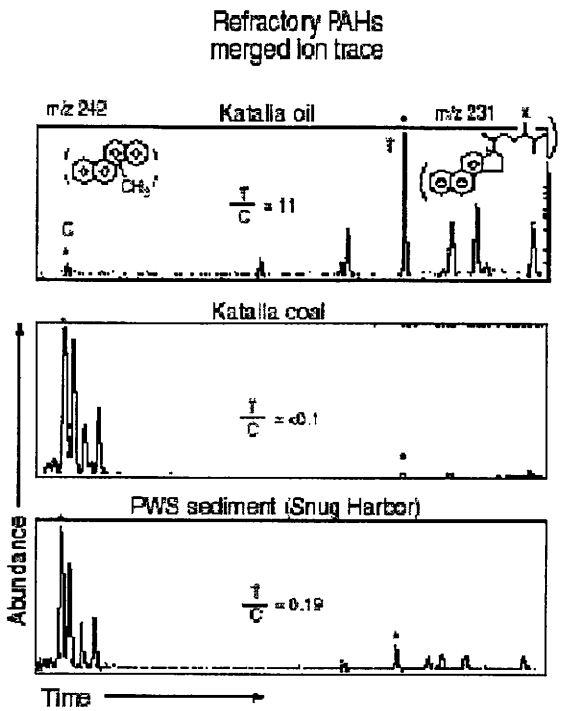
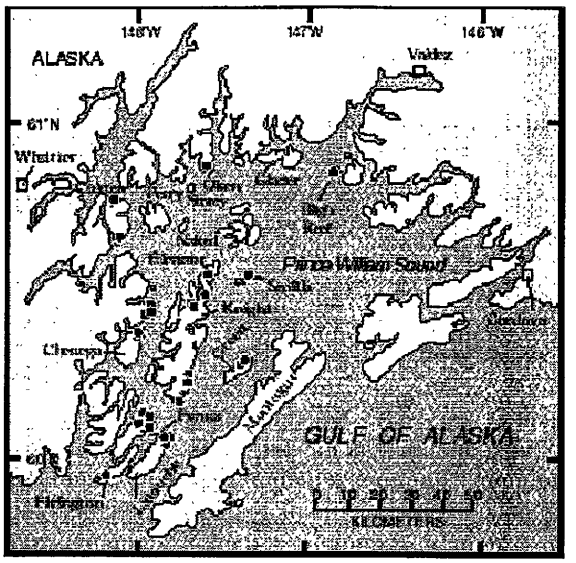
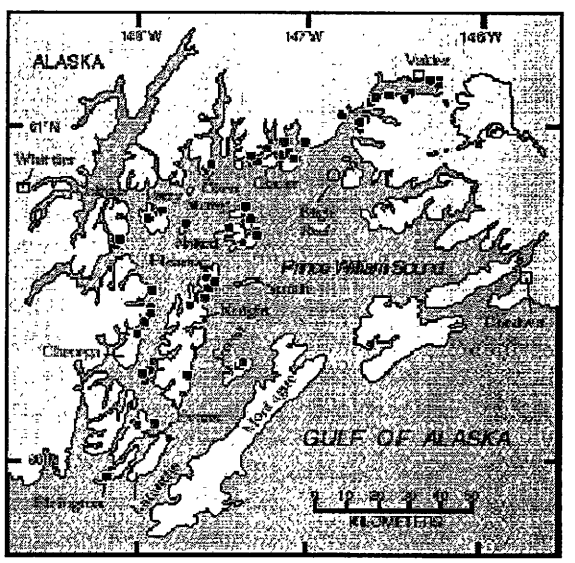


Figure 2. Refractory index ratio: GC/MS extracted ion profiles from the aromatic fraction of Katalla seep oil, Katalla coal, and a typical PWS benthic sediment. The merged trace utilizes m/z 231 for the suite of C_{26}-C_{28} triaromatic steranes (X = H, CH_3, C_2H_5) and m/z 242 for methyl chrysenes. The major peak (*) for each suite was used to calculate the refractory index.

from the ratio of the peak heights of the major peak of the C_{26} to C_{28} triaromatic sterane suite (m/z 231 extracted ion chromatogram, peak identified as consisting of the $C_{26}R$ and $C_{27}S$ epimers) to the major peak of the monomethyl chrysene suite (m/z 242 extracted ion chromatogram, first and dominant peak), as shown in Figure 2. Values for calculated parameters are given in Table 1.



A. Prince William Sound showing locations where residues of *Exxon Valdez* oil have been found.



B. Prince William Sound showing locations of tar balls related to Monterey Formation (Miocene) source rocks of California.

Figure 3. Locations of oil and tar balls.

RESULTS AND DISCUSSION

Forensic study: In the analysis of tar ball and oil samples found on the beaches of PWS it was found that the beached oils and tarballs had two distinctly different chemical signatures. Figure 3 shows the distribution of the two different families of tarry residues of these oils in our sample sets. The parameters that best identified

and correlated these tars and oil residues were carbon isotope compositions ($\delta^{13}C_{PDB}$) of the whole-oil samples and selected terpene biomarker ratios. Of particular value is the biomarker ratio [C_{26}-tricyclic terpane (S?+R?)]/C_{24}-tetracyclic terpane, called the Triplet (T) because of how it appears on m/z 191 mass chromatograms (Fig. 4). This parameter was first noticed in an earlier study of North Slope

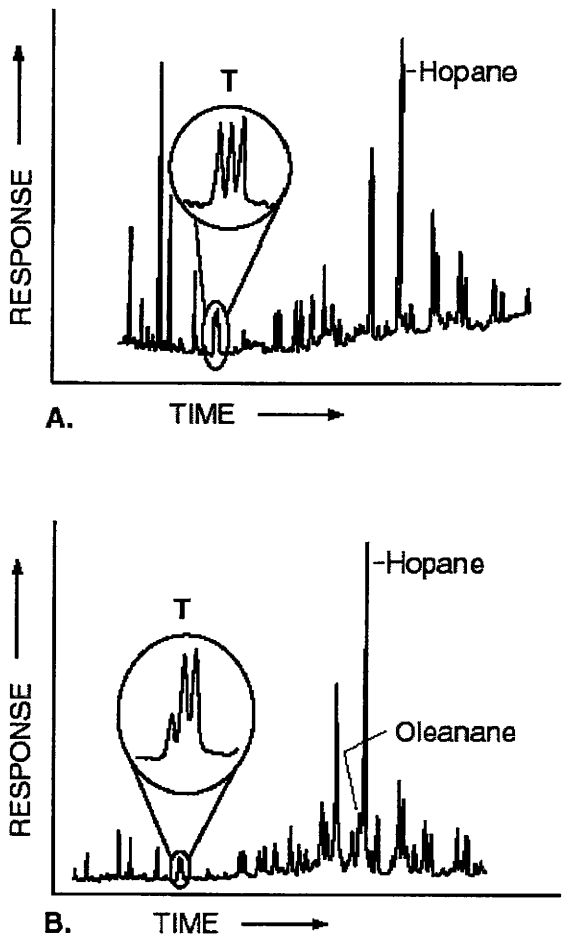


Figure 4. m/z 191 mass chromatograms showing the peaks used for the Triplet ratio and those used for the Oleanane index.

crude oils (Kvenvolden and others, 1985). Studies on PWS show that T = 2.0 ±0.1 in 25 samples of EVO (n=1) and residues (n=24) (Fig. 5A); the $\delta^{13}C$ values for 28 samples of EVO (n=1) and residues (n=27) are –29.4 ±0.1 ‰ (Fig. 5B). These parameters clearly correlate the EVO and its residues. In contrast, T = 5.1 ±0.5 in 39 samples of tar balls (Fig. 5A), and the $\delta^{13}C$ values for 61 samples of tar balls are –23.7 ±-0.2 ‰ (Fig. 5B). These values, particularly the distinctively heavy $\delta^{13}C$, are within the range of oil products sourced from the Monterey Formation of southern California (Curiale and others, 1985).

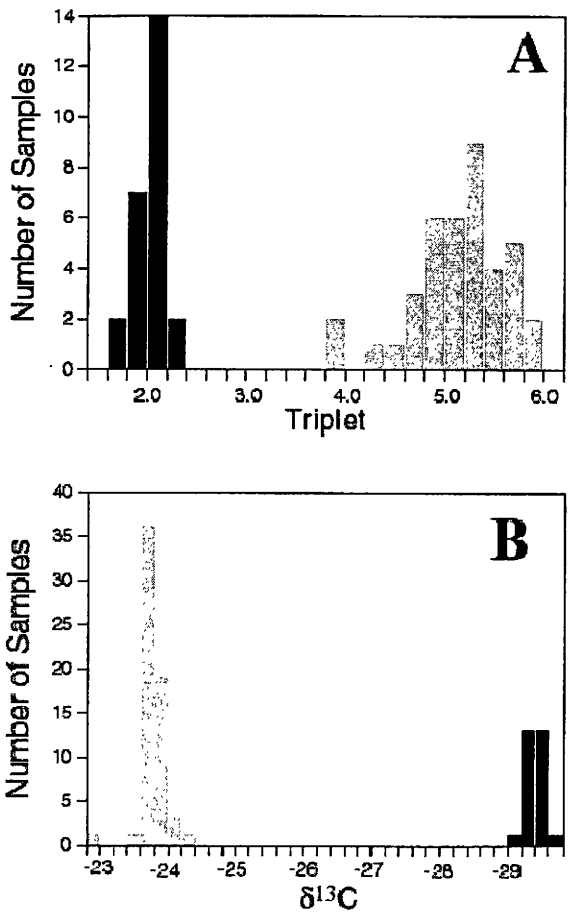


Figure 5. Triplet biomarker and stable carbon isotope value distributions for oils and tars found on PWS beaches.

In addition to compiling evidence that the original source of the second oil was indeed the Monterey Formation in southern California, a plausible explanation for its widespread distribution in PWS was necessary. The waters of PWS flow counterclockwise through the sound and out to the southwest, driven by the Alaska Coastal Current. Therefore, Valdez, the northernmost point in PWS, is an obvious possible origination point for these oils (Fig 3B). In 1964, 25 years before the EVO spill and also on Good Friday, the Great Alaskan Earthquake

occurred. Huge storage tanks of Monterey Formation California oil, which was used in the development of Alaska before North Slope Crude or Cook Inlet oil was discovered, located in the port of Old Valdez, were ruptured and destroyed in this earthquake. However, in the aftermath of the chaos caused by the 9.1 magnitude earthquake, the fate of the California oil was not documented. Kvenvolden and others (1995) and Carlson and others (1997) have suggested that this oil was disbursed throughout PWS after the earthquake and that it is the tarry residues of this oil that is retained in the recent geological record, often in the same locations as the EVO.

Background hydrocarbons in benthic sediments. Several approaches have been used to address the question of the source of the PAH background to the PWS sediments. Some of the geochemical parameters are listed in Table 1 and discussed below. Exxon's long-held claim that natural oil seeps from the Katalla/Yakataga region of the Gulf of Alaska contribute this background is based on three major geochemical correlations: the correspondance of the ratios of C2D/C2P (D = dibenzothiophene and P = phenanthrene), the presence of oleanane, a C_{30} biomarker commonly found in oils of the late Cretaceous or Tertiary and not present in EVO, and the similarity of PAH fingerprints given by the background PAH in benthic sediments and the water/suspended sediment PAH from seep streams (Bence and others, 1996). Coal is discounted as a potential source primarily due to a reported lack of coal deposits in the drainage areas of streams east of the Bering River.

An alternate source suggested by Short and others (1999) acknowledges the above-mentioned similarities, but shows that the alkylated Db/Ph ratios as well as the presence of oleanane (shown in Table 1 as an oleane/hopane index) fall within the same range for coal as well as seep oil and benthic sediment samples. These ratios are therefore inadequate discriminants. As for the purported dearth of coal sources in the area, references in Short and others (1999) show that the literature details extensive coal deposits along this reach of the Gulf of Alaska coast.

Table 1. Ranges of parameter values. See text for parameter definitions.

Parameters	PWS Background	Gulf of Alaska			
	Marine sediment (n = 6 - 10)	Marine sediment (n = 6)	Coal (n = 3)	Onshore (n = 8)	Seep Oil f = fresh; w = weathered
C2D/C2P[a]	0.11 - 0.21	0.22 – 0.25	0.17 – 0.59	0.07 – 0.31	0.18(f,w)
Oleanane Index[a]	0.19 – 0.37	0.13 – 0.14	0.08 – 0.12	0.01 – 0.22	0.12(f,w)
MSE (Kat)[b]	1.68 – 4.41	1.55 – 1.82	3.25 – 7.20	2.07 – 8.46	0.05(w)
MSE (CH)[b]	0.19 – 0.54	0.20 – 0.30	0.60 – 1.14	0.86 – 1.77	1.21(w) 2.68 (f)
RI (T/C)[b]	0 – 0.2	Š 0.1	0 - 0.02	0(most)–0.3	11(w), 13(f)

[a] Parameter used by Bence and others (1996) as evidence of naturally occurring oil seep contribution to benthic sediments

[b] Parameter used by Short and others (1999) as evidence of coal contribution to benthic sediments

Whereas Bence and others (1996) claim that there are numerous natural oil seeps in the same region and assume these seeps have sufficient outflow to deliver at least 360 to 1200 tons of petroleum per year in order to account for the loadings of PAH in PWS, Short and others (1999) claim that the seeps are small, with low productivity, and limited accessibility to Gulf of Alaska waters (for example, no oil slicks documented from these seeps into the Gulf waters, and no published reports of offshore seeps). However, coal particles eroded by natural processes would be widespread and accessible to transport to PWS. Indeed, finely divided coal particles can be seen in the intertidal area and all along the beach at Katalla. Short and others (1999) then examined other geochemical parameters. They also considered the PAH fingerprints of the oils, coals, and sediments and looked more closely at the weathering characteristics of the PAH in the seep oil and in benthic sediments. Using pattern similarity analysis, they calculated two parameters of the mean square error (MSE) of logarithmically transformed proportions of the 14 most persistent PAHs in the respective samples (Table 1). The first parameter, MSE(CH), compared patterns in samples with patterns characteristic of intertidal sediments at Constantine Harbor (CH), PWS. This site was chosen as a reference because PAH concentrations in CH sediments have remained unchanged since 1977 and are representative of deeper subtidal sediments elsewhere in PWS (Short and Heintz, 1997). The second parameter, MSE(Kat), compared the patterns of relative PAH concentrations with those in fresh Katalla seep oil, but in this case, corrected for weathering losses in the samples. Both parameters are natural log functions, with smaller numbers indicating greater similarity and larger numbers indicating less similarity. The value 0.05 of MSE(Kat) for the weathered Katalla seep oil indicates how well the weathering model accounts for weathering losses. Table 1 shows that the PAH fingerprints in PWS and Gulf of Alaska benthic sediments are very similar (MSE = 0.54) to that at CH; coal is also close (e.g., 0.60 for coal at Katalla Beach), whereas Katalla seep oil, both fresh and weathered, are very dissimilar (MSE(CH) = 2.68 and 1.21, respectively). The PAH fingerprints of the PWS benthic sediments are quite dissimilar to those of Katalla seep oil (MSE(Kat) = 1.68-4.41), even accounting for weathering.

The last parameter utilized is the refractory index. Katalla seep oil has a RI of 11 and 13. However, the benthic sediments and coal all give very low values and differ from the RI of Katalla oil by one to two orders of magnitude. The lack of a substantial presence of triaromatic steranes in the GOA and PWS benthic sediments, as reflected in the RI, is another contraindication for substantial oil input in PWS, particularly oil related to seep oil from Katalla.

One last factor considered by Short and others (1999) was the bioavailability of the PAHs in the respective potential sources. Juvenile coho salmon, collected 100 m downstream from an oil seep, were found to contain significant levels of petrogenic PAHs. However, in a comparable study, mussels further down stream and very near particulate coal outcrops had none of the petrogenic PAHs, indicating that the coal PAHs were not bioavailable and also that the oil productivity upstream was so small, or the weathering so complete, that the PAHs did not reach biota this distance away.

CONCLUSIONS

Geochemical parameters described in this study have enabled us to differentiate petroleum input sources to the recent geologic record in PWS, Alaska. First, it was found that oil washed up on the beaches in the Sound comes from two different sources—EVO from the oil spill of March 1989, and Monterey Formation, California, oil from the aftermath of the Great Earthquake of 1964. Second, evidence is contributed to the ongoing controversy as to which of two petrogenic sources of PAH is responsible for the PAH background in the benthic sediments of PWS, natural oil seeps from the coastline of the Gulf of Alaska or coal from the same area. Our studies, and cooperative work with NOAA, provide evidence that coal is the more likely source. This evidence includes a geographic and geologic framework for the coal origin and transport, geochemical parameters including weathering extrapolations and ratios of refractory constituents of the petrogenic PAH, and bioavailability experiments, all of which correlate better with a coal-sourced PAH background in the benthic sediments of PWS.

In addition to contributing to the body of information after the *Exxon Valdez* oil spill, the geochemical information and procedures obtained in these studies have implications and applications that can be carried over to other estuarine systems. For example, EVO is representative of a mixture of North Slope crude oils, and the Monterey tar balls are representative of crude oils produced from the Monterey Formation source rocks of California. Both of these types of oils are commonly transported along coastal California and into San Francisco Bay. Application of the work in PWS can help differentiate or correlate these oils and tars from spills and natural outcrops, as well as answer questions as to whether they have natural or anthropogenic origins.

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Research Articles

Genotoxicity Biomonitoring in Coal Regions Using Wild Rodent *Ctenomys torquatus* by Comet Assay and Micronucleus Test

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Coal is a mixture of a variety of chemicals, especially hydrocarbons, which may give rise to polycyclic aromatic hydrocarbons (PAH). Many PAH compounds produce mutagenic and carcinogenic effects. The quality of mineral coal in Rio Grande do Sul (RS) is low and it is typically obtained by stripping operations; it represents approximately 87% of the Brazil reserves. This report concerns the application of the Comet assay to *Ctenomys torquatus* to detect the effects of coal, comparing the results with a micronucleus (MN) assay, both using peripheral blood. This study was performed over a 2-year period in an attempt to evaluate seasonal patterns. The wild rodent is fossorial, and its geographic distribution in RS coincides with the distribution of coal reserves. Three localitions were studied: two coal fields, Butiá (in a strip coal mine region) and Candiota (near a strip coal mine), and one control region, Pelotas (no coal). At the end of 2 years, 240 rodents had been analyzed. Our results showed that coal and derivatives induced DNA and chromosomal lesions in rodent cells that were demonstrated by Comet and MN assays. These tests also demonstrated quantitative differences between field exposures (Candiota > Butiá). The Comet assay was more sensitive and also showed a direct relationship between age and damage, and an inverse relationship between temperature and damage index. Environ. Mol. Mutagen. 35:270–278, 2000. © 2000 Wiley-Liss, Inc.

Key words: coal; Comet assay; *Ctenomys torquatus*; environmental monitoring; genotoxicity; micronucleus assay

INTRODUCTION

Coal is a mixture of a variety of chemicals, especially hydrocarbons, which may give rise to polycyclic aromatic hydrocarbons (PAH). Many PAH compounds produce mutagenic and carcinogenic effects. Potentially, all technological processes associated with open fire or temperatures between 400°–600°C, which may lead to PAH, should be considered potentially hazardous [Srám et al., 1985].

Mineral coal in Rio Grande do Sul (RS), the southern state of Brazil, exceeds 30×10^9 tons, i.e., about 87% of the Brazilian reserves. The coal of this state, typically obtained by stripping operations, is low quality and generally contains 1% to 5% sulfur [Horbach et al., 1986]. It is primarily used at the Presidente Médici power plant, located in Candiota/RS. This region produces 38% of the country's coal. Consequently, a broad range of coal and derivatives (metals, hydrocarbons, etc.) is added to the chemical load of the atmosphere and water in the region. It is also well documented that coal-fired plants discharge a greater amount of radioactive material into the atmosphere than nuclear plants of comparable size [McBride et al., 1978; Kljajic et al., 1996].

Biological hazards associated with Candiota coal field were previously investigated in a pilot study, demonstrating an increase in DNA damage in *Ctenomys torquatus*, detectable by the Comet assay [Silva et al., 2000]. *C. torquatus* is a subterranean rodent endemic to southern South America [Freitas and Lessa, 1984]. Its geographic distribution in RS almost coincides with the distribution of coal reserves [Freitas, 1995]. Because damage to DNA is not immediately recognized in organisms and has broad-ranging effects, this rodent could be an important system to monitor changes in environmental genotoxicity [Petras et al., 1995].

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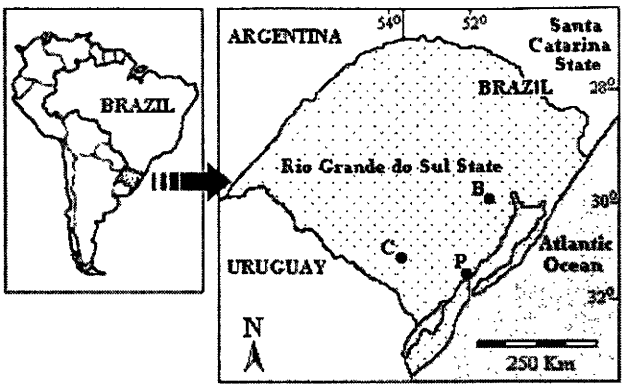

Fig. 1. Geographic localization of sampling sites: Pelotas (P), Butiá (B) and Candiota (C).

The alkaline single cell gel electrophoresis (SCG) assay or Comet assay is a new, rapid, simple, and sensitive technique for measuring and analyzing DNA breakage in individual cells [Singh et al., 1988; Tice et al., 1990; Fairbairn et al., 1995]. Potentially, any organism is suitable for investigation and only small cell samples need be used. As a result, the SCG assay is becoming a major tool for environmental biomonitoring.

The protocol that uses endemic animals to assess the biological hazards of polluted sites was developed using the Comet assay to permit genotoxicity monitoring without removing the animals from their habitat and without sacrifice [Silva et al., 2000].

The present report is concerned with the application and verification of alkaline SCG to *Ctenomys torquatus* to detect the effects of coal and to compare the results with a micronucleus (MN) assay in peripheral blood, and to verify whether seasonal patterns exist.

MATERIALS AND METHODS

Animals Sampling

Coal exposed *Ctenomys torquatus* (Octodontidae-Rodentia), were captured at two different sites in RS: Butiá, a region approximately 5 km from a strip coal mine and approximately 35 km from the Charqueadas-Jacuí coal power plant, and Candiota, which is close to a strip coal mine and near the Presidente Médici coal power plant. Reference animals, which were used as the external control, were obtained from Pelotas, a region without a coal mine (Fig. 1).

The monitoring of natural populations of rodents for genetic damage study was begun in April 1996 and continued until March 1998, one trapping per season per site. Oneida Victor (number zero) traps with a rubber cover for fossorials rodents were set where fresh earth mounds were located. Animals were anesthetized (Zoletil/Virbac, Carros Cedex, France) for blood collection and morphologic measurements, and were released at the place of capture after recuperation. Peripheral blood was obtained from foot pricks with the help of capillaries. The rodents were marked with tattoos on the hind leg, enabling the identification of animals in subsequent captures. By the end of 2 years, 240 rodents (183 females and 57 males) had been live-trapped. The *C. torquatus* age groups were determined according to the Wilks [1963] method. All work with the animals in this study was done with the permission of IBAMA (the official Brazilian environmental protection agency).

Micronucleus Assay

To verify the sensitivity of *C. torquatus*, three small number groups from Pelotas were dosed with cyclophosphamide (CP). They were treated with a volume of 0.1 ml per 10 g intraperitoneally and were sacrificed 24 hr after treatment. In addition to the test groups, negative (dosed with vehicle: water) controls were used. The bone marrow was extracted from the two femurs. Smear was made from material directly homogenized on two slides, with a drop of fetal calf serum. The slides were stained with 5% Giemsa, and coded for blind analysis. The frequency of micronucleated cells was analyzed in 2000 polychromatic erythrocytes (PCE) per animal.

The MN assay for peripheral blood was selected as the second monitoring system for comparison with alkaline SCG sensitivity. This assay was performed according to guidelines and recommendations [Heddle et al., 1983; Mavournin et al., 1990; Hayashi et al., 1994; Miller et al., 1997]. Whole blood smears were prepared on microscope slides, air dried, and stained with a mix of 60 ml Giemsa, 30 ml May Grünwald Giemsa, and 10 ml phosphate buffer (pH 5.8) for 5 min.

Subsequently, the slides were rinsed with phosphate buffer and air dried. At least four blood smears were prepared from each animal. The slides were coded for blind analysis.

The frequency of micronucleated cells was analyzed in 1,000 PCE and 4,000 normochromatic erythrocytes (NCE) per animal. The percentage of micronucleated cells by gender, age groups, and sites, observed among 1,000 cells (‰) analyzed, was calculated. Bartlett-Box test was used to evaluate the variance homogeneity of each site group. The statistical significance of the mean percentage of PCE and NCE with MN was determined using the Students' t-test. A difference of $P < 0.05$ was considered statistically significant.

Comet Assay

The alkaline Comet assay was performed as described by Singh et al. [1988], as modified in Silva et al. [2000] for field work.

Together with the blood samples from *C. torquatus*, human blood was also collected on the same day and under the same conditions. Human peripheral blood was obtained from finger pricks, with the help of capillaries. This was considered an internal control for damages, caused by manipulations, delay, or transport to the laboratory.

Blood cells (10 μl) were embedded in 95 μl of 0.75% low melting point agarose. The mixture (cell/agarose) was added to a fully frosted microscope slide coated with a layer of 300 μl of normal melting agarose (1%). After solidification, the slides were placed in lysis buffer (2.5M NaCl, 100 mM EDTA, and 10 mM Tris, pH 10.0–10.5, with freshly added 1% Triton X-100 and 10% dimethyl sulfoxide [DMSO]) for a minimum of 1 hr and a maximum of 2 weeks. All procedures were conducted in the field until lysis, in an improvised laboratory. The slide preparation and lysis needs to be done until 24 hr after blood collection. The slides were kept in lysing solution, packed, and transported in a box packed with ice to the laboratory. Subsequently, the slides were incubated in freshly made alkaline buffer (300 mM NaOH and 1 mM EDTA, pH 12.6) for 30 min. The DNA was electrophoresed for 30 min at 25 volts (0.90 V/cm) and 300 mA, and then the alkali was neutralized with 0.4M Tris (pH7.5). Finally, the DNA was stained with ethidium bromide (2 μg/ml).

To demonstrate the electrophoresis conditions and efficiency, negative and positive controls from human blood collected in the laboratory were used for each electrophoresis treatment. For a positive control, 200 μl of whole blood was mixed with 50 μl of methyl methane sulfonate (MMS-M4016/ Sigma, St. Louis, MO) at 8×10^{-5} M and 4×10^{-5} M. This mix was incubated for 2 hr at 37°C. The two concentrations were used to demonstrate different levels of damage and assay sensitivity. The result of

TABLE I. Number and Percent of Polychromatic Erythrocytes with Micronuclei (mPCE) Observed in Bone Marrow Cells of *Ctenomys torquatus* Exposed to Different Single Doses of Cyclophosphamide (CP) for 24 hours

CP dose[a] (mg/kg)	Number of rodents	Total mPCE	Total PCE analyzed	mPCE (‰)
0.0	10	14	10,000	1.4
20.0	2	26*	4,000	6.5
40.0	2	41*	4,000	10.3
60.0	2	34*	4,000	8.5

[a]CP at the indicated concentrations was administered intraperitoneally.
*Data significant at $P < 0.05/\chi^2$ test.

TABLE II. Mean Frequency of Micronucleated Erythrocytes Polychromatic (mPCE) and Normochromatic (mNCE) Observed in Blood Cells of *Ctenomys torquatus* from Pelotas, Butiá and, Candiota, by Gender

Site	N[a]	Gender	mPCE[b]	mNCE[b]
Pelotas	45	Female	0.9 ± 1.2	0.2 ± 0.4
	25	Male	1.1 ± 1.3	0.4 ± 0.5
Butiá	48	Female	1.3 ± 1.6	0.5 ± 0.6
	13	Male	1.2 ± 1.3	0.4 ± 0.3
Candiota	78	Female	1.5 ± 1.5	0.4 ± 0.4
	15	Male	1.5 ± 1.6	0.4 ± 0.4

[a]Number of animals per group.
[b]Mean value (‰) ± standard deviation.

TABLE III. Comparisons Between Age Groups, to Each Site Group, of Micronucleated Erythrocytes Polychromatic (mPCE) and Normochromatic (mNCE) Observed in Blood Cells of *Ctenomys torquatus*

Site	N[a]	Age groups	mPCE[b]	mNCE[b]
Pelotas	4	Juvenile	1.5 ± 1.0	0.6 ± 0.4
	29	Subadult	1.2 ± 1.5	0.4 ± 0.5
	37	Adult	0.8 ± 1.1	0.2 ± 0.3
Butiá	1	Juvenile	2	0.3
	15	Subadult	0.7 ± 1.2	0.3 ± 0.3
	45	Adult	1.5 ± 1.6	0.5 ± 0.6
Candiota	6	Juvenile	2.3 ± 2.0	0.6 ± 0.4
	22	Subadult	1.0 ± 1.3	0.3 ± 0.3
	65	Adult	1.6 ± 1.5	0.5 ± 0.4

[a]Number of animals per group.
[b]Mean value (‰) ± standard deviation.

each electrophoresis was considered only if the negative and positive controls demonstrated negative and positive results, respectively.

Images of 50 randomly selected cells (25 cells from each of two replicate slides) were analyzed from each animal. Comet image lengths (nuclear region plus tail) were measured in arbitrary units, with a calibrated scale in the ocular, using a fluorescence microscope equipped with an excitation filter of BP546/12 nm and a barrier filter of 590 nm. One unit was approximately 5 μm at 200× magnification.

Cells were also scored visually according to tail size into five classes ranging from undamaged (0), to maximally damaged (4), resulting in a single DNA damage score to each animal, and consequently to each studied group. Therefore, the group's damage index (DI) can range from 0 (completely undamaged, 50 cells × 0) to 200 (with maximum damage, 50 cells × 4) [Collins et al., 1995, 1997].

The Bartlett-Box test was used to evaluate the variances homogeneity of each site group. Pearson correlation and linear regression line were carried out to compare DI and temperature. Mean temperatures for each season were obtained by averaging the temperatures, by site, around the capture date. Temperature data were provided by the Meteorology Institute (8° Distrito de Meteorologia-DISME/Ministério da Agricultura).

The damage frequency (%) was calculated based on number of cells with tail vs. those without. The statistical evaluation was performed using the two-tailed Students' t-test. A difference of $P < 0.05$ was considered statistically significant.

RESULTS

MN Assay

Because the bone marrow MN assay in laboratory mouse strains is well established, our first concern was to test the sensitivity of *C. torquatus* to a known mutagen. Wild rodents showed a significant differences to a variety of CP doses (Table I).

The MN data for *C. torquatus* that were captured between autumn 1996 and summer 1998 are summarized in Table II, III, and IV. No significant difference between gender and age groups by site were observed. Three age groups for *C. torquatus* were determined by weight: (1) juveniles, females up to 125 g and males up to 135 g; (2) subadults, females from 125 to 185 g and males from 135 to 225 g; and (3) adults, above the limits found in subadults. Geographic position accounted for very little variability, with no significant differences between seasons. The Bartlett's test indicated that the variances were essentially equal. At both test sites, Candiota and Butiá, the frequency of micronucleated PCEs (mPCE) and NCEs (mNCE) was slightly higher than the concurrent control (Pelotas). The analysis of the mean percentage of micronucleated cells using the Student's t-test indicated a significant increase in mNCE ($P < 0.05$) for Butiá and in mPCE ($P < 0.05$) for Candiota (Table IV).

Table IV also presents the mean percentage (%) of mPCE and mNCE for each season per site group. Comparisons for each season and test group against Pelotas, the external control, by Students' t-test, showed very small variations. Thus, no seasonal pattern could be distinguished.

Comet Assay

The Comet assay was performed from the same blood samples used to make smears for the MN assay.

Data on the mean DI, mean DNA image length, and mean damage frequency of *C. torquatus* from Pelotas, Butiá, and Candiota for each season are presented in Table V. The DI index and frequency of damages of Candiota are significantly higher than Pelotas, for each season in which rodents were caught. The DNA image length for Candiota is also significantly larger than Pelotas, with the exception of au-

TABLE IV. Number and Mean Values of Micronucleated Erythrocytes Polychromatic (mPCE) and Normochromatic (mNCE) Observed in Blood Cells of *Ctenomys torquatus* from Pelotas, Butiá, and Candiota

	Pelotas			Butiá			Candiota		
Season/year	N[a]	mPCE[b]	mNCE[b]	N[a]	mPCE[b]	mNCE[b]	N[a]	mPCE[b]	mNCE[b]
Autumn 1996	7	2.4 ± 1.8	0.8 ± 0.6	9	1.8 ± 1.6	0.8 ± 1.4	9	2.8 ± 1.7	1.0 ± 1.8
Winter 1996	8	2.1 ± 0.6	0.8 ± 0.7	6	1.3 ± 1.0	0.8 ± 1.0	15	2.4 ± 1.4	0.7 ± 0.7
Spring 1996	4	1.8 ± 1.5	0.7 ± 0.7	7	2.4 ± 1.9	0.5 ± 0.7	15	2.0 ± 1.5	0.6 ± 0.7
Summer 1997	9	0.4 ± 0.5	0.1 ± 0.3	5	1.8 ± 1.8	0.3 ± 0.6	12	2.5 ± 3.0*	0.4 ± 0.5
Autumn 1997	11	0 ± 0	0.1 ± 0.3	9	0.9 ± 1.1*	0.2 ± 0.4	12	0.9 ± 1.1*	0.1 ± 0.3
Winter 1997	9	1.6 ± 1.1	0.2 ± 0.4	11	1.1 ± 1.9	0.5 ± 0.9	10	0.4 ± 0.5*	0.1 ± 0.3
Spring 1997	10	0.6 ± 1.0	0.03 ± 0.2	7	0.9 ± 0.2	0.5 ± 0.8	10	0.7 ± 0.7	0.1 ± 0.3
Summer 1998	12	0.3 ± 0.5	0.02 ± 0.1	7	0.4 ± 0.5	0.1 ± 0.3	10	0.7 ± 0.8	0.2 ± 0.4
Total	70	1.2 ± 0.9	0.3 ± 0.4	61	1.3 ± 0.6	0.5 ± 0.3*	93	1.6 ± 1.0*	0.4 ± 0.3

[a]Number of animals per group.
[b]Mean value (‰) ± standard deviation.
*Data significant at $P < 0.05$/Students' t-test, in relation to Pelotas group (control).

tumn 1996 ($P = 0.7$) and summer 1998 ($P = 1.7$). Butiá demonstrated a significant difference only in spring 1996 (DNA image length, $P = 2.6$) and in spring 1997 but in the latter, the DNA image length and damage frequency were lower than the control. None of blood samples from internal control showed a positive response. Negative (DI = 0–5) and positive controls (DI= 150–200) for electrophoresis demonstrated negative and positive results, respectively. The Bartlett's test indicated homogeneity of variances of each site group.

Table V also shows the mean temperature (°C) of each capture date per site. The correlation coefficient of the regression, using one-way analysis of variance, was used to compare damage and temperature per site. The correlation coefficients for Pelotas ($r = -0.30$), Butiá ($r = -0.75$), and Candiota ($r = -0.44$) were tested for significance by t, and only Butiá showed a significant correlation ($P < 0.001$). The linear regression lines from every site demonstrated a trend linking lower temperatures to more damaged cells (Fig. 2). The regression coefficients were also tested by t, and only Butiá showed a significant inclination ($P < 0.05$).

Table VI shows the significant difference between Candiota and Pelotas for DI, image length, and damage frequency. Both females and males from Candiota presented a DI significantly higher than females and males from the control, Pelotas, respectively. No difference between gender for each group was observed.

Thus, females and males were placed in a single group (Table VII), separated by age groups per site. Table VII shows that juveniles have a lower DI than subadults and adults, for each capture site (juvenile < subadult < adult). Adults from Butiá and Candiota showed DI, DNA length, and damage frequency significantly different ($P < 0.05$) from juveniles of same site. When subadult and juveniles were compared, only Butiá, showed a significant difference in DNA image length. No significant difference between age groups was demonstrated for Pelotas.

DISCUSSION

Coal extraction and burning have caused serious problems in RS, both for the mining regions (e.g., respiratory diseases, poor agriculture, etc.) and for their neighbors (e.g., acid rain in Uruguay). However, analytical techniques characterizing the levels of known pollutants do not provide insights into biological hazards associated with pollution [Salagovic et al., 1996].

Numerous assays have been developed to monitor biological hazards caused by pollutants but few genotoxicity studies have been conducted to evaluate the mutagenic potential associated with the exposure of mammalian systems [Baker et al., 1996; Silva et al., 2000], and to evaluate the chronic impact of contaminants on organisms [Belpaeme et al., 1998]. Although *C. torquatus* are fossorial rodents, they normally come up to the surface to feed and clean their burrows. They are herbivorous animals, digging their burrows with their paws and teeth. Thus, they expose themselves to the contaminants in the soil and plants, and their microenvironment to the atmosphere in the region with or without pollutants. In the present study, the usefulness of the Comet and MN assay in blood samples to evaluate chronic exposure to coal was tested on *C. torquatus*.

The first test we carried out concerned the confirmation of *C. torquatus* sensitivity. All three small number groups dosed with CP showed significant differences to the negative control. When this wild rodent, dosed with 60 mg/kg of CP, was compared with mice of the Swiss Webster outbreed line [Silva, 1994], its response showed a greater variance. In fact, the *C. torquatus* responded less strongly to CP (8.5% of mPCE) than mice (14.5% of mPCE) but the rodents that were not exposed to the drug, i.e., the negative controls, showed similar levels of damage [Ong et al., 1985; Silva, 1994]. Despite the difference between these species' responses, *C. torquatus* demonstrated a good sensitivity.

Hazards caused by coal and derivatives have been de-

TABLE V. Detection of DNA Damage in Blood Leukocytes of *Ctenomys torquatus* from Pelotas, Butiá, and Candiota, Captured from Autumn 1996 to summer 1998 and Internal Control (IC)

Season (date)	Site	N[a]	DNA image length (μm)[b]	Damage index[b]	Damage frequency (%)[b]	Mean temperature (°C)[c]
Autumn 1996	IC	04	33 ± 5	4 ± 4	4 ± 3	—
(March 23)	Pelotas	07	47 ± 6	25 ± 8	20 ± 6	20
(May 14, 16)	Butiá	10	46 ± 5	33 ± 14	23 ± 10	17
(March 25–26)	Candiota	11	49 ± 6	52 ± 12***	48 ± 11***	19
Winter 1996	IC	04	32 ± 3	5 ± 4	5 ± 2	—
(August 22–23)	Pelotas	10	37 ± 3	21 ± 5	15 ± 4	14
(July 22)	Butiá	06	50 ± 22	40 ± 46	28 ± 31	11
(August 18–20)	Candiota	16	59 ± 5***	77 ± 10***	51 ± 6***	15
Spring 1996	IC	05	27 ± 3	4 ± 3	3 ± 2	—
(December 12–13)	Pelotas	07	27 ± 1	7 ± 2	6 ± 1	23
(December 15)	Butiá	09	29 ± 2*	10 ± 6	8 ± 4	24
(December 8–10)	Candiota	15	37 ± 3***	31 ± 7***	24 ± 6***	23
Summer 1997	IC	05	30 ± 2	6 ± 5	4 ± 2	—
(March 16)	Pelotas	10	29 ± 2	8 ± 5	7 ± 4	21
(March 7,9)	Butiá	07	29 ± 2	10 ± 9	8 ± 6	22
(March 14–15)	Candiota	12	42 ± 13**	36 ± 18***	29 ± 12***	21
Autumn 1997	IC	06	29 ± 1	3 ± 3	2 ± 2	—
(June 2–3)	Pelotas	11	32 ± 3	11 ± 6	8 ± 4	13
(June 11, 18)	Butiá	09	34 ± 5	16 ± 17	10 ± 9	15
(June 1)	Candiota	12	40 ± 7**	31 ± 12***	26 ± 7***	15
Winter 1997	IC	05	28 ± 1	4 ± 3	3 ± 3	—
(July 22)	Pelotas	10	33 ± 3	15 ± 9	11 ± 7	14
(July 31)	Butiá	11	34 ± 2	20 ± 6	15 ± 4	16
(July 23–24)	Candiota	10	42 ± 12*	40 ± 27*	32 ± 16**	14
Spring 1997	IC	06	29 ± 2	4 ± 2	3 ± 2	—
(October 6–8)	Pelotas	10	36 ± 3	18 ± 4	14 ± 3	18
(December 2,5)	Butiá	08	28 ± 1***	9 ± 4	9 ± 4**	24
(October 9–10)	Candiota	10	41 ± 4**	37 ± 7***	30 ± 5***	17
Summer 1998	IC	05	29 ± 2	6 ± 5	5 ± 3	—
(January 22–23)	Pelotas	12	32 ± 3	13 ± 7	9 ± 4	22
(January 6)	Butiá	07	35 ± 8	21 ± 16	16 ± 12	24
(January 20–21)	Candiota	10	37 ± 9	29 ± 14**	25 ± 8***	22

[a]Number of animals per group.
[b]Mean values obtained from average of 50 cells per animal.
[c]Data was provided by Meteorology Institute-DISME.
*Data significant in relation to Pelotas group at $P < 0.05$, **$P < 0.01$, ***$P < 0.001$/two-tailed Students' t-test.

scribed by many authors using bacterial [Whong et al., 1983; Kleinjans et al., 1989] and human cells [Léonard et al., 1984; Srám et al., 1985; Kleinjans et al., 1989; Stierum et al., 1993]. For human cells, different techniques have been utilized, such as sister-chromatid exchange, *hprt* expression, chromosomal abnormalities, and micronucleus. In all assays, a small increase in damage was observed. Our results for *C. torquatus* from coal field regions demonstrated an increase in micronucleated cells (Tables II, III, and IV), and in cells with levels of DNA damage (Tables V, VI, VII and Fig. 3). The difference observed for coal fields from the external control region using the MN assay, although significant (Table IV), showed only a slight increase. The alkaline Comet assay showed more sensitivity, resulting in clearer differences among the groups evaluated.

The results from the MN and Comet assays show an obvious difference in sensitivity, which becomes clearer when Tables IV and V are evaluated. For the MN assay, besides a slight increase in micronucleated cells frequency (Pelotas < Butiá < Candiota), no seasonal pattern is demonstrated. Although the mean frequency of mPCE from Butiá (autumn 1997), and mPCE from Candiota (summer, autumn, and winter 1997), were significantly ($P < 0.05$) different from Pelotas; these could be a chance occurrence. For the alkaline SCG, seasonal variations were observed, demonstrating the higher sensitivity of this test (Fig. 3). These differences between tests can be explain by the biologic mechanism where the spleen captures and destroys circulating micronucleated erythrocytes in some organisms (e.g. rats) [Schegel and McGregor, 1984]. Thus, the periph-

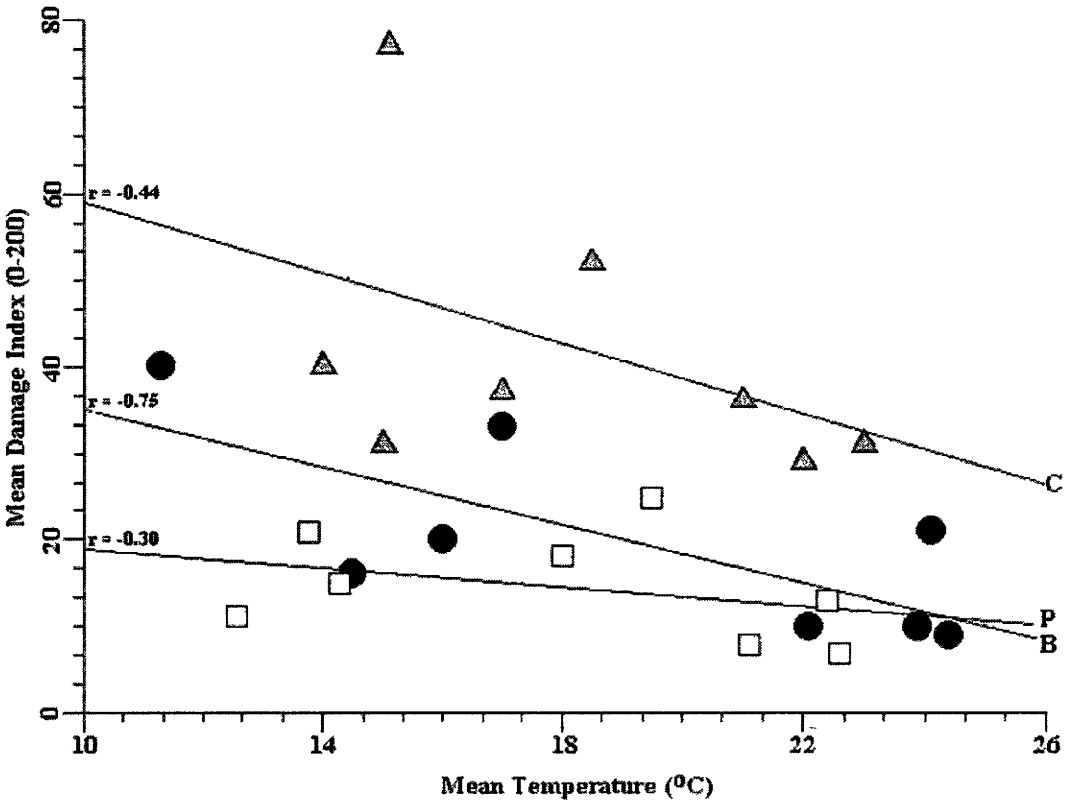

Fig. 2. Linear regression line obtained from mean damage index and mean temperature from each site and season that *Ctenomys torquatus* were captured. P, B, and C represent Pelotas (Y = 23.4–0.5X), Butiá (Y = 52.3–1.7X), and Candiota (Y = 78.6–2.0X), respectively. Pelotas, squares; Butiá, circles; Candiota, triangles.

TABLE VI. Mean Values of Damage Index in Blood Cells of *Ctenomys torquatus* by Site and Gender, Besides DNA Image Length and Damage Frequency

Site	N[a]	Gender	Damage index[b]	DNA image length (μm)[b]	Damage frequency (%)[b]
Pelotas	50	Female	14 ± 8	34 ± 7	11 ± 6
	27	Male	15 ± 8	35 ± 5	11 ± 6
Butiá	53	Female	19 ± 18	35 ± 9	14 ± 11
	14	Male	25 ± 20	35 ± 13	15 ± 18
Candiota	80	Female	45 ± 21***	45 ± 11***	35 ± 13***
	16	Male	36 ± 21***	41 ± 10*	28 ± 16***

[a]Number of animals per group.
[b]Mean values obtained from average of 50 cells per animal.
*Data significant in relation to Pelotas group at $P < 0.05$, ***$P < 0.001$/two-tailed Students' t-test.

eral blood MN assay is considered less suitable than many others tests; nevertheless, this assay is well accepted [Collaborative Study Group for the Micronucleus Test, 1992; Holden et al., 1997], mainly when the sacrifice of the animals is not recommended. The possibility of spleen capture and destruction of micronucleated erythrocytes in *C. torquatus* can be reinforced by the difference observed for the mean frequency of young and mature erythrocytes with MN, PCE, and NCE, respectively. The smaller value for NCE than PCE with MN, by site, demonstrate that the micronucleated cells are not remaining in the circulation.

Table IV also shows higher damage values for autumn and winter of 1996 than for other seasons at the three sites. Srám et al. [1996] demonstrated a high concentration of fine particles from mining districts during winter temperature inversions. Slight seasonal variations in the composition of sediments contaminated by PAHs were demonstrated by Budzinski et al. [1997]. However, our results for the seasons

TABLE VII. Comparisons Between Age Groups, to Each Site Group, of Damage Index (DI), DNA Image Length and Damage Frequency in Blood Samples of *Ctenomys torquatus*

Site	N[a]	Age groups	DI by age[b]	DNA image length (μm)[b]	Damage frequency (%)[b]
Pelotas	4	Juvenile	9 ± 7	36 ± 9	7 ± 5
	31	Subadult	13 ± 8	33 ± 6	10 ± 6
	42	Adult	16 ± 8	34 ± 5	12 ± 6
Butiá	2	Juvenile	10 ± 6	28 ± 3	7 ± 4
	17	Subadult	18 ± 24	34 ± 12*	14 ± 17
	48	Adult	21 ± 18*	36 ± 10**	15 ± 11*
Candiota	6	Juvenile	32 ± 8	38 ± 5	29 ± 15
	23	Subadult	36 ± 23	41 ± 13	28 ± 15
	67	Adult	46 ± 21**	46 ± 10***	36 ± 13*

[a]Number of animals per group.
[b]Mean values obtained from average of 50 cells per animal.
*Data significant in relation to juveniles from the same group at $P < 0.05$, **$P < 0.01$, ***$P < 0.001$/two-tailed Students' t-test.

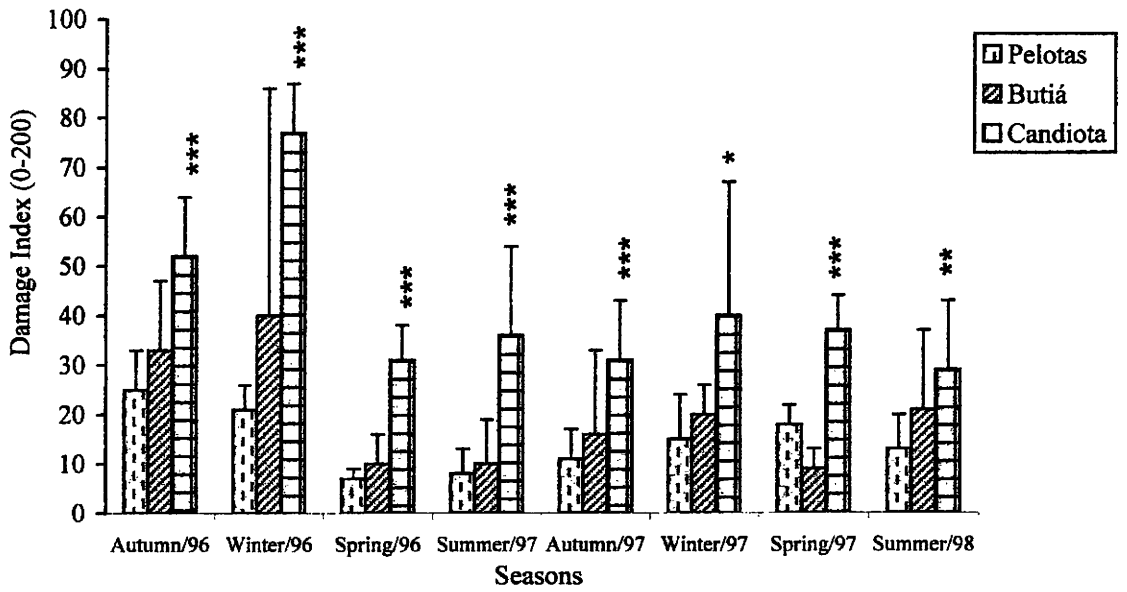

Fig. 3. Mean values of damage index in blood cells of *Ctenomys torquatus* from Pelotas, Butiá, and Candiota per season. *$P < 0.05$, **$P < 0.01$, and ***$P < 0.001$.

mentioned did not reproduce the same high values for 1997, although in the winter of 1997 a slight increase in DI occurred compared with others seasons. It should be emphasized that in 1996, various monitoring programs were implemented and systems began to be used to reduce the discharge of pollutants into the environment at the Candiota and Charqueadas-Jacuí coal power plants because of the expansion plan for the Presidente Médici coal power plant [Japan International Cooperation Agency, 1997]. This fact could explain the reduction of damaged cells from Butiá and Candiota after the winter of 1996. Studies on the evaluation of environmental quality by the Japan International Cooperation Agency (JICA) group demonstrated a higher cation/anion ratio of rain samples for the autumn and winter of 1996 for Candiota than for other samples analyzed. Among these samples, SO_x was the main anion that presented the same response, which increased during the two seasons. Besides these observations for Candiota, the two seasons mentioned were characterized by high amounts of rain, which exposed the soil and consequently the rodents, to the sulfur particulates.

Pelotas, as well as Butiá and Candiota, demonstrated higher damage values for autumn and winter of 1996; these facts should be associated with climate changes and pollutants levels. When we biomonitor a region, many variables may be present, making it practically impossible to evaluate every parameter. Errors in sampling procedures are less likely due to internal controls for each test. Ours showed only 5% with increased migration, an acceptable level.

The comparison of *C. torquatus* from Pelotas and Butiá,

showed a similar response for each season, except for the spring of 1996 and 1997. Although image length results were significant for the spring of 1996, the difference is very small. In the spring of 1997, Pelotas, the external control, presented a higher damage frequency and length than Butiá. If we observe the capture date for this season per region and respective temperatures we will see a lower temperature for Pelotas than for Butiá. The rodents from this last site were caught in summer. Regression analysis (Fig. 2) demonstrated an inverse ratio between temperature and damage but a significant correlation was demonstrated only for Butiá.

Table VI showed a longer DNA image length, DI, and damage frequency for Candiota, the region directly exposed to coal and to a coal-fueled power plant, than for Butiá and Pelotas, both females and males. Silva et al. [in prep.] demonstrated that a soil sample from Candiota had a higher total concentration of hydrocarbons (220 ppm) than Butiá (160 ppm) and Pelotas (140 ppm), thus the same relation i.e., Candiota > Butiá > Pelotas. Although the DI, image length, and damage frequency measured for females and males were statistically similar, no significant gender difference was observed. Once again, our results coincide with PAHs results from literature. Zitko et al. [1998] measured PHAs in differents organs of harp seal beaters (*Phoca groenlandica*) and did not find a difference between males and females.

Adults, subadults, and juveniles were compared (Table VII) to demonstrate a possible relationship between age and damage. The significant difference between adults and juveniles from Candiota was greater than the difference observed between rodents of same age groups from Butiá. It seems obvious that because Candiota showed a higher level of damaged cells, consequently there is a greater difference. Increases in somatic chromosome abnormalities, both structural aberrations and aneuploidy, are some of the genetic changes associated with aging [Mattevi and Salzano, 1975; Stone and Sandberg, 1995]. Similar increases in the level of damaged cells associated with age were found for whales exposed to PHAs, with the adults showing a significant increase of cytochrome P450 expression as compared with juveniles [Moore et al., 1998].

In conclusion, our results agree with previous data on coal and derivatives, mainly PAHs, and also indicate that the alkaline SCG is extremely sensitive, demonstrating seasonal/temperature differences and relationship to aging. Moreover, our study indicates that this assay is also sufficiently sensitive to detect the differences in exposure between the coal fields of Butiá and Candiota.

The evaluation for the induction of MN in peripheral blood erythrocytes, although not as sensitive as the alkaline SCG, could be useful under circumstances where genotoxicity is high. No seasonal pattern was observed but the results per region demonstrated a similar response as in SCG, with the following order of MN frequency: Pelotas < Butiá < Candiota.

Finally, *C. torquatus* was shown to be an excellent organism for use as a biomonitor and bioindicator. The rodent in this report showed enough sensitivity to become an effective monitor of biological hazards caused by coal and derivatives in our state.

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CONSENSUS SEDIMENT QUALITY GUIDELINES FOR POLYCYCLIC AROMATIC HYDROCARBON MIXTURES

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Abstract—Sediment quality guidelines (SQGs) for polycyclic aromatic hydrocarbons (PAHs) have been derived from a variety of laboratory, field, and theoretical foundations. They include the screening level concentration, effects ranges–low and–median, equilibrium partitioning concentrations, apparent effects threshold, ΣPAH model, and threshold and probable effects levels. The resolution of controversial differences among the PAH SQGs lies in an understanding of the effects of mixtures. Polycyclic aromatic hydrocarbons virtually always occur in field-collected sediment as a complex mixture of covarying compounds. When expressed as a mixture concentration, that is, total PAH (TPAH), the guidelines form three clusters that were intended in their original derivations to represent threshold (TEC = 290 μg/g organic carbon [OC]), median (MEC = 1,800 μg/g OC), and extreme (EEC = 10,000 μg/g OC) effects concentrations. The TEC/MEC/EEC consensus guidelines provide a unifying synthesis of other SQGs, reflect causal rather than correlative effects, account for mixtures, and predict sediment toxicity and benthic community perturbations at sites of PAH contamination. The TEC offers the most useful SQG because PAH mixtures are unlikely to cause adverse effects on benthic ecosystems below the TEC.

Keywords—Polycyclic aromatic hydrocarbons Mixtures Sediment quality guideline Sediment toxicity

INTRODUCTION

A plethora of marine sediment quality guidelines (SQGs) have been proposed for polycyclic aromatic hydrocarbons (PAHs) [1–10]. Existing PAH SQGs were derived from a variety of laboratory, field, and theoretical foundations. They have engendered considerable controversy over issues of correlative versus causal relations between chemistry and biological effects, bioavailability of sediment contaminants, effects of covarying chemicals and mixtures, and ecological relevance [see editorials, 11–19].

In this paper I attempt to resolve these issues and show that the different SQGs are more similar than dissimilar. The existing PAH SQGs are described and quantitatively compared. Consensus guidelines for PAHs are proposed for threshold, median, and extreme effects concentrations (TEC, MEC, EEC). The consensus guidelines are then evaluated with respect to their ability to predict sediment toxicity (10-d mortality to estuarine and marine amphipods) and in situ ecological effects (reduction in the areal species richness of macrobenthic assemblages).

EXISTING PAH SEDIMENT QUALITY GUIDELINES

Screening level concentration (SLC)

The SLC was derived from field data on PAH concentrations and the presence/absence of a number of benthic species [1]. A cumulative frequency distribution of stations at which a particular species was present was plotted against the organic carbon (OC)-normalized concentration of an individual PAH to derive the species screening level concentration (SSLC). The SSLC was defined as the concentration at the 90th percentile of this frequency distribution. The SSLCs for a large number of species were then plotted in another frequency distribution. The SLC was defined as the individual PAH concentration above which 95% of the SSLCs were found.

Effects range–low (ERL), effects range–median (ERM)

The ERL and ERM were developed from an extensive database of biological effects determined by a variety of methods (toxicity tests, field observations, other sediment guidelines including equilibrium partitioning-derived [EqP] criteria and the apparent effects threshold [AET]) [2,9]. The dry weight-normalized database for each PAH compound was sorted and the ERL and ERM identified as the lower 10th (ERL) and 50th (ERM) percentiles of effects data.

Equilibrium partitioning-derived (EqP) criteria

The EqP concentration is the OC-normalized individual PAH concentration in sediment that is in equilibrium with an interstitial water PAH concentration equal to the U.S. Environmental Protection Agency (U.S. EPA) Water Quality Criterion Final Chronic Value [3,5–7]. The U.S. EPA has proposed EqP criteria for acenaphthene, phenanthrene, and fluoranthene.

Apparent effects threshold (AET)

The AET is the dry weight-normalized individual PAH concentration above which statistically significant biological effects always occurred in the Puget Sound database used to create the values [4]. Four kinds of AET values are based on sediment toxicity tests with amphipods, oyster larvae, Microtox, and on biological effects in the field as measured by the abundance of benthic infauna. In addition, AET SQGs are expressed as the highest (HAET) and lowest (LAET) of the four kinds of AETs.

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Table 1. The ΣPAH mixture LC50 and effects range–median (ERM)[a] sediment quality guidelines for total PAHs (μg/g organic carbon [OC])

PAH	ΣPAH LC50	Mean percent of ΣTU[b]	ΣPAH mixture LC50	ERM
Naphthalene	7,146	1.0	71	210
Acenaphthylene	4,900	0.3	15	64
Acenaphthene	2,310	1.0	23	50
Fluorene	4,478	2.0	90	54
Phenanthrene	2,220	7.0	155	150
Anthracene	4,220	2.7	114	110
Low molecular weight PAH[c]			468	638
Fluoranthene	3,310	11.2	371	510
Pyrene	2,810	17.1	481	260
Benz[*a*]anthracene	2,136	5.2	111	160
Chrysene	2,136	7.9	169	280
Benzo[*b*]fluoranthene	1,096	16.4	180	188[d]
Benzo[*k*]fluoranthene	892	17.4	155	162[d]
Benzo[*a*]pyrene	1,655	10.8	179	160
High molecular weight PAH[c]			1,646	1,720
Total PAH[b]			2,114	2,358

[a] ERM at 1% OC.
[b] ΣTU = sum of toxic units.
[c] By addition.
[d] No ERM. Estimate assuming mean ratio to ΣPAH mixture LC50 for other HPAH.

ΣPAH model

The ΣPAH model estimates the probability that a PAH-contaminated sediment will be toxic to marine and estuarine amphipods [8]. Two SQGs can be derived from the ΣPAH model, the ΣPAH mixture LC50, and the ΣPAH toxicity threshold. The ΣPAH mixture LC50 is the concentration of individual compounds, low molecular weight (LPAH), high molecular weight (HPAH), or total PAHs (TPAH) that is expected when the TPAH is sufficient to cause 50% amphipod mortality (Table 1). The ΣPAH mixture LC50 is calculated as the product of the LC50 for an individual compound (e.g., in a spiked sediment toxicity test) and the mean fractional contribution of that compound to the sum of toxic units in field-collected sediments contaminated by a PAH mixture [8]. For example, the naphthalene LC50 estimated by the ΣPAH model is 7,146 μg/g OC, and naphthalene accounts for about 1% of the PAH toxic units in contaminated sediment [8]. The ΣPAH mixture LC50 for naphthalene is therefore 1% of 7,146 μg/g OC (~71 μg/g OC, Table 1). The threshold of significant amphipod toxicity occurs at 0.186 toxic units [8]. Because the ΣPAH mixture LC50 represents 1.0 toxic units, the ΣPAH toxicity threshold SQGs are 18.6% of the ΣPAH mixture LC50 SQGs (Tables 1 and 2).

Threshold effects level (TEL), probable effects level (PEL)

The TEL and PEL were derived from a biological effects data set (BEDS) that included all observations of adverse biological effects that occurred at chemical concentrations at least twofold above reference conditions, and a no effects data set that included all observations of no adverse biological effects at reference sites or at chemical concentrations within a twofold elevation above reference conditions [10]. The TEL was calculated as the geometric mean of the 15th percentile of the effects data set and the 50th percentile of the no effects data set. The PEL was calculated as the geometric mean of the 50th percentile of the effects data set and the 85th percentile of the no effects data set.

Normalization

Sediment quality guidelines have been proposed for PAH concentrations normalized on both an OC and dry weight basis.

Table 2. Sediment quality guidelines for total polycyclic aromatic hydrocarbons (TPAHs, μg/g organic carbon [OC])

	Sediment quality guidelines (SQGs)[a]									
PAH	ERL[b]	ERM[b]	TEL[b]	PEL[b]	SLC	LAET[b]	HAET[b]	EqP	ΣPAH toxicity threshold	ΣPAH mixture LC50
Naphthalene	16	210	3	39	41	210	270		13	71
Acenaphthylene	4	64	1	13	5	>56	130		3	15
Acenaphthene	2	50	1	9	6[c]	50	200	230	4	23
Fluorene	2	54	2	14	10	54	360		17	90
Phenanthrene	24	150	9	54	37	150	690	240	29	155
Anthracene	9	110	5	24	16	96	1,300		21	114
Low molecular weight PAH[d]	57	638	21	153	115	616	2,950		87	468
Fluoranthene	60	510	11	149	64	170	3,000	300	69	371
Pyrene	66	260	15	140	66	260	1,600		90	481
Benz[*a*]anthracene	26	160	7	69	26	130	510		21	111
Chrysene	38	280	11	85	38	140	920		31	169
Benzo[*b*]fluoranthene	32[c]	188[c]	7[c]	71[c]	32[c]	160	445		33	180
Benzo[*k*]fluoranthene	28[c]	162[c]	6[c]	61[c]	28[c]	160	445		29	155
Benzo[*a*]pyrene	43	160	9	76	40	160	360		33	179
High molecular weight PAH[d]	293	1,720	66	651	294	1,180	7,280		306	1,646
Total PAH[d]	350	2,358	87	804	409	1,796	10,230	211	393	2,114

[a] ERL = effects range–low [2]; ERM = effects range–median [2]; TEL = threshold effects level [10]; PEL = probable effects level [10]; SLC = screening level concentration [1]; LAET = low apparent effects threshold [4]; HAET = high apparent effects threshold [4]; EqP = U.S. Environmental Protection Agency criteria derived from equilibrium partitioning theory [3,5–7].
[b] SQG at 1% OC.
[c] No SQG. Estimate assuming mean ratio to ΣPAH mixture LC50 for other high molecular weight PAHs.
[d] By addition.

The PAH concentrations in this paper are OC-normalized to facilitate comparisons among SQGs and because of the important role of OC in determining PAH partitioning and bioavailability [3]. The mean OC concentration in the BEDS was 1.0% [10]. A sediment OC concentration of 1.0% was therefore assumed in the OC-normalization of SQGs that were originally normalized to dry weight.

Sediment guidelines for PAH mixtures

In addition to SQGs for individual PAH compounds, guidelines have been proposed for LPAH, HPAH, and TPAH. The present analysis is restricted to six LPAH compounds (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene) and seven HPAH compounds (fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene). The LPAH, HPAH, and TPAH SQGs are calculated here as the sum of the OC-normalized concentrations of the 6, 7, or 13 compounds listed above. Because different sets of compounds were included in the original derivation of LPAH, HPAH, and TPAH SQGs [2,4,8–10], the original values differ from those recalculated here. When a SQG was missing for 1 to 3 of the 13 compounds (e.g., there is no ERM for benzo[*b*]fluoranthene), it was estimated assuming the same ratio to TPAH as the guideline based on the ΣPAH mixture LC50 (Table 2). Because there are only three EqP values [5–7], an estimate of the EqP value for TPAH was made by multiplying the mean ratio of EqP to amphipod LC50 times the ΣPAH mixture LC50 for TPAH (Table 2).

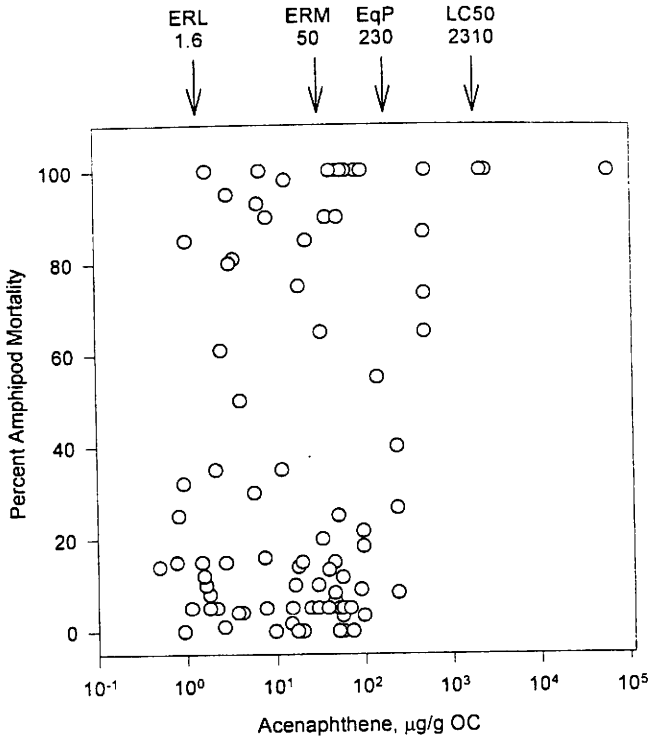

Fig. 1. Amphipod mortality in relation to acenaphthene concentration in 10-d sediment toxicity tests of sediment samples from sites of PAH contamination.

Data sets

Sediment toxicity. Two data sets were used in the analysis and comparison of SQGs in relation to sediment toxicity. The first was restricted to surveys at sites where PAHs were known to be a principal contaminant and is therefore referred to as the PAH data set [8]. It includes 102 samples from San Diego Bay, California, USA [8], Eagle Harbor, Washington, USA [20,21], Curtis Creek, Virginia, USA [22], and Halifax Harbor, Nova Scotia, Canada [23] plus data from 30 sites in Elliott Bay, Washington, USA (S.P. Ferraro, unpublished data). The second set is called the EMAP data because it includes 678 samples collected in U.S. EPA's Environmental Monitoring and Assessment Program surveys in Long Island Sound, New York, USA (1989, 1991), and the Virginian (1990, 1991) and Louisianian provinces (1991, 1992), USA. The EMAP surveys were based on a probabilistic sampling design so that sites were selected without bias toward the presence or absence of PAH contamination [24–26]. Data collected for all of the PAH and EMAP samples included 10-d sediment toxicity to amphipods (*Rhepoxynius abronius, Ampelisca abdita, Eohaustorius estuarius, Leptocheirus plumulosus,* or *Corophium volutator*) following the American Society for Testing and Materials (ASTM) protocol [27], and the sediment concentration of OC and the 13 PAH compounds listed above.

Benthic community structure. Benthos samples were collected along with sediment toxicity and chemistry samples at two of the PAH-contaminated site surveys. In San Diego Bay, a single 8-cm-diameter (50-cm^2) core was collected for benthos analysis from each of five replicate 0.1-m^2 Van Veen grabs at each station. Crustacean and mollusc species (S) retained on a 1.0-mm sieve were collected, identified, and counted to estimate areal species richness at each station, that is, S/0.025 m^2. In Elliott Bay, three 8-cm-diameter cores were collected from an unreplicated 0.1-m^2 Van Veen grab at each station. Areal species richness of crustaceans and molluscs retained on a 1.0-mm sieve was therefore estimated as S/0.015 m^2 in Elliott Bay.

COMPARISON OF SEDIMENT QUALITY GUIDELINES

The mixture paradox

Polycyclic aromatic hydrocarbons virtually always occur in field-collected sediment as a complex mixture of covarying compounds [28,29]. Thus, ecological perturbations result from the cumulative effects of multiple PAHs. A principal key to resolving differences among the SQGs is offered by what might be called the "mixture paradox." The paradox lies in the fact that an SQG derived from accurate, experimental determination of toxicologic effects caused by an individual PAH compound (e.g., through spiked-sediment experiments) will greatly underestimate ecological effects in the field that are associated with the SQG, but actually caused by the PAH mixture. As a corollary, an SQG derived from the correlation of ecological effects with the concentration of an individual PAH in field-collected sediment will greatly overestimate the effects actually caused by the single compound.

The mixture paradox is evident in the relation between amphipod toxicity and the concentration of acenaphthene in field-collected sediments (Fig. 1). The LC50 of acenaphthene to amphipods (2,310 µg/g OC) and the EqP value (230 µg/g OC), both derived from experiments with single compounds, substantially underestimate the toxicity of field-collected sediments (Fig. 1). The ERL (1.6 µg/g OC) and ERM (50 µg/g OC), derived from correlative techniques, accurately indicate low and median toxicologic effects associated with acenaphthene in the field, but are one or two orders of magnitude

below acenaphthene concentrations that could cause the observed effects (Fig. 1).

Long et al. [9] recognized that "the cumulative effects of mixtures" may tend to reduce the "apparent effective concentration of individual toxicants" and make field-derived SQGs "more protective than SQGs based upon only single-chemical approaches." Predictions of the ΣPAH model allow an explicit test of the hypothesis that field-derived SQGs represent concentrations of individual compounds in a PAH mixture whose cumulative toxicologic action is responsible for observed effects. The ΣPAH mixture LC50 guidelines (derived from spiked-sediment tests with single compounds) estimate the concentrations of individual PAHs in a mixture that would cause 50% amphipod mortality. None of the PAHs at the ΣPAH mixture LC50 SQG concentration would be sufficient, by itself, to cause significant toxicity. Note the remarkable similarity of the ERM and ΣPAH mixture LC50 guidelines (Table 1). On average these two guidelines for median effects (50% mortality or 50th percentile of ecological/toxicologic effects) differ by a factor of only 1.5. Agreement is better for the summary guidelines (LPAH, HPAH, TPAH) than for most of the guidelines for individual compounds. Clearly, each of the ERM SQGs for individual compounds is an independent estimate of the effects of the PAH mixture associated with the guideline concentration.

The results of SQG quotient (sediment concentration/SQG) analyses also provide evidence that PAH SQGs derived from correlative techniques are, in fact, mixture guidelines. Assuming additivity of the toxic effects of narcotic chemicals [8,30,31], toxicity should occur when the sum of ERM quotients exceeds unity if the ERMs reflect the effects of individual compounds. However, in a comprehensive investigation of freshwater SQGs, the frequency of toxicity of field-collected sediment samples did not increase above background levels until the sum of ERM quotients exceeded 10 and the frequency of ERM exceedances was 3 to 7 [32]. That result is consistent with the hypothesis that PAH ERMs are mixture guidelines because most of the ERMs would be simultaneously exceeded when the concentration of the PAH mixture reached a toxic level.

CONSENSUS SEDIMENT QUALITY GUIDELINES

Guidelines for individual PAHs seem inappropriate regardless of whether they are derived from correlative, experimental, or theoretical methods. Because of the mixture paradox, they will either be ecologically irrelevant or create the false impression that the individual compound has caused the observed effects. Because the effects are actually caused by multiple, covarying PAHs, it seems reasonable to define the guideline in the mixture context. In particular, a guideline based on TPAH would resolve the mixture paradox and reduce the variability among guidelines for individual compounds.

Several TPAH guidelines have been proposed, but the actual compounds included in TPAH have varied among investigations. Therefore, TPAH guidelines have been recalculated for 13 PAH compounds identified as U.S. EPA priority pollutants [33] and commonly measured in sediment surveys (Table 2).

The TPAH SQGs form three clusters that were intended in their original derivations to represent TECs, MECs, and EECs (Table 3). The TPAH guidelines in these clusters agree within a factor of about four. Excluding the TEL and PEL, which are derived from a combined effects/no effects database, the TPAH guidelines in these clusters agree within a factor of two. This agreement is remarkable because of the different theoretical, empirical, and experimental methods used in the development of the guidelines. The clusters appear to represent independent estimates of the same TPAH concentrations. Consensus SQGs for TPAH are derived simply as the arithmetic mean of the values in each cluster: TEC, 290 μg/g OC; MEC, 1,800 μg/g OC; EEC, 10,000 μg/g OC.

Table 3. Consensus sediment quality guidelines (SQGs) for total polycyclic aromatic hydrocarbons (TPAHs)[a]

SQG	TPAH (μg/g OC)	95% confidence limits
Threshold effect concentration (TEC)		
Threshold effect level	87	
Equilibrium partitioning	211	
ΣPAH toxicity threshold	393	
Effects range–low	350	
Screening level concentration	409	
Mean (consensus) TEC	290	119–461
Median effects concentration (MEC)		
Probable effects level	804	
Low apparent effects threshold	1,796	
ΣPAH mixture LC50	2,114	
Effects range–median	2,358	
Mean (consensus) MEC	1,800	682–2,854
Extreme effects concentration (EEC)		
High apparent effects threshold	10,230	
Consensus EEC	10,000	NA

[a] OC = organic carbon; NA = not applicable.

FIELD AND EXPERIMENTAL VERIFICATION OF CONSENSUS GUIDELINES

Sediment toxicity

In the data set for surveys where PAHs were the dominant ecotoxicologic factor, significant sediment toxicity (>24% mortality [34]) occurred in 2 of 36 samples (5.6%) with TPAH concentrations below the TEC (Fig. 2, Table 4). The background frequency of significant amphipod toxicity in reference marine sites is 5.0% [8]. Toxicity was significant in all 12 samples with TPAH concentrations above the EEC (Fig. 2 and Table 4). Few false negatives occurred below the TEC and no false positives occurred above the EEC.

The frequency of significantly toxic sediments increased, but not substantially, between the TEC to MEC (43% toxic) and MEC to EEC (50% toxic) concentration ranges (Fig. 2 and Table 4). Thus, a broad range of concentrations exists between the TEC and the EEC in which there is about a 50% probability of 10-d toxicity to amphipods. An SQG cannot be set within that range that would have a low frequency of both false negatives and false positives. The mean percent mortality of amphipods exposed to sediment with TPAH concentrations between the TEC and EEC guidelines was only about 36% (Table 4).

The MEC proved to be what it was expected to be, that is, an indicator of median effects. Of the 52 significantly toxic samples, 28 were less than the MEC and 24 exceeded the MEC (Fig. 2 and Table 4). The MEC lies within the transition between nontoxic and highly toxic sediment. It is literally a guide line for a median probability of adverse effects. The MEC is not an unequivocal indicator that sediments are toxic or otherwise unacceptable.

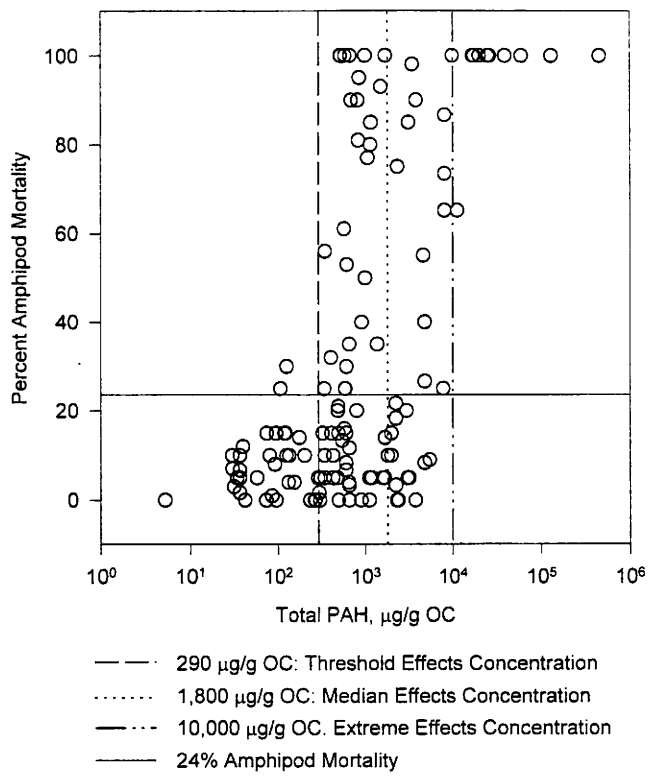

Fig. 2. Amphipod mortality in relation to total PAH concentration in 10-d sediment toxicity tests of sediment samples from sites of PAH contamination.

Sediments at relatively few sites exceed the consensus TPAH guidelines. Among 678 EMAP samples that were collected with a probabilistic sampling design from Long Island Sound in 1989 through 1990, the Virginian Province in 1990 through 1991, and the Louisianian Province in 1991, 45 (6.6%) exceeded the TEC, 2 (0.3%) exceeded the MEC, and none exceeded the EEC (Fig. 3 and Table 4). The other major difference between the EMAP data set and the PAH data set was the much higher proportion of toxic sediments below the TEC among EMAP samples (13%) than among PAH samples (5.6%) (Table 4). The increase in the frequency of toxicity at low PAH concentrations among the EMAP samples is probably attributable to other stressors. Above the TEC, the frequency of toxicity and the mean percent amphipod mortality are quite similar for the EMAP and PAH data sets, as would be expected if the consensus TPAH guidelines are valid indicators of PAH effects (Table 4). Finally, the TEC was exceeded in 20 of the 104 toxic sediments in the entire EMAP data set suggesting that PAHs alone could cause approximately 20% of the ambient sediment toxicity in the EMAP provinces.

Benthic community structure

Areal species richness of crustaceans and molluscs decreased as the consensus SQGs were exceeded in San Diego Bay (Fig. 4) and Elliott Bay (Fig. 5). In San Diego Bay, the mean number of species per 0.025 m^2 decreased from 10.5 at sites with sediment TPAH concentrations below the TEC to 6.8 at sites with sediment TPAH between the TEC and MEC (Table 4). Sediment TPAH contamination and benthic community impacts were greater in Elliott Bay where the number of species per 0.015 m^2 decreased from 12.4 between the TEC and MEC, to 9.6 between the MEC and EEC, to 3.9 at sites with TPAH concentration above the EEC (Table 4). Only one or two crustacean and mollusc species occurred in the benthic

Table 4. Sediment toxicity and benthic community structure in relation to consensus sediment quality guidelines

	Total PAH concentration (µg/g organic carbon [OC])			
	<290	290–1,800	1,800–10,000	>10,000
Sediment guideline[a]	<TEC	>TEC <MEC	>MEC <EEC	>EEC
PAH-contaminated sites				
n (%) toxic[b] samples	2 (5.6%)	26 (43%)	12 (50%)	12 (100%)
n (%) nontoxic[c] samples	34 (94%)	34 (57%)	12 (50%)	0 (0%)
Mean % amphipod mortality	7.6	34.1	38.3	97.1
EMAP sites				
n (%) toxic[b] samples	84 (13%)	19 (44%)	1 (50%)	ND[d]
n (%) nontoxic[c] samples	549 (87%)	24 (56%)	1 (50%)	
Mean % amphipod mortality	11.2%	28.3%	40%	
Crustacean and mollusc species				
San Diego Bay, California, USA				
Species/0.025 m^2: Mean	10.5	6.8	ND	ND
Range	9–12	4–11		
Elliott Bay, Washington, USA				
Species/0.015 m^2: Mean	ND	12.4	9.6	3.9
Range		10–17	1–16	1–7

[a] TEC = threshold effects concentration, 290 µg/g OC; MEC = median effects concentration, 1,800 µg/g OC; EEC = extreme effects concentration, 10,000 µg/g OC.
[b] Amphipod mortality > 24%.
[c] Amphipod mortality < 24%.
[d] ND = no data.

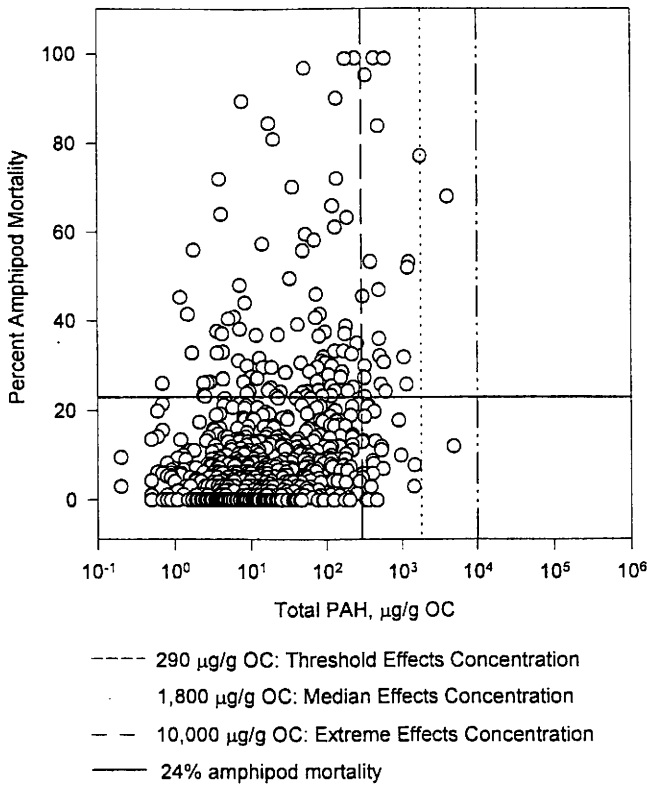

Fig. 3. Amphipod mortality in relation to total PAH concentration in 10-d sediment toxicity tests of Environmental Monitoring and Assessment Program (EMAP) sediment samples from the Virginian and Louisianian provinces, USA.

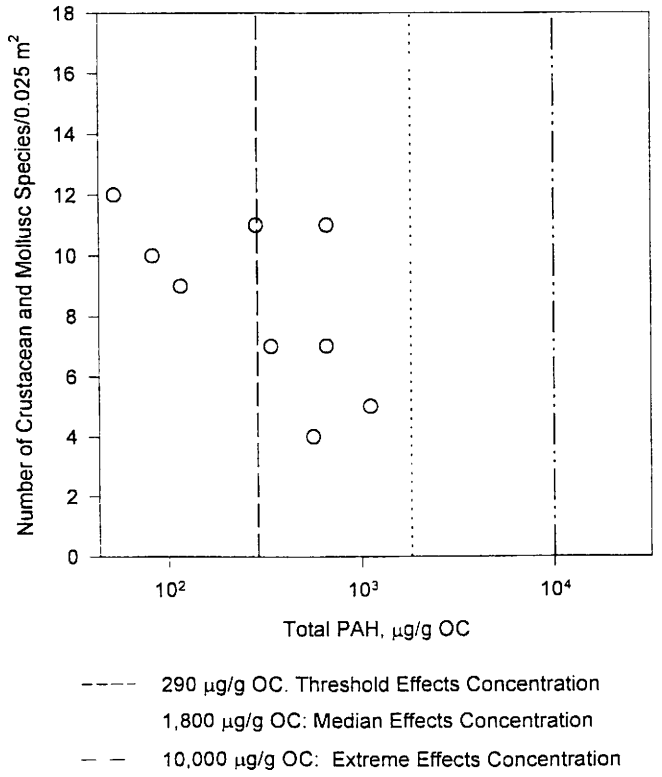

Fig. 4. Areal species richness of crustaceans and molluscs in relation to total PAH concentration in San Diego Bay, California, USA.

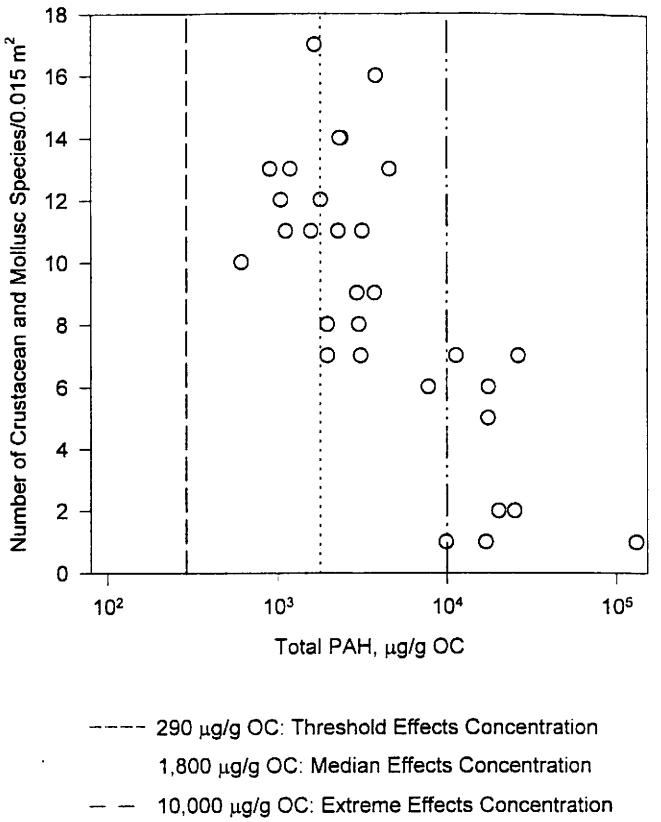

Fig. 5. Areal species richness of crustaceans and molluscs in relation to total PAH concentration in Elliott Bay, Washington, USA.

assemblage at five sites in Elliott Bay that were highly contaminated by PAHs.

DISCUSSION

Consensus guidelines

The TEC/MEC/EEC sediment quality guidelines for PAH mixtures provide a unifying synthesis of other guidelines including the SLC, ERL/ERM, EqP criteria, AET, ΣPAH, and TEL/PEL. When interpreted in the context of PAH mixtures, all of these guidelines arrive at similar concentrations for threshold, median, or extreme effects (Table 3). This similarity is unlikely to be coincidental. Rather, the agreement of guidelines derived from a diversity of theoretical and empirical approaches helps establish the validity of the consensus values. Their validity is further established by the ability of the consensus guidelines to predict sediment toxicity and benthic community perturbations at sites of PAH contamination (Table 4 and Figs. 2, 4, and 5). Expression of these guidelines for TPAH, rather than individual compounds, resolves the mixture paradox, that is, they account for mixtures and reflect causal rather than correlative effects.

Effective use of SQGs

Guidelines should guide, not dictate. The TEC offers the most useful SQG because it is reasonable to conclude that PAH mixtures are unlikely to cause adverse effects on benthic ecosystems below the TEC. The EEC indicates virtual certainty of adverse effects, but the EEC is rarely exceeded and contamination is so extreme above the EEC that the unacceptability of ecological degradation is usually obvious. The region of greatest uncertainty lies between the TEC and EEC. Here,

a broad gradient of sediment contamination occurs along which effects are increasingly more probable. The MEC is simply a point near the middle of this gradient and, therefore, should not be used to discriminate acceptable from unacceptable conditions.

Bulk sediment chemistry cannot resolve the uncertainty of toxicity and ecological effects at TPAH concentrations between the TEC and EEC. However, the issue can be resolved through independent, empirical data on sediment toxicity and benthic communities, as suggested by Long and Chapman [35] in their seminal paper on the sediment quality triad. Conclusions about the ecological effects of sediment contamination should be based on the weight of evidence among the three elements of the triad [36].

Uncertainty

Four principal sources of uncertainty exist about the consensus guidelines. First, the guidelines are based on the concentrations of the 13 parent PAHs and do not include alkylated and other PAH compounds that may contribute to biological effects. The degree to which the distribution of the 13 parent compounds is representative of the distribution of other PAHs is unknown. Second, the laboratory toxicity tests used to develop some of the guidelines from which the consensus values were derived are not sensitive to increased toxicity caused by photoactivation of PAH compounds [31,37]. Thus, effects of PAHs may be greater than expected from the guidelines, although the guidelines do correlate with the species richness of benthic assemblages exposed to ambient light (Figs. 4 and 5). Third, chemical analyses of bulk sediments may greatly overestimate bioavailability in sediments that contain inert (e.g., soot) PAH fractions [38]. In such cases, the consensus guidelines will overestimate toxicity and ecological effects caused by PAHs. Analysis of PAH concentrations in interstitial water can resolve the bioavailability issue when an inert PAH fraction is suspected. Each of these first three sources of error probably contributes to the uncertainty of effects over the broad concentration range between the TEC and EEC. Finally, additional field data, especially for benthic assemblages and other ecological indicators, are needed to validate the consensus guidelines.

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Suspended Solids, Trace Metal and PAH Concentrations and Loadings from Coal Pile Runoff to Hamilton Harbour, Ontario

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ABSTRACT. *The Kenilworth boatslip has been identified as a "hotspot" within the Hamilton Harbour Area of Concern because of highly contaminated bottom sediments. There are a variety of sources potentially contributing to this sediment contamination, including runoff from industrial coal piles. The objective of this study was to assess the contaminant characteristics associated with coal pile runoff and identify potential impacts that the runoff might have on sediment quality. Flow-proportioned samples of the coal pile runoff were collected from June through October, 1996 and analyzed for total suspended solids, trace metals, and PAHs. Loadings for selected metals and PAHs were determined using a volumetric approach that considered mean contaminant concentrations and measured or modeled flow volumes. The suspended solids and total trace metal concentrations (Al, Fe, Mn, V, Cd, Cr, Cu, Pb, Zn) often exceeded Canadian Water Quality Guidelines for the Protection of Aquatic Life. Concentrations of fluoranthene, phenanthrene, pyrene, and chrysene exceeded the provincial "Severe Effect Level" for sediment, although the bioavailability of these PAHs should be examined more thoroughly. In general, suspended solids concentration and coal pile volume were significantly correlated with the concentrations of trace metals in the coal pile runoff, while hydrometeorologic variables such as rainfall intensity, rainfall depth, and runoff volume were weakly correlated with metals concentrations. The ratios of various PAHs to naphthalene suggested that coal pile runoff could be an important contributing source to bed sediment contamination. Given the concentrations and loadings of solids, metals, and PAHs and the relatively low volume of runoff, it would be prudent to treat the coal pile discharge as a remedial action for the harbor.*

INDEX WORDS: *Hamilton Harbour, suspended sediment, trace metals, polynuclear aromatic hydrocarbons (PAHs), coal pile runoff, Severe Effect Level (SEL).*

INTRODUCTION

Hamilton Harbour, Ontario, is a recreational and industrial port primarily characterized by steel manufacturing and steel related industries which occupy the southern shore of the harbor. It is one of 42 Areas of Concern (AOCs) around the Great Lakes designated by the International Joint Commission (IJC) because of environmental impairments. Impairments identified include: loss of fisheries and wildlife habitat, restrictions on fish consumption,

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fish tumors and other deformities, beach closings, interference with drinking water, high concentrations of trace metal and organic compounds in bottom sediment, degradation of benthos, and exceedances of water and sediment quality criteria (International Joint Commission [IJC] 1989, Murphy *et al.* 1991, Ling *et al.* 1993, Remedial Action Plan [RAP] 1992, Diamond and Ling-Lamprecht 1996, Poulton *et al.* 1996). Inputs of suspended solids, trace metals and organic compounds from several industrial discharge sites contribute to these impairments (Murphy *et al.* 1991, Poulton *et al.* 1996). One source of suspended solids, trace metals and organic compounds is stormwater runoff from coal piles (Anderson and Youngstrom 1976, Davis and Boegly 1981). In 1995, 2.5 million metric tons of coal were shipped to industries within Hamilton Harbour (Statistics Canada 1997). This coal was stockpiled on open industrial property that can drain directly to the harbor, untreated. One of the areas in the harbor that receives untreated coal pile runoff is the Kenilworth boatslip.

High concentrations of suspended solids can produce adverse effects on receiving waters and aquatic biota (Scullion and Edwards 1980, Canadian Council of Resource and Environment Ministers 1993, Waters 1995). The Canadian Council of Resource and Environment Ministers (1993) mandated that for the protection of aquatic life, total suspended solids concentrations entering a waterbody should not exceed 10 mg/L when the background suspended solids concentration is $\leq$ 100 mg/L. Irvine *et al.* (1997) indicated that the ambient suspended solids concentration within the Kenilworth boatslip was in the range of 5 mg/L. Coal pile runoff studies performed by Cox *et al.* (1977) yielded mean suspended solids concentrations ranging from 190 mg/L to 650 mg/L, suggesting that the suspended solids concentrations entering the Kenilworth boatslip from coal pile runoff could be several times higher than the acceptable level established by the Canadian Council of Resource and Environment Ministers (1993). Stahl and Davis (1984) indicated that higher sulfur content coal yielded higher suspended solids concentrations within the runoff and that suspended solids concentrations increased with successive leaching events because of prolonged microbial-mediation which degraded sulphur compounds within the coal pile system.

Trace metal concentrations in coal pile runoff have been well documented through leaching simulations (Anderson and Youngstrom 1976, Davis and Boegly 1981) and in most cases concentrations exceeded guidelines established by the Canadian Council of Resource and Environment Ministers (1993). However, it has been argued that coal stockpiled at industrial sites generally receives less rain per kilogram weight compared to simulations, resulting in the overestimation of naturally leached trace metal concentrations (Davis and Boegly 1981, Stahl and Davis 1984). Concentrations of trace metals (e.g., Fe, Zn, Pb, As, Cu, Al) when leached, can be acutely toxic to biota in receiving waterbodies and cause chronic disorders in aquatic life (Wong *et al.* 1978, Scullion and Edwards 1980, Canadian Council of Resource and Environment Ministers 1993).

Relatively little is known about the characteristics of organic material leached from coal piles. The few rainfall simulation studies which do exist neither adequately describe changes that might occur in the organic content of coal during weathering nor characterize the leaching of coals in a field environment (Stahl *et al.* 1984, Fendinger *et al.* 1989). In a study performed by Fendinger *et al.* (1989), it was demonstrated that organic material in coal pile runoff was dominated by aliphatic hydrocarbons, while the concentrations of aromatic hydrocarbons were dependent upon the organic content of the coal. Stahl *et al.* (1984) indicated that PAH concentrations in runoff generally were low (50 μg/L), probably because of their low solubility in water. However, Fendinger *et al.* (1989) observed that PAHs and the suspended solids fraction in coal pile runoff were positively related. They also observed that the highest PAH concentrations occurred during the "first flush" of the event when the concentrations of suspended solids in the runoff were highest. Guidelines for PAHs in water systems have not been developed because of the complex chemistry and large number of different PAH compounds (Canadian Council of Resource and Environment Ministers 1993), but guidelines for PAHs in sediment have been established (Ontario Ministry of Environment and Energy [MOEE] 1993). Several studies have documented the potential negative impacts of PAHs on receiving waterbodies (Black 1983, Fabacher *et al.* 1988, Krantzberg and Boyd 1992, Catallo *et al.* 1995).

This study is a source evaluation of coal pile runoff discharged from an industrial coal field to the Kenilworth boatslip, Hamilton Harbour. The Kenilworth boatslip has been identified as a "hotspot" within Hamilton Harbour because of highly contaminated bottom sediments (Murphy *et*

al. 1995). Contaminated sediment remediation increasingly has been considered a viable option to improve conditions of aquatic ecosystems such as the Kenilworth boatslip (Murphy *et al.* 1995). However, to determine the success of such treatment, an understanding of contaminant loads to the proposed remediation site is necessary. Also, a better understanding of the factors influencing coal pile runoff may result in the development of strategies that can reduce runoff volume and/or contaminant loads before they migrate from the site. This study had several objectives. First, to document suspended solids, trace metals, and PAH concentrations and loadings in coal pile runoff that discharged to the Kenilworth boatslip. Contaminant concentrations were compared to established water and sediment quality guidelines to evaluate the potential impact of the discharge on aquatic biota. Second, to quantitatively evaluate the relationships between trace metals and other factors (rainfall and runoff characteristics, coal pile characteristics) to increase an understanding of contaminant input dynamics from coal piles to Hamilton Harbour. Finally, PAH ratios were compared in coal pile runoff to ratios in Hamilton Harbour bed sediments to assess relative source signatures.

METHODS

Sampling Methods

The study area was a 19,150 m^2 outdoor industrial coal storage field at a steel manufacturing facility in Hamilton, Ontario. It contained several large coal piles, which continually changed size as coal was added and/or removed. A tile system drained infiltrated and surface runoff from the coal piles and discharged it directly to the Kenilworth boatslip. An on-site gauging station was located at the discharge point to the boatslip and the coal pile runoff rate was recorded continuously as part of the MOEE Municipal and Industrial Strategy for Abatement (MISA) program.

For this study, flow measurements were recorded in the discharge flume at 15 minute intervals between 1 April 1996, and 31 October 1996, using a Badger Meter Series 2000 Obstructionless No-Loss Flowmeter. The Badger flowmeter was used to trigger an American Sigma Streamline 700 Portable Sampler to collect samples for runoff quality analysis. The pump sampler was connected to the flowmeter control panel from 1 June 1996, to 31 October 1996. The pump sampler was programmed to take a 200 mL sample from the discharge flume at a flow interval of 10 m^3. All 200 mL samples were collected in a clean 10 L glass bottle as a flow-proportioned composite sample. The flow-proportioned composite sample was removed from the field as soon as possible (normally within 5 hours) after the end of each runoff event. The composite samples were analyzed for suspended solids, trace metal, PAH, particulate organic carbon and dissolved organic carbon concentrations. Rainfall data between 1 April 1996 and 31 October 1996 were obtained from Environment Canada site 3525B YHM 6153194-153 ONT HAMILTON A located approximately 10.5 km southwest of the boatslip.

Laboratory Methods

Suspended solids concentrations were determined by filtering a 100 mL sub-sample of the composite sample onto a preweighed 0.45 μm Millipore filter. After filtration, the filter was dried at 104°C for 1 h to remove moisture and then reweighed to determine the suspended solids concentration (American Public Health Association 1985).

Two 250 mL sub-samples were collected in the laboratory from the flow-proportioned composite sample and processed for total and dissolved trace metal concentrations. The samples for the dissolved phase analysis were passed through 0.45 μm Sartorius filters and fixed with 1 mL (1:1) Seastar nitric acid, while the samples for total metals analysis were fixed with 1 mL (1:1) Seastar nitric acid without filtration (Droppo and Jaskot 1995). Trace metal analysis was performed by the National Laboratory for Environmental Testing (NLET) using inductively coupled argon plasma (ICAP) following Environment Canada Method 02-2001(Environment Canada 1994). All samples (filtered and unfiltered) were concentrated 10 times and digested using nitric acid. An analytical run normally consisted of 60 to 80 samples, 3 to 4 spiked samples, 2 spiked blanks, 4 method blanks, a control standard, 2 reference samples, 2 reference duplicate samples, 2 certified reference and 2 ASTM Type I grade reagent water samples to ensure no contamination. The certified references were TM-21 and TM-22, obtained from the National Water Research Institute, and NIST-certified Water Reference Material 1643C.

For quality assurance/quality control purposes, the calibration blank and verification standard were run after system calibration and thereafter at a rate of approximately every 11 samples. If the deviation of the calibration blank was greater than twice the

method detection limit (MDL) and/or the verification standard was greater than ± 5% from the theoretical mean, corrective measures were taken. The accuracy of the analytical method was expressed as a per cent error between the measured and certified value for the certified reference material. The per cent error typically was less than 10% for all metals. Spike recoveries were sample dependent and usually ranged from 95% for Cd to 109% for Al. The MDLs were: 0.0001 mg/L for Cd, Mn, V; 0.0002 mg/L for Cr, Cu, Ni, Pb, Zn; 0.0004 mg/L for Fe; and 0.002 mg/L for Al.

Following the removal of the 500 mL for metals analysis, the remaining volume of selected flow-proportioned samples was submitted immediately to Wastewater Technology International (WTI), Burlington, Ontario, for PAH analysis. Each sample was filtered through Whatman Grade #1 filter paper to separate the particulates from the water. The filtered particulates were analyzed directly and henceforth the results are referred to as the particulate phase PAHs, while the PAHs in the filtrate are referred to as the dissolved phase PAHs.

Analysis of the dissolved phase PAHs was adapted from U.S. EPA Method 624 (U.S. EPA 1984). Briefly, a 1 L sample was spiked with a surrogate mixture and serially extracted three times with dichloromethane under basic conditions. The combined extracts were dried over sodium sulphate. The solvent was evaporated from the extract to a final volume of 3 mL. The extract was then combined with an internal standard and analysed by gas chromatography-mass spectrometry (GC/MS). The GC/MS system was calibrated just prior to the start of each analytical run and the calibration was verified after each batch of five samples.

For QA/QC purposes with each GC/MS run of five samples a solvent blank (dichloromethane), duplicate (a random sample was divided into two equal halves and extracted separately), a method blank and a spike were done. The spike involved dividing a sample in two, with one half being spiked with six PAH surrogates and the other half being spiked with the PAH surrogates and 0.25 ml of PAH Supelpreme Target PAH mix (200 mg/L).

The analysis of the particulate phase for PAHs was adapted from U.S. EPA Method 8270 (U.S. EPA 1994). The sediment was spiked with six PAH surrogates and then Soxhlet-extracted with an acetone-hexane (59:41) mix. The extract was base-partitioned with 2% potassium bicarbonate solution. The aqueous medium was then back-extracted with hexane and the organic fractions combined. The combined organic extract was dried through sodium sulphate and concentrated for analysis by GC/MS as described previously.

The QA/QC approach for the particulate phase was similar to that of the dissolved phase. In addition to the solvent blank, method blank, duplicate and spike analyses, however, a certified sediment reference material (EC-4 or EC-1, obtained from the National Water Research Institute) was run with each batch of samples. The surrogate spike recovery for all sample batch runs (particulate and dissolved phase) averaged between 72% for naphthalene-d_8 and 88% for fluorene-d_{10}. The results of the method blank analyses for both the particulate and dissolved phases always were below the MDL for each PAH.

The same 1 L sub-sample processed for PAH concentrations also was analysed for particulate organic carbon (POC) and dissolved organic carbon (DOC). The analyses were performed by NLET using POC method 01-1090 and DOC method 01-1020 (Environment Canada 1994).

Statistical Methods

A stepwise multiple regression approach was used to estimate flow volumes for storms not sampled (because of instrument malfunction) in order to calculate suspended solids, trace metals and PAH loads entering the Kenilworth boatslip during the 7-month study period. For each measured storm event the total rainfall depth (mm), peak 15 minute rainfall intensity (mm/h), peak 1 h rainfall intensity (mm/h), antecedent hours and coal pile volume (metric tons) prior to a rainfall event were entered into the analysis as the predictor variables. Event runoff volume (m^3) from the coal field was the dependent variable. In this study a rainfall event was defined as any storm which yielded rainfall 9 mm or greater, or was greater than 12 h in duration, as such storms were observed to result in sufficient runoff volume to initiate sampling. Pearson product-moment correlation (r) was used to compare the relationship between total metal concentrations and factors possibly influencing metals concentrations in the coal pile runoff (total rainfall depth (mm); peak 15 minute rainfall intensity (mm/hr); peak 1 h rainfall intensity (mm/hr); runoff volume (m^3); antecedent number of days before the runoff event; coal pile volume (metric tons); and suspended solids concentration (mg/L)).

The distributions of all variables used in the statistical evaluations were tested for normality using

the probability plot correlation coefficient test (Filliben 1975, Vogel 1986). Qualitatively, the normal probability plots approximated a straight line, which is indicative of a normal distribution (Ryan *et al.* 1992). However, the correlations (r) between the normal scores and the raw data typically were in the 0.7 to 0.8 range, which indicates the distributions were not normally distributed at $\alpha = 0.05$. Tests using the t-distribution are, however, relatively insensitive to moderate departures from normality (Mendenhall 1979, Ryan 1990).

Loading Estimate Methods

Suspended solids, trace metals, and PAH loads were calculated using a simple volumetric approach often used to estimate contaminant loads from urban sources (e.g., Marsalek and Ng 1989, Nix 1990, Irvine *et al.* 1993, Irvine *et al.* 1998). Estimated contaminant loads were calculated using the equation:

$$L_j = C_j \cdot V \quad (1)$$

where L_j is the load of pollutant, j; C_j is the mean concentration of pollutant, j; and V is the estimated total runoff volume from the coal piles for the field season; $V = \Sigma Q_i$ when Q_i is the event runoff volume.

RESULTS

Concentrations of Suspended Solids, Trace Metals, and PAHs

During the sampling period 32 rainstorms occurred and flow volume was recorded successfully for 17 of these events. Flow-proportioned composite samples from these 17 events were collected for suspended solids analysis. The mean suspended solids concentration representing the 17 storms was 2,188 mg/L, with a standard deviation of 3,402 mg/L.

Fifteen of the 17 storm events were analysed for total and dissolved phase trace metal concentrations. The mean and standard deviation for selected total trace metals are compared to Canadian Water Quality Guidelines in Table 1. Results for the dissolved phase of some metals (Al, Cd, Cu, Pb) were below the MDL in some samples. Therefore, mean values had to be estimated from a censored data set, which was not the case for the total metals results in Table 1 (the total metals results always were above MDL). Various methods for estimating the mean of a censored data set have been proposed (Newman *et al.* 1989, El-Shaarawi and Dolan 1989, Dolan and El-Shaarawi 1991). Often, however, a value of one-half the MDL is used to calculate the mean and this approach was taken in this study. The mean concentrations for the dissolved phase were (in mg/L): Al-0.056; Cd-0.00013; Cr-0.0025; Cu-0.001; Fe-0.64; Mn-0.94; Ni-0.024; Pb-0.0004; V-11.1; Zn-0.014.

Four storm events were sampled for particulate phase PAH concentrations and six storm events for dissolved phase PAH concentrations. The mean concentrations for selected PAHs are compared to guideline levels in Table 2. The PAHs shown in Table 2 were selected for illustrative purposes and represent PAHs that commonly are reported in the literature. Ontario Ministry of the Environment and Energy (1993) concentrations for particulate phase PAHs were normalized for direct comparison using the recorded total organic carbon content (determined by summing the particulate and dissolved phase organic carbon contents measured in the field samples), following the method of MOEE (1993). Polynuclear aromatic hydrocarbons with particularly high concentrations were fluoranthene, phenanthrene, pyrene and chrysene which exceeded

TABLE 1. Selected mean (total) trace metal concentrations.

	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
Mean	3.2	0.0019	0.024	0.035	15.5	1.3	0.05	0.022	15.55	0.28
S.D.	3.4	0.0015	0.024	0.028	14.4	0.5	0.03	0.018	16.76	0.3
CWQG	0.1	0.0018	0.02	0.004	0.3	N.S.	0.15	0.007	N.S.	0.03

#— total trace metal concentrations (mg/L); n = 15
S.D.— standard deviation
CWQG—Canadian Water Quality Guideline for Protection of Aquatic Life; N.S.- no standard

TABLE 2. Selected mean polynuclear aromatic hydrocarbon (PAH) concentrations.

	Fluoranthene	Phenanthrene	Benzo(a)pyrene	Pyrene	Chrysene
Mean	208.2 (4.5)	284.3 (6.1)	71 (0.9)	139.9 (3.1)	46.6 (0.7)
S.D.	254.3 (2.1)	338.5 (3.3)	85.4 (0.2)	173.2 (1.4)	48.7 (0.2)
MOEE Guideline	102	95	144	85	46

#—particulate bound PAH concentrations (g/g); n = 4
(#)—dissolved PAH concentrations (g/L); n = 6
NOTE—Ministry of the Environment and Energy [MOEE] guideline for particulate bound PAHs

TABLE 3. Selected trace metal loads.

	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
g*	30,966 (897)	18 (2)	238 (25)	340 (20)	150,018 (6,237)	12,621 (9,128)	477 (233)	213 (12)	150,640 (107,173)	2,720 (132)
g/d	144.7 (4.2)	0.1 (0.01)	1.1 (0.11)	1.6 (0.09)	701.1 (29.1)	59.0 (42.7)	2.2 (1.1)	1.0 (0.1)	703.9 (500.8)	12.7 (0.6)

#—total trace metal loads
(#)—dissolved trace metal loads
* mass discharged during study period (1 April 1996, to 31 October 1996)

the MOEE "Severe Effect Level" (SEL) for particulate phase PAHs.

Estimated Runoff Volume

The stepwise regression indicated that event rainfall depth (mm) and coal pile volume (metric tons) were the two most influential predictors and the resulting equation was:

$$\text{Flow Volume} = 125.2 + 22.4 \cdot (\text{rainfall depth}) - 0.00076 \cdot (\text{coal pile volume}) \quad (2)$$

where the r^2 was 0.74, the standard error of the estimate (σ) was 180, and rainfall depth and coal pile volume were significant at the 0.001 and 0.025 levels, respectively.

Combining the observed runoff volume for the 17 sampled storm events with runoff volume of the 15 storm events estimated using equation 2, the total coal field runoff volume for the 32 storm events between 1 April 1996, and 31 October 1996, was 9,690 m^3. This runoff represented approximately 96% of the rainfall depth falling on the coal field site during that period. The remaining 4% of the rainfall would be partitioned between evaporation, storage within the piles, or overland flow from areas near the shoreline (and bypassing the tile drains). The unmeasured overland flow therefore would produce a minimal effect on the loading estimates.

Suspended Solids, Trace Metal, and PAH Loading Estimates

Loading estimates of suspended solids, trace metals and PAHs entering the boatslip from coal pile runoff were calculated according to equation 1. The suspended solids load entering the boatslip from the coal field during the study period (1 April 1996, to 31 October 1996) was 21,202 kg (or 99 kg/d). Trace metal and PAH loading estimates are presented in Tables 3 and 4, respectively.

Metals Correlations

Table 5 presents the correlation results between total metals concentrations observed during runoff events and factors that may affect these metals concentrations. There was a significant positive correlation (α = 0.05) for all metals concentrations (except V) and suspended solids concentration. The relationships between total metals concentrations and other variables were weaker. After suspended

TABLE 4. Selected polynuclear aromatic hydrocarbon (PAH) loads.

	Fluoranthene	Phenanthrene	Benzo(a)pyrene	Pyrene	Chrysene
g*	4,413 (44)	6,027 (59)	1,505 (7)	2,965 (30)	988 (7)
g/d	20.6 (0.20)	28.2 (0.27)	7 (0.04)	13.9 (0.14)	4.6 (0.03)

#—particulate bound PAH loads
(#)—dissolved PAH loads
* mass discharged during study period (1 April 1996, to 31 October 1996)

TABLE 5. Correlation (r) matrix of total trace metal concentrations and runoff factors.

Variable	Al	Cd	Cr	Cu	Fe	Ni	Pb	V	Zn
Total Rainfall Depth (mm)	–0.358	–0.425	–0.31	–0.361	–0.405	–0.057	–0.423	–0.317	–0.336
Peak 15 min. Rainfall (mm/hr)	0.238	**0.56**	0.467	0.312	0.422	0.281	0.326	0.314	0.347
Peak 1 h Rainfall (mm/hr)	0.03	–0.048	–0.012	0.013	–0.065	–0.08	–0.16	0.007	0.077
Runoff Volume (m^3)	–0.235	–0.282	–0.136	–0.17	–0.203	0.162	–0.21	–0.438	–0.363
Antecedent Days before Runoff Event	–0.291	–0.462	–0.329	–0.476	–0.342	–0.064	–0.356	–0.468	–0.438
Coal Pile Volume (metric tons)	–0.475	**–0.621**	–0.329	**–0.524**	–0.436	0.07	–0.375	**–0.567**	**–0.647**
Suspended Solids Concentration (mg/L)	**0.873**	**0.881**	**0.919**	**0.736**	**0.917**	**0.652**	**0.901**	0.349	**0.879**

Bold face correlations are significant at $\alpha = 0.05$

solids concentration, coal pile volume had the strongest relationship with metals concentrations, the correlation being significant ($\alpha = 0.05$) for four of the nine metals. Peak 15 minute rainfall intensity was the hydrometeorologic variable that had the strongest relationship with metals concentrations, but this relationship was only significant ($\alpha = 0.05$) for one metal.

PAH Ratios

Figure 1 shows the ratios between the various PAHs analyzed in this study and naphthalene (NaP). A variety of studies have used PAH ratios in bed sediment as a semi-quantitative indicator of source (Furlong *et al.* 1988, Zhang *et al.* 1993, Benner *et al.* 1995), because the exact source(s) often may not be known. More sophisticated statistical/receptor modeling also has been applied recently to help source-apportion PAHs in sediments (Christensen *et al.* 1997, Sharma *et al.* 1997). The receptor modeling approach was not needed in this study since it was possible to determine PAH ratios for a well-known source (coal pile runoff). The calculated ratios can be used as a benchmark to assist future sediment studies in Hamilton Harbour and other areas in evaluating possible sources. The PAH ratios for coal pile runoff also are compared with those for coal tar, coal and wood gasification, highway dust, and air filter coke oven emissions in Figure 1. In Figure 2, the ratios for the coal pile runoff are compared to the PAH ratios for coal tar

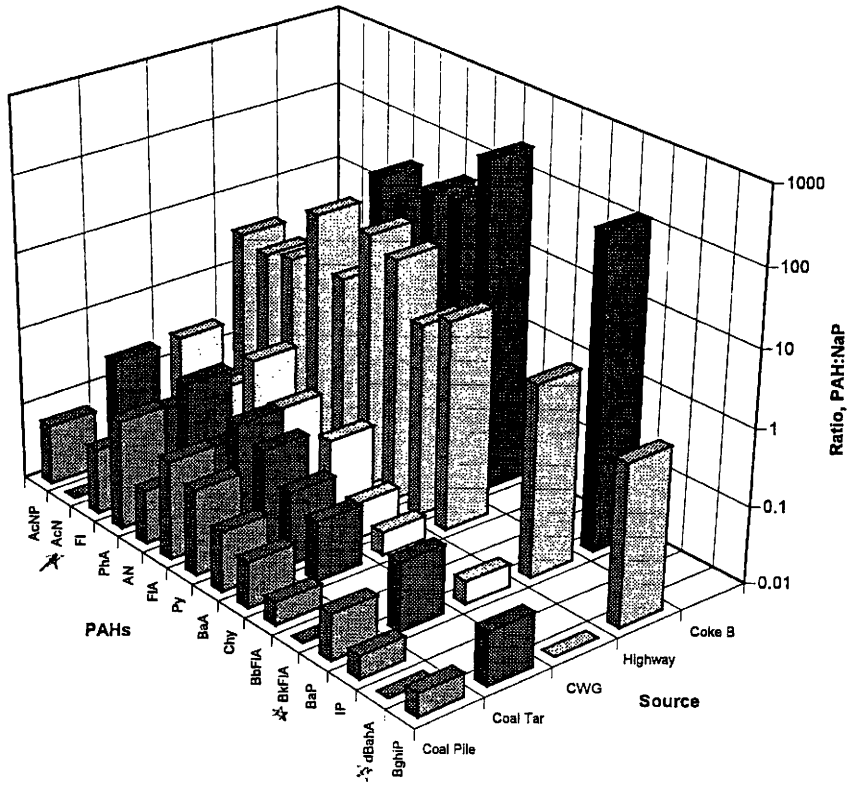

FIG. 1. Ratios of mean particulate phase PAHs in the coal pile runoff samples (n = 4) to NaP. Also shown are ratios of PAHs to NaP for other sources as reported by Christensen et al. *(1997). Abbreviations are: naphthalene (NaP), acenaphthylene (AcNP), acenaphthene (AcN), fluorene (Fl), phenanthrene (PhA), anthracene (AN), fluoranthene (Fla), pyrene (Py), benzo(a)anthracene (BaA), chrysene (Chy), benzo(b)fluoranthene (BbFlA), benzo(k)fluoranthene (BkFlA), benzo(a)pyrene (BaP), indeno(1,2,3-c,d)pyrene (IP), dibenzo(a,h)anthracene (dBahA), and benzo(g,h,i)perylene (BghiP); coal and wood gasification (CWG), highway dust (highway), and air filter coke oven emissions (Coke B).*

contaminated sediment from Hamilton Harbour as reported by Murphy *et al.* 1991.

DISCUSSION

The mean suspended solids concentration of 2,188 mg/L observed in the coal pile runoff exceeded the Canadian Water Quality Guideline of 10 mg/L (based on ambient suspended solids concentration being ≤ 100 mg/L). Ling *et al.* (1993), in summarizing MOEE data, reported an ambient suspended solids concentration of 10 mg/L for the entire harbor, which is comparable to the 5 mg/L level reported by Irvine *et al.* (1997) for the Kenilworth boatslip. High concentrations of suspended solids, as noted previously, can have a negative impact on aquatic biota, including fishes.

Several trace metals within coal pile runoff exceeded Canadian Water Quality Guidelines, which is consistent with results documented by Cox *et al.* (1977) and Davis and Boegly (1981). Total trace metal concentrations observed in this study may be chronically toxic to aquatic organisms at various trophic levels (Warnick and Bell 1969, Wong *et al.* 1978, Krantzberg and Boyd 1992) but would not be high enough to cause lethal effects to several aquatic insects and fish species (Warnick and Bell

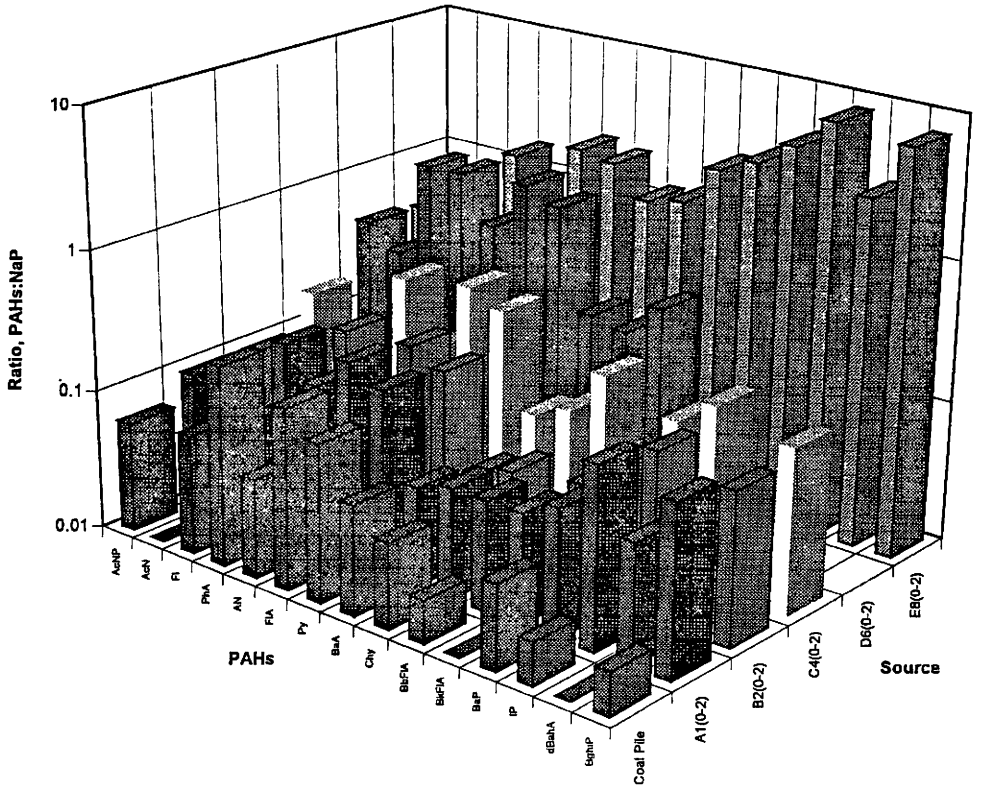

FIG. 2. Ratios of mean particulate phase PAHs in the coal pile runoff samples to NaP. Also shown are the ratios for bed sediment samples from Hamilton Harbour reported by Murphy et al. *(1991). For a discussion of the bed sediment samples, see text.*

1969), although higher concentrations may be associated with individual runoff events.

Diamond and Ling-Lamprecht (1996) summarized metal loading estimates to the entire harbor that were contained in various government reports. Metal loads from the coal pile site were less than 1% of the loads from the sewage treatment plants or direct industrial (cooling water) discharges. This comparison does not include discharges from other coal fields in the harbor, but in a general mass balance framework for the entire harbor, the monitored coal pile site could be viewed as a relatively small source of metals. Given the elevated concentrations, however, there is potential for localized habitat impact in the boatslip.

The correlation analysis (Table 5) indicated that the strongest relationship existed between total metal concentrations and suspended solids concentrations in the runoff. This is not surprising since many metals have an affinity for particles (Allen 1986, Karlsson *et al.* 1987, Droppo and Jaskot 1995). A negative relationship was found between total metal concentrations and coal pile volume (significant at $\alpha = 0.05$ for Cd, Cu, V, and Zn). This may be reflective of the larger coal piles possessing structural characteristics conducive to infiltration and storage (fresh, less compacted, with a minimal surface seal). No significant relationships were found between metals concentrations and total rainfall depth, peak 1 h rainfall intensity, flow volume, or number of antecedent days before a runoff event. In general, the strongest relationship between metals concentrations and a hydrometeorologic variable was observed for the peak 15 minute rainfall intensity. This is consistent with soil erosion research that has shown higher intensity rainfall over a short period of time influences particulate erosion rates (Wischmeier and Smith 1958, Foster *et al.* 1982, James and Irvine 1992). As noted previously, there was a significant relationship between metals

concentrations and suspended solids, so it is reasonable that the metals concentrations also would be correlated with a variable that can influence suspended solids concentrations.

Ontario Ministry of the Environment and Energy (1993) guidelines indicated that PAH concentrations observed in the particulate phase of coal pile runoff may produce severe impairments to the receiving waters of the Kenilworth boatslip. In this study it was observed that PAH concentrations associated with suspended solids in some cases (chrysene) were similar to those documented by Fendinger *et al.* (1989), but for others the results reported here were up to two orders of magnitude higher. The results were more similar to PAH concentrations found in bottom sediments collected in an effluent channel from a coking plant, as reported by Griest (1980) and for coal tar as presented by Christensen *et al.* (1997). The differences in these results as compared to Fendinger *et al.* (1989) may be related to several factors, including the age and weathering of the coal used in the experiments, the general PAH concentrations associated with different coals, and the experimental design (including field and analytical methods). The dissolved phase PAH concentrations were similar to those documented by Stahl *et al.* (1984), but again were higher than those reported by Fendinger *et al.* (1989).

While there are several environmental factors that can affect the particulate to dissolved phase partitioning, PAHs often are more associated with the particulate phase because of their nonpolar nature and general low solubility in water (Allen 1986, Hemond and Fechner 1994). For example, Griest (1980) reported that PAH concentrations in the bed sediment of the effluent channel from a coking plant were three to four orders of magnitude higher than concentrations in the overlying water. Data from Fendinger *et al.* (1989) and this study (Table 2) also indicated that PAH concentrations associated with the particulate phase of coal pile runoff were orders of magnitude greater than those in the dissolved phase.

Although PAHs may not be acutely lethal to aquatic organisms, these organic compounds may produce chronic effects such as cellular abnormalities, fin and gill erosion, and liver, pancreatic, testes, and eye-lens diameter alterations in fish, suppression of benthic organism diversity and alteration of bacterial and aquatic plant communities (Hass and Applegate 1975, Payne 1978, Black 1983, Fabacher *et al.* 1988, Murphy *et al.* 1991). As an added complexity, however, it may be possible that the concentration of PAHs associated with coal particles could exceed MOEE guidelines, but they may not be bioavailable. It is therefore possible that the concentrations of PAHs observed in the sediment fraction of coal pile runoff may have less impact upon the aquatic biota than the MOEE guidelines would suggest (Carlson *et al.* 1979, Bender *et al.* 1987, Chapman *et al.* 1996). More specific testing on the bioavailability of PAHs in coal pile runoff to Hamilton Harbour should be done.

In this study, the ratios of various PAHs to NaP in the coal pile runoff were most similar to the ratios reported for coal tar, and coal and wood gasification (Fig. 1). Murphy *et al.* (1991) reported concentrations of various PAHs for bed sediment in an area of Hamilton Harbour that was impacted by runoff from a different coal field than the one sampled in this study. The PAH to NaP ratios for the upper 2 cm of sediments are shown in Figure 2. Samples Mur A1(0–2), B2(0–2), and C4(0–2) exhibited ratios more similar to the coal pile runoff ratios than samples Mur D6(0–2) and E8(0–2). Murphy *et al.* (1991) described samples Mur A1(0–2), B2(0–2), and C4(0–2) as being solid, shiny, dark black (tarry), while samples Mur D6(0–2) and E8(0–2) were described as having streaks of shiny, dark black. The former three samples were located adjacent to the coal pile discharge pipe, while the latter two samples were located further from the pipe. Other sources therefore may have contributed to samples Mur D6(0–2) and E8(0–2), as reflected by their different signature. A subsequent study performed by Murphy *et al.* (1995) also indicated that sediments within the Kenilworth boatslip were highly contaminated with coal tar. The most contaminated of these sediments were located adjacent to industry outfall pipes, and in particular, the coal pile discharge pipe discussed in this study. Figure 2 suggests that coal pile runoff may be an important source of PAH contamination for some areas of Hamilton Harbour.

Diamond and Ling-Lamprecht (1996) indicated that there was relatively little information regarding PAH loadings to the harbor, with the exception of direct industrial discharges for a small number of PAHs. Based on the data presented by Diamond and Ling-Lamprecht (1996), the loading of benzo(a)-pyrene from the coal pile site represents 1.5% of the total industrial loading to the harbor. Although the coal pile loading represents a relatively small percentage of the industrial loading, it appears that coal pile runoff can result in significant localized contamination of bed sediment.

Between 1982 and 1992, 32 to 36 million metric tons of coal per year were shipped across the Great Lakes from U.S. harbors, destined for both U.S. and Canadian ports (Waxmonsky 1992). A survey done by Price *et al.* (1989) indicated that electric power utilities in the basin maintain their coal piles within confined areas, capturing and treating the runoff before discharge to a receiving water body. It is unknown how effective these systems are, or whether docks that temporarily store the coal prior to shipping follow similar treatment procedures. Given the potentially negative impacts of coal pile runoff, a basin-wide survey of coal handling practices and pre-treatment of discharges should be conducted.

CONCLUSION

This study specifically quantified contaminant concentrations and loadings from an industrial coal field site rather than estimating these values through a laboratory simulation approach as often is done. Therefore, this study avoided the problem of scale and extrapolating results from a laboratory simulation to the field situation.

Coal pile runoff resulted in quantifiable loads of suspended solids, trace metals and PAHs which may produce negative impacts upon the aquatic biota within the receiving waters of the Kenilworth boatslip. Ratios of various PAHs to NaP were similar for coal pile runoff, coal tar, and coal and wood gasification. Furthermore, the ratios were similar for the coal pile runoff and bed sediment in areas receiving coal pile discharge. This indicates that the coal pile signature can be seen in bed sediment and in the absence of runoff data, the environmental history of bed sediment can be effectively reconstructed using ratios reported in the literature.

Measures taken to contain stockpiled coal and treat runoff could be effective in reducing harmful loads of suspended solids, trace metals and PAHs to receiving waters of the Great Lakes basin. This could be particularly true in the local case of the Kenilworth boatslip where the relatively small volume of discharge with high concentrations of particle-bound contaminants might be efficiently treated through construction of some type of settling basin.

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Sources of Polycyclic Aromatic Hydrocarbons in Sediments of the Kinnickinnic River, Wisconsin

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ABSTRACT. *A chemical mass balance (CMB) model was developed and used to apportion both point and nonpoint sources of polycyclic aromatic hydrocarbons (PAHs) in six dated sediment cores. The cores were collected in 1994 from a stretch of the Kinnickinnic River between the Becher Street Bridge and the Wisconsin Wrecking Company Wharf, Milwaukee, Wisconsin, and had PAH concentrations of 80 to 1,000 ppm. This work was done in order to identify major PAH sources to this IJC Area of Concern which is important for pollution modeling and management. The source fingerprints were taken from the literature. Coke oven emissions and coal-wood gasification or coal tar are the main local PAH sources, whereas highway dust provides an important nonpoint input since the 1920s. Coal-wood gasification ceases to be a significant source after 1950–'60. Factor analysis based on nonnegative constraint of factor scores and loadings, and oblique rotations, supports this apportionment, but points also to deficiencies in the CMB source profile for coke oven emissions. It appears that the now defunct Milwaukee Solvay Coke Co. was a major source. The influence of geophysical factors and chemical and biological fractionation of the selected PAH compounds appears to be small.*

INDEX WORDS: *PAHs, Milwaukee Harbor, sediments, Lake Michigan, chemical mass balance model, factor analysis, source apportionment.*

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are of concern because of their carcinogenic properties (Neff 1979). PAHs have their origin in both natural and anthropogenic processes. However, several studies have indicated that the anthropogenic input of PAHs to aquatic sediments far exceeds natural sources (NAS 1971). Major human activities which produce PAHs include pyrolysis of wood to produce charcoal and carbon black, coke production, manufacturing of gas fuel, power generation from fossil fuels, combustion of fuels in internal combustion engines, incineration of industrial and domestic wastes, oil refinery and chemical engineering operations, aluminum manufacturing, etc.. By-products of these processes which contain significant amount of PAHs have been dumped on the land, in the water, or buried at subsurface sites. Airborne particulates, generated from these processes and carrying PAHs, are transported worldwide in the atmosphere, and usually find their final destination in soils, and in sediments of aquatic systems.

Differences in the pattern of PAH mixtures reflect different sources and pathways, and thus provide a basis for the analysis of their sources. Traditional approaches of PAH source analysis use ratios of specific compounds (for example, phenanthrene to anthracene, fluoranthene to pyrene), alkyl homologue distribution pattern, or the presence of compounds indicative of a particular source (Laflamme and Hites 1978, Lake *et al.* 1979, Zhang *et al.* 1993, Furlong *et al.* 1988, Benner *et al.* 1995). These methods, however, involve only a small portion of PAH data produced by an analytical laboratory. Thus, they are often unable to resolve sources at all, or with sufficient accuracy, and may be considered incomplete with respect to the number of PAHs that preferably should be involved in the apportionment.

The Milwaukee Harbor estuary is one of the designated Areas of Concern (AOC) of the Interna-

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tional Joint Commission (IJC). This work was done in conjunction with the Remedial Action Committee of the AOC.

Singh *et al.* (1993), considering PAH compound profiles, used a chemical mass balance model to determine nonpoint sources of PAHs in the Milwaukee Harbor Estuary. Similar approaches have been applied to determine sources of organic pollutants in air (Sexton *et al.* 1985, Li and Kamens 1993, Venkataraman and Friedlander 1994, Kenski *et al.* 1995).

This approach is extended here to include both point and nonpoint sources of PAHs deposited in dated aquatic sediments. An in-depth discussion of model uncertainty, based in part on an alternative constrained factor analytical method, is included. We consider also the horizontal distribution of sediment PAHs over of the given stretch of the Kinnickinnic River.

CHEMICAL MASS BALANCE MODEL

The two basic assumptions of the chemical mass balance (CMB) model are, (1) the amount of a chemical pollutant in the sediment at a specific site is the sum of the amounts of this chemical from each independent contributing source, and can be expressed by equation [1], and (2) the ratio between the concentration in the sample of a chemical from a given source and the concentration of the same chemical in the source material is the same for all the chemicals under study (no change in source profile between source and receptor), and can be characterized by a single contribution factor α_i. The expression for the PAHs is,

$$F_j = \sum_{i=1}^{n} \Phi_{ji}\alpha_i + e_j \ (1 \le j \le m) \tag{1}$$

where F_j is the measured concentration of the jth PAH compound in the sample, Φ_{ji} is the concentration of jth PAH in the ith source, α_i is the source contribution factor of the ith source, e_j is the error associated with the jth PAH, n is the number of sources, and m is the number of PAH marker compounds used in the model. In order to characterize source profiles Φ_{ji} (ppm), we define an average molecular weight $(M.W.)_i$,

$$(M.W.)_i = \frac{\sum_{j=1}^{m} \Phi_{ji}}{\sum_{j=1}^{m} \frac{\Phi_{ji}}{(m.w.)_{ji}}} \tag{2}$$

where $(m.w.)_{ji}$ is the molecular weight of PAH compound j in source i. The contribution factors (α_i's) are determined by multiple linear regression using a least-squares method in which the weighted error (equivalent to χ^2) is minimized. The second assumption can also be expressed as a requirement that the source profile, i.e., the relative abundance of PAH compounds, does not change between source and receptor. This definition of α_i is more general than the original one (Friedlander 1973) where α_i simply is the mass fraction of material originating from source i, and where the sum of all α_i's, therefore equals unity. While the latter definition implies mass balance for both bulk material (sediment) and PAHs, our version indicates only mass balance for the PAHs.

The relative contribution P_i of total PAHs from source i is calculated for each source according to

$$P_i = \frac{\alpha_i \sum_{j=1}^{m} \Phi_{ji}}{\alpha_1 \sum_{j=1}^{m} \Phi_{j1} + \alpha_2 \sum_{j=1}^{m} \Phi_{j2} + \ldots + \alpha_n \sum_{j=1}^{m} \Phi_{jn}} \tag{3}$$

The uncertainty δP_i is calculated from

$$\delta P_i = P_i \sqrt{\left(\frac{\delta N}{N}\right)^2 + \left(\frac{\delta D}{D}\right)^2} \tag{4}$$

where $P_i = N/D$

$$\delta N = \delta\alpha_i \sum_{j=1}^{m} \Phi_{ji}$$

$$\delta D = \left(\left(\delta\alpha_1 \sum_{j=1}^{m} \Phi_{j1}\right)^2 + \left(\delta\alpha_2 \sum_{j=1}^{m} \Phi_{j2}\right)^2 + \ldots + \left(\delta\alpha_n \sum_{j=1}^{m} \Phi_{jn}\right)^2 \right)^{1/2}$$

N and D are the numerator and denominator, respectively, of equation [3], and the uncertainties $\delta\alpha_i$ are calculated as in Henry *et al.* (1984).

In order to assess the closeness or goodness of fit between the calculated values of PAHs as determined by the model and the measured values, χ^2 and the multiple linear correlation coefficient R^2 were also determined. The χ^2 was calculated based on the equation:

$$\chi^2 = \sum_{j=1}^{m} \frac{(F_j - F_j')^2}{(r.e.)_k^2 F_j^2 + \sum_{i=1}^{n} (r.e.)_i^2 (\alpha_i \Phi_{ji})^2} \quad (5)$$

where F_j and F_j' are measured and calculated concentrations, respectively, of the jth PAH in the sample. This equation is derived from eq. (11) of Henry *et al.* (1984) using the relative errors $(r.e.)_k$ and $(r.e.)_i$ of the measurements, and the source profile i, respectively. We assume that these relative errors do not vary much from compound to compound such that

$$(r.e.)_k = \frac{\sigma F_j}{F_j} \qquad (r.e.)_i = \frac{\sigma \Phi_{ji}}{\Phi_{ji}} \quad (6)$$

where σ indicates standard errors.

From statistics it is well known that a good fit between measured and calculated values is obtained when χ^2 equals the number of degrees of freedom (df) when df > 4. In this case, each term of the sum in eq. [5] corresponding to the number of degrees of freedom, df = m − n assumes a value close to one since $F_j - F_j'$ then is comparable to the overall error, i.e., the square root of the denominator in eq. [5]. The remaining n terms may be thought of as being zero since n model parameters have been determined from the experimental data.

In applying eq. [5], initial α_i's are calculated assuming that $(r.e.)_i = 0$. Next, revised α_i's are determined using known $(r.e.)_i$'s and the initial set of α_i's. Further iterations were not necessary since the α_i's converge rapidly. For the measured relative error we use 0, 0.2, and 0.4, and then estimate by inter- or extrapolation the $(r.e.)_k$ corresponding to χ^2 = df. If the resulting relative error is ≤ 50%, the fit is considered satisfactory. When the relative error is between 50 and 70%, the fit is fair, and unsatisfactory for larger relative errors. The advantage of considering $(r.e.)_k$ for χ^2 = df rather than χ^2 itself is that $(r.e.)_k$, in contrast to χ^2, can be related directly to the acceptable range of relative errors regardless of the number of degrees of freedom.

METHODS

Sediment Data

During June of 1994, six vibra cores, each 2 to 3 meters long, were collected from a stretch of the Kinnickinnic River, close to downtown Milwaukee and between Becher Street Bridge and the Wisconsin Wrecking Company Wharf using R/V Pelagos. During sampling, aluminum irrigation pipes of 6.7 cm inner diameter were vibrated down into the sediment through clamps and a flexible coupling to a gasoline engine on board the research vessel. The sampling locations are marked in the map shown in Figure 1. This area was determined to be a "hot spot" of PAH contamination in the Milwaukee Harbor Estuary through our earlier work (Ni *et al.* 1992).

Each core was sliced into 15 sections, and each section was analyzed for porosity, grain size distribution, organic content (loss on ignition), and dated by measuring the ^{137}Cs and ^{210}Pb activities. Sedimentation rate was calculated according to a linear regression of log excess ^{210}Pb activity against cumulative mass of the sediment core. Sixteen PAH compounds were determined for each sample, including naphthalene (NaP), acenaphthylene (AcNP), acenaphthene (AcN), fluorene (Fl), phenanthrene (PhA), anthracene (AN), fluoranthene (FlA), pyrene (Py), benz[a]anthracene (BaA), chrysene (Chy), benzo[b]fluoranthene (BbFlA), benzo[k]fluoranthene (BkFlA), benzo[a]pyrene (BaP), indeno[123-cd]pyrene (IP), dibenz[a,h]anthracene (dBahA), and benzo[ghi]perylene (BghiP). Detailed procedures of sampling, sediment characterization, PAH analysis including quality assurance/quality control (QA/QC), and radioactivity analysis are reported by Li *et al.* (1995).

Complete experimental results of sediment PAHs for the entire Milwaukee Harbor Estuary are presented elsewhere (Li *et al.* 1996). Only those compounds whose concentrations were determined with satisfactory chromatographic separations and above the method detection limits (0.3–1 ppm) were considered in the CMB modeling. Further reductions in the number of compounds included were made based on available source fingerprint data. Our aim was to have at least four degrees of freedom. Based on this, we selected seven compounds for five cores and eight for one (VC-2). NaP, Fl, PhA, AN, Py, BaA, BaP were chosen for VC-5 and 6, and Fl, PhA, AN, FlA, Py, BaA, BaP for VC-1, 3, and 4. NaP is included in the first set because NaP was mainly present in VC-2, 5, and 6. Also, FlA was included in the second set because coal-wood gasification (CWG), for which FlA data were not available, was not a significant source for VC-1, 2, 3, and 4. Thus, for VC-2 we used all eight compounds.

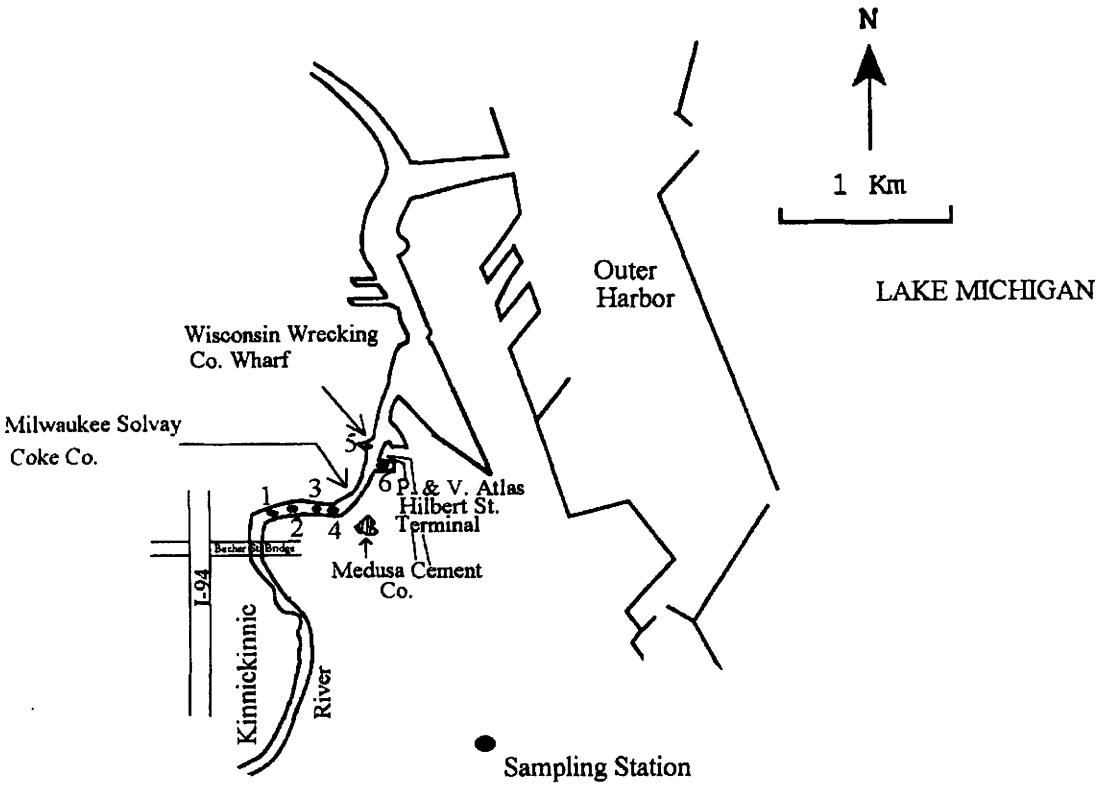

FIG. 1. Partial map of the Milwaukee Harbor Estuary with sampling sites on the Kinnickinnic River.

Source Fingerprints

The majority of the PAHs found in the environment originates from incomplete combustion of fossil fuels including wood, coal, and petroleum. Most PAH data used in this study as fingerprints of these sources were drawn from the literature (NRC 1983, Wise *et al.* 1988, Neff 1979, Singh *et al.* 1993). They are summarized in Table 1 and illustrated in Figures 2–4. A blank cell in Table 1 means that there is no information about the PAH compound for the given source as for FlA in CWG or Chy in Coke-A and Coke-B. The HWY concentrations represent averages of three samples. Note that the average molecular weights for Coke-B, HWY, CT, and CWG decrease in the given order, probably reflecting the temperature at which the PAHs were formed. The fact that the HWY PAH concentrations are orders of magnitude lower than PAH concentrations of other sources presents no particular difficulty since the α's (equation 1) will be adjusted accordingly by the least-squares procedure. The important thing is that each source profile is distinct and that its relative error (coefficient of variation) is known and within the same general range (0.03–0.4). In order to improve the comparability of source profiles, and since the apportionment results (P_i, equation 3) do not depend on a constant factor in the source profile, the coke oven (Fig. 2) and coal and coal-wood gasification profiles (Fig. 3) have been normalized to Py (1,000 ppm).

Coke production and fuel gas manufacturing were among the major industrial activities in the study area until the mid 1970s. In fact, sediment core VC-6 was taken from a site near the previous Milwaukee Solvay Coke Company, which operated its coke ovens from 1902 until the 1970s. It is likely that the high PAH concentration in the sediment deposited during that period at that location originated from the products of this company, which include metallurgical coke, coal tar, coal gas, and some aromatic chemicals (M.L. Morgan, personal communication, 1994). However, a chemical inventory of the company is not available. Compositions of two types of PAH sources, namely Coke-A and Coke-B,

TABLE 1. ***PAH concentrations in several sources (ppm).***

Parameter	Coke-A[a]	Coke-B[a]	CT[b]	CWG[c]	GEET[d]	HWY[e]
NaP		17.2[h]	1,160.0	236.0		0.26
AcNP			252.0	53.6		
AcN						0.65
Fl	75.3	17.2	136.0	28.9		0.83
PhA	680.1	540.6	462.0	94.0		4.75
AN	209.3	391.2	101.0	32.7		1.00
FlA	1,270.0	704.4	322.0		972.0	5.58
Py	977.2	826.4	235.0	31.3	1,770.0	3.95
BaA	536.8	3,838.1	102.0	6.3	61.7	0.84
Chy			71.7	3.8	175.0	1.42
BaP	566.9	2,147.9	95.8	3.8	31.5	0.82
BghiP			53.7	0.7	51.0	0.33
C.V.[f]		0.40	0.03	0.20		0.29
M.W.[g]		222.7	152.4	147.9		189.0

[a]Air-filter of coke oven emissions (NRC 1983 p. 2-23)
[b]Coal tar (Wise *et al.* 1988)
[c]Coal and wood gasification , Ill#6 coal & wood pellets (NRC 1983, pp. 2–13)
[d]Gas engine exhaust tar (Neff 1979 p. 36)
[e]Highway dust (Singh *et al.* 1993)
[f]Coefficient of variation
[g]Average molecular weight (NaP, Fl, PhA, AN, Py, BaA, BaP)
[h]Assumed upper limit

were obtained from analyzing the samples collected from a glass fiber and a 0.8 μm porosity silver membrane filter, respectively, of coke oven emissions (Lao *et al.* 1975). These coke data were also listed in Neff (1979) and NRC (1983). Data listed in Table 1 for Coke-A and Coke-B are the geometric means of two sets of data, i.e., samples 1 and 2 for Coke-A, and samples 3 and 4 for Coke-B (Fig. 2).

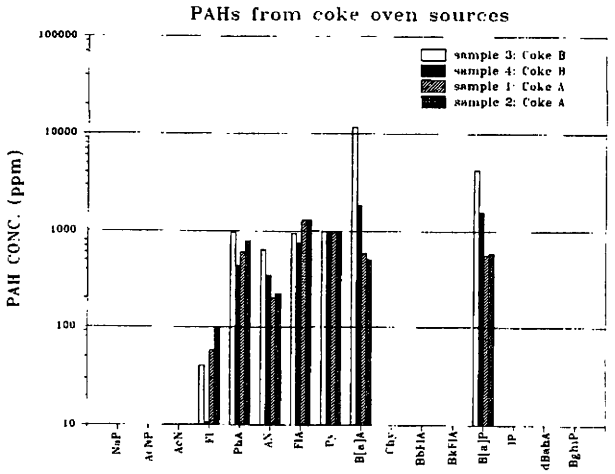

FIG. 2. PAH concentrations in coke oven emissions, normalized to Py (1,000 ppm) (NRC 1983, pp. 2–23)

In urban areas with heavy traffic, vehicular exhaust and, therefore, highway dust (HWY) can be a significant sources of PAHs. Gasoline engine exhaust tar (GEET) contains significant amount of PAHs including some proven carcinogens such as benzo[a]pyrene and chrysene. Pyrene is the most abundant constituent, accounting for approximately 50% of total PAHs in GEET (Table 1).

Other important anthropogenic PAH sources may

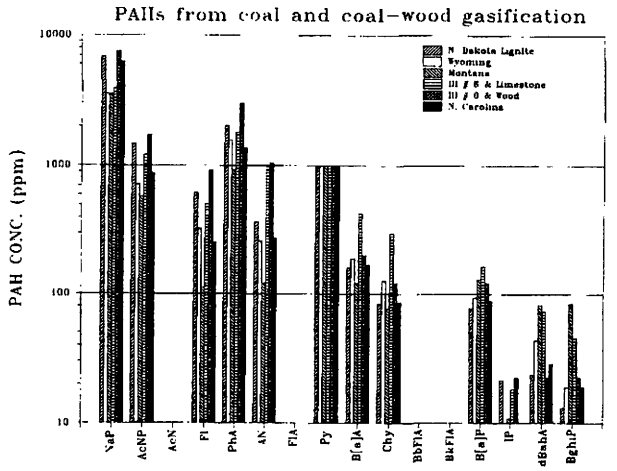

FIG. 3. PAH concentrations resulting from gasification of various coals and coal blends, normalized to Py (1,000 ppm) (NRC 1983, pp. 2–13)

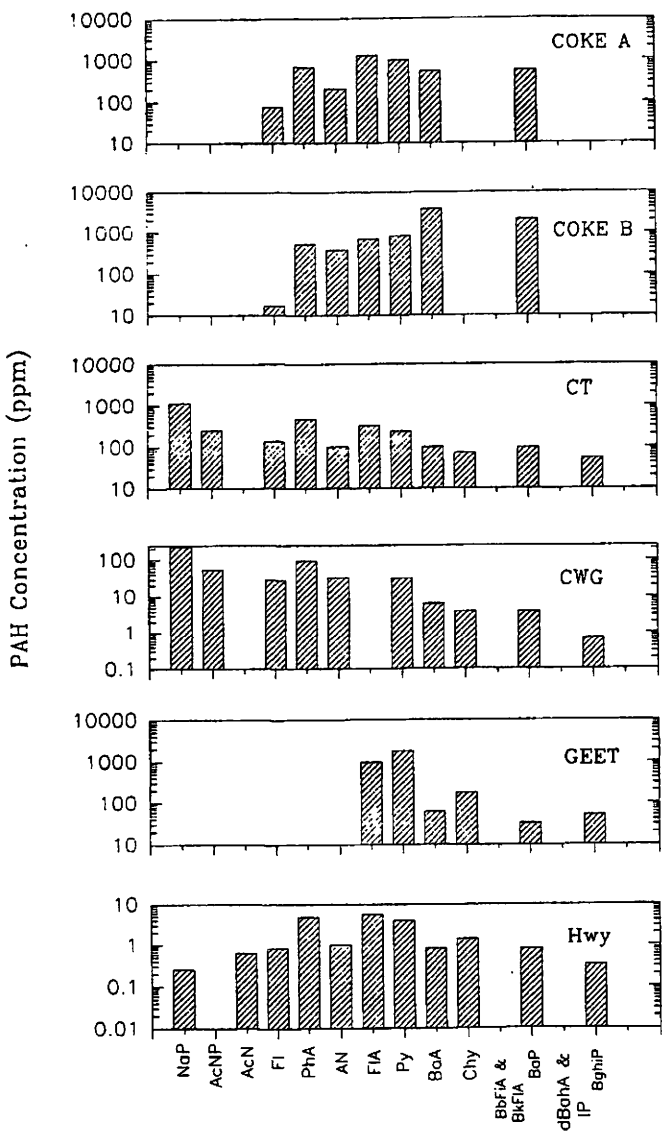

FIG. 4. PAH concentrations in sources used for CMB modeling.

include, but are not limited to, power generation using coal, or oil, petroleum refining, catalyst regeneration, incineration of solid industrial and domestic wastes, as well as leakage and spills of petroleum-based products from various activities. PAHs may also enter the environment from various non-point sources in addition to those considered in this study.

Modeling Procedure

For each core segment, several cases were considered in which different combinations of sources were evaluated as possible contributing sources. The number of degrees of freedom (df) which is the difference between the number of PAH compounds involved and the number of possible contributing sources, should as high as possible, and was kept ≥ 4. In order to obtain a source apportionment that would be physically meaningful, and comparable from segment to segment, and from core to core, the following objectives in the modeling were maintained: (a) as much as possible to use the same PAH compounds for all segments, (b) to the extent possible to use the same sources for all segments, and (c) to use known information about possible sources, and to have the average source molecular weights distributed evenly and span the range of average sample molecular weights.

As discussed above, the first objective was met by using Fl, PhA, AN, Py, BaA, BaP for all six cores. In addition, FlA was added for VC-1, 3, 4, NaP for VC-5, 6, and both FlA and NaP for core VC-2. The second and third objectives were met by using Coke-B, HWY, and CWG as general sources for all six cores. We found that the average molecular weights of these sources in all cases spanned the average sample molecular weights. These sources are also in accordance with known information about PAH contamination in the area. Note that coal tar (CT) is almost indistinguishable from CWG, but that the latter source gives slightly lower measured relative errors for $\chi^2 = \text{df}$.

The uncertainty of the experimental sediment data, σF_j in equation [6], is expressed as the relative standard deviation or error $(\text{r.e.})_k$ which is calculated by analyzing sample duplicates on different days, several weeks apart. A relative error of 0.3–0.4 was typical. This is then the basis for the earlier statement that the model fit is considered satisfactory for $(\text{r.e.})_k \leq 50\%$, fair for $50\% \leq (\text{r.e.})_k \leq 70\%$, and unsatisfactory for $(\text{r.e.})_k \geq 70\ \%$.

In an attempt to verify the results obtained by CMB modeling, factor scores and loadings were calculated by principal component analysis (PCA). We used a version of Ozeki *et al's.* (1995) method in which the data matrix has only positive elements and where nonnegative constraints are imposed on both the score and the loading matrices. This is achieved through a series of oblique rotations in which the basic factor analysis equation is maintained. The advantage of this method over conventional PCA is that factor scores may be directly interpreted as the source contribution of a given sample (segment), and that, similarly, the loading matrix directly provides information

on the unknown source profiles. The number of sources included depends on the eigenvalue structure of the covariance matrix. Sources corresponding to the largest eigenvalues which account for ≥ 80% of the variance of the data were considered significant, and were, therefore, retained. Since core VC-6 goes furthest back in time (1895) and has the most complicated CMB source pattern, the PCA technique was applied to this core. In order to obtain maximum comparability between the CMB and the PCA results, the PAH compounds considered in PCA were the same as those included in the CMB model (NaP, Fl, PhA, AN, Py, BaA, BaP).

A second check on the results of the PAH source analysis for core VC-6 was made by investigating elemental carbon particles of chemically isolated carbon fractions from each layer (Griffin and Goldberg 1983). Oven dried sediment was treated with HCl and HF to remove carbonates and metals and to dissolve silicates. Next, organic compounds were oxidized with H_2O_2 in preparation for scanning electron microscopy (Top-Con, ABT-32). The classification of carbon particles according to their source (wood, oil, or coal) was then performed on 100 randomly selected particles for each layer following the morphology guidelines of Griffin and Goldberg (1979).

RESULTS AND DISCUSSION

A summary of results of radionuclide and PAH analysis for core VC-6, which is used as an example of applying the CMB model, is given in Table 2. From the ^{210}Pb activities it is seen that the sedimentation rate is reasonably constant. Total PAH concentrations for all cores are shown in Figures 5 and 6. From Figure 6, it is seen that core VC-6 spans the time period from 1895 to 1991, and that the maximal total PAH level is 610 ppm occurring in 1902. Levels are also high (590–580 ppm) in 1916 and 1923. The top layer has a moderate PAH concentration of 140 ppm.

Relative contributions (P_i) with uncertainties of Coke-B and CWG to the total PAHs, determined by the CMB model for all six locations in the study area, are also shown in Figures 5 and 6. The HWY contribution is 100% minus the sum of the contributions from Coke-B and CWG. Relative errors of measured concentrations for χ^2 = df are 11–55% for all cores except VC-2 for which the relative errors are 55–67%. Coke-B, HWY, and CWG are significant sources in VC-5 and 6, whereas only Coke-B

TABLE 2. ^{210}Pb and ^{137}Cs activities, dates of layers, selected PAH concentrations, and average PAH molecular weights of sediment core VC-6.

Depth (cm)	Net ^{210}Pb Activity[a] (dpm/g)	^{137}Cs Activity (dpm/g)	Sedimentation Rate Date[b]	PAH (ppm)[c]								
				NaP	Fl	PhA	AN	FlA	Py	BaA	BaP	M.W.[d]
0–17	6.29	0.54	1991	0.50	0.76	10.5	1.25	25.1	21.6	9.4	10.8	206.4
17–34	3.15	0.47	1984	0.77	0.71	9.3	1.30	23.5	19.9	7.5	7.0	203.0
34–51	8.19	2.90	1977	0.72	1.68	22.5	2.44	65.5	54.7	20.5	24.1	206.9
51–68	2.20	2.23	1970	5.69	2.54	31.7	3.49	69.0	55.4	26.0	22.9	200.5
68–85	3.69	8.52	1963	0.92	2.60	34.2	3.71	66.4	57.1	24.7	26.0	204.4
85–102	1.64	3.04	1957	7.53	2.43	26.6	3.43	62.2	49.9	30.8	22.6	200.7
102–119	1.84	0.00	1950	3.57	2.34	22.6	3.38	48.5	40.3	24.5	17.3	202.3
119–136	0.00	0.05	1943	36.2	3.72	18.8	6.89	60.6	54.8	36.8	18.6	183.9
136–153	0.36	0.01	1936	49.9	4.36	40.0	6.76	65.5	59.0	53.4	17.6	181.2
153–170	0.56	0.09	1929	65.0	5.44	43.1	8.76	66.3	63.5	62.1	22.6	179.3
170–187	1.52	0.06	1923	43.3	5.00	50.7	9.62	87.8	80.5	76.4	34.3	190.1
187–204	0.57	0.00	1916	67.4	4.91	48.6	8.22	78.1	75.4	77.2	28.1	182.4
204–221	0.73	0.01	1909	58.6	3.20	22.5	4.77	54.3	53.8	40.3	15.7	175.1
221–238	0.43	0.00	1902	144.0	4.30	48.0	10.00	66.1	67.3	60.0	23.4	164.8
238–255	0.47	0.00	1895	50.9	5.65	46.7	6.57	53.0	46.4	52.1	17.0	179.3

[a]Net ^{210}Pb Activity = measured ^{210}Pb activity - supported ^{210}Pb activity (1.4 dpm/g).
[b]Based on a constant sedimentation rate of 2.384 g/cm^2/year, determined from ^{210}Pb activity data.
[c]Based on dry weight of sediment sample.
[d]Average molecular weight (NaP, Fl, PhA, AN, Py, BaA, BaP).

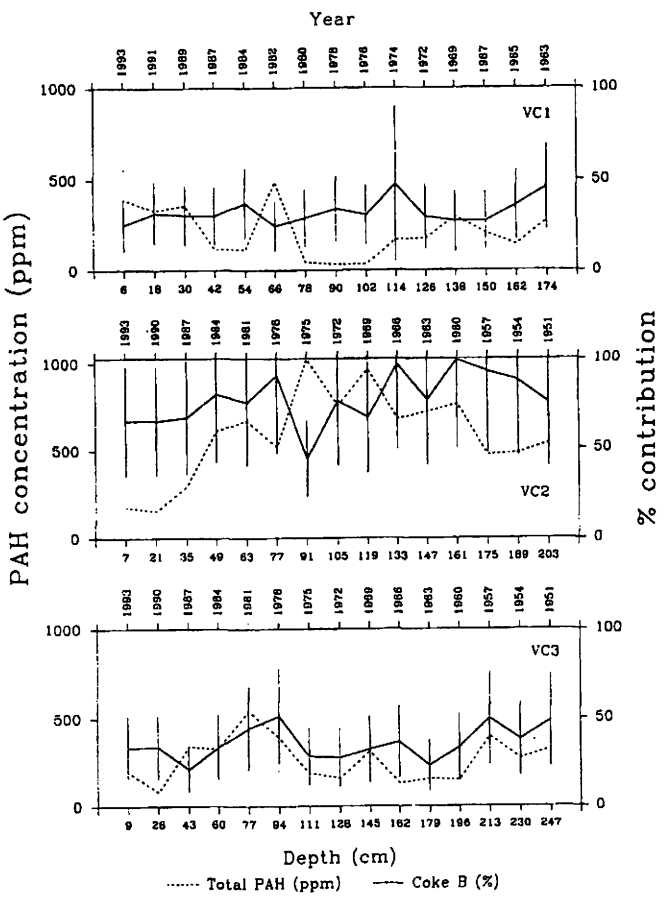

FIG. 5. Total PAH concentration and Coke-B contribution vs. depth and year of cores VC-1, 2, and 3.

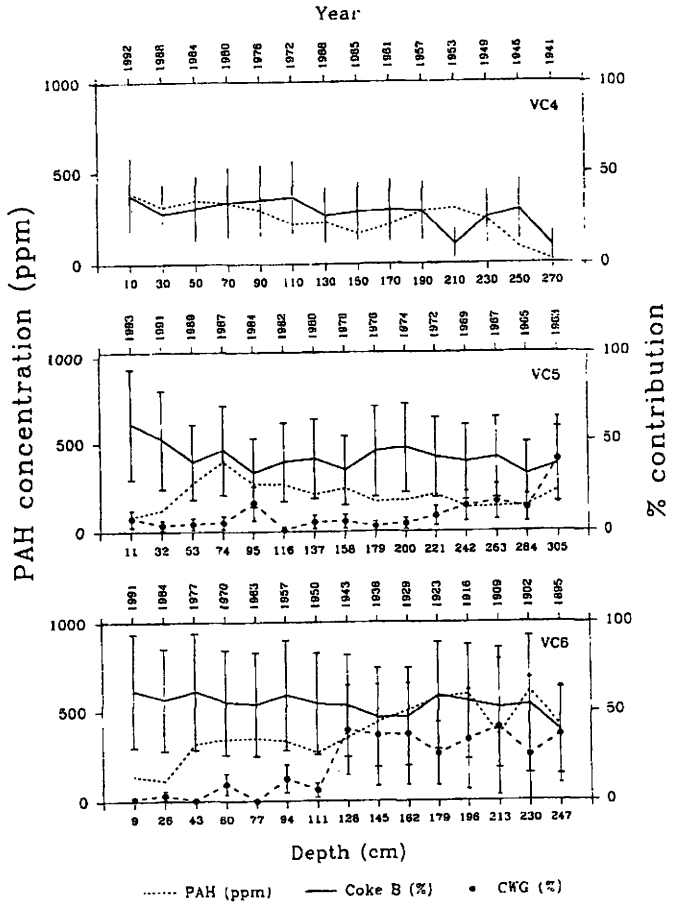

FIG. 6. Total PAH concentration and Coke-B & CWG contribution vs. depth and year of cores VC-4, 5, and 6.

and HWY are important for cores VC-1, 2, 3, and 4. Note that there is a rough correlation between total PAH concentrations and the sum of Coke-B and CWG contributions. This would be expected since the latter sources are local. In particular, the highest PAH concentrations of 800–1,020 ppm in VC-2 are accompanied by high Coke-B contributions of 50 to more than 90% (Fig. 5).

Figure 7 shows a detailed comparison for VC-6 of the contributions of the HWY, CWG, and Coke-B along with scores calculated from PCA using the three highest eigenvalues. As may be seen from this figure, there is a remarkable agreement between the CMB and factor analysis (FA) results for CWG. The loading vectors, determined by PCA, and corresponding to these scores are correctly categorized, based on a Q^2 criterion for log of the normalized vectors (Kuik *et al.* 1993), according to the assumed CMB source profiles (Fig. 8). Thus, the HWY loading vector fits in fact best with the HWY source profile used in CMB modeling, and the CWG and Coke-B loadings provide similarly optimal fits to the corresponding actual source profiles. NaP and Fl are excluded in the HWY and CWG profiles, respectively, because their values became negative as a result of the oblique rotations. Also, actual values of NaP and Fl were treated as outliers for the Coke-B fit. This may indicate that the Coke-B source profile used in CMB modeling (Fig. 2) is deficient in that the low-molecular weight compounds are underestimated. One possible reason is that these compounds primarily are in the vapor phase, and, therefore, are not strongly retained on the filter.

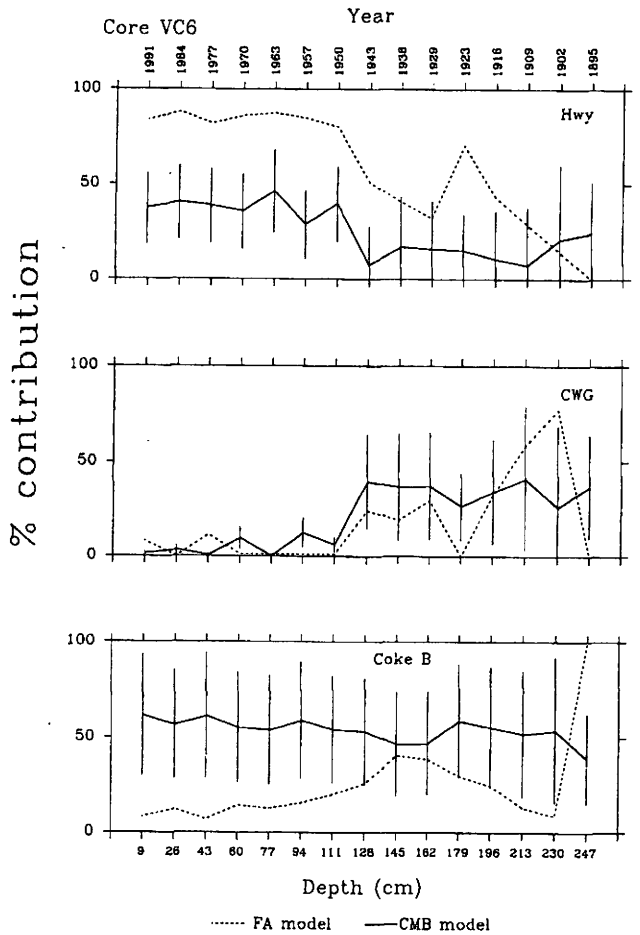

FIG. 7. Percent contribution to PAHs of HWY, CWG, and Coke-B sources vs. depth and year of core VC-6. Results obtained by CMB modeling are compared to scores derived from factor analysis (FA).

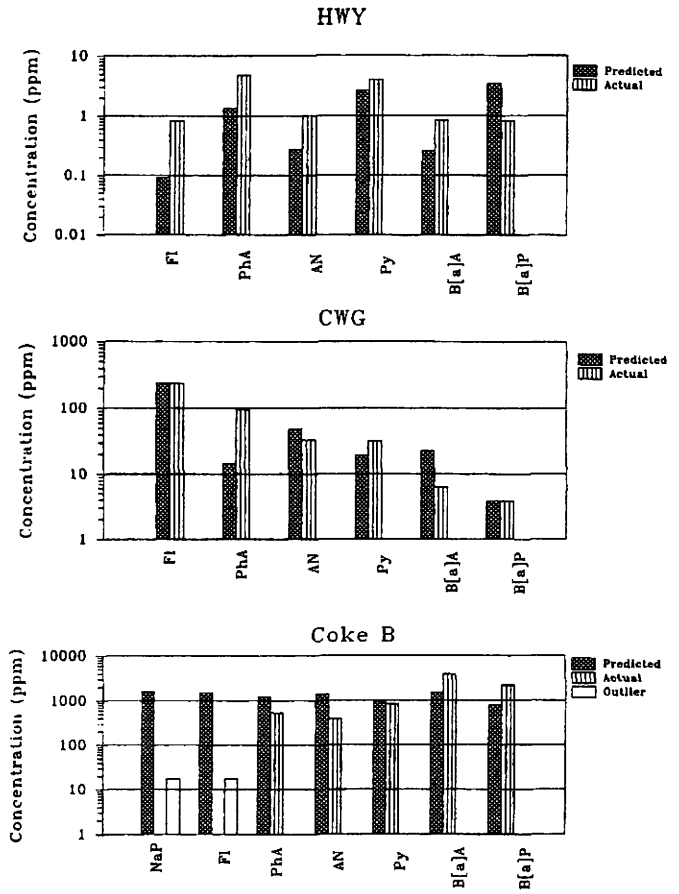

FIG. 8. Comparison of source profiles for HWY, CWG, and Coke-B used in CMB modeling with normalized loading vectors derived from factor analysis (FA).

PAH Sources

From Figures 5 and 6 it is seen that the HWY source in the top layers is highest (≅ 65%) in cores VC-1, 3, and 4, and 35–40% in the other cores. Also, this source increases toward the top in cores VC-2 and 6, to some extent so in VC-1 and 3, but not in VC-4 and 5. The latter anomaly may be caused by redistribution of PAHs within the system. CWG, which is found in VC-5 and 6, becomes small after 1950–60, and appears to reflect the actual history of coal gasification or possibly coal tar production in the area. The highest PAH concentrations are associated with high contributions of Coke-B and CWG (VC-2 and 6).

Figure 7 provides a confirmation of the CMB results for CWG, partial confirmation for HWY, and an indication that Coke-B before 1923 and after 1943 are overestimated by the CMB model. The latter result is based on the fact that the FA model for Coke-B follows the actual activities of the now defunct Milwaukee Solvay Coke Co. and that the Coke-B source profile for CMB modeling appeared deficient with respect to the low-molecular weight compounds Fl and NaP (Fig. 8). Figure 9 provides an independent confirmation of the HWY results of Figure 7 in that oil particles are much more abundant in the upper layers. Also, the results for wood particles indicate that coal rather than coal-wood gasification was predominant. There is not much difference between the corresponding source profiles (Fig. 3).

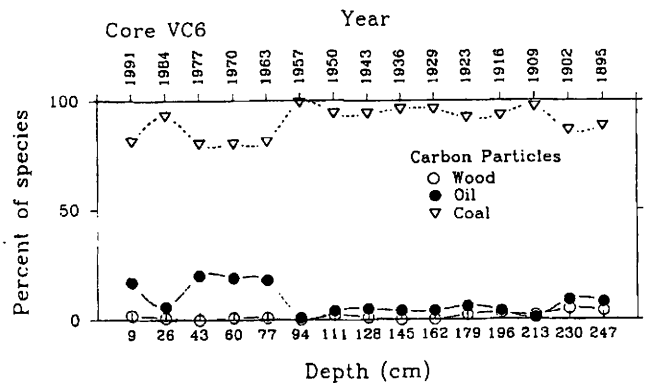

FIG. 9. Percent carbon particles from wood, oil, and coal burning.

larger than one, it is reasonable to assume that smaller particles of high PAH content have replaced larger particles of low PAH content at the receptor compared to the source. This is consistent with the fact that larger particles, e.g., sand, have a lower PAH content than smaller organic carbon-silt particles (< 74 μm) (Ab Razak *et al.* 1996), and that the larger particles would tend to settle out before reaching the sample sites due to gravity according to Stokes law.

A comparison of measured and calculated PAH concentrations of the above sections of VC-6 is shown in Figure 10. The calculated concentrations are obtained from

$$F_j' = \sum_{i=1}^{n} \Phi_{ji}\alpha_i$$

using the previously introduced notation. Measured values are shown with error bars for χ^2 = df. Note that although source profile errors are not shown in this figure, they are implicitly included in the calculated values. In view of these conditions, the agreement between measured and calculated PAH concentrations is quite good.

Statistical Analysis

Statistical results for selected sections of core VC-6 are presented in Table 3. From this table it is seen that the multiple correlation coefficient R^2 is between 0.51 and 0.71 and that the relative error for χ^2 = df is between 40 and 53%. The sum of α_i's ranges from 0.92 to 3.25. Since this sum mainly is

TABLE 3. Statistical results of CMB modeling for selected sections of sediment core VC-6 (df = 4).

Core Section	PAH Sources	α	P_i	χ^2	R^2	Σα	R.E.[a] (%)
6-2	Coke-B	0.00203 ± 0.00086	0.561 ± 0.286	5.25	0.604	0.93	45
	CWG	0.00201 ± 0.00150	0.0309 ± 0.025				
	HWY	0.925 ± 0.365	0.408 ± 0.199				
6-5	Coke-B	0.00594 ± 0.0027	0.535 ± 0.289	5.81	0.705	3.25	46
	CWG	-0.000194 ± 0.0023	0.0010 ± 0.011				
	HWY	3.240 ± 1.216	0.466 ± 0.224				
6-7	Coke-B	0.00558 ± 0.0024	0.539 ± 0.284	3.95	0.633	2.61	40
	CWG	0.0112 ± 0.0068	0.0603 ± 0.0406				
	HWY	2.60 ± 1.07	0.401 ± 0.202				
6-9	Coke-B	0.00884 ± 0.00384	0.464 ± 0.276	6.06	0.547	2.15	43
	CWG	0.126 ± 0.00825	0.367 ± 0.283				
	HWY	2.02 ± 3.08	0.170 ± 0.268				
6-11	Coke-B	0.0163 ± 0.00638	0.585 ± 0.301	4.65	0.644	2.80	43
	CWG	0.132 ± 0.0770	0.263 ± 0.177				
	HWY	2.65 ± 3.27	0.152 ± 0.194				
6-14	Coke-B	0.0125 ± 0.00507	0.534 ± 0.385	8.14	0.510	3.23	53
	CWG	0.106 ± 0.169	0.253 ± 0.429				
	HWY	3.11 ± 5.57	0.213 ± 0.402				

[a]Relative error at χ^2 = df

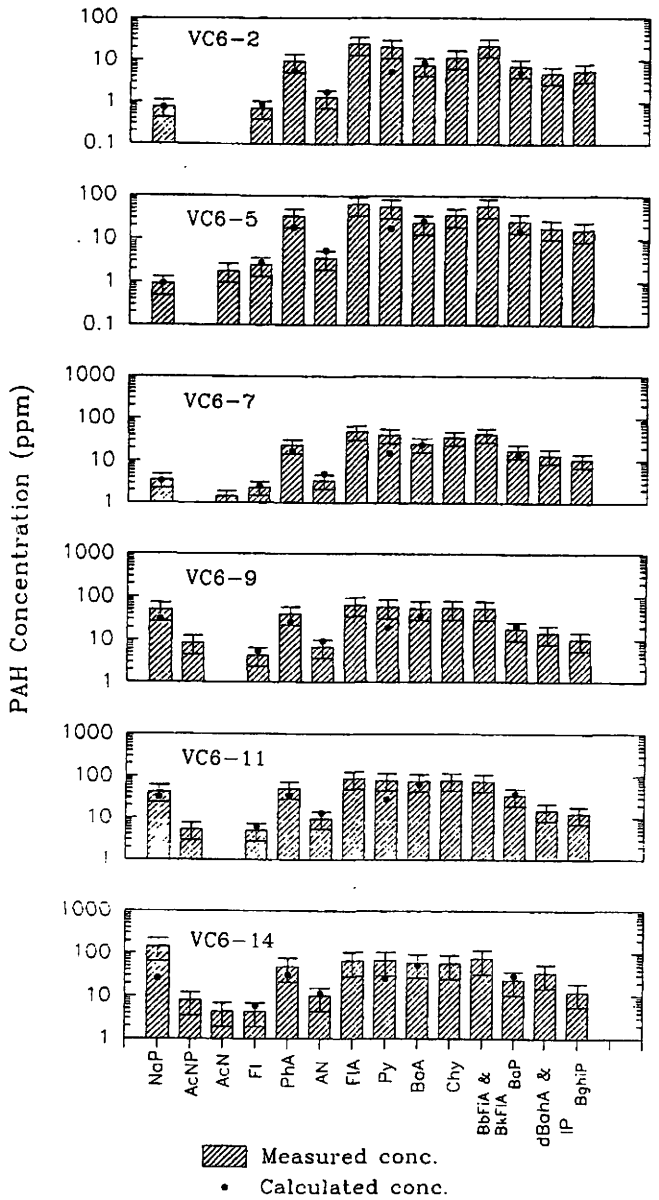

FIG. 10. Measured and calculated PAH concentrations for selected sections of core VC-6.

Model Limitations and Potential

Geochemical and geophysical factors can influence the PAH concentrations found in sediments. The source resolution could conceivably also be affected by these factors through particle size. However, since properties such as loss on ignition (7–12%), porosity (0.5–0.6), and grain size distribution (clay 8–10%, silt 25–40%, and sand 50–60%) were fairly similar for all six cores, except VC-1 (Li *et al.* 1995), we believe that the results are minimally influenced by these factors. For VC-1, there was a virtual absence of clay and silt in layers 4, 5, 7, 8, and 9. The loss on ignition (< 3%) and the porosity (0.35–0.4) were also low there. As a result, the corresponding PAH levels were depressed (Fig. 5).

If sediment mixing were significant, it could influence the results of the chemical mass balance model by homogenizing the sediment. From ^{7}Be measurements (Li *et al.* 1995), we found, however, that mixing is restricted to the upper ~2 cm which is much smaller than the typical sediment interval thickness of 10–20 cm. Thus, mixing is not likely to influence the results.

A fundamental requirement of the chemical mass balance model as expressed in equation [1] is that the PAH compound profile from a given source is the same at the source and the receptor. Any fractionation, i.e., differential alteration of the PAH profile between source and receptor, must be known in order to be taken into account. While we allow all PAH compounds to be changed with the same factor, as in the case of addition or subtraction of large inert particles to the sample, we assume here that there is no fractionation. This assumption seems to be justified by (a) the sums of the source contribution factors α are fairly close to one and, (b) the marker compounds NaP, Fl, PhA, An, FlA, Py, BaA, and BaP (Table 2) are fairly conservative and do not appear to be subject to significant volatilization, biodegradation, or photooxidation. Compounds such as naphthalene and anthracene which can be volatilized (NaP) or photodegraded (AN) may here be suitable marker compounds because the transport path in the environment is short, so that the PAHs are quickly buried in the sediments.

While PAH degradation is known to occur in the water column by microbial attack or photolysis (Callahan *et al.* 1979), most of the PAHs would rapidly be incorporated in the sediments where they are protected form further degradation (Hinga *et al.* 1980, Saylor and Sherill 1983). According to Hinga and Pilson (1987), BaA buried in sediment may remain stable in anoxic layers. The rapid sedimentation rate (2.8–9.8 cm/yr) in the Kinnickinnic River, and the shallowness of the river itself, may therefore explain why fractionation of the PAHs is of minor significance in this system.

The development of CMB models for PAHs in

aquatic systems merits further attention. Improved source resolution can be achieved by expanding the list of suitable marker compounds and by measuring corresponding source fingerprints. The use of alternative source resolution techniques to confirm the sources is desirable.

CONCLUSIONS

A chemical mass balance model for PAHs in aquatic sediments has been developed. The model is similar to CMB models currently used in air quality studies (Sexton *et al.* 1985, Kenski *et al.* 1995). Source fingerprints for Coke-A, Coke-B, coal tar (CT), coal-wood gasification (CWG), gas engine exhaust tar (GEET), or highway dust (Hwy) were taken from the literature (NRC 1983, Neff 1979, Singh *et al.* 1993, Wise *et al.* 1988). The number of marker compounds is here either eight (NaP, Fl, PhA, AN, FlA, Py, BaA, and BaP), or seven when either NaP or FlA are left out. The importance of consistent geochemical and geophysical factors as well as the stability of marker compounds is emphasized.

The model is successfully applied to dated sediments of the Kinnickinnic River between the Becher Street Bridge and the Wisconsin Wrecking Company Wharf. This area is heavily contaminated with PAHs (80–1,000 ppm). One major source appears to be the former Milwaukee Solvay Coke Co. which produced coke and performed coal gasification from around 1900 to the late 1970s. Other possible sources include railroads and highway runoff. The horizontal and vertical distribution of PAHs is in accordance with this picture. PAHs from highway runoff peaks in the upper layers of most cores. Coal-wood gasification or coal tar is highest in cores VC-5, and VC-6 close to the former Milwaukee Solvay Coke Co. Coke-B peaks in VC-2. Maximum total PAH concentrations are found in cores (VC-2, 6) with high Coke-B and CWG contributions.

The value of using CMB models in dated cores is demonstrated for core VC-6 which spans the time period from 1895 to 1991. From 1895 to 1950 the PAHs came from Coke-B and coal-wood gasification or coal tar. Highway runoff becomes important in the 1920s, decreases during 1930–'40, and peaks in the most recent layers. This would be expected based on the historical development of automobile traffic. The source apportionment for core VC-6 is supported by a principal component analysis using nonnegative constraints on factor scores and loadings, and by elemental carbon particle analysis.

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Sources of Polycyclic Aromatic Hydrocarbons in Sediments of the Kinnickinnic River, Wisconsin

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ABSTRACT. *A chemical mass balance (CMB) model was developed and used to apportion both point and nonpoint sources of polycyclic aromatic hydrocarbons (PAHs) in six dated sediment cores. The cores were collected in 1994 from a stretch of the Kinnickinnic River between the Becher Street Bridge and the Wisconsin Wrecking Company Wharf, Milwaukee, Wisconsin, and had PAH concentrations of 80 to 1,000 ppm. This work was done in order to identify major PAH sources to this IJC Area of Concern which is important for pollution modeling and management. The source fingerprints were taken from the literature. Coke oven emissions and coal-wood gasification or coal tar are the main local PAH sources, whereas highway dust provides an important nonpoint input since the 1920s. Coal-wood gasification ceases to be a significant source after 1950–'60. Factor analysis based on nonnegative constraint of factor scores and loadings, and oblique rotations, supports this apportionment, but points also to deficiencies in the CMB source profile for coke oven emissions. It appears that the now defunct Milwaukee Solvay Coke Co. was a major source. The influence of geophysical factors and chemical and biological fractionation of the selected PAH compounds appears to be small.*

INDEX WORDS: *PAHs, Milwaukee Harbor, sediments, Lake Michigan, chemical mass balance model, factor analysis, source apportionment.*

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are of concern because of their carcinogenic properties (Neff 1979). PAHs have their origin in both natural and anthropogenic processes. However, several studies have indicated that the anthropogenic input of PAHs to aquatic sediments far exceeds natural sources (NAS 1971). Major human activities which produce PAHs include pyrolysis of wood to produce charcoal and carbon black, coke production, manufacturing of gas fuel, power generation from fossil fuels, combustion of fuels in internal combustion engines, incineration of industrial and domestic wastes, oil refinery and chemical engineering operations, aluminum manufacturing, etc.. By-products of these processes which contain significant amount of PAHs have been dumped on the land, in the water, or buried at subsurface sites. Airborne particulates, generated from these processes and carrying PAHs, are transported worldwide in the atmosphere, and usually find their final destination in soils, and in sediments of aquatic systems.

Differences in the pattern of PAH mixtures reflect different sources and pathways, and thus provide a basis for the analysis of their sources. Traditional approaches of PAH source analysis use ratios of specific compounds (for example, phenanthrene to anthracene, fluoranthene to pyrene), alkyl homologue distribution pattern, or the presence of compounds indicative of a particular source (Laflamme and Hites 1978, Lake *et al.* 1979, Zhang *et al.* 1993, Furlong *et al.* 1988, Benner *et al.* 1995). These methods, however, involve only a small portion of PAH data produced by an analytical laboratory. Thus, they are often unable to resolve sources at all, or with sufficient accuracy, and may be considered incomplete with respect to the number of PAHs that preferably should be involved in the apportionment.

The Milwaukee Harbor estuary is one of the designated Areas of Concern (AOC) of the Interna-

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tional Joint Commission (IJC). This work was done in conjunction with the Remedial Action Committee of the AOC.

Singh *et al.* (1993), considering PAH compound profiles, used a chemical mass balance model to determine nonpoint sources of PAHs in the Milwaukee Harbor Estuary. Similar approaches have been applied to determine sources of organic pollutants in air (Sexton *et al.* 1985, Li and Kamens 1993, Venkataraman and Friedlander 1994, Kenski *et al.* 1995).

This approach is extended here to include both point and nonpoint sources of PAHs deposited in dated aquatic sediments. An in-depth discussion of model uncertainty, based in part on an alternative constrained factor analytical method, is included. We consider also the horizontal distribution of sediment PAHs over of the given stretch of the Kinnickinnic River.

CHEMICAL MASS BALANCE MODEL

The two basic assumptions of the chemical mass balance (CMB) model are, (1) the amount of a chemical pollutant in the sediment at a specific site is the sum of the amounts of this chemical from each independent contributing source, and can be expressed by equation [1], and (2) the ratio between the concentration in the sample of a chemical from a given source and the concentration of the same chemical in the source material is the same for all the chemicals under study (no change in source profile between source and receptor), and can be characterized by a single contribution factor α_i. The expression for the PAHs is,

$$F_j = \sum_{i=1}^{n} \Phi_{ji}\alpha_i + e_j \ (1 \le j \le m) \tag{1}$$

where F_j is the measured concentration of the jth PAH compound in the sample, Φ_{ji} is the concentration of jth PAH in the ith source, α_i is the source contribution factor of the ith source, e_j is the error associated with the jth PAH, n is the number of sources, and m is the number of PAH marker compounds used in the model. In order to characterize source profiles Φ_{ji} (ppm), we define an average molecular weight $(M.W.)_i$,

$$(M.W.)_i = \frac{\sum_{j=1}^{m} \Phi_{ji}}{\sum_{j=1}^{m} \frac{\Phi_{ji}}{(m.w.)_{ji}}} \tag{2}$$

where $(m.w.)_{ji}$ is the molecular weight of PAH compound j in source i. The contribution factors (α_i's) are determined by multiple linear regression using a least-squares method in which the weighted error (equivalent to χ^2) is minimized. The second assumption can also be expressed as a requirement that the source profile, i.e., the relative abundance of PAH compounds, does not change between source and receptor. This definition of α_i is more general than the original one (Friedlander 1973) where α_i simply is the mass fraction of material originating from source i, and where the sum of all α_i's, therefore equals unity. While the latter definition implies mass balance for both bulk material (sediment) and PAHs, our version indicates only mass balance for the PAHs.

The relative contribution P_i of total PAHs from source i is calculated for each source according to

$$P_i = \frac{\alpha_i \sum_{j=1}^{m} \Phi_{ji}}{\alpha_1 \sum_{j=1}^{m} \Phi_{j1} + \alpha_2 \sum_{j=1}^{m} \Phi_{j2} + \ldots + \alpha_n \sum_{j=1}^{m} \Phi_{jn}} \tag{3}$$

The uncertainty δP_i is calculated from

$$\delta P_i = P_i \sqrt{\left(\frac{\delta N}{N}\right)^2 + \left(\frac{\delta D}{D}\right)^2} \tag{4}$$

where $P_i = N/D$

$$\delta N = \delta\alpha_i \sum_{j=1}^{m} \Phi_{ji}$$

$$\delta D = \left(\left(\delta\alpha_1 \sum_{j=1}^{m} \Phi_{j1}\right)^2 + \left(\delta\alpha_2 \sum_{j=1}^{m} \Phi_{j2}\right)^2 + \ldots + \left(\delta\alpha_n \sum_{j=1}^{m} \Phi_{jn}\right)^2 \right)^{1/2}$$

N and D are the numerator and denominator, respectively, of equation [3], and the uncertainties $\delta\alpha_i$ are calculated as in Henry *et al.* (1984).

In order to assess the closeness or goodness of fit between the calculated values of PAHs as determined by the model and the measured values, χ^2 and the multiple linear correlation coefficient R^2 were also determined. The χ^2 was calculated based on the equation:

$$\chi^2 = \sum_{j=1}^{m} \frac{(F_j - F_j')^2}{(r.e.)_k^2 F_j^2 + \sum_{i=1}^{n} (r.e.)_i^2 (\alpha_i \Phi_{ji})^2} \quad (5)$$

where F_j and F_j' are measured and calculated concentrations, respectively, of the jth PAH in the sample. This equation is derived from eq. (11) of Henry *et al.* (1984) using the relative errors $(r.e.)_k$ and $(r.e.)_i$ of the measurements, and the source profile i, respectively. We assume that these relative errors do not vary much from compound to compound such that

$$(r.e.)_k = \frac{\sigma F_j}{F_j} \qquad (r.e.)_i = \frac{\sigma \Phi_{ji}}{\Phi_{ji}} \quad (6)$$

where σ indicates standard errors.

From statistics it is well known that a good fit between measured and calculated values is obtained when χ^2 equals the number of degrees of freedom (df) when df > 4. In this case, each term of the sum in eq. [5] corresponding to the number of degrees of freedom, df = m − n assumes a value close to one since $F_j - F_j'$ then is comparable to the overall error, i.e., the square root of the denominator in eq. [5]. The remaining n terms may be thought of as being zero since n model parameters have been determined from the experimental data.

In applying eq. [5], initial α_i's are calculated assuming that $(r.e.)_i = 0$. Next, revised α_i's are determined using known $(r.e.)_i$'s and the initial set of α_i's. Further iterations were not necessary since the α_i's converge rapidly. For the measured relative error we use 0, 0.2, and 0.4, and then estimate by inter- or extrapolation the $(r.e.)_k$ corresponding to χ^2 = df. If the resulting relative error is ≤ 50%, the fit is considered satisfactory. When the relative error is between 50 and 70%, the fit is fair, and unsatisfactory for larger relative errors. The advantage of considering $(r.e.)_k$ for χ^2 = df rather than χ^2 itself is that $(r.e.)_k$, in contrast to χ^2, can be related directly to the acceptable range of relative errors regardless of the number of degrees of freedom.

METHODS

Sediment Data

During June of 1994, six vibra cores, each 2 to 3 meters long, were collected from a stretch of the Kinnickinnic River, close to downtown Milwaukee and between Becher Street Bridge and the Wisconsin Wrecking Company Wharf using R/V Pelagos. During sampling, aluminum irrigation pipes of 6.7 cm inner diameter were vibrated down into the sediment through clamps and a flexible coupling to a gasoline engine on board the research vessel. The sampling locations are marked in the map shown in Figure 1. This area was determined to be a "hot spot" of PAH contamination in the Milwaukee Harbor Estuary through our earlier work (Ni *et al.* 1992).

Each core was sliced into 15 sections, and each section was analyzed for porosity, grain size distribution, organic content (loss on ignition), and dated by measuring the ^{137}Cs and ^{210}Pb activities. Sedimentation rate was calculated according to a linear regression of log excess ^{210}Pb activity against cumulative mass of the sediment core. Sixteen PAH compounds were determined for each sample, including naphthalene (NaP), acenaphthylene (AcNP), acenaphthene (AcN), fluorene (Fl), phenanthrene (PhA), anthracene (AN), fluoranthene (FlA), pyrene (Py), benz[a]anthracene (BaA), chrysene (Chy), benzo[b]fluoranthene (BbFlA), benzo[k]fluoranthene (BkFlA), benzo[a]pyrene (BaP), indeno[123-cd]pyrene (IP), dibenz[a,h]anthracene (dBahA), and benzo[ghi]perylene (BghiP). Detailed procedures of sampling, sediment characterization, PAH analysis including quality assurance/quality control (QA/QC), and radioactivity analysis are reported by Li *et al.* (1995).

Complete experimental results of sediment PAHs for the entire Milwaukee Harbor Estuary are presented elsewhere (Li *et al.* 1996). Only those compounds whose concentrations were determined with satisfactory chromatographic separations and above the method detection limits (0.3–1 ppm) were considered in the CMB modeling. Further reductions in the number of compounds included were made based on available source fingerprint data. Our aim was to have at least four degrees of freedom. Based on this, we selected seven compounds for five cores and eight for one (VC-2). NaP, Fl, PhA, AN, Py, BaA, BaP were chosen for VC-5 and 6, and Fl, PhA, AN, FlA, Py, BaA, BaP for VC-1, 3, and 4. NaP is included in the first set because NaP was mainly present in VC-2, 5, and 6. Also, FlA was included in the second set because coal-wood gasification (CWG), for which FlA data were not available, was not a significant source for VC-1, 2, 3, and 4. Thus, for VC-2 we used all eight compounds.

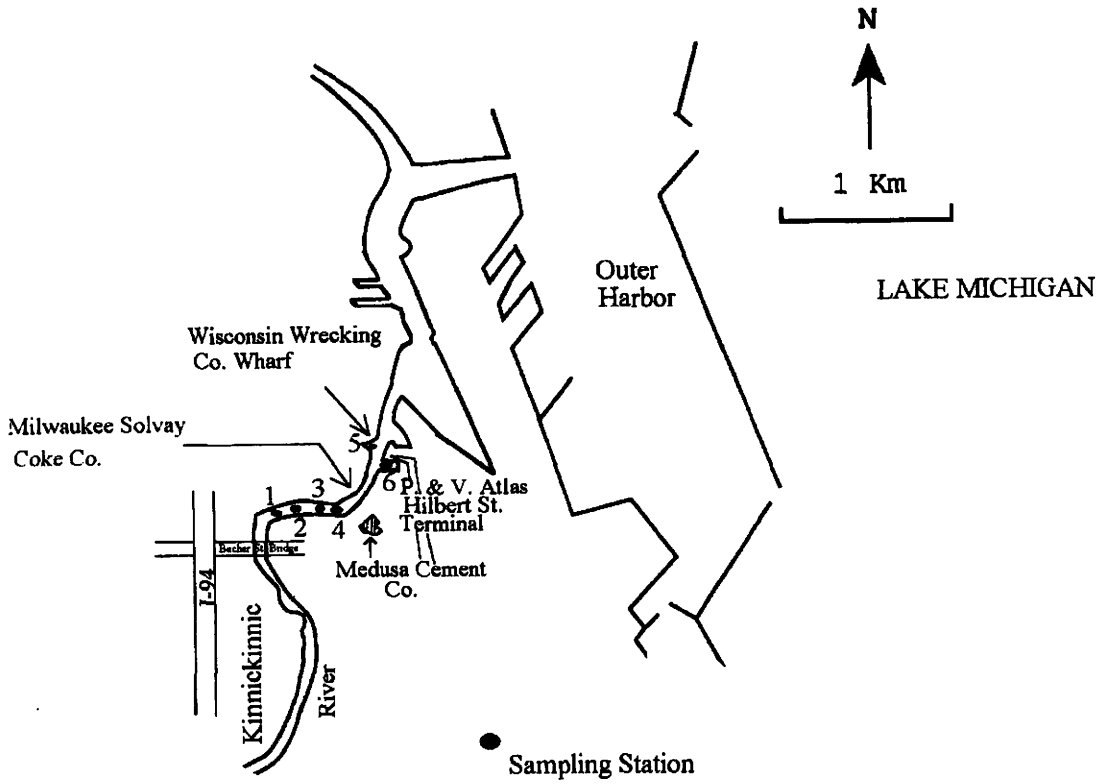

FIG. 1. Partial map of the Milwaukee Harbor Estuary with sampling sites on the Kinnickinnic River.

Source Fingerprints

The majority of the PAHs found in the environment originates from incomplete combustion of fossil fuels including wood, coal, and petroleum. Most PAH data used in this study as fingerprints of these sources were drawn from the literature (NRC 1983, Wise *et al.* 1988, Neff 1979, Singh *et al.* 1993). They are summarized in Table 1 and illustrated in Figures 2–4. A blank cell in Table 1 means that there is no information about the PAH compound for the given source as for FlA in CWG or Chy in Coke-A and Coke-B. The HWY concentrations represent averages of three samples. Note that the average molecular weights for Coke-B, HWY, CT, and CWG decrease in the given order, probably reflecting the temperature at which the PAHs were formed. The fact that the HWY PAH concentrations are orders of magnitude lower than PAH concentrations of other sources presents no particular difficulty since the α's (equation 1) will be adjusted accordingly by the least-squares procedure. The important thing is that each source profile is distinct and that its relative error (coefficient of variation) is known and within the same general range (0.03–0.4). In order to improve the comparability of source profiles, and since the apportionment results (P_i, equation 3) do not depend on a constant factor in the source profile, the coke oven (Fig. 2) and coal and coal-wood gasification profiles (Fig. 3) have been normalized to Py (1,000 ppm).

Coke production and fuel gas manufacturing were among the major industrial activities in the study area until the mid 1970s. In fact, sediment core VC-6 was taken from a site near the previous Milwaukee Solvay Coke Company, which operated its coke ovens from 1902 until the 1970s. It is likely that the high PAH concentration in the sediment deposited during that period at that location originated from the products of this company, which include metallurgical coke, coal tar, coal gas, and some aromatic chemicals (M.L. Morgan, personal communication, 1994). However, a chemical inventory of the company is not available. Compositions of two types of PAH sources, namely Coke-A and Coke-B,

TABLE 1. PAH concentrations in several sources (ppm).

Parameter	Coke-A[a]	Coke-B[a]	CT[b]	CWG[c]	GEET[d]	HWY[e]
NaP		17.2[h]	1,160.0	236.0		0.26
AcNP			252.0	53.6		
AcN						0.65
Fl	75.3	17.2	136.0	28.9		0.83
PhA	680.1	540.6	462.0	94.0		4.75
AN	209.3	391.2	101.0	32.7		1.00
FlA	1,270.0	704.4	322.0		972.0	5.58
Py	977.2	826.4	235.0	31.3	1,770.0	3.95
BaA	536.8	3,838.1	102.0	6.3	61.7	0.84
Chy			71.7	3.8	175.0	1.42
BaP	566.9	2,147.9	95.8	3.8	31.5	0.82
BghiP			53.7	0.7	51.0	0.33
C.V.[f]		0.40	0.03	0.20		0.29
M.W.[g]		222.7	152.4	147.9		189.0

[a]Air-filter of coke oven emissions (NRC 1983 p. 2-23)
[b]Coal tar (Wise *et al.* 1988)
[c]Coal and wood gasification , Ill#6 coal & wood pellets (NRC 1983, pp. 2–13)
[d]Gas engine exhaust tar (Neff 1979 p. 36)
[e]Highway dust (Singh *et al.* 1993)
[f]Coefficient of variation
[g]Average molecular weight (NaP, Fl, PhA, AN, Py, BaA, BaP)
[h]Assumed upper limit

were obtained from analyzing the samples collected from a glass fiber and a 0.8 μm porosity silver membrane filter, respectively, of coke oven emissions (Lao *et al.* 1975). These coke data were also listed in Neff (1979) and NRC (1983). Data listed in Table 1 for Coke-A and Coke-B are the geometric means of two sets of data, i.e., samples 1 and 2 for Coke-A, and samples 3 and 4 for Coke-B (Fig. 2).

In urban areas with heavy traffic, vehicular exhaust and, therefore, highway dust (HWY) can be a significant sources of PAHs. Gasoline engine exhaust tar (GEET) contains significant amount of PAHs including some proven carcinogens such as benzo[a]pyrene and chrysene. Pyrene is the most abundant constituent, accounting for approximately 50% of total PAHs in GEET (Table 1).

Other important anthropogenic PAH sources may

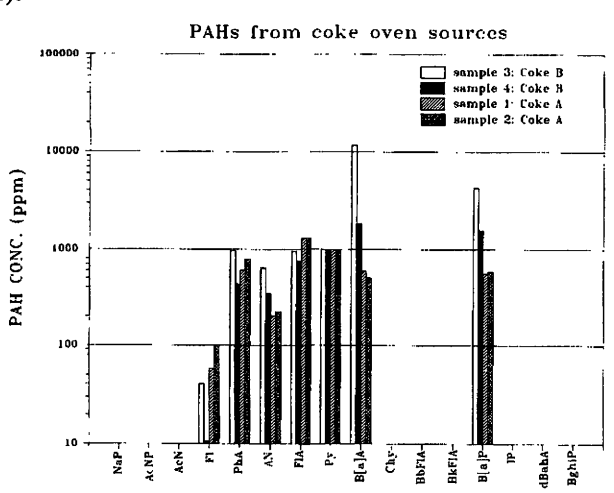

FIG. 2. PAH concentrations in coke oven emissions, normalized to Py (1,000 ppm) (NRC 1983, pp. 2–23)

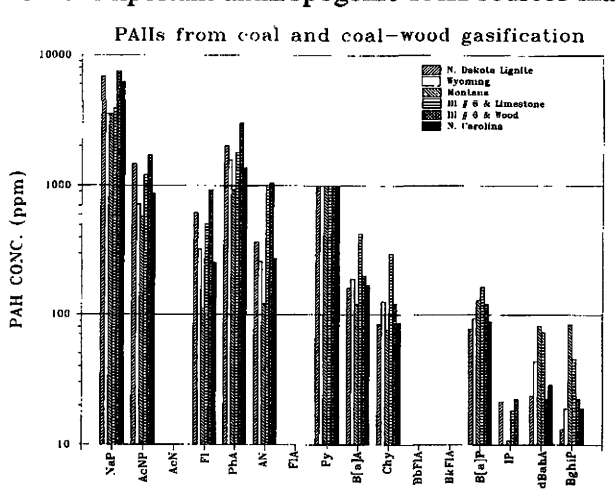

FIG. 3. PAH concentrations resulting from gasification of various coals and coal blends, normalized to Py (1,000 ppm) (NRC 1983, pp. 2–13)

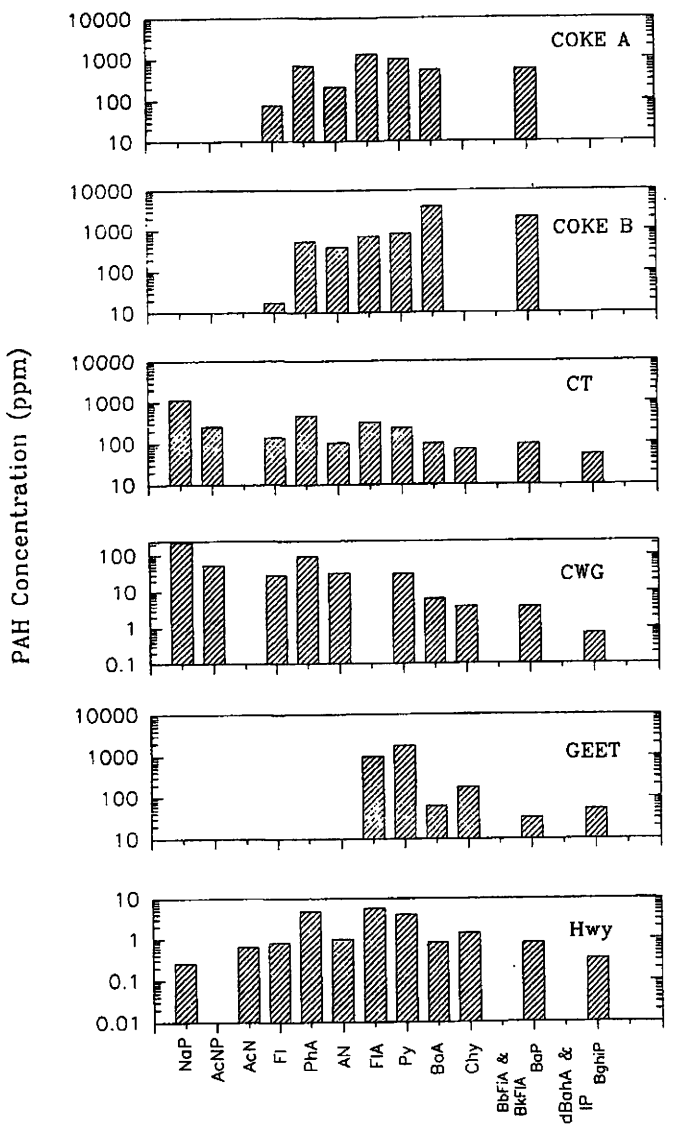

FIG. 4. PAH concentrations in sources used for CMB modeling.

include, but are not limited to, power generation using coal, or oil, petroleum refining, catalyst regeneration, incineration of solid industrial and domestic wastes, as well as leakage and spills of petroleum-based products from various activities. PAHs may also enter the environment from various non-point sources in addition to those considered in this study.

Modeling Procedure

For each core segment, several cases were considered in which different combinations of sources were evaluated as possible contributing sources. The number of degrees of freedom (df) which is the difference between the number of PAH compounds involved and the number of possible contributing sources, should as high as possible, and was kept ≥ 4. In order to obtain a source apportionment that would be physically meaningful, and comparable from segment to segment, and from core to core, the following objectives in the modeling were maintained: (a) as much as possible to use the same PAH compounds for all segments, (b) to the extent possible to use the same sources for all segments, and (c) to use known information about possible sources, and to have the average source molecular weights distributed evenly and span the range of average sample molecular weights.

As discussed above, the first objective was met by using Fl, PhA, AN, Py, BaA, BaP for all six cores. In addition, FlA was added for VC-1, 3, 4, NaP for VC-5, 6, and both FlA and NaP for core VC-2. The second and third objectives were met by using Coke-B, HWY, and CWG as general sources for all six cores. We found that the average molecular weights of these sources in all cases spanned the average sample molecular weights. These sources are also in accordance with known information about PAH contamination in the area. Note that coal tar (CT) is almost indistinguishable from CWG, but that the latter source gives slightly lower measured relative errors for $\chi^2 = \text{df}$.

The uncertainty of the experimental sediment data, σF_j in equation [6], is expressed as the relative standard deviation or error $(\text{r.e.})_k$ which is calculated by analyzing sample duplicates on different days, several weeks apart. A relative error of 0.3–0.4 was typical. This is then the basis for the earlier statement that the model fit is considered satisfactory for $(\text{r.e.})_k \leq 50\%$, fair for $50\% \leq (\text{r.e.})_k \leq 70\%$, and unsatisfactory for $(\text{r.e.})_k \geq 70\ \%$.

In an attempt to verify the results obtained by CMB modeling, factor scores and loadings were calculated by principal component analysis (PCA). We used a version of Ozeki *et al's.* (1995) method in which the data matrix has only positive elements and where nonnegative constraints are imposed on both the score and the loading matrices. This is achieved through a series of oblique rotations in which the basic factor analysis equation is maintained. The advantage of this method over conventional PCA is that factor scores may be directly interpreted as the source contribution of a given sample (segment), and that, similarly, the loading matrix directly provides information

on the unknown source profiles. The number of sources included depends on the eigenvalue structure of the covariance matrix. Sources corresponding to the largest eigenvalues which account for ≥ 80% of the variance of the data were considered significant, and were, therefore, retained. Since core VC-6 goes furthest back in time (1895) and has the most complicated CMB source pattern, the PCA technique was applied to this core. In order to obtain maximum comparability between the CMB and the PCA results, the PAH compounds considered in PCA were the same as those included in the CMB model (NaP, Fl, PhA, AN, Py, BaA, BaP).

A second check on the results of the PAH source analysis for core VC-6 was made by investigating elemental carbon particles of chemically isolated carbon fractions from each layer (Griffin and Goldberg 1983). Oven dried sediment was treated with HCl and HF to remove carbonates and metals and to dissolve silicates. Next, organic compounds were oxidized with H_2O_2 in preparation for scanning electron microscopy (Top-Con, ABT-32). The classification of carbon particles according to their source (wood, oil, or coal) was then performed on 100 randomly selected particles for each layer following the morphology guidelines of Griffin and Goldberg (1979).

RESULTS AND DISCUSSION

A summary of results of radionuclide and PAH analysis for core VC-6, which is used as an example of applying the CMB model, is given in Table 2. From the ^{210}Pb activities it is seen that the sedimentation rate is reasonably constant. Total PAH concentrations for all cores are shown in Figures 5 and 6. From Figure 6, it is seen that core VC-6 spans the time period from 1895 to 1991, and that the maximal total PAH level is 610 ppm occurring in 1902. Levels are also high (590–580 ppm) in 1916 and 1923. The top layer has a moderate PAH concentration of 140 ppm.

Relative contributions (P_i) with uncertainties of Coke-B and CWG to the total PAHs, determined by the CMB model for all six locations in the study area, are also shown in Figures 5 and 6. The HWY contribution is 100% minus the sum of the contributions from Coke-B and CWG. Relative errors of measured concentrations for χ^2 = df are 11–55% for all cores except VC-2 for which the relative errors are 55–67%. Coke-B, HWY, and CWG are significant sources in VC-5 and 6, whereas only Coke-B

TABLE 2. ^{210}Pb and ^{137}Cs activities, dates of layers, selected PAH concentrations, and average PAH molecular weights of sediment core VC-6.

Depth (cm)	Net ^{210}Pb Activity[a] (dpm/g)	^{137}Cs Activity (dpm/g)	Sedimentation Rate Date[b]	PAH (ppm)[c]								
				NaP	Fl	PhA	AN	FlA	Py	BaA	BaP	M.W.[d]
0–17	6.29	0.54	1991	0.50	0.76	10.5	1.25	25.1	21.6	9.4	10.8	206.4
17–34	3.15	0.47	1984	0.77	0.71	9.3	1.30	23.5	19.9	7.5	7.0	203.0
34–51	8.19	2.90	1977	0.72	1.68	22.5	2.44	65.5	54.7	20.5	24.1	206.9
51–68	2.20	2.23	1970	5.69	2.54	31.7	3.49	69.0	55.4	26.0	22.9	200.5
68–85	3.69	8.52	1963	0.92	2.60	34.2	3.71	66.4	57.1	24.7	26.0	204.4
85–102	1.64	3.04	1957	7.53	2.43	26.6	3.43	62.2	49.9	30.8	22.6	200.7
102–119	1.84	0.00	1950	3.57	2.34	22.6	3.38	48.5	40.3	24.5	17.3	202.3
119–136	0.00	0.05	1943	36.2	3.72	18.8	6.89	60.6	54.8	36.8	18.6	183.9
136–153	0.36	0.01	1936	49.9	4.36	40.0	6.76	65.5	59.0	53.4	17.6	181.2
153–170	0.56	0.09	1929	65.0	5.44	43.1	8.76	66.3	63.5	62.1	22.6	179.3
170–187	1.52	0.06	1923	43.3	5.00	50.7	9.62	87.8	80.5	76.4	34.3	190.1
187–204	0.57	0.00	1916	67.4	4.91	48.6	8.22	78.1	75.4	77.2	28.1	182.4
204–221	0.73	0.01	1909	58.6	3.20	22.5	4.77	54.3	53.8	40.3	15.7	175.1
221–238	0.43	0.00	1902	144.0	4.30	48.0	10.00	66.1	67.3	60.0	23.4	164.8
238–255	0.47	0.00	1895	50.9	5.65	46.7	6.57	53.0	46.4	52.1	17.0	179.3

[a]Net ^{210}Pb Activity = measured ^{210}Pb activity - supported ^{210}Pb activity (1.4 dpm/g).
[b]Based on a constant sedimentation rate of 2.384 g/cm^2/year, determined from ^{210}Pb activity data.
[c]Based on dry weight of sediment sample.
[d]Average molecular weight (NaP, Fl, PhA, AN, Py, BaA, BaP).

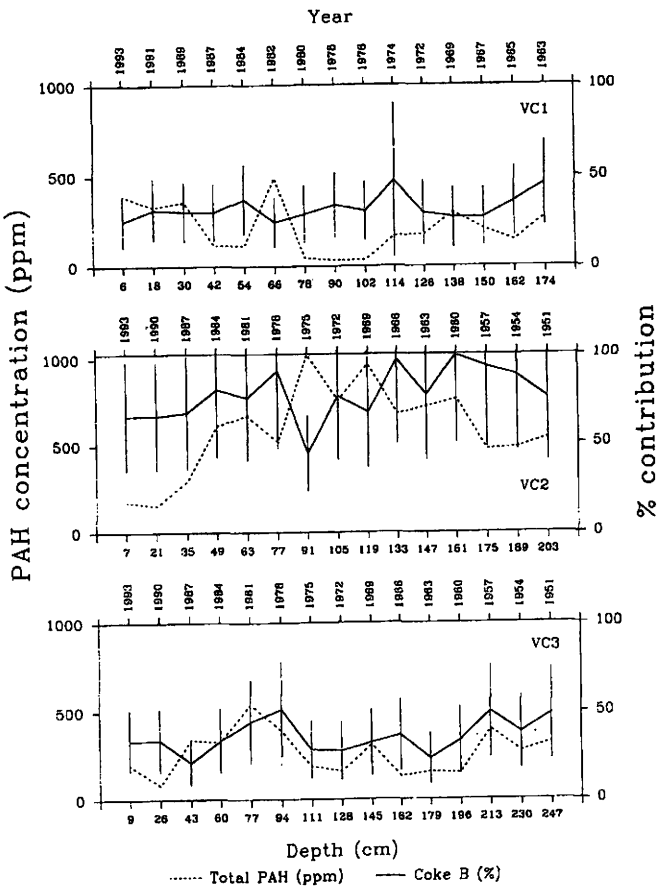

FIG. 5. Total PAH concentration and Coke-B contribution vs. depth and year of cores VC-1, 2, and 3.

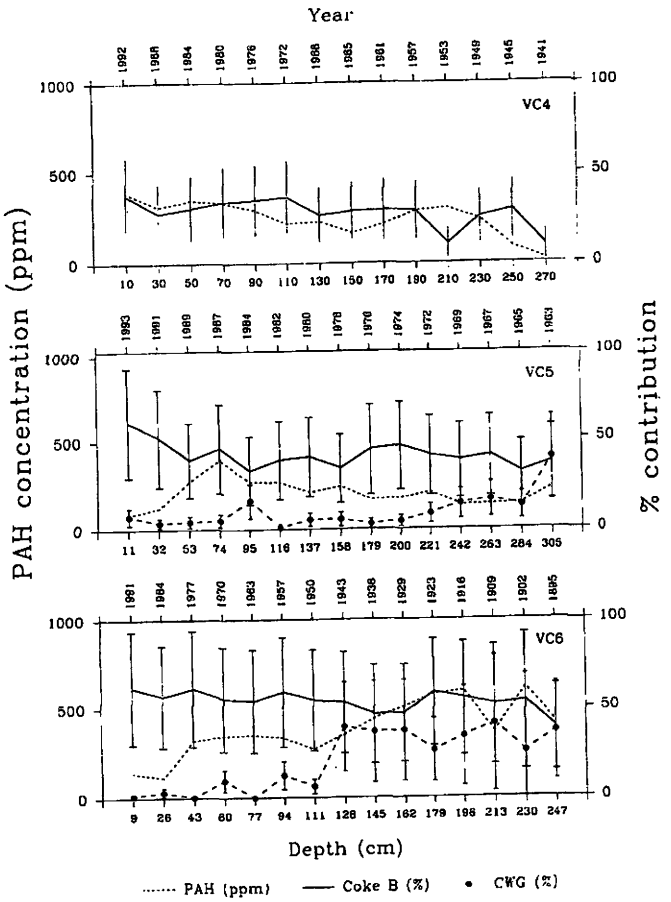

FIG. 6. Total PAH concentration and Coke-B & CWG contribution vs. depth and year of cores VC-4, 5, and 6.

and HWY are important for cores VC-1, 2, 3, and 4. Note that there is a rough correlation between total PAH concentrations and the sum of Coke-B and CWG contributions. This would be expected since the latter sources are local. In particular, the highest PAH concentrations of 800–1,020 ppm in VC-2 are accompanied by high Coke-B contributions of 50 to more than 90% (Fig. 5).

Figure 7 shows a detailed comparison for VC-6 of the contributions of the HWY, CWG, and Coke-B along with scores calculated from PCA using the three highest eigenvalues. As may be seen from this figure, there is a remarkable agreement between the CMB and factor analysis (FA) results for CWG. The loading vectors, determined by PCA, and corresponding to these scores are correctly categorized, based on a Q^2 criterion for log of the normalized vectors (Kuik *et al.* 1993), according to the assumed CMB source profiles (Fig. 8). Thus, the HWY loading vector fits in fact best with the HWY source profile used in CMB modeling, and the CWG and Coke-B loadings provide similarly optimal fits to the corresponding actual source profiles. NaP and Fl are excluded in the HWY and CWG profiles, respectively, because their values became negative as a result of the oblique rotations. Also, actual values of NaP and Fl were treated as outliers for the Coke-B fit. This may indicate that the Coke-B source profile used in CMB modeling (Fig. 2) is deficient in that the low-molecular weight compounds are underestimated. One possible reason is that these compounds primarily are in the vapor phase, and, therefore, are not strongly retained on the filter.

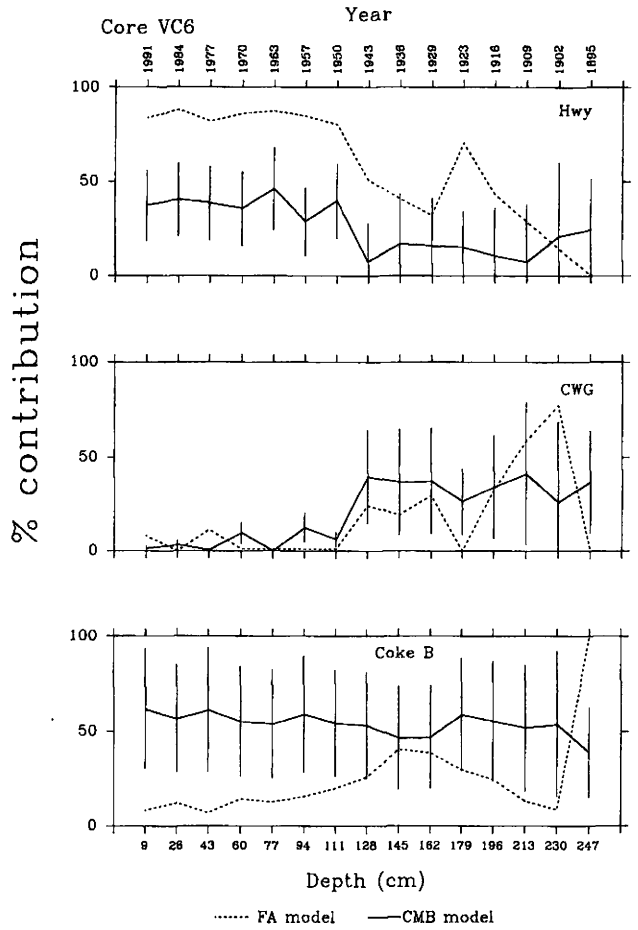

FIG. 7. Percent contribution to PAHs of HWY, CWG, and Coke-B sources vs. depth and year of core VC-6. Results obtained by CMB modeling are compared to scores derived from factor analysis (FA).

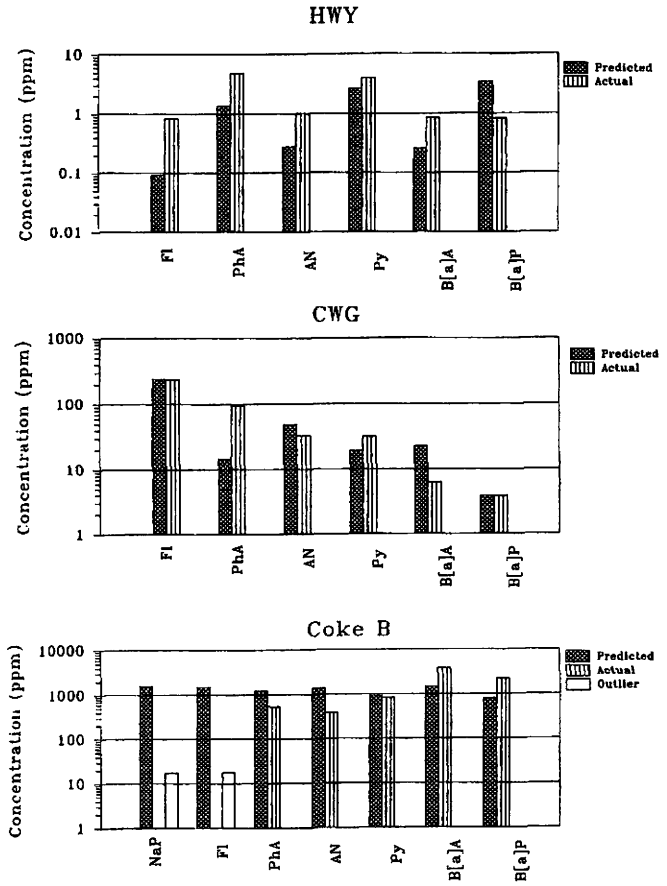

FIG. 8. Comparison of source profiles for HWY, CWG, and Coke-B used in CMB modeling with normalized loading vectors derived from factor analysis (FA).

PAH Sources

From Figures 5 and 6 it is seen that the HWY source in the top layers is highest (≅ 65%) in cores VC-1, 3, and 4, and 35–40% in the other cores. Also, this source increases toward the top in cores VC-2 and 6, to some extent so in VC-1 and 3, but not in VC-4 and 5. The latter anomaly may be caused by redistribution of PAHs within the system. CWG, which is found in VC-5 and 6, becomes small after 1950–60, and appears to reflect the actual history of coal gasification or possibly coal tar production in the area. The highest PAH concentrations are associated with high contributions of Coke-B and CWG (VC-2 and 6).

Figure 7 provides a confirmation of the CMB results for CWG, partial confirmation for HWY, and an indication that Coke-B before 1923 and after 1943 are overestimated by the CMB model. The latter result is based on the fact that the FA model for Coke-B follows the actual activities of the now defunct Milwaukee Solvay Coke Co. and that the Coke-B source profile for CMB modeling appeared deficient with respect to the low-molecular weight compounds Fl and NaP (Fig. 8). Figure 9 provides an independent confirmation of the HWY results of Figure 7 in that oil particles are much more abundant in the upper layers. Also, the results for wood particles indicate that coal rather than coal-wood gasification was predominant. There is not much difference between the corresponding source profiles (Fig. 3).

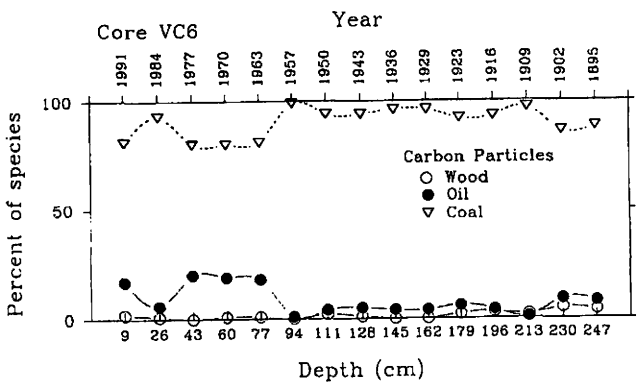

FIG. 9. Percent carbon particles from wood, oil, and coal burning.

larger than one, it is reasonable to assume that smaller particles of high PAH content have replaced larger particles of low PAH content at the receptor compared to the source. This is consistent with the fact that larger particles, e.g., sand, have a lower PAH content than smaller organic carbon-silt particles (< 74 μm) (Ab Razak *et al.* 1996), and that the larger particles would tend to settle out before reaching the sample sites due to gravity according to Stokes law.

A comparison of measured and calculated PAH concentrations of the above sections of VC-6 is shown in Figure 10. The calculated concentrations are obtained from

$$F_j' = \sum_{i=1}^{n} \Phi_{ji}\alpha_i$$

using the previously introduced notation. Measured values are shown with error bars for χ^2 = df. Note that although source profile errors are not shown in this figure, they are implicitly included in the calculated values. In view of these conditions, the agreement between measured and calculated PAH concentrations is quite good.

Statistical Analysis

Statistical results for selected sections of core VC-6 are presented in Table 3. From this table it is seen that the multiple correlation coefficient R^2 is between 0.51 and 0.71 and that the relative error for χ^2 = df is between 40 and 53%. The sum of α_i's ranges from 0.92 to 3.25. Since this sum mainly is

TABLE 3. Statistical results of CMB modeling for selected sections of sediment core VC-6 (df = 4).

Core Section	PAH Sources	α	P_i	χ^2	R^2	Σα	R.E.[a] (%)
6-2	Coke-B	0.00203 ± 0.00086	0.561 ± 0.286	5.25	0.604	0.93	45
	CWG	0.00201 ± 0.00150	0.0309 ± 0.025				
	HWY	0.925 ± 0.365	0.408 ± 0.199				
6-5	Coke-B	0.00594 ± 0.0027	0.535 ± 0.289	5.81	0.705	3.25	46
	CWG	-0.000194 ± 0.0023	0.0010 ± 0.011				
	HWY	3.240 ± 1.216	0.466 ± 0.224				
6-7	Coke-B	0.00558 ± 0.0024	0.539 ± 0.284	3.95	0.633	2.61	40
	CWG	0.0112 ± 0.0068	0.0603 ± 0.0406				
	HWY	2.60 ± 1.07	0.401 ± 0.202				
6-9	Coke-B	0.00884 ± 0.00384	0.464 ± 0.276	6.06	0.547	2.15	43
	CWG	0.126 ± 0.00825	0.367 ± 0.283				
	HWY	2.02 ± 3.08	0.170 ± 0.268				
6-11	Coke-B	0.0163 ± 0.00638	0.585 ± 0.301	4.65	0.644	2.80	43
	CWG	0.132 ± 0.0770	0.263 ± 0.177				
	HWY	2.65 ± 3.27	0.152 ± 0.194				
6-14	Coke-B	0.0125 ± 0.00507	0.534 ± 0.385	8.14	0.510	3.23	53
	CWG	0.106 ± 0.169	0.253 ± 0.429				
	HWY	3.11 ± 5.57	0.213 ± 0.402				

[a]Relative error at χ^2 = df

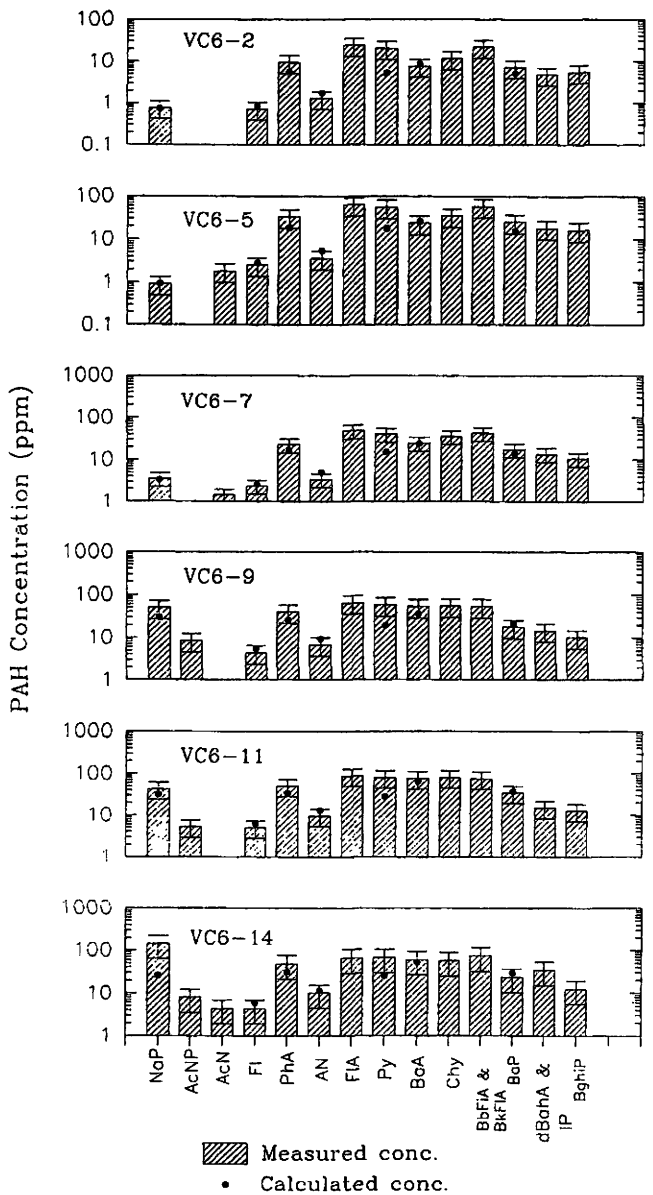

FIG. 10. Measured and calculated PAH concentrations for selected sections of core VC-6.

Model Limitations and Potential

Geochemical and geophysical factors can influence the PAH concentrations found in sediments. The source resolution could conceivably also be affected by these factors through particle size. However, since properties such as loss on ignition (7–12%), porosity (0.5–0.6), and grain size distribution (clay 8–10%, silt 25–40%, and sand 50–60%) were fairly similar for all six cores, except VC-1 (Li *et al.* 1995), we believe that the results are minimally influenced by these factors. For VC-1, there was a virtual absence of clay and silt in layers 4, 5, 7, 8, and 9. The loss on ignition (< 3%) and the porosity (0.35–0.4) were also low there. As a result, the corresponding PAH levels were depressed (Fig. 5).

If sediment mixing were significant, it could influence the results of the chemical mass balance model by homogenizing the sediment. From ^{7}Be measurements (Li *et al.* 1995), we found, however, that mixing is restricted to the upper ~2 cm which is much smaller than the typical sediment interval thickness of 10–20 cm. Thus, mixing is not likely to influence the results.

A fundamental requirement of the chemical mass balance model as expressed in equation [1] is that the PAH compound profile from a given source is the same at the source and the receptor. Any fractionation, i.e., differential alteration of the PAH profile between source and receptor, must be known in order to be taken into account. While we allow all PAH compounds to be changed with the same factor, as in the case of addition or subtraction of large inert particles to the sample, we assume here that there is no fractionation. This assumption seems to be justified by (a) the sums of the source contribution factors α are fairly close to one and, (b) the marker compounds NaP, Fl, PhA, An, FlA, Py, BaA, and BaP (Table 2) are fairly conservative and do not appear to be subject to significant volatilization, biodegradation, or photooxidation. Compounds such as naphthalene and anthracene which can be volatilized (NaP) or photodegraded (AN) may here be suitable marker compounds because the transport path in the environment is short, so that the PAHs are quickly buried in the sediments.

While PAH degradation is known to occur in the water column by microbial attack or photolysis (Callahan *et al.* 1979), most of the PAHs would rapidly be incorporated in the sediments where they are protected form further degradation (Hinga *et al.* 1980, Saylor and Sherill 1983). According to Hinga and Pilson (1987), BaA buried in sediment may remain stable in anoxic layers. The rapid sedimentation rate (2.8–9.8 cm/yr) in the Kinnickinnic River, and the shallowness of the river itself, may therefore explain why fractionation of the PAHs is of minor significance in this system.

The development of CMB models for PAHs in

aquatic systems merits further attention. Improved source resolution can be achieved by expanding the list of suitable marker compounds and by measuring corresponding source fingerprints. The use of alternative source resolution techniques to confirm the sources is desirable.

CONCLUSIONS

A chemical mass balance model for PAHs in aquatic sediments has been developed. The model is similar to CMB models currently used in air quality studies (Sexton *et al.* 1985, Kenski *et al.* 1995). Source fingerprints for Coke-A, Coke-B, coal tar (CT), coal-wood gasification (CWG), gas engine exhaust tar (GEET), or highway dust (Hwy) were taken from the literature (NRC 1983, Neff 1979, Singh *et al.* 1993, Wise *et al.* 1988). The number of marker compounds is here either eight (NaP, Fl, PhA, AN, FlA, Py, BaA, and BaP), or seven when either NaP or FlA are left out. The importance of consistent geochemical and geophysical factors as well as the stability of marker compounds is emphasized.

The model is successfully applied to dated sediments of the Kinnickinnic River between the Becher Street Bridge and the Wisconsin Wrecking Company Wharf. This area is heavily contaminated with PAHs (80–1,000 ppm). One major source appears to be the former Milwaukee Solvay Coke Co. which produced coke and performed coal gasification from around 1900 to the late 1970s. Other possible sources include railroads and highway runoff. The horizontal and vertical distribution of PAHs is in accordance with this picture. PAHs from highway runoff peaks in the upper layers of most cores. Coal-wood gasification or coal tar is highest in cores VC-5, and VC-6 close to the former Milwaukee Solvay Coke Co. Coke-B peaks in VC-2. Maximum total PAH concentrations are found in cores (VC-2, 6) with high Coke-B and CWG contributions.

The value of using CMB models in dated cores is demonstrated for core VC-6 which spans the time period from 1895 to 1991. From 1895 to 1950 the PAHs came from Coke-B and coal-wood gasification or coal tar. Highway runoff becomes important in the 1920s, decreases during 1930–'40, and peaks in the most recent layers. This would be expected based on the historical development of automobile traffic. The source apportionment for core VC-6 is supported by a principal component analysis using nonnegative constraints on factor scores and loadings, and by elemental carbon particle analysis.

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Prediction of sediment toxicity using consensus-based freshwater sediment quality guidelines

United States Geological Survey (USGS) final report for
the U.S. Environmental Protection Agency (USEPA)
Great Lakes National Program Office (GLNPO)

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Abstract

The primary objectives of this study were to: (1) evaluate the ability of consensus-based SQGs (sediment quality guidelines) to predict toxicity in a freshwater database for field-collected sediments in the Great Lakes basin; (2) evaluate the ability of SQGs to predict sediment toxicity on a regional geographic basis elsewhere in North America; and (3) compare approaches for evaluating the combined effects of chemical mixtures on the toxicity of field-collected sediments. A database was developed from 92 published reports which included a total of 1657 samples with high-quality matching sediment toxicity and chemistry data. The database was comprised primarily of 10- to 14-day or 28- to 42-day toxicity tests with the amphipod *Hyalella azteca* (designated as the HA10 or HA28 tests) and 10- to 14-day toxicity tests with the midges *Chironomus tentans* or *C. riparius* (designated as the CS10 test). Endpoints reported in these tests were primarily survival or growth. Because field-collected sediments typically contain complex mixtures of contaminants, the predictive ability of a sediment assessment is likely to increase when SQGs are used in combination to classify toxicity of sediments. For this reason, the evaluation of the predictive ability of probable effect concentrations (PECs) was conducted to determine the incidence of effects above and below various mean PEC quotients (mean quotients of 0.1, 0.5, 1.0, and 5.0). The PECs are SQGs that were established as concentrations of individual chemicals above which adverse effects in sediments are expected to frequently occur. A PEC quotient was calculated for each chemical in each sample in the database by dividing the concentration of a chemical by the PEC for that chemical. A mean quotient was calculated for each sample by summing the individual quotient for each chemical and then dividing this sum by the number of PECs evaluated.

When mean quotients were calculated using an approach of equally weighting up to 10 reliable PECs (PECs for metals, total polycyclic aromatic hydrocarbons (PAHs), total polychlorinated biphenyls (PCBs), and sum DDE), there was an overall increase in the incidence of toxicity with an increase in the mean quotient in all three tests. For example in the HA10 test, the toxicity of samples was 20% at mean quotients of <0.1 and increased to 67% at mean quotients of >5.0. Similarly, for the CS10 test there was a 20% incidence of toxicity at mean quotients of <0.1 increasing to a 64% incidence of toxicity at mean quotients of >5.0. In contrast, the incidence of toxicity in the HA28 test was only 8% at mean quotients of <0.1 and increased to 91% at mean quotients of >1.0. In all three tests, there was a consistent increase in the toxicity at mean quotients of >0.5. However, the overall incidence of toxicity was greater in the HA28 test compared to the short-term tests.

The incidence of toxicity at mean quotients of <0.1 was somewhat higher in the HA10 and CS10 tests (20%) compared to the HA28 test (8%). This toxicity at low mean quotients does not appear to be related to total organic carbon in sediment. There was insufficient information in the database to evaluate effects of grain size on toxicity. Unmeasured contaminants in these field-collected sediments or contaminants for which we do not have reliable PECs (i.e., pesticides, herbicides) may have contributed to this toxicity at low mean quotients. Alternatively, the data for HA10 and CS10 tests were obtained from numerous laboratories which may have contributed to variability in the data reported in these studies. In contrast, a limited number of laboratories conducted most of the HA28 tests.

The reason for the higher incidence of toxicity with increasing mean quotients in the HA28 test compared to the short-term tests may be due to the duration of the exposure or the sensitivity of

growth in the longer HA28 test. A 50% incidence of toxicity in the HA28 test corresponds to a mean quotient of 0.63 when survival or growth were used to classify a sample as toxic. By comparison, a 50% incidence of toxicity is expected at a mean quotient of 3.2 when survival alone was used to classify a sample as toxic in the HA28 test. In the CS10 test, a 50% incidence of toxicity is expected at a mean quotient of 9.0 when survival alone was used to classify a sample as toxic or at a mean quotient of 3.5 when survival or growth were used to classify a sample as toxic. In contrast, similar mean quotients resulted in a 50% incidence of toxicity in the HA10 test when survival alone (mean quotient of 4.5) or when survival or growth (mean quotient of 3.4) were used to classify a sample as toxic. Results of these analyses indicate that both the duration of the exposure and the endpoints measured can influence whether a sample is found to be toxic or not. The longer-term tests in which growth and survival are measured tended to be more sensitive than shorter-term tests, with acute to chronic ratios on the order of 6 indicated for *H. azteca*.

We were also interested in determining the predictive ability of PEC quotients for major classes of compounds. Therefore, we evaluated the incidence of toxicity based on a mean quotient for metals, a quotient for total PAHs, or a quotient for total PCBs. Different patterns of toxicity associated with the various procedures for calculating quotients were observed. For example in the HA28 test, a relatively abrupt increase in toxicity was associated with elevated PCBs alone or with elevated PAHs alone, compared to the pattern of a gradual increase in toxicity observed with quotients calculated using a combination of metals, PAHs, and PCBs. These analyses indicate that the different patterns in toxicity may be the result of unique chemical signals associated with individual contaminants. While mean quotients can be used to classify samples as toxic or non-toxic, individual quotients might be useful in helping to identify substances that may be causing or substantially contributing to the observed toxicity.

We chose to make comparisons across geographic areas using mean quotients calculated by equally weighting the contribution of the three major classes of compounds (metals, or PAHs, or PCBs). This approach assumes that these three diverse groups of chemicals exert some form of joint toxic action. Use of this approach also maximized the number of samples that were used to make comparisons across geographic areas. Generally, there was an increase in the incidence of toxicity with increasing mean PEC quotients within most of the regions, basins, and areas for all three toxicity tests. For the HA10 and HA28 tests, the incidence of toxicity for samples from each of the Great Lakes and within the areas of each Great Lake was relatively consistent with the overall pattern of toxicity in the entire database. However, the relationship between the incidence in toxicity and mean quotients in the CS10 test was more variable among geographic areas compared to either the HA10 or HA28 test. The results of these analyses indicate that the consensus-based PECs can be used to reliably predict toxicity of sediments on both a regional and national basis.

This paper presents results of the first analyses completed on the entire freshwater sediment database. Some of the additional analyses planned for the database that are beyond the scope of this paper include: (1) comparing approaches for designating samples as toxic; (2) evaluating logistic-regression models; (3) identifying a list of optimal analytes for broad scale application and testing the relative efficacy of the mean versus the sum PEC quotients; (4) evaluating the influence of grain size and ammonia on the incidence of toxicity; and (5) developing a guidance manual for conducting an integrated assessment of sediment contamination.

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Acknowledgments

We thank the members of the Sediment Advisory Group on Sediment Quality Assessment for insight and guidance in developing the procedures for evaluating the predictive ability of freshwater sediment quality guidelines. We would also like to thank Kathie Adare, Peter Landrum, and Rick Swartz for providing helpful review comments on the report. Although information in this report was developed in part by the USGS, USEPA, and NOAA, the report may not necessarily reflect the reviews of these organizations and no official endorsement should be inferred. Sediment quality guidelines (SQGs) can be used as one of several tools to assess contaminated sediments; however, there is no intent expressed or implied that these guidelines represent USGS, USEPA, or NOAA sediment quality criteria. Information in this report and the development of the database have been funded in part by the USEPA Great Lakes National Program Office, USEPA Office of Research and Development, USEPA Office of Water, Minnesota Pollution Control Agency, and National Research Council of Canada. This report has been reviewed in accordance with USEPA and USGS policy.

Introduction

Numerical sediment quality guidelines (SQGs) have been developed by a variety of federal, state, and provincial agencies across North America using matching sediment chemistry and biological effects data. These SQGs have been routinely used to interpret historical data, identify potential problem chemicals or areas at a site, design monitoring programs, classify hot spots and rank sites, and make decisions for more detailed studies (Long and MacDonald 1998). Additional suggested uses for SQGs include identifying the need for source controls of problem chemicals before release, linking chemical sources to sediment contamination, triggering regulatory action, and establishing target remediation objectives (USEPA 1997). Numerical SQGs, when used with other tools such as sediment toxicity tests, bioaccumulation, and benthic community surveys, can provide a powerful weight of evidence for assessing the hazards associated with contaminated sediments (Ingersoll et al. 1997).

A critical component in the application of SQGs for assessing sediment quality is a demonstration of the ability of the guidelines to predict the absence or presence of toxicity in field-collected sediments (Ingersoll et al. 1996, Smith et al. 1996, Long et al. 1998a, Swartz 1999, Fairey et al. 2000, MacDonald et al. 2000a,b). This paper is the fourth in a series that is intended to address the ability of various SQGs to predict toxicity in contaminated sediments. The first paper in the series focused on resolving the "mixture paradox" that is associated with the application of empirically-derived SQGs for individual polycyclic aromatic hydrocarbons (PAHs). In this case, the paradox was addressed by developing consensus-based SQGs for total PAHs (Swartz 1999). A second paper developed and evaluated consensus-based SQGs for total polychlorinated biphenyls (PCBs) to address a similar mixture paradox for that group of contaminants (MacDonald et al. 2000b).

A third paper developed consensus-based SQGs for freshwater sediments (MacDonald et al. 2000a). The published SQGs for 28 chemical substances were assembled and classified into two categories in accordance with their original narrative intent. These published SQGs were then used to develop two consensus-based SQGs for each contaminant, including a threshold effect concentration (TEC; below which adverse effects are not expected to occur) and a probable effect concentration (PEC; above which adverse effects are expected to frequently occur; Table 1; MacDonald et al. 2000a). A preliminary evaluation of the predictive ability of these consensus-based SQGs for freshwater sediment was conducted using a database of 347 samples obtained from 15 separate studies. The results of these three previous investigations demonstrated that the consensus-based SQGs provide a unifying synthesis of the existing guidelines, reflect causal rather than correlative effects, and account for the effects of contaminant mixtures in sediment (Swartz 1999, MacDonald et al. 2000a,b).

The primary objective of this fourth paper is to further evaluate the predictive ability of the consensus-based PECs developed by MacDonald et al. (2000a). The database used by MacDonald et al. (2000a) was expanded to include a total of 1657 samples from 92 published reports with high-quality matching sediment toxicity and chemistry data. The majority of the data from these reports were for 10- to 28-day toxicity tests with the amphipod *Hyalella azteca* or 10- to 14-day toxicity tests with the midges *Chironomus tentans* or *C. riparius*. The endpoints

measured in these toxicity tests primarily included survival or growth of test organisms at the end of the sediment exposures. A second objective of this paper is to evaluate the predictive ability of these PECs on a regional basis within the larger database. We were interested in determining if there are differences in the predictive ability of the PECs across the entire database compared to various geographic areas within the database, such as all of the samples from the Great Lakes or all of the samples from an area within a Great Lake, such as Indiana Harbor or Waukegan Harbor located within Lake Michigan.

Methods

Development of consensus-based sediment quality guidelines

Individual SQGs for freshwater ecosystems have previously been developed using a variety of approaches (Table 1). Each of these approaches has certain advantages and limitations which influence their application in the sediment quality assessment process (Ingersoll et al. 1997). In an effort to focus on the agreement among these various published SQGs, consensus-based SQGs were developed by MacDonald et al. (2000a) for 28 chemicals of concern in freshwater sediments (i.e., metals, PAHs, PCBs, and pesticides). For each contaminant of concern, two consensus-based SQGs were developed from published SQGs, including a threshold effect concentration (TEC) and a probable effect concentration (PEC). The TECs were calculated by determining the geometric mean of the SQGs that were included in this category (MacDonald et al. 2000a). Likewise, consensus-based PECs were calculated by determining the geometric mean of the PEC-type values (Table 1). The geometric mean, rather than the arithmetic mean or median, was calculated because it provides an estimate of central tendency that is not unduly affected by extreme values and because the distributions of the SQGs were not known (MacDonald et al. 2000a). Consensus-based TECs or PECs were calculated only if three of more published SQGs were available for a chemical substance or group of substances. The evaluations of toxicity in the present study were based on the use of PECs because TECs were developed to provide an estimate of conditions where toxicity would not be expected and PECs were developed to provide an estimate of conditions where toxicity would be expected. Evaluations of SQGs in the present study were based on dry-weight concentrations because previous studies have demonstrated that normalization of SQGs for PAHs or PCBs to total organic carbon (Barrick et al. 1988, Long et al. 1995, Ingersoll et al. 1996) or normalization of metals to acid-volatile sulfides (Long et al. 1998b) did not improve the predictions of toxicity in field-collected sediments.

The consensus-based PECs listed in Table 1 were critically evaluated by MacDonald et al. (2000a) to determine if they would provide effective tools for assessing sediment quality conditions in freshwater ecosystems. The criteria for evaluating the reliability of the consensus-based PECs were adapted from Long et al. (1998a). Specifically, the individual TECs were considered to provide a reliable basis for assessing the quality of freshwater sediments if >75% of the sediment samples were correctly predicted to be not toxic. Similarly, the individual PEC for each substance was considered to be reliable if >75% of the sediment samples were correctly predicted to be toxic using the PEC. Therefore, the target levels of both false positives (i.e., samples incorrectly classified as toxic) and false negatives (i.e., samples incorrectly classified as

not toxic) was 25% using the TEC and PEC. To assure that the results of this evaluation were not unduly influenced by the number of sediment samples, the various SQGs were considered to be reliable only if a minimum of 20 samples were included in the evaluation (i.e., 20 samples above at a PEC or 20 samples below a TEC; CCME 1995). The results of this evaluation described in MacDonald et al. (2000a) indicated that most of the TECs (i.e., 21 of 28) provide an accurate basis for predicting the absence of sediment toxicity. Similarly, most of the PECs (i.e., 16 of 28) provide an accurate basis for predicting sediment toxicity (Table 1).

A reliable TEC or PEC was not available for mercury, an important contaminant of concern in sediments (Table 1). This lack of reliability is most likely due to the speciation of mercury in the sediments, as well as the ability of methyl mercury to bioaccumulate in organisms. Sediment quality guidelines developed using a tissue residue approach are needed to establish safe sediment concentrations for human health and piscivorus-wildlife receptors (Ingersoll et al. 1997). For this report, only direct toxic effects on benthic invertebrates are considered in the evaluation of the predictability of the consensus-based SQGs.

Development of the sediment toxicity database

To support the development of the sediment toxicity database, matching sediment chemistry and biological effects data were compiled for various freshwater locations across North America (in addition to the data that were used in the analyses performed by MacDonald et al. 2000a). Candidate data sets were identified by reviewing the published literature and by contacting individuals active in the field of sediment quality assessment. More than 1500 documents were reviewed and evaluated to obtain the data required to evaluate SQGs in the present study. Because these data sets were generated for a wide variety of purposes, each study was critically-evaluated to assure the quality of the data used for evaluating the predictive ability of the SQGs (Long et al. 1998a, Ingersoll and MacDonald 1999). Data from individual studies were considered acceptable for use in the present study if:

- The study was conducted in a freshwater location in North America;
- Appropriate procedures were used to collect, handle, and store sediments (e.g., ASTM 2000, USEPA 2000);
- Matching sediment chemistry and biological effects data were reported and concentrations of contaminants were measured in each sample or treatment group.
- Minimum data quality requirements were reported. For example, analytical detection limits were lower than freshwater probable effect levels (PEL; Smith et al. 1996), accuracy and precision were within acceptable limits, and analytes were not present at detectable levels in method blanks;
- Appropriate analytical methods were used to generate chemistry data. For metals, concentrations of total metals needed to be reported. However, other measures of metal concentrations were used (i.e., simultaneously extracted metals) if sufficient information was available to demonstrate that these measures are comparable to total metal concentrations (Ingersoll et al. 1996, 1998). For organic compounds, the concentrations needed to be measured using gas chromatography-mass spectroscopy, high pressure liquid chromatography, or comparable methods; and,

- Toxicity tests needed to meet test acceptability criteria outlined in ASTM (2000) and USEPA (2000) and endpoints measured needed to be ecologically relevant (likely to influence the viability of the organism in the field) or needed to be indicative of ecologically-relevant endpoints.

Using these selection criteria, a total of 92 freshwater data sets were incorporated into a database that included 1657 individual sediment samples. The toxicity tests in this database primarily include tests with the amphipod, *Hyalella azteca*; the midges, *Chironomus tentans* or *C. riparius*; the mayfly, *Hexagenia limbata*; the oligochaete, *Lumbriculus variegatus*; the daphnids, *Ceriodaphnia dubia* or *Daphnia magna*; and, the bacterium, *Vibrio fisheri* (Microtox). We selected a subset of the samples from this database that reported sediment chemistry for at least one of the substances for which reliable SQGs were listed in Table 1. We then selected a subset of these resultant samples with matching toxicity data for the amphipod *Hyalella azteca* or the midges *Chironomus tentans* or *C. riparius*. Tests with *H. azteca* and *Chironomus* spp. were selected because the samples that were tested represented a broader geographic area compared to the other tests in the database. The selected studies provided 670 samples for *H. azteca* 10- to 14-day tests (designated as HA10), 160 samples for *H. azteca* 28- to 42-day tests (designated as HA28) and 632 samples for *Chironomus* spp. 10- to 14-day tests (CS10; 556 of the samples were for tests with *C. tentans* and 76 of the samples were for tests with *C. riparius*). We combined the data for the two midge species due to the limited amount of data for *C. riparius*. Preliminary analyses of the database indicated similar sensitivity for these two species of midge. The selected studies represented a broad range in both sediment toxicity and contamination. A total of 28% of the samples were toxic in the HA10 test, 35% of the samples were toxic in the HA28 test, and 27% of the samples were toxic in the CS10 test (28% of the samples were toxic in the *C. tentans* tests and 21% of the samples were toxic in the *C. riparius* tests). Toxicity of samples was determined as a significant reduction in survival or growth relative to a control or reference sediment (as designated in the original study or determined using appropriate statistical procedures). Sexual maturation and reproduction were periodically reported in the HA28 test; however, these two additional endpoints did not identify any additional samples as toxic relative to effects reported on survival or growth of amphipods.

The total PCB concentration in each sediment sample in the database was calculated by summing dry-weight concentrations of individual congeners. If only aroclors concentrations were reported, total PCBs were calculated as the sum concentration of all individual aroclors. If both congeners and aroclors were reported, the congeners were used to calculate the concentration total PCBs in a sample. If only total PCBs was reported for a sample, then this value was used. The total PAH concentration in each sediment sample was generally calculated by summing the dry-weight concentrations from as many of the following 13 compounds that were reported: acenaphthene, acenaphthylene, anthracene, fluorene, 2-methylnaphthalene, naphthalene, phenanthrene, benz(a)anthracene, dibenz(a,h)anthracene, benzo(a)pyrene, chrysene, fluoranthene, and pyrene. Total PAHs were calculated using eight or less of these individual PAHs for <5% of the samples in the database. In calculating total PCBs or total PAHs, half the detection limit was used for compounds reported below the detection limit. Similarly, half of the detection limit was used for concentrations of metals below the detection limit. For DDTs, the concentrations of p,p'-DDD and o,p'-DDD, p,p'-DDE and o,p'-DDE, and p,p'-DDT and o,p'-DDT were summed to calculate

the concentrations of sum DDD, sum DDE, and, sum DDT, respectively. Total DDT was calculated by summing the concentrations of sum DDD, sum DDE, and, sum DDT. If all individual PCBs, PAHs, DDD, DDE, or DDT were less that the detection limit, the detection limits were summed and reported as a less than value for the sum.

Analysis of data

The initial evaluation of predictive ability by MacDonald et al. (2000a) focused primarily on determining the ability of each SQG, when applied alone, to correctly classify samples as toxic or not toxic. Because field-collected sediments typically contain complex mixtures of contaminants, the predictive ability of these sediment quality assessment tools is likely to increase when the SQGs are used in combination to classify toxicity of sediments. For this reason, the evaluation of the predictive ability of the SQGs in the present study was conducted to determine the incidence of effects above and below various mean PEC quotients (mean quotients of 0.1, 0.5, 1.0, and 5.0; Ingersoll et al. 1998, Long et al. 1998a, Fairey et al. 2000).

A PEC quotient was calculated for each chemical in each sample in the database by dividing the concentration of a chemical by the PEC for that chemical. A mean quotient was then calculated for each sample by summing the individual quotient for each chemical and dividing this sum by the number of reliable PECs evaluated. MacDonald et al. (2000a) found that some PEC values were more reliable predictors of toxicity and that use of only these PECs reduced the variability in the prediction of sediment toxicity compared to using all available PECs. The PEC for total PAHs, instead of the PECs for the individual PAHs, was used in the calculation to avoid double accounting of the PAH data (MacDonald et al. 2000a). This resulted in the use of up to 10 reliable PECs in calculating the mean quotient (arsenic, cadmium, chromium, copper, lead, nickel, zinc, total PAHs, total PCBs, and sum DDE; Table1 and designated "Mean - all" in Table 2). This approach to the calculation of mean quotients weighs each of the chemicals and chemical classes equally (Ingersoll et al. 1998, Long et al. 1998a, MacDonald et al. 2000a).

In the present study, a second approach was also used to calculate mean PEC quotients. We were interested in equally weighting the contribution of metals, PAHs, and PCBs in the evaluation of sediment chemistry and toxicity (assuming these three diverse groups of chemicals exert some form of joint toxic action). For this reason, we first calculated an average PEC quotient for up to seven metals in a sample. A mean quotient was then calculated for each sample by summing the average quotient for metals, the quotient for total PAHs, and the quotient for total PCBs, and then dividing this sum by three (n = 3 quotients/sample; designated "Mean - MPP (and)" in Table 2). Another approach for evaluating mean quotients was to calculate the mean of the average quotient for metals, the quotient for total PAHs, or the quotient for total PCBs (n = 1 to 3 quotients/sample; designated "Mean - MPP (or)" in Table 2). Hence, the "Mean - MPP (or)" approach uses any or all of the three classes of contaminants as available. For example, if a sample only had a measure of total PAHs and total PCBs, then the mean quotient would be calculated using just the quotients for these two classes of compounds. In contrast, the "Mean - MPP (and)" approach only uses samples with measures of metals, total PAHs, and total PCBs. Sum DDE was not included in these calculations of the mean quotient because there were a limited number of samples in the database with elevated concentrations of DDE and we were

interested in equally weighting the contributions of the major groups of contaminants in the database (metals, total PAHs, and total PCBs). Therefore, the differences in this "MPP approach" from the approach used by MacDonald et al. (2000a) are: (1) an average quotient for metals was used instead of the individual quotients for metals and (2) sum DDE was not used in the calculation.

Results and Discussion

Evaluation of approaches for calculation of mean PEC quotients

The results of the evaluations of the incidence of sediment toxicity within ranges of mean PEC quotients in the entire database for each of the three tests (HA10, HA28, CS10) are summarized in Table 2. When mean quotients were calculated using the approach of weighting equally up to 10 reliable PECs (designated "Mean - all" in Table 2), there was an increase in the incidence of toxicity with an increase in the mean quotient in all three tests. For the HA10 test, the incidence of toxicity was 20% at mean quotients of <0.1 and increased to 67% at mean quotients of >5.0. Similarly, for the CS10 test there was a 20% incidence of toxicity at mean quotients of <0.1 increasing to a 64% incidence of toxicity at mean quotients of >5.0. In contrast, the incidence of toxicity in the HA28 test was only 8% at mean quotients of <0.1 and increased to 91% at mean quotients of >1.0 (the incidence of toxicity at a quotient >5.0 was not calculated for the HA28 test due to a limited number of samples above a quotient of 5.0; Table 2).

Long et al. (1998a) conducted a similar analysis of the incidence of toxicity in sediment tests using a database developed for 10-day marine amphipod tests (n=1068). The incidence of toxicity was only 12% at mean quotients of <0.1 (quotients calculated using either marine effect range median (ERM) or probable effect level (PEL) guidelines; Long et al. 1998a). In the present study, the incidence of toxicity at mean quotients of <0.1 was somewhat higher in the HA10 and CS10 tests (20%) compared to the tests with marine amphipods (12%; Long et al. 1998a) or the HA28 test (8%; Table 2).

The reason for this higher incidence of toxicity at mean quotients of <0.1 in the HA10 and CS10 tests is not clear. This toxicity at low mean quotients does not appear to be related to total organic carbon in sediment. There was insufficient information in the database to evaluate effects of grain size on toxicity. USEPA (2000) and ASTM (2000) reported that amphipods and midges are relatively intolerant to effects of sediment grain size. Unmeasured contaminants in these field-collected sediments or contaminants for which we do not have reliable PECs (i.e., pesticides, herbicides) may have contributed to this toxicity at low mean quotients (see discussion of Figures 1 and 2 below). Alternatively, the data for HA10 and CS10 tests were obtained from numerous laboratories which may have contributed to variability in the data reported in these studies. In contrast, a limited number of laboratories conducted most of the toxicity tests for the marine amphipod or HA28 tests.

In all three tests, there was a consistent increase in the toxicity at mean quotients of >0.5 (designated "Mean - all" in Table 2). However, the overall incidence of toxicity was greater in the HA28 test (91% toxicity at mean quotients of >1.0) compared to the short-term tests (57%

toxicity at mean quotients of >1.0 and 67% toxicity at mean quotients of >5.0 in the HA10 test and 51% toxicity at mean quotients of >1.0 and 64% toxicity at mean quotients of >5.0 in the CS10 test). Similarly, Long et al. (1998a) reported a 56 to 71% incidence of toxicity at mean quotients of >1.0 in the 10-day sediment tests with marine amphipods. The reason for the higher incidence of toxicity in the HA28 test compared to the short-term tests may be due to the duration of the exposure or the sensitivity of growth in the longer HA28 test (see discussion of Figures 1 and 2 below). However, comparisons of the sensitivity between these tests needs to be made with some caution. There were very few samples in the database where tests were conducted using splits of the same samples. Therefore, the differences observed in the responses of organisms may also be due to differences in the types of sediments evaluated in the individual databases for each test.

We were also interested in determining the predictive ability of PEC quotients for major classes of compounds. Therefore, we evaluated the incidence of toxicity based on an average quotient for metals, a quotient for total PAHs, or a quotient for total PCBs (second, third, and fourth rows for each toxicity test listed in Table 2). For the HA10 test, the incidence of toxicity across quotients of <0.1 to >1.0, based on metals alone, total PAHs alone, or total PCBs alone were similar to the incidence of toxicity that was calculated for the mean quotient using up to10 PECs (designated "Mean - all" in Table 2). The incidence of toxicity in the HA10 test was somewhat higher at quotients >5.0 for total PAHs (80%) or total PCBs (73%) compared to metals alone (62%).

For the CS10 test, the incidence of toxicity was also similar across quotients of <0.1 to >5.0, calculated based on metals alone compared to a mean quotient calculated using up to 10 PECs (designated "Mean - all" in Table 2). However, the incidence of toxicity at a total PCB quotient <0.1 was 46%, suggesting that other compounds may be contributing to toxicity at low concentrations of PCBs. The incidence of toxicity in the CS10 test was somewhat higher for quotients based solely on total PAHs compared to quotients based on metals alone, total PCBs alone, or mean quotients calculated using up to 10 PECs. These analyses suggest that the CS10 test may be more sensitive to PAHs compared to the other chemical classes.

For the HA28 test, the incidence of toxicity was similar across the quotients of <0.1 to >1.0, calculated based on metals alone compared to a mean quotient calculated using up to 10 PECs (designated "Mean - all" in Table 2). However, the incidence of toxicity at quotient of 0.1 to <0.5 was higher for PAHs (61%) compared to the other three quotients (6 to 20% toxicity for metals alone, total PCBs alone, or mean quotients based on up to 10 PECs). The incidence of toxicity at PCB quotients of <1.0 was lower (4 to 17%), while the incidence of toxicity at a PCB quotient of >1.0 was higher (97%) compared to the other three quotients. Results of these analyses indicate a relatively abrupt increase in toxicity associated with elevated PCBs alone or elevated PAHs alone compared to the pattern of a gradual increase toxicity observed with quotients calculated using the up to 10 PECs (designated "Mean - all" in Table 2). These results suggest that *H. azteca* may be more sensitive to PAHs and PCBs in longer-term tests than it is to metals.

In the next analysis, we were interested evaluating the incidence in toxicity by equally weighting

the combined influence of metals, PAHs, and PCBs in a sample. A mean PEC quotient was calculated for each sample by summing the average quotient for metals, the quotient for total PAHs, and the quotient for total PCBs, and then dividing this sum by three (designated as "Mean - MPP (and)" in Table 2). This calculation was done for only those samples with reported concentrations of metals, total PAHs, and total PCBs (266 of 670 samples in the HA10 test, 109 of 160 samples in the HA28 test, and 177 of 632 samples in the CS10 test). Results of this analysis indicate a higher incidence of toxicity in the HA10 (66%), HA28 (100%), and CS10 (60%) tests at mean quotients >1.0 based on an equal weighting of metals, total PAHs, and total PCBs compared to a mean quotient calculated using up to 10 PECs (57, 91, and 51%, respectively; designated "Mean- all" in Table 2).

The different patterns of toxicity associated with these various procedures for calculating quotients may be the result of unique chemical signals associated with individual contaminants in each sample. For example, there was a higher incidence in toxicity with quotients calculated using total PCBs alone compared to quotients calculated using metals alone in the HA10 test. Alternatively, these different patterns may also be influenced by the total number of samples used to make these comparisons. For example, there were 670 total samples for the HA10 test. Of these 670 samples, 623 had metal chemistry data, 488 had measured concentrations of total PAHs, 326 had measured concentrations of total PCBs, and all three of these classes of compounds were measured in only 266 samples. In order to determine the influence of sample number on the observed incidence of toxicity, we first selected the same samples used in the analysis described in the previous paragraph (samples in which metals, total PAHs, and total PCBs were all measured). Quotients were then calculated for these subsets of samples: (1) using up to 10 PECs (designated "Mean - all (select1)"), (2) using up to 9 PECs (not including DDE; designated "Mean - all (select2)", or (3) using metals alone ("mean - metals (select2)"), total PAHs alone ("total PAHs (select2)"), or total PCBs alone ("total PCBs (select2)"; Table 2).

Results of these analyses indicate that the incidence of toxicity for all three tests was similar in these subsets of samples using the three procedures to calculate mean quotients ("Mean - MPP (and)" versus "Mean - all (select1)" versus "Mean - all (select2)"). In the HA10 test, the incidence of toxicity in the subset of samples (n=266) was similar based on an average quotient for metals alone, a quotient for total PAHs alone, or a quotient for total PCBs alone compared to the "Mean - all (select2)". In contrast, there were different patterns of toxicity associated with individual classes of compounds in the subsets of samples in the HA28 (n=109) or CS10 (n=177) tests where metals, PAHs, and PCBs were all reported. In the HA28 test, a relatively abrupt increase in toxicity was associated with elevated PCBs alone or with elevated PAHs alone, compared to the pattern of a gradual increase toxicity observed with quotients calculated using the "Mean - all (select2)". Similarly in the CS10 test, a increase in toxicity was observed at lower quotients of PAHs alone or metals alone compared to the pattern of a gradual increase toxicity observed with quotients calculated using the "Mean - all (select2)".

These analyses indicate that the different patterns in toxicity may be the result of unique chemical signals associated with individual contaminants in samples rather than the result of a limited number of samples used to make these comparisons. However, we could only make these comparisons with a limited number of samples where metals, PAHs, and PCBs were all reported.

Fairey et al. (2000) conducted a similar analysis of a larger marine database for amphipods and found that the number and type of SQGs used in the calculation of a mean quotient influenced the predictions of sediment toxicity to amphipods. The incidence of toxicity to amphipods increased with increasing numbers of contaminants included in the derivation of the mean quotient (Fairey et al. 2000). While mean quotients can be used to classify samples as toxic or non-toxic, individual quotients might be useful in helping to identify substances that may be causing or substantially contributing to the observed toxicity (MacDonald et al. 2000b).

To use all samples in the database and equally weight the contribution of metals, PAHs, and PCBs, a final analysis was conducted where the mean quotient was calculated as the average of the three major classes available in a sample. For example, if a sample only had a measure of total PAHs and total PCBs, then the mean quotient would be calculated using just the quotients for these two classes of compounds (designated as "Mean – MPP (or)" in Table 2). Results of these analyses indicate that the incidence of toxicity in all three tests was similar when either "Mean - all" (based on up to 10 PECs) or "Mean - MPP (or)" were used to calculate the mean quotients (Table 2).

Evaluation of exposure duration and endpoints measured in toxicity tests

In Figures 1 and 2, we evaluated the relationship between mean PEC quotients and the incidence of toxicity as a function of the duration of the exposure or of the endpoints measured in the toxicity tests. In this analysis, a mean quotient for each sample was calculated using the "Mean - MPP (or)" approach. The samples within each test were ranked in ascending order by mean quotient. The incidence of toxicity and geometric mean of the mean quotients within groups of 20 samples for the HA10 and CS10 tests or within groups of 10 samples for the HA28 test was then plotted (Figures 1 and 2, Appendix 1). The geometric mean, rather than the arithmetic mean or median of the quotients, was calculated because it provides an estimate of central tendency that is not unduly affected by extreme values and because the distributions of the mean quotients were not known.

In Figure 1, samples were classified as toxic based on an adverse effect on survival or growth in the three tests. Results of these analyses plotted in Figure 1 are consistent with the analyses presented in Table 2. Importantly, the incidence of toxicity increases with increasing level of contamination in all three tests. This increase was particularly pronounced at mean quotients of >0.5 in all three tests. There was a slightly elevated incidence of toxicity at the very lowest mean quotient in all three tests. Long et al. (1998a) also observed an elevated incidence of toxicity with marine amphipods at low mean quotients. Long et al. (1998a) suggested that these samples were sometimes fine-grained sediments with low concentrations of organic carbon and detectable concentrations of butyltins, chlorinated pesticides, alkyl-substituted PAHs, ammonia, or other substances not accounted for with the SQGs. In the present study, the incidence of toxicity at low mean quotients did not appear to be related to total organic carbon in sediment. There was insufficient information in the database to evaluate effects of grain size on toxicity. USEPA (2000) and ASTM (2000) reported that amphipods and midges were relatively intolerant to effects of sediment grain size.

We also evaluated relationships between the toxicity and mean quotients calculated using up to 10 reliable PECs or mean quotients calculated using all of the available PECs in Table 1 regardless of their reliability (plots not included in this paper). An increase in toxicity was observed with increasing contamination using either 10 reliable PECs or all of the PECs to calculate mean quotients. However, the variability was higher when all of the PECs listed in Table 1 were used in this analysis. Therefore, the use of reliable PECs improved the relationship between mean PEC quotients and the incidence of toxicity.

In Figure 2, samples in the three tests were classified as toxic based on an adverse effect on survival alone or based on an adverse effect on survival or growth. The relationship between the incidence of toxicity and the geometric mean of the mean quotients was best described by a three parameter logistic model (SigmaPlot 1997; Figure 2; see Appendix 1 for the equations and coefficients). The best fit of the data was observed in the HA28 test ($r^2 = 0.79$ based on survival or 0.93 based on survival or growth) relative to the HA10 test ($r^2 = 0.73$ based on survival or 0.78 based on survival or growth) or CS10 test ($r^2 = 0.56$ based on survival or 0.76 based on survival or growth; Figure 2). In the HA10 test, the relationship between toxicity and mean quotient was similar when either survival alone or survival or growth together were used to classify a sample as toxic. However, in the HA28 and CS10 tests, the relationship between the incidence of toxicity and mean quotient was different when survival or growth were used to classify a sample as toxic compared to survival alone (Figure 2).

The incidence of toxicity in the HA28 and CS10 tests based on survival or growth was often double the incidence of toxicity based on survival alone at mean quotients of >0.3. A 50% incidence of toxicity in the HA28 test corresponds to a mean quotient of 0.63 when survival or growth were used to classify a sample as toxic (Figure 2, Appendix 1). By comparison, a 50% incidence of toxicity was estimated at a mean quotient of 3.2 when survival alone was used to classify a sample as toxic in the HA28 test. In the CS10 test, a 50% incidence of toxicity was estimated at a mean quotient of 9.0 when survival alone was used to classify a sample as toxic or at a mean quotient of 3.5 when survival or growth were used to classify a sample as toxic. In contrast, similar mean quotients resulted in a 50% incidence of toxicity in the HA10 test when survival alone (mean quotient of 4.5) or when survival or growth (mean quotient of 3.4) were used to classify a sample as toxic.

Results of these analyses indicate that both the duration of the exposure and the endpoint measured can influence whether a sample is found to be toxic or not. Again, comparisons of the sensitivity between these tests needs to be made with some caution. There were very few samples in the freshwater database where tests were conducted using splits of the same samples. Therefore, the differences observed in the responses of organisms may also be due to differences in the types of sediments evaluated in the individual databases for each test. Nevertheless, it appears that longer-term tests in which survival and growth are measured tend to be more sensitive than short-term tests, with acute to chronic ratios on the order of 6 indicated for *H. azteca*. Similar differences in sensitivity of *H. azteca* have been observed in 10- and 42-day water-only exposures to cadmium, fluoranthene or DDD (unpublished data).

Evaluation of the predictive ability of mean PEC quotients across various geographical areas with the database

A primary objective of this paper was to determine if there were differences in the predictive ability of PEC quotients within geographic areas compared to the entire database. We chose to make these comparisons of geographic areas using the "MPP (or)" mean quotients calculated as the mean of the average quotient for metals, the quotient for total PAHs, or the quotient for total PCBs (Table 2). Use of this approach maximized the number of samples used in the evaluation and equally weighted the contribution of the three major classes of compounds (metals, or PAHs, or PCBs) to the observed incidence of toxicity. The relationship between the incidence of toxicity and mean quotients is presented in Tables 3 to 5 for the entire database and for various geographical areas represented within the database. Designation of region, basin, and area for each geographic area in Tables 3 to 5 is based on information obtained from the original report or by contacting the authors of the report. Comparisons of toxicity among the entire geographic areas listed in Tables 3 to 5 should be done with caution given the limited number of samples from each area (i.e., only 5 samples for the HA10 test from the entire Buffalo River). Samples were grouped by geographic areas in Table 3 to 5 to determine how well toxicity and mean quotients correspond in the entire database compared to subsets of samples within the database. Control samples were not included within each geographical area. However, the incidence of toxicity with and without control samples was similar for the entire database (first and second rows for each of the three tests listed in Tables 3 to 5).

For the HA10 test, there was typically an increase in the incidence of toxicity with an increase in the mean quotient within most of the regions, basins, and areas (Table 3). The incidence of toxicity for samples from each of the Great Lakes and within the areas of each Great Lake was relatively consistent with the overall pattern of toxicity in the entire database. No one area influenced the overall incidence of toxicity for the HA10 test. However, the absolute incidence of toxicity differed somewhat between areas. For example, the incidence of toxicity for the Great Lakes samples in the HA10 test (n=313) was 14% at mean quotients of <0.1, 68% at mean quotients of >1.0, and 78% at mean quotients of >5.0. This compares to an incidence of toxicity for the entire database (n=654) of 19% at mean quotients of <0.1, 54% at mean quotients of >1.0, and 71% at mean quotients of >5.0. Hence, at mean quotients of >1.0 there was about a 14% higher incidence of toxicity for samples from the Great Lakes compared to the entire database for the HA10 test. The lower incidence of toxicity for samples from non-Great Lakes areas was primarily due to the lower incidence of toxicity at mean quotients >1.0 for samples from the states of New York (7%, n=15), Oregon (40%, n=20), and Washington (50%, n=34).

In the HA10 test, there was also a higher incidence of toxicity at mean quotients of <0.1 for a limited number of samples from the lower Mississippi River (89%, n=9) and from the Temblader River in California (75%, n=4) compared to the entire database. These samples contributed to the 22% incidence of toxicity that was observed for samples from non-Great Lakes areas at quotients of <0.1 (n=89). By comparison, only a 14% incidence of toxicity was evident for samples with quotients of <0.1 for Great Lakes areas (n=51). One of the reasons for the difference between non-Great Lakes samples and Great Lakes samples may be due to

contaminants associated with agricultural practices in the non-Great Lakes areas (i.e., herbicides or pesticides) that contributed to the toxicity of these samples independently of elevated metals, PAHs, or PCBs.

In the HA28 test, there was also an increase in the incidence of toxicity with an increase in the mean quotient within most of the regions, basins, and areas (Table 4). The incidence of toxicity for samples from each of the Great Lakes and within areas of each Great Lake was relatively consistent with the overall pattern of toxicity in the entire database. Similarly, the incidence in toxicity for samples from the Great Lakes was consistent with the incidence in toxicity for samples from non-Great Lakes areas. Therefore, no one area influenced the overall incidence of toxicity within the HA28 test. There were a relatively high number of non-toxic samples (n= 51 of 53) with low mean quotients from the upper Mississippi River. The incidence of toxicity for the Great Lakes samples (n=42) was 13% at mean quotients of <0.5, 71% at mean quotients of 0.5 to <1.0, and 100% at mean quotients of >1.0. This pattern is consistent with incidence of toxicity for the entire database (n=151) of 17% at mean quotients of <0.5, 56% at mean quotients of 0.5 to <1.0, and 97% at mean quotients of >1.0 (Table 4).

In the CS10 test, there was typically an increase in the incidence of toxicity with an increase in the mean quotient within most of the regions, basins, and areas (Table 5). The incidence of toxicity for the Great Lakes samples (n=463) was 14% at mean quotients of <0.1, 56% at mean quotients of >1.0, and 71% at mean quotients of >5.0. This pattern is consistent with incidence of toxicity for the entire database (n=611) of 20% at mean quotients of <0.1, 52% at mean quotients of >1.0, and 68% at mean quotients of >5.0. The incidence of toxicity for samples from each of the Great Lakes and within the areas of each Great Lake was relatively consistent with the overall pattern of toxicity in the entire database; however, there were some exceptions to this pattern. A lower incidence of toxicity was observed at mean quotients of >1.0 for samples from the St. Mary's River (41%, n=17), Fox River and Green Bay (0%, n=8), Menominee River (38%, n= 8), and White Lake Montague (25%, n=8). However, at mean quotients of >5.0, there was a more consistent pattern in the incidence of toxicity in the CS10 test. An exception to this pattern at mean quotients >5.0 was observed for samples from the St. Mary's River (38%, n=8) and White Lake Montague (25%, n=4). Similarly, a lower incidence in toxicity was observed at mean quotients of >5.0 for samples from the state of Washington (50%, n=4).

In the CS10 test, there was also a higher incidence of toxicity at mean quotients of <0.1 for a limited number of samples from Sheboygan Harbor (75%, n=4), from the lower Mississippi River (89%, n=9), and from the Trinity River (67%, n=3). The samples from the Lower Mississippi River and Trinity River contributed to the 53% incidence of toxicity that was observed for samples from non-Great Lakes areas with quotients of <0.1 (n=19). By comparison, only a 14% incidence of toxicity was evident for samples with quotients of <0.1 for Great Lakes areas (n=99). Again, one of the reasons for the difference between non-Great Lakes samples and Great Lakes samples may be due to contaminants associated with agricultural practices in the non-Great Lakes areas (i.e., herbicides or pesticides) that contributed to the toxicity of these samples independently of elevated metals, PAHs, or PCBs.

In summary, there was generally an increase in the incidence of toxicity with increasing mean PEC quotients within most of the regions, basins, and areas for all three tests (Tables 3 to 5). For the HA10 and HA28 tests, the incidence of toxicity for samples from each of the Great Lakes and within the areas of each Great Lake was relatively consistent with the overall pattern of toxicity in the entire database. However, the relationship between the incidence in toxicity and mean quotients in the CS10 test was more variable among geographic areas compared to either the HA10 or HA28 test. The results of these analyses indicate that the consensus-based PECs can be used to reliably predict toxicity of sediments on both a regional and national basis.

Future analyses planned for the database

This paper presents results of the first analyses completed on the entire freshwater sediment database. Some of the additional analyses planned for the database (beyond the scope of this paper) are listed below:

- **Approaches for designating samples as toxic.** In the present study, samples were designated as toxic in the three tests based on a significant reduction in survival or a sublethal endpoint (typically growth) relative to a control or reference sediment. This designation of toxicity utilized the results of statistical analyses presented in each of the original studies. Alternatively, Long et al. (1998a) classified sediments in a marine amphipod database as either marginally toxic (significantly reduced relative to the control) or as highly toxic (significantly reduced relative to the control with a reduction greater than a minimum significant difference; MSD). The MSD was established by Long et al. (1998a) using a power analysis of data from 10-day marine amphipod tests (Thursby et al.1997). Long et al. (1998a) and Field et al. (1999) reported reduced variability in the relationship between toxicity and sediment contamination when toxicity was evaluated using a standardized approach. Future analyses of the freshwater database will compare relationships between toxicity and contamination using marginally toxic versus highly toxic sediments. This classification may be based on a power analysis to establish an MDS for each endpoint in each of the three tests. Alternatively, the MDS for each endpoint may be established using results of round-robin testing (USEPA 2000). This latter procedure is currently being investigated for use in classifying the toxicity of freshwater samples in a revision to the report on the incidence and severity of sediment contamination in surface waters of the United States (USEPA 1997; Scott Ireland, USEPA, Washington, DC, personal communication). Classification of sediments as either marginally or highly toxic may help to reduce the variability in the observed relationship between toxicity and mean quotients. Additionally, this analysis may help to address the higher incidence of toxicity at mean quotients of <0.1 in the HA10 and CS10 tests compared to the HA28 tests.

- **Logistic-regression modeling of the freshwater database.** Field et al. (1999) described a procedure for evaluating matching marine sediment chemistry and toxicity data using logistic regression models. These models can be used to estimate the probability of observing an effect at any contaminant concentration. The models were developed for marine amphipods using a large database (n=2524) from a variety of geographic areas.

The results of preliminary analyses using these techniques indicate that the freshwater database may have too few samples to adequately develop these regression models. However, evaluations are ongoing to determine how well the regression models developed from the marine database can be used to predict responses of organisms in the freshwater database.

- **Optimal list of analytes for broad scale application and test of the relative efficacy of the mean versus the sum PEC quotient.** Further comparisons are needed of approaches for calculating the PEC quotient. Calculation of a mean quotient may include analytes which have limited toxicological importance. The significant toxicological contribution of a few chemicals may be averaged out by the use of the mean quotient. Analyses need to be conducted to identify an optimal list of analytes for broad scale application and to test the relative efficacy of the mean versus the sum PEC quotient. Even if the mean quotient continues to be the best at predicting toxicity, identification of an optimal list of analytes would be useful. If a consistent set of analytes is applied, the sum and the mean quotient will mathematically equivalent.

- **Influence of sediment grain size and ammonia on the incidence of toxicity.** Data on grain size and pore-water ammonia, pH, and water hardness were obtained for some studies evaluated in this paper. Future analyses of the database will evaluate the influence of either grain size or ammonia on the response of the test organisms in the HA10, HA28, or CS10 tests. ASTM (2000) and USEPA (2000) provide the following guidance for dealing with the influence of grain size or ammonia in toxicity tests with freshwater sediments.

  Natural physico-chemical characteristics such as grain size or organic carbon can potentially influence the response of test organisms. ASTM (2000) and USEPA (2000) summarize results from a variety of studies and conclude *H. azteca* can tolerate a wide range in grain size and organic matter in 10- to 42-day tests with sediments. Larvae of *C. tentans* in 10-day tests were tolerant of a wide range of grain size if ash-free dry weight was used to account for the influence of inorganic material in the gut. The content of organic matter in sediments does not appear to affect survival of *C. tentans* larvae in sediments; but, may be important with respect to larval growth. Future analyses of the database will evaluate potential relationships between grain size or organic carbon of sediments on the toxicity in the HA10, HA28, or CS10 tests.

  Ammonia in pore water may contribute to the toxicity of some sediments in fresh water. The toxicity of ammonia to *C. tentans* is dependent on pH whereas the toxicity of ammonia to *H. azteca* is also dependent on water hardness (ASTM 2000, USEPA 2000). Water-only LC50 values may provide suitable screening values for potential ammonia toxicity; however, higher concentrations may be necessary to actually induce ammonia toxicity in sediment exposures, particularly for *H. azteca* due to avoidance. ASTM (2000) and USEPA (2000) cite studies which describe procedures for conducting toxicity identification evaluations (TIEs) for pore-water or whole-sediment samples to determine if ammonia is contributing to the toxicity of sediment samples. Future analyses of the

database will evaluate potential relationships between pore-water ammonia, pH, and water hardness on toxicity in the HA10, HA28, or CS10 tests. These analyses will focus on the HA28 test due to limited data available for the HA10 or CS10 tests.

- **Guidance manual for conducting an integrated assessment of sediment contamination.** Work is in progress to develop a guidance manual for USEPA Great Lakes National Program Office that can be used to assess sediment quality and determine the need for remediation at a site. Specifically, this guidance manual will describe procedures for combining results of sediment toxicity, bioaccumulation, benthic communities surveys, and sediment chemistry in an integrated evaluation of ecological risk. Development of this guidance manual is being coordinated with ongoing efforts to develop similar guidance by the Department of the Interior and by Environment Canada. Additional analyses of the freshwater database will be used to help develop this guidance. Specifically, these analyses will focus on determining which endpoints provide the most sensitive and cost effective measures of sediment contamination.

Summary

The primary objectives of this study were to: (1) evaluate the ability of consensus-based PECs to predict toxicity in a freshwater database for field-collected sediments in the Great Lakes basin; (2) evaluate the ability of these PECs to predict sediment toxicity on a regional geographic basis elsewhere in North America; and (3) compare approaches for evaluating the combined effects of chemical mixtures on the toxicity of field-collected sediments. When mean quotients were calculated using an approach of equally weighting up to 10 reliable PECs (PECs for metals, total PAHs, total PCBs, and sum DDE), there was an increase in the incidence of toxicity with an increase in the mean quotient in all three tests. A consistent increase in the toxicity in all three tests occurred at mean quotients of >0.5. However, the overall incidence of toxicity was greater in the HA28 test compared to the short-term tests. The reason for the higher incidence of toxicity in the HA28 test compared to the short-term tests may be due to the duration of the exposure or the sensitivity of growth in the longer HA28 test. However, comparisons of the sensitivity between these tests needs to be made with some caution. There were very few samples in the database where tests were conducted using splits of the same samples. Therefore, the differences observed in the responses of organisms may also be due to differences in the types of sediments evaluated in the individual databases for each test. Nevertheless, it appears that longer-term tests in which survival and growth are measured tend to be more sensitive than shorter-term tests, with acute to chronic ratios on the order of 6 indicated for *H. azteca.*

We were also interested in determining the predictive ability of PEC quotients for major classes of compounds. Therefore, we evaluated the incidence of toxicity based on a mean quotient for metals, a quotient for total PAHs, or a quotient for total PCBs. Different patterns of toxicity associated with the other procedures for calculating quotients were observed. For example in the HA28 test, a relatively abrupt increase in toxicity was associated with elevated PCBs alone or with elevated PAHs alone, compared to the pattern of a gradual increase toxicity observed with quotients calculated using a combination of metals, PAHs, and PCBs. These analyses indicate that the different patterns in toxicity may be the result of unique chemical signals associated with individual contaminants in samples. While mean quotients can be used to classify samples as toxic or non-toxic, individual quotients might be useful in helping to identify substances that may be causing or substantially contributing to the observed toxicity.

We chose to make comparisons across geographic areas using mean quotients calculated by equally weighting the contribution of the three major classes of compounds (metals, or PAHs, or PCBs). This approach assumes that these three diverse groups of chemicals exert some form of joint toxic action. Use of this approach also maximized the number of samples that were used to make comparisons across geographic areas. Generally, there was an increase in the incidence of toxicity increasing with mean PEC quotients within most of the regions, basins, and areas for all three toxicity tests. The incidence of toxicity for samples from each of the Great Lakes and within the areas of each Great Lake was relatively consistent with the overall pattern of toxicity in the entire database for the HA10 and HA28 tests. However, the relationship between the incidence in toxicity and mean quotients in the CS10 test was more variable among geographic areas compared to either the HA10 or HA28 test. Results of these analyses indicate that the

PECs developed using a database from across North America can be used to reliably predict toxicity of sediments on a regional basis.

One of the primary goals of sediment quality assessments is to evaluate the effects of contaminated sediments on benthic communities in the field (Ingersoll et al. 1997). Swartz et al. (1994) evaluated sediment quality conditions along a sediment contamination gradient of total DDT using information from 10-day toxicity tests with amphipods, sediment chemistry, and the abundance of benthic amphipods in the field. Survival of amphipods (*Eohaustorius estuarius*, *Rhepoxynius abronius*, and *H. azteca*) in laboratory toxicity tests was positively correlated to the abundance of amphipods in the field and negatively correlated to total DDT concentrations. The toxicity threshold for amphipods in 10-day sediment toxicity tests was about 300 μg total DDT/g organic carbon. The threshold for reduction in abundance of amphipods in the field was about 100 μg total DDT/g organic carbon. Therefore, correlations between toxicity, contamination, and the status of benthic macroinvertebrates in the field indicate that 10-day sediment toxicity tests can provide a reliable indicator of the presence of adverse levels of sediment contamination in the field. However, these short-term toxicity tests may be under protective of sublethal effects of contaminants on benthic communities in the field.

Similarly, Canfield et al. (1994, 1996, 1998) evaluated the composition of benthic invertebrate communities in sediments in a variety of locations including the Great Lakes, the upper Mississippi River, and the Clark Fork River in Montana. Results of these benthic invertebrate community assessments were compared to SQGs (ERMs) and 28-day sediment toxicity tests with *H. azteca*. Good concordance was evident between measures of laboratory toxicity, SQGs, and benthic invertebrate community composition in extremely contaminated samples. However, in moderately contaminated samples, less concordance was observed between the composition of the benthic community and either laboratory toxicity tests or SQGs. The laboratory toxicity tests better identified chemical contamination in sediments compared to many of the commonly used measures of benthic invertebrate community structure. As the status of benthic invertebrate communities may reflect other factors such as habitat alteration in addition to effects of contaminants, the use of longer-term toxicity tests in combination with SQGs may provide a more sensitive and protective measure of potential toxic effects of sediment contamination on benthic communities compared to use of 10-day toxicity tests.

This paper presents results of the first analyses completed on the entire freshwater sediment database. Some of the additional analyses planned for the database that are beyond the scope of this paper include: (1) comparing approaches for designating samples as toxic; (2) evaluating logistic-regression models; (3) identifying a list of optimal analytes for broad scale application and testing the relative efficacy of the mean verses the sum PEC quotient; (4) evaluating the influence of grain size and ammonia on the incidence of toxicity; and (5) developing a guidance manual for conducting an integrated assessment of sediment contamination.

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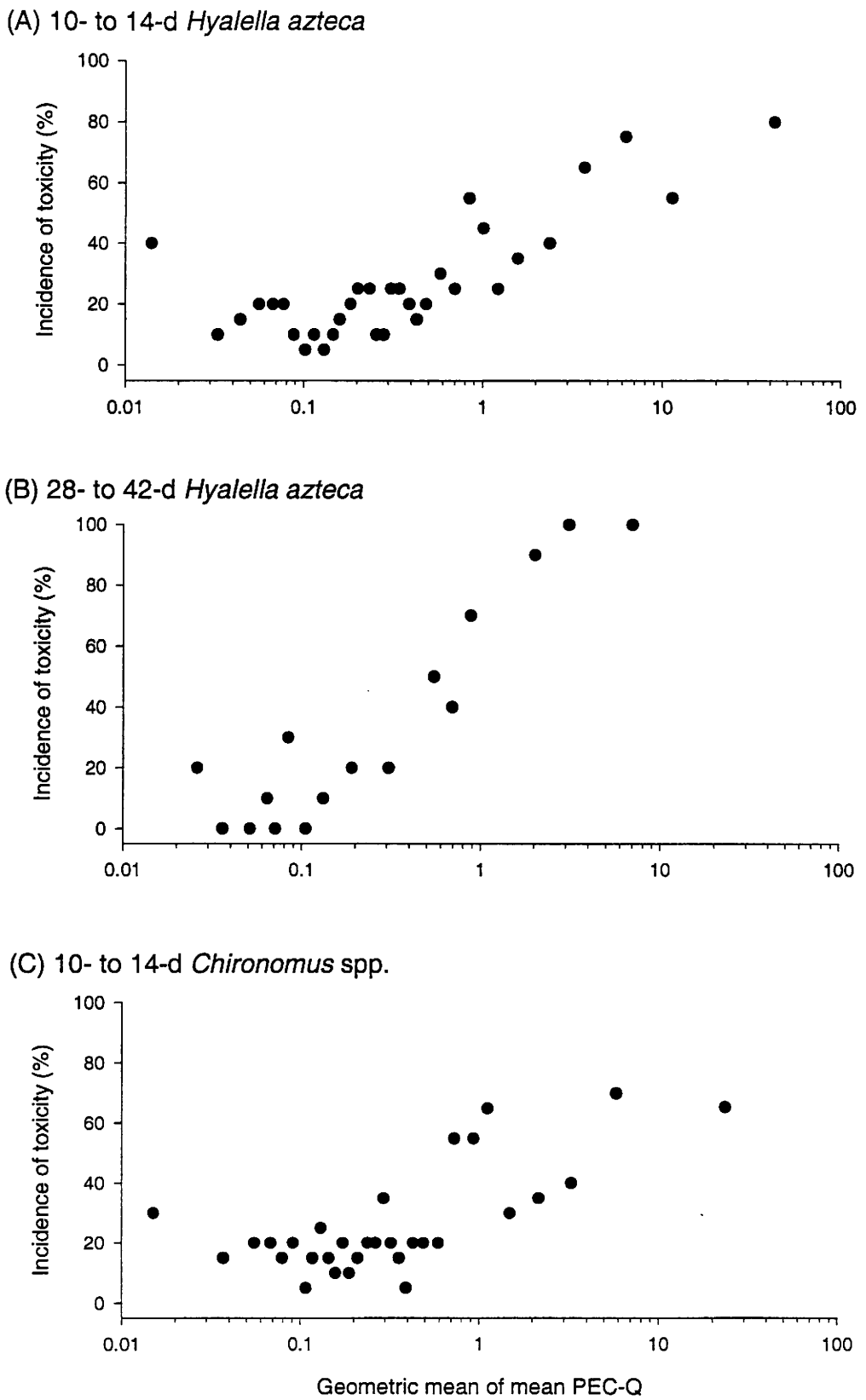

Figure 1. Relationship between the geometric mean of the mean PEC quotients and the incidence of toxicity in the three tests, based on survival or growth. The average is based on 20 samples/data point in Figures 1A and 1C (except for the data point for the highest average of the mean quotients where n=19 to 30), and 10 samples/data point for Figure 1B (see Appendix 1 for detail).

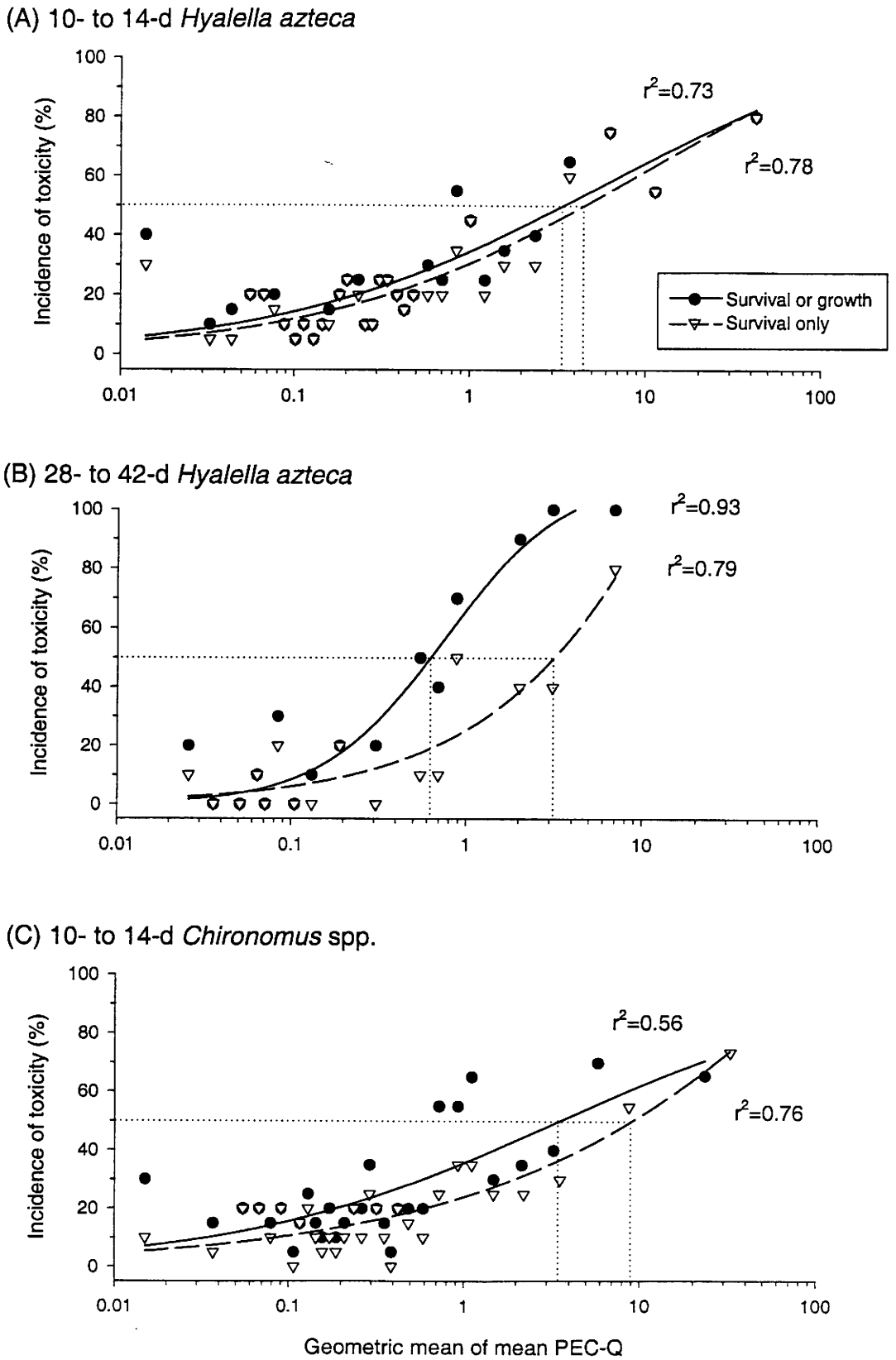

Figure 2. Relationship between the geometric mean of the mean PEC quotients and the incidence of toxicity in the three tests, based on survival or growth, or based on survival alone. The dotted line represents a 50% incidence of toxicity. See legend for Figure 1 for additional detail.

Table 1. Sediment quality guidelines that reflect probable effect concentrations (PECs; i.e., above which harmful effects are likely to be observed; MacDonald et al. 2000a). An "*" designates a reliable PEC (>20 samples and >75% correct classification as toxic).

Substance	PEL	SEL	TET	ERM	PEL-HA28	Consensus-Based PEC
Metals (in mg/kg DW)						
Arsenic	17	33	17	85	48	33.0*
Cadmium	3.53	10	3	9	3.2	4.98*
Chromium	90	110	100	145	120	111*
Copper	197	110	86	390	100	149*
Lead	91.3	250	170	110	82	128*
Mercury	0.486	2	1	1.3	NG	1.06
Nickel	36	75	61	50	33	48.6*
Zinc	315	820	540	270	540	459*
Polycyclic Aromatic Hydrocarbons (in µg/kg DW)						
Anthracene	NG	3700	NG	960	170	845
Fluorene	NG	1600	NG	640	150	536
Naphthalene	NG	NG	600	2100	140	561*
Phenanthrene	515	9500	800	1380	410	1170*
Benz[a]anthracene	385	14800	500	1600	280	1050*
Benzo(a)pyrene	782	14400	700	2500	320	1450*
Chrysene	862	4600	800	2800	410	1290*
Fluoranthene	2355	10200	2000	3600	320	2230
Pyrene	875	8500	1000	2200	490	1520*
Total PAHs	NG	100000	NG	35000	3400	22800*
Polychlorinated Biphenyls (in µg/kg DW)						
Total PCBs	277	5300	1000	400	240	676*
Organochlorine Pesticides (in µg/kg DW)						
Chlordane	8.9	60	30	6	NG	17.6
Dieldrin	6.67	910	300	8	NG	61.8
Sum DDD	8.51	60	60	20	NG	28.0
Sum DDE	6.75	190	50	15	NG	31.3*
Sum DDT	NG	710	50	7	NG	62.9
Total DDTs	4450	120	NG	350	NG	572
Endrin	62.4	1300	500	45	NG	207
Heptachlor Epoxide	2.74	50	30	NG	NG	16.0
Lindane (gamma-BHC)	1.38	10	9	NG	NG	4.99

PEL = Probable effect level; dry weight (Smith *et al.* 1996).
SEL = Severe effect level, dry weight (Persaud *et al.* 1993).
TET = Toxic effect threshold; dry weight (EC & MENVIQ 1992).
ERM = Effects range median; dry weight (Long and Morgan 1991).
PEL-HA28 = Probable effect level for *Hyalella azteca*; 28-day test; dry weight (USEPA 1996).
NG = No guideline.

Table 2. Incidence of sediment toxicity within ranges of PEC quotients (calculated using various approaches) for freshwater tests based on survival or growth.

PEC quotient[1]	Incidence of toxicity (%) based on mean PEC quotients (number of samples in parentheses)						Total number of samples
	<0.1	0.1 to <0.5	0.5 to <1.0	1.0 to <5.0	>1.0	>5.0	
***Hyalella azteca* 10- to 14-day tests**							
Mean - all	20 (102)	16 (336)	36 (80)	52 (103)	57 (152)	67 (49)	670
Mean - metals	20 (104)	19 (354)	39 (72)	63 (72)	63 (51)	62 (21)	623
Total PAHs	20 (178)	26 (160)	23 (47)	37 (54)	57 (103)	80 (49)	488
Total PCBs	26 (109)	21 (91)	46 (49)	51 (47)	60 (77)	73 (30)	326
Mean - MPP (and)	19 (79)	26 (89)	38 (34)	49 (35)	66 (64)	86 (29)	266
Mean - all (select1)	19 (36)	23 (128)	32 (38)	67 (42)	70 (64)	77 (22)	266
Mean - all (select2)	22 (46)	22 (121)	33 (40)	64 (39)	73 (59)	90 (20)	266
Mean - metals (select2)	23 (40)	24 (139)	33 (45)	81 (31)	86 (42)	100 (11)	266
Total PAHs (select2)	25 (123)	33 (76)	35 (20)	49 (33)	64 (47)	100 (14)	266
Total PCBs (select2)	20 (98)	25 (61)	47 (43)	47 (34)	59 (64)	73 (30)	266
Mean - MPP (or)	18 (147)	16 (288)	37 (73)	41 (92)	54 (162)	71 (70)	670
***Hyalella azteca* 28- to 42-day tests**							
Mean - all	8 (51)	11 (47)	57 (28)	NC[2]	91 (34)	NC	160
Mean - metals	8 (50)	20 (51)	62 (37)	NC	86 (22)	NC	160
Total PAHs	17 (98)	61 (46)	56 (9)	NC	86 (7)	NC	160
Total PCBs	4 (26)	6 (35)	17 (12)	NC	97 (36)	NC	109
Mean - MPP (and)	4 (45)	6 (18)	50 (18)	NC	100 (28)	NC	109
Mean - all (select1)	5 (44)	5 (17)	50 (22)	NC	100 (26)	NC	109
Mean - all (select2)	5 (40)	5 (21)	50 (22)	NC	100 (26)	NC	109
Mean - metals (select2)	5 (40)	25 (24)	60 (33)	NC	100 (12)	NC	109
Total PAHs (select2)	8 (57)	64 (37)	55 (9)	NC	100 (6)	NC	109
Total PCBs (select2)	4 (26)	6 (35)	17 (12)	NC	97 (36)	NC	109
Mean - MPP (or)	10 (63)	13 (39)	56 (27)	NC	97 (31)	NC	160
***Chironomus* spp. 10- to 14-day tests**							
Mean - all	20 (90)	19 (333)	33 (95)	44 (75)	51 (114)	64 (39)	632
Mean - metals	22 (88)	23 (338)	25 (89)	39 (61)	44 (84)	57 (23)	599
Total PAHs	14 (178)	33 (133)	57 (28)	67 (33)	74 (53)	85 (20)	392
Total PCBs	46 (91)	22 (49)	36 (33)	53 (51)	58 (74)	70 (23)	247
Mean - MPP (and)	29 (21)	35 (78)	35 (26)	50 (34)	60 (52)	78 (18)	177
Mean - all (select1)	29 (7)	37 (98)	29 (34)	47 (17)	66 (38)	81 (21)	177
Mean - all (select2)	33 (6)	35 (98)	33 (36)	61 (23)	68 (37)	79 (14)	177
Mean - metals (select2)	8 (12)	43 (107)	22 (36)	75 (12)	82 (22)	90 (10)	177
Total PAHs (select2)	27 (64)	33 (73)	77 (13)	85 (20)	81 (27)	71 (7)	177
Total PCBs (select2)	48 (58)	23 (31)	34 (32)	35 (34)	48 (56)	68 (22)	177
Mean - MPP (or)	20 (121)	17 (313)	43 (63)	43 (88)	52 (132)	68 (44)	629

[1]**Description of quotients:**

Mean - all: based on the PECs for each of the reliable metals, total PAHs, total PCBs, or sum DDE listed in Table 1 (n = 1 to 10 quotients/sample).

Mean - metals: based on the PECs for reliable metals listed in Table 1 (n = 1 to 7 quotients/sample).

Total PAHs: based on the PEC for total PAHs listed in Table 1 (n = 1 quotient/sample).

Total PCBs: based on the PEC for total PCBs listed in Table 1 (n = 1 quotient/sample).

Mean - MPP (and): based on reliable PECs for the average metals quotient, the total PAH quotient, and the total PCB quotient (n = 3 quotients/sample).

Mean - all (select1): based on the PECs for each of the reliable metals, total PAHs, total PCBs, or sum DDE listed in Table 1 using only samples with measured metals, total PAHs and total PCBs (n = 4 to 10 quotients/sample).

Mean - all (select2): based on the PECs for each of the reliable metals, total PAHs, or total PCBs listed in Table 1 using only samples with measured metals, total PAHs and total PCBs (n = 3 to 9 quotients/sample).

Mean - metals (select2), total PAHs (select2), or total PCBs (select2): based on the average quotient for metals, the quotient for total PAHs, or the quotient for total PCBs using only samples with measured metals, total PAHs and total PCBs.

Mean - MPP (or): based on the reliable PECs for the average metals quotient, total PAH quotient, or total PCB quotient (n = 1 to 3 quotients/sample).

[2]**NC:** Not calculated.

Table 3. Incidence of sediment toxicity within ranges of PEC quotients for the *Hyallela azteca* 10- to 14-day test in various geographic areas within the database based on survival or growth. PEC quotients were calculated as the mean of the average quotients for metals, a quotient for total PAHs, or a quotient for total PCBs ("Mean - MPP (or)" from Table 2). The numbers of samples are included within the parentheses.

Region	Basin	Area	Toxicity (%)	Incidence of toxicity (%) based on mean PEC quotients					
				<0.1	0.1 to <0.5	0.5 to <1.0	1.0 to <5.0	>1.0	>5.0
North America		All (with controls)	28 (670)	18 (147)	16 (288)	37 (73)	41 (92)	54 (162)	71 (70)
		All (w/o controls)	29 (654)	19 (140)	17 (279)	37 (73)	41 (92)	54 (162)	71 (70)
Great Lakes		All	35 (313)	14 (51)	18 (137)	47 (38)	60 (50)	68 (87)	78 (37)
	Lake Erie	All	63 (30)	(0)	0 (4)	67 (15)	75 (8)	82 (11)	100 (3)
		Buffalo River	100 (5)	(0)	(0)	100 (3)	100 (2)	100 (2)	(0)
		Clinton River	67 (12)	(0)	(0)	63 (8)	75 (4)	75 (4)	(0)
		Maumee River	46 (13)	(0)	0 (4)	50 (4)	50 (2)	80 (5)	100 (3)
	Lake Huron	Saginaw River	10 (10)	(0)	0 (6)	0 (2)	50 (2)	50 (2)	(0)
	Lake Michigan	All	60 (90)	50 (6)	40 (25)	33 (9)	69 (26)	76 (50)	83 (24)
		Burns Waterway	0 (3)	(0)	0 (1)	(0)	(0)	0 (2)	0 (2)
		Fox River	0 (6)	0 (1)	0 (3)	0 (1)	0 (1)	0 (1)	(0)
		Indiana Harbor	71 (41)	0 (1)	25 (4)	29 (7)	77 (13)	90 (29)	100 (16)
		Lake Michigan	0 (4)	(0)	0 (4)	(0)	(0)	(0)	(0)
		Menominee River	80 (5)	(0)	(0)	(0)	80 (5)	80 (5)	(0)
		Sheboygan Harbor	72 (18)	75 (4)	75 (12)	(0)	0 (1)	50 (2)	100 (1)
		Waukegan Harbor	67 (3)	(0)	0 (1)	100 (1)	(0)	100 (1)	100 (1)
		Waushara County	0 (2)	(0)	(0)	(0)	0 (2)	0 (2)	(0)
		White Lake Montague	75 (8)	(0)	(0)	(0)	100 (4)	75 (8)	50 (4)
	Lake Ontario	All	19 (26)	(0)	19 (21)	100 (1)	0 (1)	0 (4)	0 (3)
		Genesee River	38 (13)	(0)	33 (12)	100 (1)	(0)	(0)	(0)
		Oswego River	0 (7)	(0)	0 (7)	(0)	(0)	(0)	(0)
		Sturgeon Lake	0 (6)	(0)	0 (2)	(0)	0 (1)	0 (4)	0 (3)
	Lake Superior	St. Louis River	18 (157)	9 (45)	12 (81)	38 (11)	38 (13)	55 (20)	86 (7)
Non-Great Lakes		All	24 (341)	22 (89)	16 (142)	26 (35)	19 (42)	39 (75)	64 (33)
Lower Mississippi River		Tennessee	89 (9)	89 (9)	(0)	(0)	(0)	(0)	(0)
Chesapeake Bay		All	50 (12)	50 (6)	40 (5)	100 (1)	(0)	(0)	(0)
State of California		All	38 (8)	75 (4)	0 (1)	0 (1)	0 (2)	0 (2)	(0)
		San Francisco Bay	0 (4)	(0)	0 (1)	0 (1)	0 (2)	0 (2)	(0)
		Temblader River	75 (4)	75 (4)	(0)	(0)	(0)	(0)	(0)
State of Florida		Miami-Dade County	22 (88)	12 (49)	27 (30)	57 (7)	50 (2)	50 (2)	(0)
State of New York	Hudson River	New York Lakes	4 (28)	0 (5)	0 (6)	0 (2)	7 (14)	7 (15)	0 (1)
State of Oregon	Columbia River	Lower Columbia River	15 (60)	0 (1)	3 (29)	0 (10)	0 (5)	40 (20)	53 (15)
State of Texas		Trinity River	15 (40)	0 (5)	17 (35)	(0)	(0)	(0)	(0)
State of Washington		All*	27 (92)	0 (10)	14 (35)	23 (13)	28 (18)	50 (34)	75 (16)
		Columbia River*	14 (35)	0 (10)	18 (17)	100 (2)	0 (4)	0 (6)	0 (2)
		Puget Sound	35 (57)	(0)	11 (18)	9 (11)	36 (14)	61 (28)	86 (14)
Nova Scotia, Canada		All	100 (4)	(0)	100 (1)	100 (1)	100 (1)	100 (2)	100 (1)

* One sample from British Columbia included in this total.

Table 4. Incidence of sediment toxicity within ranges of PEC quotients for the *Hyalella azteca* 28- to 42-day test in various geographic areas within the database based on survival or growth. PEC quotients were calculated as the mean of the average quotients for metals, a quotient for total PAHs, or a quotient for total PCBs ("Mean - MPP (or)" from Table 2). The numbers of samples are included within the parentheses.

Region	Basin	Area	Toxicity (%)	Incidence of toxicity (%) based on mean PEC quotients					
				<0.1	0.1 to <0.5	0.5 to <1.0	1.0 to <5.0	>1.0	>5.0
North America		All (with controls)	35 (160)	10 (63)	13 (39)	56 (27)	96 (25)	97 (31)	100 (6)
		All (w/o controls)	37 (151)	10 (63)	17 (30)	56 (27)	96 (25)	97 (31)	100 (6)
Great Lakes		All	79 (42)	(0)	13 (8)	71 (7)	100 (22)	100 (27)	100 (5)
	Lake Erie	Buffalo River	80 (5)	(0)	(0)	67 (3)	100 (2)	100 (2)	(0)
	Lake Huron	Saginaw River	30 (10)	(0)	0 (6)	50 (2)	100 (2)	100 (2)	(0)
	Lake Michigan	All	96 (27)	(0)	50 (2)	100 (2)	100 (18)	100 (23)	100 (5)
		Indiana Harbor	100 (4)	(0)	(0)	(0)	100 (1)	100 (4)	100 (3)
		Waukegan Harbor	96 (23)	(0)	50 (2)	100 (2)	100 (17)	100 (19)	100 (2)
Non-Great Lakes		All	21 (109)	10 (63)	18 (22)	50 (20)	67 (3)	75 (4)	100 (1)
Upper Mississippi River		All	4 (53)	4 (45)	0 (8)	(0)	(0)	(0)	(0)
State of Alabama	Gulf of Mexico	Mobile Bay	0 (5)	(0)	0 (4)	(0)	0 (1)	0 (1)	(0)
State of Maine	Kennebec River	Brunswick	25 (4)	0 (2)	50 (2)	(0)	(0)	(0)	(0)
State of Maryland	Chesapeake Bay	Aberdeen	75 (4)	100 (1)	0 (1)	100 (2)	(0)	(0)	(0)
State of Montana	Pend Oreille River	Clark Fork River	62 (13)	50 (2)	50 (2)	57 (7)	100 (1)	100 (2)	100 (1)
State of Texas		All	20 (15)	15 (13)	50 (2)	(0)	(0)	(0)	(0)
	Gulf of Mexico	Galveston Bay	60 (5)	50 (4)	100 (1)	(0)	(0)	(0)	(0)
		Rio Grande	0 (5)	0 (5)	(0)	(0)	(0)	(0)	(0)
		Trinity River	0 (4)	0 (3)	0 (1)	(0)	(0)	(0)	(0)
		Austin	0 (1)	0 (1)	(0)	(0)	(0)	(0)	(0)
Washington D.C.	Chesapeake Bay	Chesapeake Bay	40 (15)	(0)	33 (3)	36 (11)	100 (1)	100 (1)	(0)

Table 5. Incidence of sediment toxicity within ranges of PEC quotients for the *Chironomus* spp. 10- to 14-day test in various geographic areas within the database based on survival or growth. PEC quotients were calculated as the mean of the average quotients for metals, a quotient for total PAHs, or a quotient for total PCBs ("Mean - MPP (or)" from Table 2). The numbers of samples are included within the parentheses.

Region	Basin	Area	Toxicity (%)	Incidence of toxicity (%) based on mean PEC quotients					
				<0.1	0.1 to <0.5	0.5 to <1.0	1.0 to <5.0	>1.0	>5.0
North America		All (with controls)	27 (629)	20 (121)	17 (313)	43 (63)	43 (88)	52 (132)	68 (44)
		All (w/o controls)	28 (611)	20 (118)	17 (298)	43 (63)	43 (88)	52 (132)	68 (44)
Great Lakes		All	30 (463)	14 (99)	20 (211)	51 (45)	47 (70)	56 (108)	71 (38)
	Lake Erie	All	45 (73)	21 (19)	38 (26)	71 (17)	70 (10)	64 (11)	0 (1)
		Buffalo River	40 (5)	(0)	(0)	67 (3)	0 (2)	0 (2)	(0)
		Clinton River	100 (12)	(0)	(0)	100 (8)	100 (4)	100 (4)	(0)
		Elmira, Ontario, Canada	33 (6)	20 (5)	100 (1)	(0)	(0)	(0)	(0)
		St. Clair River	39 (44)	21 (14)	47 (19)	33 (6)	75 (4)	60 (5)	0 (1)
		Wheatly	0 (6)	(0)	0 (6)	(0)	(0)	(0)	(0)
	Lake Huron	All	46 (48)	25 (4)	47 (19)	67 (6)	45 (11)	42 (19)	38 (8)
		Saginaw River	10 (10)	(0)	0 (6)	0 (2)	50 (2)	50 (2)	(0)
		St. Mary's River	55 (38)	25 (4)	69 (13)	100 (4)	44 (9)	41 (17)	38 (8)
	Lake Michigan	All	37 (89)	33 (9)	23 (30)	20 (5)	33 (27)	49 (45)	72 (18)
		Burns Waterway Harbor	0 (3)	(0)	0 (1)	(0)	(0)	0 (2)	0 (2)
		East River	0 (1)	(0)	0 (1)	(0)	(0)	0 (0)	0 (0)
		Fox River & Green Bay	0 (18)	0 (1)	0 (6)	0 (3)	0 (8)	0 (8)	(0)
		Grand River	33 (3)	(0)	0 (1)	(0)	0 (1)	50 (2)	100 (1)
		Indiana Harbor	100 (14)	(0)	(0)	(0)	100 (6)	100 (14)	100 (8)
		Kenosha Harbor	0 (1)	(0)	(0)	0 (1)	(0)	(0)	(0)
		Kewanee Harbor	0 (2)	0 (2)	(0)	(0)	(0)	(0)	(0)
		Lake Michigan	20 (5)	0 (1)	25 (4)	(0)	(0)	(0)	(0)
		Menominee River	27 (11)	0 (1)	0 (2)	(0)	29 (7)	38 (8)	100 (1)
		Port Washington Harbor	0 (2)	(0)	0 (2)	(0)	(0)	(0)	(0)
		Sheboygan Harbor	56 (18)	75 (4)	50 (12)	(0)	0 (1)	50 (2)	100 (1)
		Waukegan Harbor	67 (3)	(0)	0 (1)	100 (1)	(0)	100 (1)	100 (1)
		White Lake Montague	25 (8)	(0)	(0)	(0)	25 (4)	25 (8)	25 (4)
	Lake Ontario	All	17 (89)	11 (19)	5 (56)	50 (4)	71 (7)	80 (10)	100 (3)
		Hamilton Harbor	60 (5)	(0)	(0)	100 (1)	50 (4)	50 (4)	(0)
		Lake Ontario	3 (63)	7 (15)	2 (47)	0 (1)	(0)	(0)	(0)
		Niagra River	63 (8)	(0)	0 (2)	50 (2)	100 (3)	100 (4)	100 (1)
		Oswego River	27 (11)	25 (4)	29 (7)	(0)	(0)	(0)	(0)
		Sturgeon Lake	100 (2)	(0)	(0)	(0)	(0)	100 (2)	100 (2)
	Lake Superior	All	22 (164)	8 (48)	16 (80)	31 (13)	47 (15)	65 (23)	100 (8)
		St. Louis River	21 (155)	9 (47)	14 (76)	27 (11)	46 (13)	67 (21)	100 (8)
		Black River	57 (7)	0 (1)	67 (3)	100 (1)	50 (2)	50 (2)	(0)
		Lake Superior	0 (1)	(0)	(0)	0 (1)	(0)	(0)	(0)
		Wisconsin State	0 (1)	(0)	0 (1)	(0)	(0)	(0)	(0)
Non-Great Lakes		All	22 (148)	53 (19)	12 (87)	22 (18)	28 (18)	33 (24)	50 (6)
Lower Mississippi River		Tennessee	89 (9)	89 (9)	(0)	(0)	(0)	(0)	(0)
State of Montana	Pend Oreille River	Clark Fork River	15 (13)	0 (2)	0 (2)	14 (7)	100 (1)	50 (2)	0 (1)
State of New York	Hudson River	New York Lakes	9 (23)	0 (5)	0 (5)	50 (2)	9 (11)	9 (11)	(0)
State of Texas		Trinity River	13 (72)	67 (3)	10 (68)	0 (1)	(0)	(0)	(0)
State of Washington		All	30 (27)	(0)	18 (11)	29 (7)	40 (5)	44 (9)	50 (4)
Nova Scotia, Canada		All	75 (4)	(0)	100 (1)	0 (1)	100 (1)	100 (2)	100 (1)

Appendix 1. Summary of the data presented in Figures 1 and 2.

10- to 14-day *Hyalella azteca*					28- to 42-day *Hyalella azteca*					10- to 14-day *Chironomus* spp.					
N	Survival or growth		Survival only		N	Survival or growth		Survival only		Survival or growth			Survival only		
	Geomean of mean Q	Toxic (%)	Geomean of mean Q	Toxic (%)		Geomean of mean Q	Toxic (%)	Geomean of mean Q	Toxic (%)	N	Geomean of mean Q	Toxic (%)	N	Geomean of mean Q	Toxic (%)
20	0.014	40	0.014	30	10	0.026	20	0.026	10	20	0.015	30	20	0.015	10
20	0.033	10	0.033	5	10	0.036	0	0.036	0	20	0.037	15	20	0.037	5
20	0.044	15	0.044	5	10	0.051	0	0.051	0	20	0.055	20	20	0.055	20
20	0.056	20	0.056	20	10	0.064	10	0.064	10	20	0.068	20	20	0.068	20
20	0.067	20	0.067	20	10	0.071	0	0.071	0	20	0.079	15	20	0.079	10
20	0.077	20	0.077	15	10	0.084	30	0.084	20	20	0.091	20	20	0.091	20
20	0.088	10	0.088	10	10	0.105	0	0.105	0	20	0.107	5	20	0.107	0
20	0.102	5	0.102	5	10	0.132	10	0.132	0	20	0.117	15	20	0.117	15
20	0.114	10	0.114	10	10	0.191	20	0.191	20	20	0.130	25	20	0.130	20
20	0.130	5	0.130	5	10	0.307	20	0.307	0	20	0.144	15	20	0.144	10
20	0.146	10	0.146	10	10	0.550	50	0.550	10	20	0.157	10	20	0.157	5
20	0.159	15	0.159	10	10	0.696	40	0.696	10	20	0.173	20	20	0.173	10
20	0.183	20	0.183	20	10	0.881	70	0.881	50	20	0.188	10	20	0.188	5
20	0.202	25	0.202	25	10	2.022	90	2.022	40	20	0.210	15	20	0.210	10
20	0.235	25	0.235	20	10	3.119	100	3.119	40	20	0.239	20	20	0.239	20
20	0.257	10	0.257	10	10	7.000	100	7.000	80	20	0.265	20	20	0.265	10
20	0.282	10	0.282	10						20	0.294	35	20	0.294	25
20	0.309	25	0.309	25						20	0.322	20	20	0.322	20
20	0.344	25	0.344	25						20	0.357	15	20	0.357	10
20	0.390	20	0.390	20						20	0.390	5	20	0.390	0
20	0.429	15	0.429	15						20	0.426	20	20	0.426	20
20	0.483	20	0.483	20						20	0.489	20	20	0.489	15
20	0.582	30	0.582	20						20	0.590	20	20	0.590	10
20	0.701	25	0.701	20						20	0.728	55	20	0.728	25
20	0.847	55	0.847	35						20	0.931	55	20	0.931	35
20	1.013	45	1.013	45						20	1.116	65	20	1.116	35
20	1.224	25	1.224	20						20	1.490	30	20	1.490	25
20	1.582	35	1.582	30						20	2.164	35	20	2.222	25
20	2.386	40	2.386	30						20	3.281	40	20	3.555	30
20	3.711	65	3.711	60						20	5.837	70	20	8.779	55
20	6.276	75	6.276	75						29	23.400	66	19	32.608	74
20	11.339	55	11.339	55											
30	42.350	80	42.350	80											
Equation:		$y=a/[1+(x/x_0)^b]$													
a	114.017		122.465			111.803		447.821			99.488			397.523	
b	-0.479		-0.488			-1.247		-0.639			-0.474			-0.366	
x_0	5.687		9.535			0.745		81.279			3.442			1804.374	
Predict mean quotient at 50% incidence of toxicity															
	3.4		4.5			0.63		3.2			3.5			9.0	

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Particle-Scale Understanding of the Bioavailability of PAHs in Sediment

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This study reports results of sediment bioslurry treatment and earthworm bioaccumulation for polycyclic aromatic hydrocarbon (PAH) contaminants found in sediment dredged from Milwaukee Harbor. A significant finding was that bioslurry treatment reduced PAHs on the sediment clay/silt fraction but not on the sediment coal-derived fraction and that PAH reduction in the clay/silt fraction correlated with substantial reduction in earthworm PAH bioaccumulation. These findings are used to infer PAH bioavailability from characterization of particle-scale PAH distribution, association, and binding among the principal particle fractions in the sediment. The results are consistent with work showing that the sediment comprised two principal particle classes for PAHs, coal-derived and clay/silt, each having much different PAH levels, release rates, and desorption activation energies. PAH sorption on coal-derived particles is associated with minimal biodegradation, slow release rates, and high desorption activation energies, while PAH sorption on clay/silt particles is associated with significant potential biodegradability, relatively fast release rates, and lower desorption activation energies. These characteristics are attributed to fundamental differences in the organic matter to which the PAHs are sorbed. Although the majority of the PAHs are found preferentially on coal-derived particles, the PAHs on the clay/silt sediment fraction are more mobile and available, and thus potentially of greater concern. This study demonstrates that a suite of tests comprising both bioassays and particle-scale investigations provide a basis to assess larger-scale phenomena of biotreatment of PAH-impacted sediments and bioavailability and potential toxicity of PAH contaminants in sediments. Improved understanding of contaminant bioavailability aids decision-making on the effectiveness of biotreatment of PAH-impacted sediments and the likelihood for possible reuse of dredged sediments as reclaimed soil or fill.

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Introduction

Approximately 400 million cubic yards of sediment are dredged from United States ports, harbors, and waterways each year to maintain the nation's navigation system. It is estimated that approximately 10% of these dredged materials are impacted by organic and inorganic contaminants (*1*). Contaminated dredged materials are generally discharged into diked, confined disposal facilities (CDFs). Many CDFs are filled or reaching their design capacity, and economic treatments are sought to extend the life of CDFs by reclaiming dredged material for reuse as fill or soil.

The reuse of dredged material as reclaimed soil will extend the operational life of CDFs while benefiting the environment through reclamation of topsoil and fill material. However, dredged harbor sediments contaminated with polycyclic aromatic hydrocarbons (PAHs) face very stringent cleanup standards prior to reuse. The reuse of contaminant-impacted dredged material is restricted to terrestrial application; therefore, the material generally must meet either state soil or solid waste cleanup criteria. This is a serious impediment for reuse of dredged materials. In Wisconsin, for example, the use of contaminated dredged material for topsoil is governed by suggested generic soil cleanup levels (*2*). If the contaminated dredged material is reused as fill material, it falls under Wisconsin's regulation for the beneficial use of industrial byproducts (*3*). As shown in Table 1, for use in nonindustrial (topsoil) or residential (fill material) applications, certain PAH contaminants such as benzo[*a*]pyrene and dibenz[*a*,*h*]anthracene must be cleaned up to as low as 8.8 ppb (*2*, *4*). These levels are practically unachievable using bioreclamation technologies. Thus, relatively low-cost, natural cleanup processes such as composting may not meet cleanup standards. These low-level cleanup standards assume that the PAHs are readily available and may result in environmental exposure. While there is growing awareness that contaminant availability and risk should determine cleanup levels, adequate tools to evaluate and understand contaminant availability in dredged materials are lacking. As is the case with contaminated soils (*5*), conservative, low-level cleanup standards are invoked, wherein sediment cleanup is driven by total contaminant mass removal not bioavialability (*6*). Consequently, the adherence and slow release of PAHs from geosorbents is both an obstacle to remediation (*7*, *8*) and a challenge to concepts about cleanup standards and risks (*5*, *9*).

Bioremediation of PAH-contaminated sediments often results in high residual concentrations that do not satisfy the minimum standards for reuse as soil (*10*). It is believed that residual PAH concentrations are caused by the limited bioavailability of PAHs. Operational, physicochemical tests are being developed to assess contaminant bioavailability and to evaluate the potential feasibility of biological treatments to meet cleanup objectives. Often such tests are based on the determination of readily available PAHs as measured by release into the water phase. These tests may involve long-term, batch rate of release experiments with the uptake of dissolved PAHs onto a solid sorbent (*11*, *12*) and the data evaluated using an empirical first-order or a two-site model consisting of two first-order expressions (*13*). Thermal techniques may be useful in conjunction with aqueous desorption tests to characterize the available fraction (*14*).

Study Objectives. The primary question addressed in this work was whether the macroscopic bioavailability behavior of PAHs in dredged sediment could be explained by particle-scale characterizations of PAH distribution, association, and

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TABLE 1. Comparison of PAH Concentrations (mg/kg) in Untreated Milwaukee CDF Sediment and Wisconsin Required Cleanup Levels (mg/kg) for Reuse of Dredged Material

		WI generic soil cleanup levels			WI solid waste cleanup levels	
compd	concn	GW pathway	nonindustrial	industrial	unrestricted	restricted
naphthalene[a]	1.2	0.4	20	110	600	6000
2-methylnaphthalene	2.1	20	600	40000	na	na
acenaphthylene	0.1	0.7	18	360	8.8	88
acenaphthene	1.9	38	900	60000	900	9000
fluorene	2.3	100	600	40000	600	6000
phenanthrene[a]	15.4	1.8	18	390	0.88	8.8
anthracene	3.1	3000	5000	300000	5000	50000
fluoranthene	21.8	500	600	40000	600	6000
pyrene	17.7	8700	500	30000	500	5000
chrysene[a]	9.8	37	8.8	390	8.8	88
benzo[*a*]anthracene[a]	6.9	17	0.088	3.9	0.088	0.88
benzo[*b*]fluoranthrene[a]	7.6	360	0.088	3.9	0.088	0.88
benzo[*k*]fluoranthrene[a]	6.3	870	0.88	39	0.88	8.8
benzo[*a*]pyrene[a]	7.0	48	0.0088	0.39	0.0088	0.08
indeno[1,2,3-*c,d*]pyrene[a]	5.6	680	0.088	3.9	0.088	0.88
dibenz[*a,h*]anthracene[a]	1.1	38	0.0088	0.39	0.0088	0.088
benzo[*g,h,i*]perylene[a]	5.1	6800	1.8	39	0.88	8.8

[a] Denotes PAHs that exceed at least one of the cleanup levels required for reuse of dredged materials. Generic soil cleanup levels are for reuse as topsoil or near-surface soil. Nonindustrial and industrial soil cleanup levels are based on direct contact pathways. Groundwater (GW) pathway cleanup levels assume reuse will be in areas where the material will come into contact with groundwater. Restricted solid waste cleanup levels limit the reuse to capped, roadfill, or nonresidential applications. Unrestricted solid waste cleanup levels are based on unrestricted reuse as fill material. Compiled from refs *2* and *3*.

binding with sediment. To this end, the research comprised aerobic bioslurry testing and earthworm PAH uptake studies before and after bioslurry treatment. These data were interpreted in view of recent reporting (*14, 15*) of particle-scale measurements of PAH distribution, organic matter association, release rates, and desorption binding energies for this sediment.

Milwaukee Confined Disposal Facility (CDF). The sediment used in this study was obtained from the Jones Island Confined Disposal Facility (CDF), commonly known as the Milwaukee CDF and operated by the Milwaukee Harbor Port Authority. Shown in Figure 1 is the 44-acre CDF located in the South Milwaukee Harbor. Constructed in 1975 with a maximum thickness of 10 m, it serves as a disposal facility for maintenance-dredged materials unsuitable for open-lake disposal. The majority of the CDF was filled via hydraulic dredging and consists of consolidated, fine-grained material. Borings from the Milwaukee CDF indicate 50 mg/kg total PAH near the surface (within 2 m), 275 mg/kg at 5 m, and 100 mg/kg at 7 m (*16*). Samples for this work were collected in fall 1996 by backhoe at a depth of 4 m, placed in a 55-gal drum and sealed on site, shipped via refrigerated truck to the Environmental Laboratory, U.S. Army Engineer Research and Development Center, and stored at 4 °C for 2 yr prior to use.

Experimental Methods

Homogenization of Dredged Materials. Drummed sediment was placed in an aluminum trough and homogenized for 6 h using a heavy-duty mixer. Wet sieving removed material larger than 2 mm. Sievings were poured into a 55-gal drum and allowed to settle for 1 month at 4 °C, and then the overlying water layer was removed using a peristaltic pump. The sediment was homogenized again prior to sampling and loading the bioslurry reactors.

Bioslurry Reactor System. The bioslurry reactor system comprised six 5-L reactors. Two reactors were controls (anaerobic and poisoned), and four were active (aerobic) reactors. Each bioreactor received 5.3 kg (wet weight) of dredged material, which consisted of 56.5% solids. To produce a 30% (by volume) slurry, 3.5 L of modified Stanier's basal media (*17*) was added to each reactor. The media did not

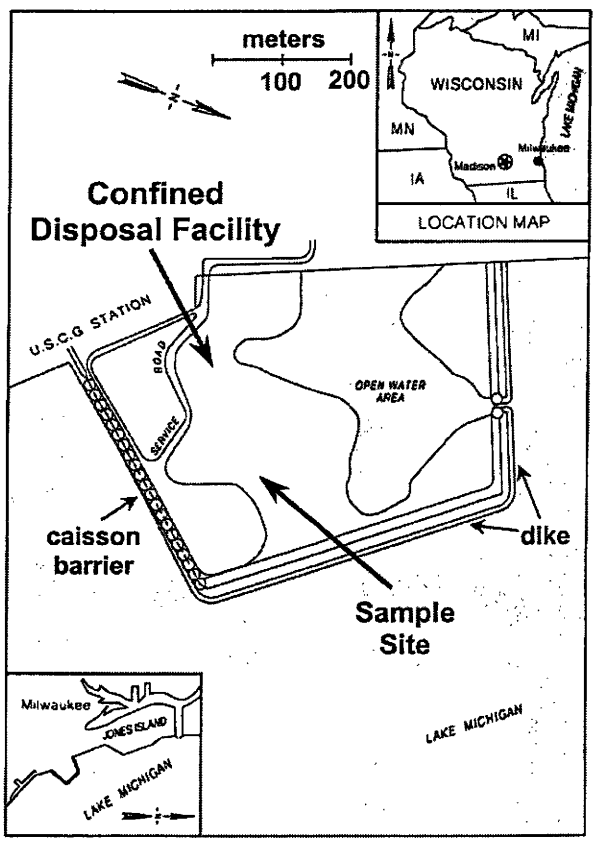

FIGURE 1. Site map of Milwaukee Confined Disposal Facility and sample site. The sample was collected at a depth of 4 m.

contain any carbon source. The reactors had two 3.8-in impellers mounted to a mixing shaft. The lower impeller was positioned about 1 in. from the bottom of the reactor, and the upper impeller was mounted about 3 in. above the lower impeller. Each reactor had three diffuser stones in the bottom that bubbled either argon (control reactors) or air (aerobic

reactors). The gas was fed from compressed gas cylinders and passed through double charcoal filters before entering the bioreactors. The reactors were continuously stirred at 350 rpm. The reactors were vented to a fume hood. Off-gas monitoring in related tests showed no significant loss of PAHs by volatilization.

The anaerobic reactors were poisoned with 500 ppm each of sodium azide and mercuric chloride. Initial biomass analyses indicated that the poisoning was not effective in killing the microbial community for longer than a few days. Thus another 500 ppm of both compounds was added 18 d into the experiment, 1000 ppm 1 week later, and 750 ppm every 3 weeks thereafter. This maintained poisoned, anaerobic controls, as shown by streaking the slurry onto nutrient agar plates and incubating for 72 h. The bioreactors were tested daily for pH, dissolved oxygen, oxidation–reduction potential, and temperature and for nitrate and phosphate initially every 2 days and then weekly after the first month. Carbon, nitrogen, and phosphorus ratios were maintained at 100:10:1, with the carbon content based on the sediment total organic carbon content. Dissolved oxygen was maintained in the range of 8–9 mg/L for the aerobic reactors with pH 7.0.

Each month sediment was sampled using 50-mL pipets after allowing the reactors to settle for 1 h. Samples were collected from five different locations and at three different depths (top, middle, and bottom) within each reactor. The collected slurry was placed in sterile screw-top containers and centrifuged at 8000 rpm for 20 min, and the supernatant was decanted; the solids were placed in a pan lined with sterile aluminum foil and mixed thoroughly and placed into sample vials. At the end of the test, the reactor was emptied, and a composite sample was collected. All sampling tools were autoclaved prior to use.

Physical Separation. The whole sediment was separated into four size fractions (>1000, 1000–250, 250–63, and <63 μm) for purposes of determining PAH presence and availability among sediment fractions. The larger size fractions (>63 μm) comprised primarily sandy grains, coal-derived particles, and woody material. It was possible to wash off the lighter fractions (coal and wood) from the heavier sand by swirling with water in a beaker and draining off the entrained lighter particles. Materials in the fine fraction (<63 μm) were density separated using a cesium chloride solution having a specific gravity of 1.8 (*15*). Five grams of wet sediment and 40 mL of cesium chloride solution were centrifuged at 200 rpm for 10 min in 50-mL glass centrifuge tubes. The fine coal-derived and wood particles floated, were decanted, and were collected on filter paper and rinsed with water several times. The heavy clay and silt fractions were similarly washed several times to remove cesium chloride. Each of these density-separated fractions was placed in cold storage.

Desorption Analyses. Room temperature, batch, desorption kinetic studies evaluated the mass transfer of the PAHs from the whole and separated fractions of sediment to Tenax beads (*15*). Duplicate rate of release tests followed procedures reported previously by Ghosh et al. (*15*) and others (*18, 19*). Contaminated sediment (2.0 g) and Tenax beads (0.5 g, 40–60 mesh, Suppelco, PA) were added to 15-mL glass vials containing 10 mL of deionized water and continuously mixed on a rotator. Mercuric chloride (1.0 mg) was added to the mixture to prevent biological growth. At sampling times, the Tenax beads were harvested by allowing the sediment to settle, and the Tenax beads to float up. The Tenax beads were removed from the glass vials, and fresh Tenax beads were added. PAHs were extracted from the Tenax beads by agitating the beads in 10 mL of hexane and acetone (50:50 mixture) for 12 h and repeating twice. The extracts were then combined and concentrated, cleaned using silica gel, and analyzed by GC-FID.

Thermal program desorption (TPD) measurements employed a gas chromatograph quadrupole mass spectrometer (GCQ-MS) with a direct insertion probe manufactured by Thermoquest. These tests evaluated binding activation energies, as interpreted from TPD rate responses, for PAHs from untreated and bioslurry treated sediment. TPD tests followed procedures described by Talley (*20*), which showed that the release of PAHs is dependent both on PAH molecular weight and the character of the sorbent material. Milligram-level samples of whole sediment and separated fractions were placed into the mass spectrometer via a 1 mm diameter glass vial inserted in the probe. The temperature of the probe containing the sample glass vial was then increased at 10 °C/min from 30 to 400 °C. As the probe heated, the volatilized compounds were ionized, selectively filtered in the quadrupole, and detected in the mass spectrometer. The high sensitivity of the GCQ-MS enabled sample size down to the particle level. The thermogram data reduction techniques are described in Ghosh et al. (*14*).

Chemical Analyses. PAH concentrations were determined by analysis of four replicate samples from the sieved and mixed sediment prior to placing in the bioslurry reactors. After the bioslurry reactors were loaded, samples were collected monthly from each reactor and analyzed for PAHs by Soxhlet extraction and GC/MS analysis for PAHs using EPA Method 3540. GC-FID was used for PAH analyses on whole sediment and separated size fractions to determine PAH distribution by particle size and density. These analyses followed EPA Method 3550B with ultrasonic extraction and silica gel cleanup by EPA Method 3630C (*15*). Samples were analyzed for the 16 PAHs on the EPA Priority Pollutant List as well as for methyl naphthalene. Transmission FTIR analysis was performed with a Mattson ATI FTIR–NIR spectrometer using sediment particles ground and formed into KBr pellets.

Microbial Analyses. Microcosm studies used radiolabeled phenanthrene, pyrene, chrysene, and benzo[*a*]pyrene to confirm that viable PAH-degrading microorganisms were present in the sediment. The aerobic systems were evaluated for acetate, phenanthrene, pyrene, chrysene, and benzo[*a*]-pyrene mineralization. Anaerobic systems were tested for acetate and phenanthrene mineralization. Microcosm studies were conducted on sediment collected from each bioslurry reactor after 18 h of mixing and then monthly thereafter. One gram (wet weight) of slurry material was placed into 15-mL Teflon-lined screw-cap test tubes to which was added 2.7 mL of the modified Stanier's basal media (*17*) and 20 000 DPM amount of ^{14}C-labeled substrate in triplicate for each substrate. A modified version of the method described by Fulthorpe et al. (*21*) assessed microbial activity in which glass fiber filters (Whatman, Maidstone, U.K.), 10 mm diameter and saturated in 1 M barium hydroxide, were placed into the caps of screw-top test tubes to trap evolved $^{14}CO_2$ (*31*). The filters were placed in 15-mL scintillation cocktail (Ultima Gold, Packard Instruments Co., Downers Grove, IL) and counted twice with a top count microplate scintillation counter (Packard Instrument Co., Downers Grove, IL). Counts were corrected for background and counting efficiency using the external standard method described by the manufacturer.

Polar lipid fatty acid analyses (PLFA), as described by White and Ringelberg (*22*), identified the level of biomass present in the sediment and provided information about the microbial community structure. The total lipid extractant was separated into neutral, glyco-, and polar lipid fractions (*23*) and prepared for gas chromatography/mass spectrometry (GC/MS) by mild alkaline methanolic transesterification (*31*). Peak identities were confirmed using a gas chromatograph-mass selective detector (Hewlett-Packard GC6890-5973 MSD) with electron impact ionization at 70 eV. DNA analysis targeted the presence of select genes known to be present during active PAH degradation. Total DNA was isolated from

triplicate 500-mg slurry samples using a mini-bead beater system as described by Borneorneman et al. (*24*) and purified using Fast DNA SPIN Kit (FastPrep7 Instrument FP120; BIO 101, Vista, CA). Total DNA was suspended in 50 μL of molecular biology grade H_2O (Five prime-Three prime, WI) and stored at −20 °C (*31*).

Earthworm Bioassays. Earthworm acute toxicity and bioaccumulation bioassays evaluated the adverse effects of the sediment PAHs to *Eisenia fetida*. In as much as dredged sediment for the Milwaukee CDF was disposed on land and reuse of dredged sediment would involve terrestrial application, earthworm bioassays were determined to be most appropriate test for toxicity end point assessments. The use of these organisms as indicators of environmental pollution is well-documented (*25, 26*). Acute toxicity was assessed by earthworm survival in 14-day tests following EPA procedures (*27, 28*). Earthworms were exposed in a static system of the untreated sediment mixtures and artificial soil (70% sand, 20% kaolin, and 10% peat). Ten concentrations of sediment (100%, 75%, 50%, 25%, 12.5%, 6.25%, 3.125%, 1.56%, 0.78%, and 0%) were prepared in triplicate, where the percent concentration refers to the amount of contaminated sediment present in the test with 100 g dry weight total in covered 250-mL flasks with air holes. The 0% concentration (100% artificial soil) served as the control. After being mixed, the test sediment was hydrated to 75% of water-holding capacity with deionized water. Ten earthworms were placed into each jar on the surface of the sediment. The jars were capped and stored in a humidity-controlled room at 25 °C. Test results were based on earthworm survival.

Earthworm bioaccumulation tests followed a modified ASTM method E1676-97 (*29*) where 500 g of sediment was collected from each reactor at the conclusion of the bioslurry tests. After the sample was homogenized, three test containers were filled with 160 g each. Sixteen earthworms were added to each test container. The sediment and artificial soil were hydrated to 75% of water-holding capacity, covered with cotton muslin cloth to allow the passage of air, and stored in a humidity-controlled room for 28 d. A few flakes of powdered oatmeal were added to the surface of each test container to attract the earthworms to the surface, resulting in greater earthworm mobility and activity. At the end of the 28 d, the earthworms were rinsed with dechlorinated water and placed in glass vials lined with filter paper. The worms remained in the vials (2 per vial) for 1 d in order to allow their gullet to cleanse. The worms were then placed in a −70 °C freezer. On the day of chemical analysis, the worms were removed from the freezer and freeze-dried in a lyophilizer, producing a dry earthworm powdery material for Soxhlet extraction (EPA Method 3540) and analysis by GC/MS. Bioaccumulation tests were performed on untreated and final biotreated sediment.

Results and Discussion

Sediment Composition. Composite sediment samples were separated into two density fractions: (i) specific gravity <1.8 comprising mainly coal-derived material with some plant and woody matter and (ii) specific gravity >1.8 comprising clay, silt, and sand. Elemental analyses using SEM with wavelength dispersive X-ray showed silica the most abundant material in the heavier, >63 μm size fraction, and clays dominant in the heavier, <63 μm size fraction (*15*). The second most abundant particle class within all size fractions comprised high-carbon content black particles, principally coal-derived with some coal as determined by petrography microanalysis under reflected light of polished particles (ASTM standard methods for coal analysis: D2797, D2798, D2799). Historic coal coking, coal gasification, and coal shipping operations are believed to be the source of this material (*30*). The sediment mass distribution by size and density showed clay and silt comprised about 60% of the sediment by weight and sand particles greater than 63 μm about 35% of the sediment. Thus, the heavy sediment fraction constituted 95% of the sediment by weight, while the light fraction, comprising coal-derived, wood material, and plant debris constituted the remaining 5% of the sediment weight.

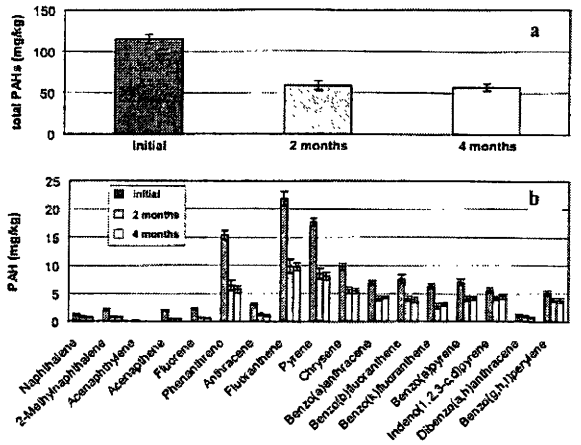

FIGURE 2. Bioslurry treatment results: (a) total PAH concentrations for initial sample, second and fourth month; (b) individual PAH concentrations for initial sample, second and fourth month. There was a 49% reduction of total PAHs by month 2 and a 50% reduction by month 4. Error bars indicate ± 1 SD.

Distribution of PAHs in Sediment. Total PAHs were 115 ± 5.7 mg/kg as determined by Soxhlet extraction and GC/MS analysis of composite samples prior to bioslurry treatment. The distribution of PAHs in whole sediment is shown in Figure 2, among which fluoranthene had the highest concentration at 21.8 mg/kg. Ten of the 17 PAH compounds exceeded either the Wisconsin suggested generic soil cleanup levels (*2*) or the solid waste cleanup levels for the beneficial use of industrial byproducts (*3, 4*), as indicated in Table 1.

The coal-derived/wood material and debris contained 62% of the total PAHs, with 38% of the total PAHs associated with the sand, clay, and silt in the sediment (*15*). Although the clays and silt were the most abundant component in the sediment at about 60 wt %, this size fraction accounted for only about one-third of the total PAHs. A significant observation is that the coal-derived/wood material and debris comprised only 5% of the sediment mass but contained more than three-fifths of the total PAHs. The clay/silt fraction contained about 52 mg/kg total PAHs as compared to as much as several thousand mg/kg total PAHs in the light <63 μm size fraction. Additional analysis involving separation of wood-derived particles from coal in the lighter density fraction showed more than 95% of PAHs in the lighter fraction were associated with coal-derived particles. Thus, we refer to this lighter density fraction as coal-derived in the rest of the paper.

Reduction of PAHs by Bioslurry Treatment. Bioslurry treatment was conducted for 4 months with one reactor sacrificed after 2 months. There was a small amount of reduction of PAHs for the control reactors in which samplings at 2 and 3 months showed average PAH levels of 100 mg/kg as compared to 115 mg/kg initially. This slight decrease in total PAH concentration was judged not significant and was most likely a consequence of the difficulty of sampling representatively from the reactors versus sampling from the initial whole sediment composite prior to filling the reactors.

Average concentrations of total and individual PAHs for the active bioreactors for the initial sample before biotreatment and at months 2 and 4 after biotreatment are shown in Figure 2. No significant change in PAH concentrations occurred between 2 and 4 months of treatment, and thus the

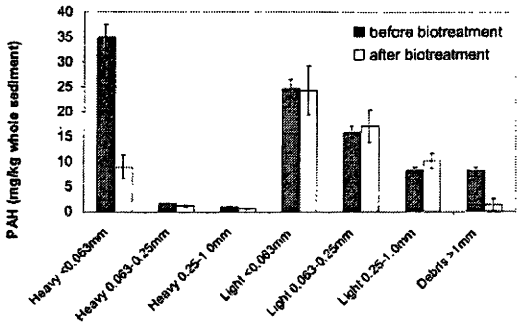

FIGURE 3. PAH reduction in sediment fractions before and after bioslurry treatment. These values are based on the contribution of each fraction to the total PAH concentration of 90 mg/kg as measured by GC-FID. Error bars indicate ± 1 SD based on analysis of four reactors.

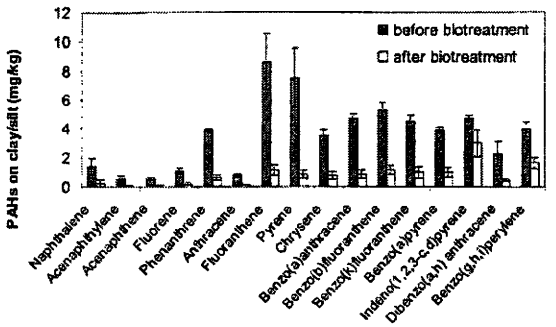

FIGURE 4. PAH concentrations for the Milwaukee CDF clay/silt fraction (heavy, <63 μm) before and after bioslurry treatment. Error bars indicate ± 1 SD based on analysis of four reactors.

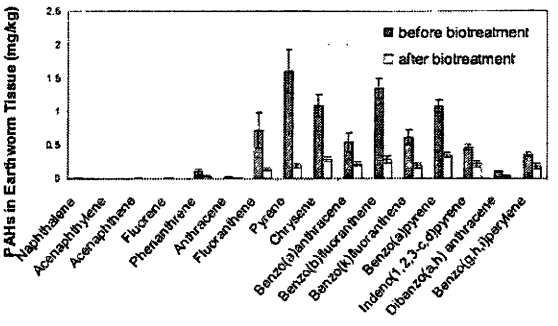

FIGURE 5. Measurement of the bioaccumulation of PAHs by earthworms (*Eisenia fetida*) from Milwaukee CDF sediment before and after biotreatment. Error bars indicate ± 1 SD.

2-month reactor data were included in an overall average for determining final PAH reduction.

The aerobic bioreactors showed a net reduction in total extractable PAH of approximately 50% over the 4-month study from an average of 115 mg/kg to 57 mg/kg. As shown in Figure 2b, all PAH compounds decreased in concentration. The greatest decrease was 64% that occurred for PAHs in the 128–178 MW range, followed by 51% reduction in the 202–228 MW range. The higher molecular mass compounds in the 252–278 MW range showed an average 38% decrease.

A total of 500 g of sediment samples was collected from each of the four bioslurry reactors after 2 or 4 months of treatment to assess PAH biodegradation by examination of sediment particle size and type. Average PAH reductions by size fraction for all reactors are shown in Figure 3, and these data reveal a significant difference in the extent of PAH biodegradation among the sediment particle types. A marked distinction in the biotreatability of PAHs among the heavy and light density fractions was evident. PAH biodegradation was achieved mainly within the <63 μm heavy fraction comprising the clays and silt, for which there was 75% reduction in PAHs. The coal-derived material, which was the principal PAH-containing component in >63 μm to 1 mm size fractions, showed no reduction in PAH concentrations. The apparent reduction in the PAHs in the >1 mm light fraction, which included more friable woody material and debris, is believed to be due attrition rather than biodegradation because the particle mass decreased in this size fraction during bioslurry treatment.

The data in Figure 3 suggest that the PAHs on the <63 μm clay/silt fractions are largely available for biodegradation and that the PAHs on the coal-derived <63 μm to 1 mm size fractions are not available to the microorganisms during bioslurry treatment. The lack of change of PAHs in the coal-derived fraction clearly indicates that the PAHs on this fraction are not bioavailable to the microorganisms. In contrast, data in Figure 4 show for the <63 μm clay/silt fraction that all PAHs monitored in this study were reduced as a result of biotreatment of the sediment. The largest percent reduction (>85%) was achieved for fluoranthene and pyrene, which were the most prominent PAHs in the clay/silt fraction.

Biodegradation Capability of Indigenous Microorganisms. Radiolabeled microcosm studies were performed with material from bioslurry bioreactors to assess whether Milwaukee CDF sediment contained indigenous microorganisms capable of degrading PAHs. These results showed that viable PAH-degrading organisms were present in the sediment throughout the study and that mineralization rates for each of the PAHs examined was greatest at 1 and 2 months.

PLFA analyses revealed that microbial biomass was relatively low in the control reactors averaging less than 8000 total pmol of PLFA g^{-1} through 3 months. Biomass in the active reactors ranged from slightly less than 10 000 total pmol of PLFA g^{-1} initially to almost 50000 total pmol of PLFA g^{-1} at 2 months, decreasing to about 30 000 total pmol of PLFA g^{-1} by 4 months (*31*). Biomass increased during the first 2 months of the study during the time that the total PAH concentration showed a concomitant decrease in concentration. These data provide supporting evidence of a microbial link to the PAH degradation and that the aerobic reactors contained viable PAH-degrading microorganisms.

The DNA analyses of the sediment at the start of the study showed gene encoding enzymes associated with aromatic degradation (naphthalene dioxygenase, biphenyl dioxygenase, catechol 2,3-dioxygenase, toluene monooxygenase, and alkane hydroxylase) were present in copy numbers below the detection limit of the assay (<1 gene copy per gram). By the first and second month of bioslurry treatment, the copy numbers for each of the genes assayed increased to the maximum detectable number—10 000 copies g^{-1}. This correlates strongly to the microbial biomass increase and to the decrease in PAH concentrations. The increase in the copies of these genes and increase in microbial biomass is consistent with observed mineralization response for phenanthrene, pyrene, and chrysene detected in the microcosm studies.

Earthworm Toxicity and Bioaccumulation. Earthworm acute toxicity tests with sediment prior to biotreatment showed a 100% survival rate, indicating that the PAHs present initially in the sediment were not toxic to induce death. Earthworm bioaccumulation tests were performed on sediment before bioslurry treatment and after 4 months of bioslurry treatment. The bioaccumulation results for individual PAHs are shown in Figure 5. These data comprise an average of the results from 192 earthworms exposed to sediment before treatment and 144 earthworms exposed to sediment after 4 months of bioslurry treatment. Each reactor was evaluated in triplicate with 16 earthworms per subsample for extraction and analyses. The uptake of total PAHs in

earthworm tissue from the untreated sediment was 8.1 mg/kg. Earthworm uptake after bioslurry treatment was reduced to 2.0 mg/kg. This represents a 75% reduction in total PAH uptake. Seven PAHs (naphthalene, 2-methylnaphthalene, acenaphthene, fluorene, fluoranthene, pyrene, and benzo-[*b*]fluoranthene) showed reductions in bioaccumulation over 80% as a result of bioslurry treatment. Every PAH showed at least 56% reduction in uptake in the earthworm tissue.

When comparing Figures 4 and 5, a similar trend is apparent. Both the clay/silt fraction (Figure 4) and the earthworm uptake (Figure 5) showed 75% PAH reduction as a result of bioslurry treatment, while the coal-derived fraction showed no reduction in PAHs. Thus, a strong correlation exists between the individual PAHs biodegraded and a beneficial effect on lowered bioaccumulation as measured by earthworm tissue uptake. This observation suggests that only the PAHs in the clay/silt fraction comprise the readily available fraction to both microorganisms and earthworms.

PAH Rate of Release and Availability. The binding and association of PAHs with the silt/clay and coal-derived particles were assessed by PAH rate of release experiments at room temperature, PAH binding activation energy assessments using thermal programmed desorption, and sorbent organic matter characterizations using infrared microspectroscopy.

Desorption kinetic studies were conducted with the whole sediment and separated fractions to investigate the availability of PAHs (*15*). The 100-d desorption kinetic tests with whole sediment showed that approximately 40% of the PAHs were released quickly within about 1 month, while the remaining approximately 60% were strongly bound and not released over 100 d. Thus, approximately 40% of the PAHs in the whole sediment may constitute a readily available fraction. An important finding from tests with separated particles was that the clay/silt and coal-derived fractions showed much different PAH release rates. The PAHs associated with the coal-derived fraction appear strongly bound, as only about 8% of the PAHs in the 63−250 μm coal-derived fraction were released in 100 d. In contrast, desorption data from the clay/silt fraction indicate a higher availability with nearly 80% of the PAHs in this fraction readily desorbing within two months. These trends mirror the results from the bioslurry tests, wherein the majority of the PAHs in the clay/silt fraction apparently are bioavailable and degraded in comparison to the coal-derived material. The majority of the PAHs in the coal-derived material apparently are not bioavailable during bioslurry treatment nor desorbed in long-term tests. Thus, a supposition from these data is that the majority of the PAHs associated with the coal-derived particles may not be bioavailable for degradation nor exhibit a highly toxic response as inferred from the bioslurry and bioaccumulation tests.

Thermal Programmed Desorption Analysis of PAH Release from Untreated Sediment. The thermodynamics of the desorption process for the <63 μm clay/silt fraction and the 63−250 μm coal-derived fraction was investigated by the effect of temperature on PAH desorption, as measured by thermal programmed desorption MS. Room temperature desorption data for individual PAH mass homologues was used to determine the fast and slow desorbing PAH fraction and the respective apparent first-order or effective diffusive rate for four PAH mass homologues in each particle class (*14*). The effect of temperature on the desorption rate was modeled as an activated first-order or diffusion process with the activation energy determined by fitting the thermal programmed desorption data. These results showed that the coal-derived and clay/silt particles had much different PAH desorption activation energies. PAH binding with the coal-derived particles was associated with high activation energies, i.e., in the range of 115−139 kJ/mol. Activation energy values

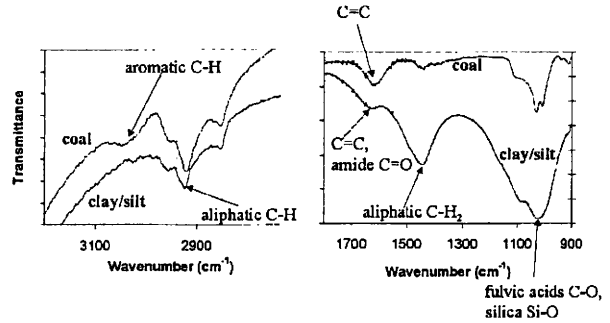

FIGURE 6. Comparison of infrared absorbance spectra of coal-derived particles in sediment and clay/silt particles. The coal-derived particles show higher absorbance of aromatic C−H stretch and a higher absorbance for C=C indicating a much more aromatic nature of the coal−carbon as compared to the organic matter associated with the sediment clay/silt matrix. The clay/silt material also showed higher absorbance for oxygen-containing groups.

greater than 60 kJ/mol may be associated with diffusion through polymeric materials (*32, 33*). In contrast, PAHs associated with the clay/silt material had much lower desorption activation energies, i.e., in the range of 37−41 kJ/mol. Low values of desorption activation energies in the range of 10−50 kJ/mol have been reported for pore diffusion (*33, 34*). TPD analysis of coal-derived particles after bioslurry treatment showed little or no change in response, while TPD analysis of clay/silt particles showed marked decrease in mass ions, consistent with PAH reduction in this fraction.

Infrared Analysis of Sorbent Organic Matter. Infrared (IR) absorption analysis investigated the differences in organic matter character between the two primary classes of sediment particle types in the Milwaukee Harbor sediment. Separated clay/silt particles and coal-derived particles from the sediment were ground and mixed with KBr to form a pellet for transmission IR analysis. As shown in Figure 6, the IR absorption spectra of the coal-derived particles and the clay/silt particles have marked differences. The coal-derived particles show a higher absorbance of aromatic C−H stretching vibrations and C=C stretching vibrations indicating a much more aromatic nature of the coal−carbon as compared to the organic matter associated with the sediment clay/silt matrix. The clay/silt material also showed higher IR absorbance associated with oxygen-containing groups and aliphatic $C-H_2$ bending vibrations. Thus, the coal-derived particles are more aromatic and nonpolar and provide a substrate that is more conducive to the binding of the highly aromatic PAH molecules. For example, it has been shown that carbon-normalized partition coefficients (K_{oc}) of phenanthrene and TCE for highly aromatic sorbents such as soot and coal are 2−3 orders of magnitude higher as compared to that for natural organic matter (*35−37*). The differences in release rates and desorption activation energies of PAHs may thus be attributed to fundamental differences in the organic matter to which the PAHs are bound. These characteristics are then manifested in larger-scale phenomena of PAH biodegradability and bioaccumulation.

Relevance to Sediment Management. We show in this work that the PAHs associated with the fine clay/silt fraction are potentially the PAH contaminants of greatest concern. PAHs associated with the clay/silt fraction comprise about one-third of the total PAHs in this sediment, and this is the PAH fraction that is much more mobile and biodegradable, and if reduced in total mass results in substantial improvement with respect to earthworm bioaccumulation. In contrast, PAHs associated with coal-derived materials are much less available, not biotreatable, and apparently are not significant with respect to bioaccumulation by earthworms. Thus, an hypothesis from our work is that PAHs in the coal-

derived fraction are potentially much less of a concern for protection of the environment, even though the PAHs in this fraction comprise the majority of the PAHs in the sediment. Consequently, decisions about dredged sediment quality criteria and treatment and material reuse should focus on the PAHs associated with the available fraction, which in this case comprises those PAHs in clays and silt. Determining which sediments pose greatest risk and which do not is of greatest concern in deciding whether sediments need active management. The work presented here provides support for the hypothesis that total concentrations of a particular hydrophobic organic contaminant in sediment does not translate directly to risk.

The approach presented in this work, which included both particle-scale mechanistic characterizations and larger-scale bioassay tests, provides a framework to improve decision-making regarding the management and treatment of PAH-impacted sediments. We demonstrate that PAH behavior at the particle-scale is relevant to understanding larger-scale phenomena of PAH contaminant availability and bioaccumulation. By recognizing that both labile and residual fractions of PAH contamination may exist and that these fractions are associated with identifiable sediment components, it is possible to justify treatments that focus on the fraction of concern. This will increase the likelihood for reuse of dredged and deposited sediment and suggest alternatives for in situ management, while being protective of the environment.

Some suggestions on how the new knowledge in this study might be applied include the following. Biotreatment to a low bioavailability end point may be a reasonable objective. An intensive treatment process to separate the high- and low-risk sediment fractions might be economical in some instances. Addition of coal-derived carbon to sediments as a treatment approach may promote in situ stabilization of organic contaminants. More broadly, using information from this work to understand and explain low bioavailability of PAHs and other hydrophobic organic contaminants in sediments and perhaps to justify low-intensity management approaches will be an important benefit.

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Suspended Solids, Trace Metal and PAH Concentrations and Loadings from Coal Pile Runoff to Hamilton Harbour, Ontario

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ABSTRACT. *The Kenilworth boatslip has been identified as a "hotspot" within the Hamilton Harbour Area of Concern because of highly contaminated bottom sediments. There are a variety of sources potentially contributing to this sediment contamination, including runoff from industrial coal piles. The objective of this study was to assess the contaminant characteristics associated with coal pile runoff and identify potential impacts that the runoff might have on sediment quality. Flow-proportioned samples of the coal pile runoff were collected from June through October, 1996 and analyzed for total suspended solids, trace metals, and PAHs. Loadings for selected metals and PAHs were determined using a volumetric approach that considered mean contaminant concentrations and measured or modeled flow volumes. The suspended solids and total trace metal concentrations (Al, Fe, Mn, V, Cd, Cr, Cu, Pb, Zn) often exceeded Canadian Water Quality Guidelines for the Protection of Aquatic Life. Concentrations of fluoranthene, phenanthrene, pyrene, and chrysene exceeded the provincial "Severe Effect Level" for sediment, although the bioavailability of these PAHs should be examined more thoroughly. In general, suspended solids concentration and coal pile volume were significantly correlated with the concentrations of trace metals in the coal pile runoff, while hydrometeorologic variables such as rainfall intensity, rainfall depth, and runoff volume were weakly correlated with metals concentrations. The ratios of various PAHs to naphthalene suggested that coal pile runoff could be an important contributing source to bed sediment contamination. Given the concentrations and loadings of solids, metals, and PAHs and the relatively low volume of runoff, it would be prudent to treat the coal pile discharge as a remedial action for the harbor.*

INDEX WORDS: *Hamilton Harbour, suspended sediment, trace metals, polynuclear aromatic hydrocarbons (PAHs), coal pile runoff, Severe Effect Level (SEL).*

INTRODUCTION

Hamilton Harbour, Ontario, is a recreational and industrial port primarily characterized by steel manufacturing and steel related industries which occupy the southern shore of the harbor. It is one of 42 Areas of Concern (AOCs) around the Great Lakes designated by the International Joint Commission (IJC) because of environmental impairments. Impairments identified include: loss of fisheries and wildlife habitat, restrictions on fish consumption,

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fish tumors and other deformities, beach closings, interference with drinking water, high concentrations of trace metal and organic compounds in bottom sediment, degradation of benthos, and exceedances of water and sediment quality criteria (International Joint Commission [IJC] 1989, Murphy *et al.* 1991, Ling *et al.* 1993, Remedial Action Plan [RAP] 1992, Diamond and Ling-Lamprecht 1996, Poulton *et al.* 1996). Inputs of suspended solids, trace metals and organic compounds from several industrial discharge sites contribute to these impairments (Murphy *et al.* 1991, Poulton *et al.* 1996). One source of suspended solids, trace metals and organic compounds is stormwater runoff from coal piles (Anderson and Youngstrom 1976, Davis and Boegly 1981). In 1995, 2.5 million metric tons of coal were shipped to industries within Hamilton Harbour (Statistics Canada 1997). This coal was stockpiled on open industrial property that can drain directly to the harbor, untreated. One of the areas in the harbor that receives untreated coal pile runoff is the Kenilworth boatslip.

High concentrations of suspended solids can produce adverse effects on receiving waters and aquatic biota (Scullion and Edwards 1980, Canadian Council of Resource and Environment Ministers 1993, Waters 1995). The Canadian Council of Resource and Environment Ministers (1993) mandated that for the protection of aquatic life, total suspended solids concentrations entering a waterbody should not exceed 10 mg/L when the background suspended solids concentration is $\leq$ 100 mg/L. Irvine *et al.* (1997) indicated that the ambient suspended solids concentration within the Kenilworth boatslip was in the range of 5 mg/L. Coal pile runoff studies performed by Cox *et al.* (1977) yielded mean suspended solids concentrations ranging from 190 mg/L to 650 mg/L, suggesting that the suspended solids concentrations entering the Kenilworth boatslip from coal pile runoff could be several times higher than the acceptable level established by the Canadian Council of Resource and Environment Ministers (1993). Stahl and Davis (1984) indicated that higher sulfur content coal yielded higher suspended solids concentrations within the runoff and that suspended solids concentrations increased with successive leaching events because of prolonged microbial-mediation which degraded sulphur compounds within the coal pile system.

Trace metal concentrations in coal pile runoff have been well documented through leaching simulations (Anderson and Youngstrom 1976, Davis and Boegly 1981) and in most cases concentrations exceeded guidelines established by the Canadian Council of Resource and Environment Ministers (1993). However, it has been argued that coal stockpiled at industrial sites generally receives less rain per kilogram weight compared to simulations, resulting in the overestimation of naturally leached trace metal concentrations (Davis and Boegly 1981, Stahl and Davis 1984). Concentrations of trace metals (e.g., Fe, Zn, Pb, As, Cu, Al) when leached, can be acutely toxic to biota in receiving waterbodies and cause chronic disorders in aquatic life (Wong *et al.* 1978, Scullion and Edwards 1980, Canadian Council of Resource and Environment Ministers 1993).

Relatively little is known about the characteristics of organic material leached from coal piles. The few rainfall simulation studies which do exist neither adequately describe changes that might occur in the organic content of coal during weathering nor characterize the leaching of coals in a field environment (Stahl *et al.* 1984, Fendinger *et al.* 1989). In a study performed by Fendinger *et al.* (1989), it was demonstrated that organic material in coal pile runoff was dominated by aliphatic hydrocarbons, while the concentrations of aromatic hydrocarbons were dependent upon the organic content of the coal. Stahl *et al.* (1984) indicated that PAH concentrations in runoff generally were low (50 μg/L), probably because of their low solubility in water. However, Fendinger *et al.* (1989) observed that PAHs and the suspended solids fraction in coal pile runoff were positively related. They also observed that the highest PAH concentrations occurred during the "first flush" of the event when the concentrations of suspended solids in the runoff were highest. Guidelines for PAHs in water systems have not been developed because of the complex chemistry and large number of different PAH compounds (Canadian Council of Resource and Environment Ministers 1993), but guidelines for PAHs in sediment have been established (Ontario Ministry of Environment and Energy [MOEE] 1993). Several studies have documented the potential negative impacts of PAHs on receiving waterbodies (Black 1983, Fabacher *et al.* 1988, Krantzberg and Boyd 1992, Catallo *et al.* 1995).

This study is a source evaluation of coal pile runoff discharged from an industrial coal field to the Kenilworth boatslip, Hamilton Harbour. The Kenilworth boatslip has been identified as a "hotspot" within Hamilton Harbour because of highly contaminated bottom sediments (Murphy *et*

al. 1995). Contaminated sediment remediation increasingly has been considered a viable option to improve conditions of aquatic ecosystems such as the Kenilworth boatslip (Murphy *et al.* 1995). However, to determine the success of such treatment, an understanding of contaminant loads to the proposed remediation site is necessary. Also, a better understanding of the factors influencing coal pile runoff may result in the development of strategies that can reduce runoff volume and/or contaminant loads before they migrate from the site. This study had several objectives. First, to document suspended solids, trace metals, and PAH concentrations and loadings in coal pile runoff that discharged to the Kenilworth boatslip. Contaminant concentrations were compared to established water and sediment quality guidelines to evaluate the potential impact of the discharge on aquatic biota. Second, to quantitatively evaluate the relationships between trace metals and other factors (rainfall and runoff characteristics, coal pile characteristics) to increase an understanding of contaminant input dynamics from coal piles to Hamilton Harbour. Finally, PAH ratios were compared in coal pile runoff to ratios in Hamilton Harbour bed sediments to assess relative source signatures.

METHODS

Sampling Methods

The study area was a 19,150 m^2 outdoor industrial coal storage field at a steel manufacturing facility in Hamilton, Ontario. It contained several large coal piles, which continually changed size as coal was added and/or removed. A tile system drained infiltrated and surface runoff from the coal piles and discharged it directly to the Kenilworth boatslip. An on-site gauging station was located at the discharge point to the boatslip and the coal pile runoff rate was recorded continuously as part of the MOEE Municipal and Industrial Strategy for Abatement (MISA) program.

For this study, flow measurements were recorded in the discharge flume at 15 minute intervals between 1 April 1996, and 31 October 1996, using a Badger Meter Series 2000 Obstructionless No-Loss Flowmeter. The Badger flowmeter was used to trigger an American Sigma Streamline 700 Portable Sampler to collect samples for runoff quality analysis. The pump sampler was connected to the flowmeter control panel from 1 June 1996, to 31 October 1996. The pump sampler was programmed to take a 200 mL sample from the discharge flume at a flow interval of 10 m^3. All 200 mL samples were collected in a clean 10 L glass bottle as a flow-proportioned composite sample. The flow-proportioned composite sample was removed from the field as soon as possible (normally within 5 hours) after the end of each runoff event. The composite samples were analyzed for suspended solids, trace metal, PAH, particulate organic carbon and dissolved organic carbon concentrations. Rainfall data between 1 April 1996 and 31 October 1996 were obtained from Environment Canada site 3525B YHM 6153194-153 ONT HAMILTON A located approximately 10.5 km southwest of the boatslip.

Laboratory Methods

Suspended solids concentrations were determined by filtering a 100 mL sub-sample of the composite sample onto a preweighed 0.45 μm Millipore filter. After filtration, the filter was dried at 104°C for 1 h to remove moisture and then reweighed to determine the suspended solids concentration (American Public Health Association 1985).

Two 250 mL sub-samples were collected in the laboratory from the flow-proportioned composite sample and processed for total and dissolved trace metal concentrations. The samples for the dissolved phase analysis were passed through 0.45 μm Sartorius filters and fixed with 1 mL (1:1) Seastar nitric acid, while the samples for total metals analysis were fixed with 1 mL (1:1) Seastar nitric acid without filtration (Droppo and Jaskot 1995). Trace metal analysis was performed by the National Laboratory for Environmental Testing (NLET) using inductively coupled argon plasma (ICAP) following Environment Canada Method 02-2001(Environment Canada 1994). All samples (filtered and unfiltered) were concentrated 10 times and digested using nitric acid. An analytical run normally consisted of 60 to 80 samples, 3 to 4 spiked samples, 2 spiked blanks, 4 method blanks, a control standard, 2 reference samples, 2 reference duplicate samples, 2 certified reference and 2 ASTM Type I grade reagent water samples to ensure no contamination. The certified references were TM-21 and TM-22, obtained from the National Water Research Institute, and NIST-certified Water Reference Material 1643C.

For quality assurance/quality control purposes, the calibration blank and verification standard were run after system calibration and thereafter at a rate of approximately every 11 samples. If the deviation of the calibration blank was greater than twice the

method detection limit (MDL) and/or the verification standard was greater than ± 5% from the theoretical mean, corrective measures were taken. The accuracy of the analytical method was expressed as a per cent error between the measured and certified value for the certified reference material. The per cent error typically was less than 10% for all metals. Spike recoveries were sample dependent and usually ranged from 95% for Cd to 109% for Al. The MDLs were: 0.0001 mg/L for Cd, Mn, V; 0.0002 mg/L for Cr, Cu, Ni, Pb, Zn; 0.0004 mg/L for Fe; and 0.002 mg/L for Al.

Following the removal of the 500 mL for metals analysis, the remaining volume of selected flow-proportioned samples was submitted immediately to Wastewater Technology International (WTI), Burlington, Ontario, for PAH analysis. Each sample was filtered through Whatman Grade #1 filter paper to separate the particulates from the water. The filtered particulates were analyzed directly and henceforth the results are referred to as the particulate phase PAHs, while the PAHs in the filtrate are referred to as the dissolved phase PAHs.

Analysis of the dissolved phase PAHs was adapted from U.S. EPA Method 624 (U.S. EPA 1984). Briefly, a 1 L sample was spiked with a surrogate mixture and serially extracted three times with dichloromethane under basic conditions. The combined extracts were dried over sodium sulphate. The solvent was evaporated from the extract to a final volume of 3 mL. The extract was then combined with an internal standard and analysed by gas chromatography-mass spectrometry (GC/MS). The GC/MS system was calibrated just prior to the start of each analytical run and the calibration was verified after each batch of five samples.

For QA/QC purposes with each GC/MS run of five samples a solvent blank (dichloromethane), duplicate (a random sample was divided into two equal halves and extracted separately), a method blank and a spike were done. The spike involved dividing a sample in two, with one half being spiked with six PAH surrogates and the other half being spiked with the PAH surrogates and 0.25 ml of PAH Supelpreme Target PAH mix (200 mg/L).

The analysis of the particulate phase for PAHs was adapted from U.S. EPA Method 8270 (U.S. EPA 1994). The sediment was spiked with six PAH surrogates and then Soxhlet-extracted with an acetone-hexane (59:41) mix. The extract was base-partitioned with 2% potassium bicarbonate solution. The aqueous medium was then back-extracted with hexane and the organic fractions combined. The combined organic extract was dried through sodium sulphate and concentrated for analysis by GC/MS as described previously.

The QA/QC approach for the particulate phase was similar to that of the dissolved phase. In addition to the solvent blank, method blank, duplicate and spike analyses, however, a certified sediment reference material (EC-4 or EC-1, obtained from the National Water Research Institute) was run with each batch of samples. The surrogate spike recovery for all sample batch runs (particulate and dissolved phase) averaged between 72% for naphthalene-d_8 and 88% for fluorene-d_{10}. The results of the method blank analyses for both the particulate and dissolved phases always were below the MDL for each PAH.

The same 1 L sub-sample processed for PAH concentrations also was analysed for particulate organic carbon (POC) and dissolved organic carbon (DOC). The analyses were performed by NLET using POC method 01-1090 and DOC method 01-1020 (Environment Canada 1994).

Statistical Methods

A stepwise multiple regression approach was used to estimate flow volumes for storms not sampled (because of instrument malfunction) in order to calculate suspended solids, trace metals and PAH loads entering the Kenilworth boatslip during the 7-month study period. For each measured storm event the total rainfall depth (mm), peak 15 minute rainfall intensity (mm/h), peak 1 h rainfall intensity (mm/h), antecedent hours and coal pile volume (metric tons) prior to a rainfall event were entered into the analysis as the predictor variables. Event runoff volume (m^3) from the coal field was the dependent variable. In this study a rainfall event was defined as any storm which yielded rainfall 9 mm or greater, or was greater than 12 h in duration, as such storms were observed to result in sufficient runoff volume to initiate sampling. Pearson product-moment correlation (r) was used to compare the relationship between total metal concentrations and factors possibly influencing metals concentrations in the coal pile runoff (total rainfall depth (mm); peak 15 minute rainfall intensity (mm/hr); peak 1 h rainfall intensity (mm/hr); runoff volume (m^3); antecedent number of days before the runoff event; coal pile volume (metric tons); and suspended solids concentration (mg/L)).

The distributions of all variables used in the statistical evaluations were tested for normality using

the probability plot correlation coefficient test (Filliben 1975, Vogel 1986). Qualitatively, the normal probability plots approximated a straight line, which is indicative of a normal distribution (Ryan *et al.* 1992). However, the correlations (r) between the normal scores and the raw data typically were in the 0.7 to 0.8 range, which indicates the distributions were not normally distributed at $\alpha = 0.05$. Tests using the t-distribution are, however, relatively insensitive to moderate departures from normality (Mendenhall 1979, Ryan 1990).

Loading Estimate Methods

Suspended solids, trace metals, and PAH loads were calculated using a simple volumetric approach often used to estimate contaminant loads from urban sources (e.g., Marsalek and Ng 1989, Nix 1990, Irvine *et al.* 1993, Irvine *et al.* 1998). Estimated contaminant loads were calculated using the equation:

$$L_j = C_j \bullet V \qquad (1)$$

where L_j is the load of pollutant, j; C_j is the mean concentration of pollutant, j; and V is the estimated total runoff volume from the coal piles for the field season; $V = \Sigma Q_i$ when Q_i is the event runoff volume.

RESULTS

Concentrations of Suspended Solids, Trace Metals, and PAHs

During the sampling period 32 rainstorms occurred and flow volume was recorded successfully for 17 of these events. Flow-proportioned composite samples from these 17 events were collected for suspended solids analysis. The mean suspended solids concentration representing the 17 storms was 2,188 mg/L, with a standard deviation of 3,402 mg/L.

Fifteen of the 17 storm events were analysed for total and dissolved phase trace metal concentrations. The mean and standard deviation for selected total trace metals are compared to Canadian Water Quality Guidelines in Table 1. Results for the dissolved phase of some metals (Al, Cd, Cu, Pb) were below the MDL in some samples. Therefore, mean values had to be estimated from a censored data set, which was not the case for the total metals results in Table 1 (the total metals results always were above MDL). Various methods for estimating the mean of a censored data set have been proposed (Newman *et al.* 1989, El-Shaarawi and Dolan 1989, Dolan and El-Shaarawi 1991). Often, however, a value of one-half the MDL is used to calculate the mean and this approach was taken in this study. The mean concentrations for the dissolved phase were (in mg/L): Al-0.056; Cd-0.00013; Cr-0.0025; Cu-0.001; Fe-0.64; Mn-0.94; Ni-0.024; Pb-0.0004; V-11.1; Zn-0.014.

Four storm events were sampled for particulate phase PAH concentrations and six storm events for dissolved phase PAH concentrations. The mean concentrations for selected PAHs are compared to guideline levels in Table 2. The PAHs shown in Table 2 were selected for illustrative purposes and represent PAHs that commonly are reported in the literature. Ontario Ministry of the Environment and Energy (1993) concentrations for particulate phase PAHs were normalized for direct comparison using the recorded total organic carbon content (determined by summing the particulate and dissolved phase organic carbon contents measured in the field samples), following the method of MOEE (1993). Polynuclear aromatic hydrocarbons with particularly high concentrations were fluoranthene, phenanthrene, pyrene and chrysene which exceeded

TABLE 1. Selected mean (total) trace metal concentrations.

	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
Mean	3.2	0.0019	0.024	0.035	15.5	1.3	0.05	0.022	15.55	0.28
S.D.	3.4	0.0015	0.024	0.028	14.4	0.5	0.03	0.018	16.76	0.3
CWQG	0.1	0.0018	0.02	0.004	0.3	N.S.	0.15	0.007	N.S.	0.03

#— total trace metal concentrations (mg/L); n = 15
S.D.— standard deviation
CWQG—Canadian Water Quality Guideline for Protection of Aquatic Life; N.S.- no standard

TABLE 2. Selected mean polynuclear aromatic hydrocarbon (PAH) concentrations.

	Fluoranthene	Phenanthrene	Benzo(a)pyrene	Pyrene	Chrysene
Mean	208.2	284.3	71	139.9	46.6
	(4.5)	(6.1)	(0.9)	(3.1)	(0.7)
S.D.	254.3	338.5	85.4	173.2	48.7
	(2.1)	(3.3)	(0.2)	(1.4)	(0.2)
MOEE Guideline	102	95	144	85	46

#—particulate bound PAH concentrations (g/g); n = 4
(#)—dissolved PAH concentrations (g/L); n = 6
NOTE—Ministry of the Environment and Energy [MOEE] guideline for particulate bound PAHs

TABLE 3. Selected trace metal loads.

	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
g*	30,966	18	238	340	150,018	12,621	477	213	150,640	2,720
	(897)	(2)	(25)	(20)	(6,237)	(9,128)	(233)	(12)	(107,173)	(132)
g/d	144.7	0.1	1.1	1.6	701.1	59.0	2.2	1.0	703.9	12.7
	(4.2)	(0.01)	(0.11)	(0.09)	(29.1)	(42.7)	(1.1)	(0.1)	(500.8)	(0.6)

#—total trace metal loads
(#)—dissolved trace metal loads
* mass discharged during study period (1 April 1996, to 31 October 1996)

the MOEE "Severe Effect Level" (SEL) for particulate phase PAHs.

Estimated Runoff Volume

The stepwise regression indicated that event rainfall depth (mm) and coal pile volume (metric tons) were the two most influential predictors and the resulting equation was:

$$\text{Flow Volume} = 125.2 + 22.4 \cdot (\text{rainfall depth}) - 0.00076 \cdot (\text{coal pile volume}) \quad (2)$$

where the r^2 was 0.74, the standard error of the estimate (σ) was 180, and rainfall depth and coal pile volume were significant at the 0.001 and 0.025 levels, respectively.

Combining the observed runoff volume for the 17 sampled storm events with runoff volume of the 15 storm events estimated using equation 2, the total coal field runoff volume for the 32 storm events between 1 April 1996, and 31 October 1996, was 9,690 m^3. This runoff represented approximately 96% of the rainfall depth falling on the coal field site during that period. The remaining 4% of the rainfall would be partitioned between evaporation, storage within the piles, or overland flow from areas near the shoreline (and bypassing the tile drains). The unmeasured overland flow therefore would produce a minimal effect on the loading estimates.

Suspended Solids, Trace Metal, and PAH Loading Estimates

Loading estimates of suspended solids, trace metals and PAHs entering the boatslip from coal pile runoff were calculated according to equation 1. The suspended solids load entering the boatslip from the coal field during the study period (1 April 1996, to 31 October 1996) was 21,202 kg (or 99 kg/d). Trace metal and PAH loading estimates are presented in Tables 3 and 4, respectively.

Metals Correlations

Table 5 presents the correlation results between total metals concentrations observed during runoff events and factors that may affect these metals concentrations. There was a significant positive correlation ($\alpha = 0.05$) for all metals concentrations (except V) and suspended solids concentration. The relationships between total metals concentrations and other variables were weaker. After suspended

TABLE 4. Selected polynuclear aromatic hydrocarbon (PAH) loads.

	Fluoranthene	Phenanthrene	Benzo(a)pyrene	Pyrene	Chrysene
g*	4,413 (44)	6,027 (59)	1,505 (7)	2,965 (30)	988 (7)
g/d	20.6 (0.20)	28.2 (0.27)	7 (0.04)	13.9 (0.14)	4.6 (0.03)

#—particulate bound PAH loads
(#)—dissolved PAH loads
* mass discharged during study period (1 April 1996, to 31 October 1996)

TABLE 5. Correlation (r) matrix of total trace metal concentrations and runoff factors.

Variable	Al	Cd	Cr	Cu	Fe	Ni	Pb	V	Zn
Total Rainfall Depth (mm)	–0.358	–0.425	–0.31	–0.361	–0.405	–0.057	–0.423	–0.317	–0.336
Peak 15 min. Rainfall (mm/hr)	0.238	**0.56**	0.467	0.312	0.422	0.281	0.326	0.314	0.347
Peak 1 h Rainfall (mm/hr)	0.03	–0.048	–0.012	0.013	–0.065	–0.08	–0.16	0.007	0.077
Runoff Volume (m^3)	–0.235	–0.282	–0.136	–0.17	–0.203	0.162	–0.21	–0.438	–0.363
Antecedent Days before Runoff Event	–0.291	–0.462	–0.329	–0.476	–0.342	–0.064	–0.356	–0.468	–0.438
Coal Pile Volume (metric tons)	–0.475	**–0.621**	–0.329	**–0.524**	–0.436	0.07	–0.375	**–0.567**	**–0.647**
Suspended Solids Concentration (mg/L)	**0.873**	**0.881**	**0.919**	**0.736**	**0.917**	**0.652**	**0.901**	0.349	**0.879**

Bold face correlations are significant at $\alpha = 0.05$

solids concentration, coal pile volume had the strongest relationship with metals concentrations, the correlation being significant ($\alpha = 0.05$) for four of the nine metals. Peak 15 minute rainfall intensity was the hydrometeorologic variable that had the strongest relationship with metals concentrations, but this relationship was only significant ($\alpha = 0.05$) for one metal.

PAH Ratios

Figure 1 shows the ratios between the various PAHs analyzed in this study and naphthalene (NaP). A variety of studies have used PAH ratios in bed sediment as a semi-quantitative indicator of source (Furlong *et al.* 1988, Zhang *et al.* 1993, Benner *et al.* 1995), because the exact source(s) often may not be known. More sophisticated statistical/receptor modeling also has been applied recently to help source-apportion PAHs in sediments (Christensen *et al.* 1997, Sharma *et al.* 1997). The receptor modeling approach was not needed in this study since it was possible to determine PAH ratios for a well-known source (coal pile runoff). The calculated ratios can be used as a benchmark to assist future sediment studies in Hamilton Harbour and other areas in evaluating possible sources. The PAH ratios for coal pile runoff also are compared with those for coal tar, coal and wood gasification, highway dust, and air filter coke oven emissions in Figure 1. In Figure 2, the ratios for the coal pile runoff are compared to the PAH ratios for coal tar

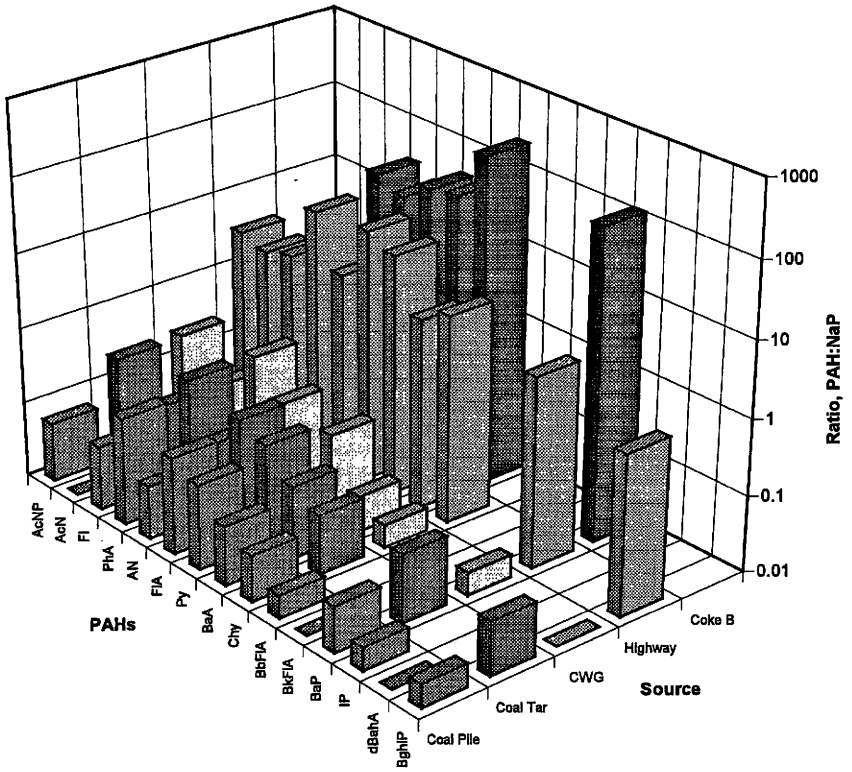

FIG. 1. Ratios of mean particulate phase PAHs in the coal pile runoff samples (n = 4) to NaP. Also shown are ratios of PAHs to NaP for other sources as reported by Christensen et al. *(1997). Abbreviations are: naphthalene (NaP), acenaphthylene (AcNP), acenaphthene (AcN), fluorene (Fl), phenanthrene (PhA), anthracene (AN), fluoranthene (Fla), pyrene (Py), benzo(a)anthracene (BaA), chrysene (Chy), benzo(b)fluoranthene (BbFlA), benzo(k)fluoranthene (BkFlA), benzo(a)pyrene (BaP), indeno(1,2,3-c,d)pyrene (IP), dibenzo(a,h)anthracene (dBahA), and benzo(g,h,i)perylene (BghiP); coal and wood gasification (CWG), highway dust (highway), and air filter coke oven emissions (Coke B).*

contaminated sediment from Hamilton Harbour as reported by Murphy *et al.* 1991.

DISCUSSION

The mean suspended solids concentration of 2,188 mg/L observed in the coal pile runoff exceeded the Canadian Water Quality Guideline of 10 mg/L (based on ambient suspended solids concentration being ≤ 100 mg/L). Ling *et al.* (1993), in summarizing MOEE data, reported an ambient suspended solids concentration of 10 mg/L for the entire harbor, which is comparable to the 5 mg/L level reported by Irvine *et al.* (1997) for the Kenilworth boatslip. High concentrations of suspended solids, as noted previously, can have a negative impact on aquatic biota, including fishes.

Several trace metals within coal pile runoff exceeded Canadian Water Quality Guidelines, which is consistent with results documented by Cox *et al.* (1977) and Davis and Boegly (1981). Total trace metal concentrations observed in this study may be chronically toxic to aquatic organisms at various trophic levels (Warnick and Bell 1969, Wong *et al.* 1978, Krantzberg and Boyd 1992) but would not be high enough to cause lethal effects to several aquatic insects and fish species (Warnick and Bell

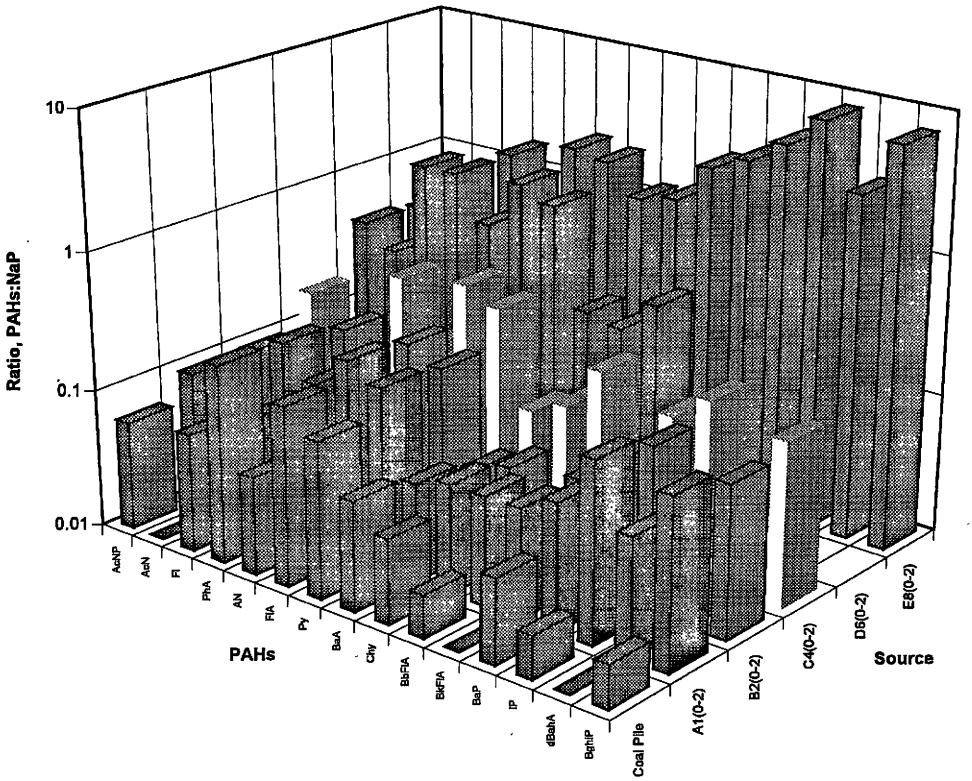

FIG. 2. Ratios of mean particulate phase PAHs in the coal pile runoff samples to NaP. Also shown are the ratios for bed sediment samples from Hamilton Harbour reported by Murphy et al. *(1991). For a discussion of the bed sediment samples, see text.*

1969), although higher concentrations may be associated with individual runoff events.

Diamond and Ling-Lamprecht (1996) summarized metal loading estimates to the entire harbor that were contained in various government reports. Metal loads from the coal pile site were less than 1% of the loads from the sewage treatment plants or direct industrial (cooling water) discharges. This comparison does not include discharges from other coal fields in the harbor, but in a general mass balance framework for the entire harbor, the monitored coal pile site could be viewed as a relatively small source of metals. Given the elevated concentrations, however, there is potential for localized habitat impact in the boatslip.

The correlation analysis (Table 5) indicated that the strongest relationship existed between total metal concentrations and suspended solids concentrations in the runoff. This is not surprising since many metals have an affinity for particles (Allen 1986, Karlsson *et al.* 1987, Droppo and Jaskot 1995). A negative relationship was found between total metal concentrations and coal pile volume (significant at $\alpha = 0.05$ for Cd, Cu, V, and Zn). This may be reflective of the larger coal piles possessing structural characteristics conducive to infiltration and storage (fresh, less compacted, with a minimal surface seal). No significant relationships were found between metals concentrations and total rainfall depth, peak 1 h rainfall intensity, flow volume, or number of antecedent days before a runoff event. In general, the strongest relationship between metals concentrations and a hydrometeorologic variable was observed for the peak 15 minute rainfall intensity. This is consistent with soil erosion research that has shown higher intensity rainfall over a short period of time influences particulate erosion rates (Wischmeier and Smith 1958, Foster *et al.* 1982, James and Irvine 1992). As noted previously, there was a significant relationship between metals

concentrations and suspended solids, so it is reasonable that the metals concentrations also would be correlated with a variable that can influence suspended solids concentrations.

Ontario Ministry of the Environment and Energy (1993) guidelines indicated that PAH concentrations observed in the particulate phase of coal pile runoff may produce severe impairments to the receiving waters of the Kenilworth boatslip. In this study it was observed that PAH concentrations associated with suspended solids in some cases (chrysene) were similar to those documented by Fendinger *et al.* (1989), but for others the results reported here were up to two orders of magnitude higher. The results were more similar to PAH concentrations found in bottom sediments collected in an effluent channel from a coking plant, as reported by Griest (1980) and for coal tar as presented by Christensen *et al.* (1997). The differences in these results as compared to Fendinger *et al.* (1989) may be related to several factors, including the age and weathering of the coal used in the experiments, the general PAH concentrations associated with different coals, and the experimental design (including field and analytical methods). The dissolved phase PAH concentrations were similar to those documented by Stahl *et al.* (1984), but again were higher than those reported by Fendinger *et al.* (1989).

While there are several environmental factors that can affect the particulate to dissolved phase partitioning, PAHs often are more associated with the particulate phase because of their nonpolar nature and general low solubility in water (Allen 1986, Hemond and Fechner 1994). For example, Griest (1980) reported that PAH concentrations in the bed sediment of the effluent channel from a coking plant were three to four orders of magnitude higher than concentrations in the overlying water. Data from Fendinger *et al.* (1989) and this study (Table 2) also indicated that PAH concentrations associated with the particulate phase of coal pile runoff were orders of magnitude greater than those in the dissolved phase.

Although PAHs may not be acutely lethal to aquatic organisms, these organic compounds may produce chronic effects such as cellular abnormalities, fin and gill erosion, and liver, pancreatic, testes, and eye-lens diameter alterations in fish, suppression of benthic organism diversity and alteration of bacterial and aquatic plant communities (Hass and Applegate 1975, Payne 1978, Black 1983, Fabacher *et al.* 1988, Murphy *et al.* 1991). As an added complexity, however, it may be possible that the concentration of PAHs associated with coal particles could exceed MOEE guidelines, but they may not be bioavailable. It is therefore possible that the concentrations of PAHs observed in the sediment fraction of coal pile runoff may have less impact upon the aquatic biota than the MOEE guidelines would suggest (Carlson *et al.* 1979, Bender *et al.* 1987, Chapman *et al.* 1996). More specific testing on the bioavailability of PAHs in coal pile runoff to Hamilton Harbour should be done.

In this study, the ratios of various PAHs to NaP in the coal pile runoff were most similar to the ratios reported for coal tar, and coal and wood gasification (Fig. 1). Murphy *et al.* (1991) reported concentrations of various PAHs for bed sediment in an area of Hamilton Harbour that was impacted by runoff from a different coal field than the one sampled in this study. The PAH to NaP ratios for the upper 2 cm of sediments are shown in Figure 2. Samples Mur A1(0–2), B2(0–2), and C4(0–2) exhibited ratios more similar to the coal pile runoff ratios than samples Mur D6(0–2) and E8(0–2). Murphy *et al.* (1991) described samples Mur A1(0–2), B2(0–2), and C4(0–2) as being solid, shiny, dark black (tarry), while samples Mur D6(0–2) and E8(0–2) were described as having streaks of shiny, dark black. The former three samples were located adjacent to the coal pile discharge pipe, while the latter two samples were located further from the pipe. Other sources therefore may have contributed to samples Mur D6(0–2) and E8(0–2), as reflected by their different signature. A subsequent study performed by Murphy *et al.* (1995) also indicated that sediments within the Kenilworth boatslip were highly contaminated with coal tar. The most contaminated of these sediments were located adjacent to industry outfall pipes, and in particular, the coal pile discharge pipe discussed in this study. Figure 2 suggests that coal pile runoff may be an important source of PAH contamination for some areas of Hamilton Harbour.

Diamond and Ling-Lamprecht (1996) indicated that there was relatively little information regarding PAH loadings to the harbor, with the exception of direct industrial discharges for a small number of PAHs. Based on the data presented by Diamond and Ling-Lamprecht (1996), the loading of benzo(a)-pyrene from the coal pile site represents 1.5% of the total industrial loading to the harbor. Although the coal pile loading represents a relatively small percentage of the industrial loading, it appears that coal pile runoff can result in significant localized contamination of bed sediment.

Between 1982 and 1992, 32 to 36 million metric tons of coal per year were shipped across the Great Lakes from U.S. harbors, destined for both U.S. and Canadian ports (Waxmonsky 1992). A survey done by Price *et al.* (1989) indicated that electric power utilities in the basin maintain their coal piles within confined areas, capturing and treating the runoff before discharge to a receiving water body. It is unknown how effective these systems are, or whether docks that temporarily store the coal prior to shipping follow similar treatment procedures. Given the potentially negative impacts of coal pile runoff, a basin-wide survey of coal handling practices and pre-treatment of discharges should be conducted.

CONCLUSION

This study specifically quantified contaminant concentrations and loadings from an industrial coal field site rather than estimating these values through a laboratory simulation approach as often is done. Therefore, this study avoided the problem of scale and extrapolating results from a laboratory simulation to the field situation.

Coal pile runoff resulted in quantifiable loads of suspended solids, trace metals and PAHs which may produce negative impacts upon the aquatic biota within the receiving waters of the Kenilworth boatslip. Ratios of various PAHs to NaP were similar for coal pile runoff, coal tar, and coal and wood gasification. Furthermore, the ratios were similar for the coal pile runoff and bed sediment in areas receiving coal pile discharge. This indicates that the coal pile signature can be seen in bed sediment and in the absence of runoff data, the environmental history of bed sediment can be effectively reconstructed using ratios reported in the literature.

Measures taken to contain stockpiled coal and treat runoff could be effective in reducing harmful loads of suspended solids, trace metals and PAHs to receiving waters of the Great Lakes basin. This could be particularly true in the local case of the Kenilworth boatslip where the relatively small volume of discharge with high concentrations of particle-bound contaminants might be efficiently treated through construction of some type of settling basin.

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Local Impacts of Coal Mines and Power Plants across Canada. II. Metals, Organics and Toxicity in Sediments

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A Canada-wide survey was undertaken to study local impacts of coal mines and coal-fired electrical generating stations. The first part dealt with thallium in waters and sediments. This, Part II, deals with metals and organics in sediments as well as sediment toxicity to four different organisms. Several elevated metal and PAH concentrations as well as high toxicity (based on biological sediment guidelines) were observed compared to uncontaminated sites. Based on Ontario's sediment guidelines, most of the studied sediments fell in the "marginally to significantly polluted" category of sediment quality, although two belonged to the "grossly polluted" class due to the extremely high concentrations of some metals. The observed diversity of PAHs and near-unity carbon preference indices indicate non-biological origins of the studied sediments. In this initial study, four different organisms, *Chironomus riparius, Hyalella azteca, Hexagenia* spp. (*Hexagenia limbata*) and *Tubifex tubifex* were used to determine sediment toxicity, which showed 50% of the tested sites were highly stressed.

Key words: **coal mine, power plant, sediment quality guidelines, metal pollution, organics, carbon preference index, toxicity, biological sediment guidelines, bioassay endpoint, ordination space**

Introduction

Coal is Canada's most abundant fossil fuel. Its annual production and consumption exceed 78 and 55 million tonnes, respectively (Table 1, Canadian Coal Statistics 1997). Across Canada there are 35 active coal mines and 25 coal-fired generating stations (Tables 2 and 3). Coal is also important to the Canadian economy, and its exports are worth $2 billion (Natural Resources Canada 1994).

The effects of coal production and consumption, however, may be detrimental to the environment. For example, Murphy et al. (1999) investigated local impacts of a rural power plant on lichen abundance in a New England forest, taking into account the wind direction, distance and sides of trees. They reported measurable ecological impacts on the adjoining plant community, which were caused by the emissions from the power plant. Wehner et al. (1999) reported that the primary emissions of particulates from coal power plants may have important impacts on climate

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Table 1. Production, consumption, import and export of coal in Canada (in tonnes)

Province	Production	Consumption	Import	Export
British Columbia	27,892,747	200,817	—	27,278,581
Alberta	36,343,416	26,264,343	—	9,181,069
Saskatchewan	11,652,553	10,018,189	—	—
Manitoba	—	263,829	185,572	—
Ontario	—	13,877,042	11,393,496	—
Quebec	—	732,265	750,265	—
New Brunswick	170,958	1,326,676	1,150,622	—
Nova Scotia	2,632,994	3,051,199	—	49,924
Total	78,692,668	55,734,360	13,479,955	36,509,574

change. Smith and Carson (1977) reported that the air emissions from coal-burning power plants form the largest collective source of thallium discharged atmospherically. Cheam et al. (2000) recently made a Canada-wide survey on local impacts of the coal-related operations on surrounding waters and sediments and found very high thallium concentrations at several sites. This paper describes the impacts in terms of concentrations of heavy metals and organics in surrounding sediments, as well as toxicity of these sediments to aquatic invertebrates.

Materials and Methods

Sediment Sampling and Handling

The coal mines and power plants across Canada, including their locations, salable production, accessibility and sampling protocols, have been described in Part I (Cheam et al. 2000). Several sites for initial examination were selected in this study. Thirty-two sediment samples were collected, 17 from power plant sites and 15 from mine sites. A mini Ponar sampler (1 to 2 L) or an Eckman sampler was used to collect sediment samples. For trace metals and bioassay tests, all containers, bags, spoons and other utensils used were plastic; glass bottles were used to collect sediment samples for organic parameters.

Sediment samples were refrigerated at 4°C until use. For inorganic and organic parameters, 250-mL bottles were used to contain wet sediments, which were freeze-dried, crushed, sieved and subsampled for the determination of heavy metals and organics. For toxicity tests and for each site, five 1-L replicate samples (for five replicate tests) were collected and placed into plastic bags, and then refrigerated.

Analytical Methods and Analytes

Trace metals in sediments were determined using inductively coupled

Table 2. List of all active coal mines in Canada and their owners

Principal mines and their owners
(1997 data from the The Coal Association of Canada)

British Columbia
- Quinsam, Quinsam Coal Corporation
- Bullmoose, Teck Corporation
- Quintette, Teck Corporation
- Fording River, Fording Coal Ltd.
- Greenhills, Fording Coal Ltd.
- Line Creek, Line Creek Resources Ltd.
- Elkview, Teck Corporation
- Coal Mountain, Fording Coal Ltd.

Alberta
- Smokey River, Smokey River Coal Ltd.
- Obed, Luscar Ltd.
- Highvale, TransAlta Utilities Corporation
- Whitewood, TransAlta Utilities Corporation
- Luscar, Luscar Ltd.
- Gregg River, Manalta Coal Ltd.
- Coal Valley, Luscar Ltd.
- Genesee, Edmonton Power & Fording Coal Ltd.
- Vesta, Alberta Power Ltd.
- Paintearth, Luscar Ltd.
- Montgomery, Manalta Coal Ltd.
- Sheerness, Luscar Ltd.

Saskatchewan
- Poplar River, Manalta Coal Ltd.
- Utility, SaskPower
- Boundary Dam, Luscar Ltd.
- Costello, Manalta Coal Ltd.
- Shand, Luscar Ltd.
- Bienfait, Luscar Ltd.

New Brunswick
- NB Coal (Minto), NB Coal Ltd.

Nova Scotia
- Prince, Cape Breton Development Corporation
- Phalen, Cape Breton Development Corporation

Minor mines
(Natural Resources Canada 1998)

Alberta
- Dodds
- Egg Lake

Nova Scotia
- Stellarton
- Thomas Brogan
- Evans
- Thorbourn

Table 3. List of coal-based electrical generating stations and their owners

Alberta
Sundance, TransAlta Utilities Corporation
Wabamun, TransAlta Utilities Corporation
Keephills, TransAlta Utilities Corporation
Battle River, Alberta Power Ltd.
H.R. Milner, Alberta Power Ltd.
Sheerness, Alberta Power Ltd. and TransAlta Utilities Corporation
Genesee, Edmonton Power
Saskatchewan
Boundary Dam, Saskpower
Poplar River, Saskpower
Shand, Saskpower
Manitoba
Brandon, Manitoba Hydro
Selkirk, Manitoba Hydro
Ontario
Nanticoke, Ontario Hydro
Lakeview, Ontario Hydro
Lambton, Ontario Hydro
Thunder Bay, Ontario Hydro
Atikokan, Ontario Hydro
New Brunswick
Belledune, New Brunswick Power
Dalhousie, New Brunswick Power
Grand Lake, New Brunswick Power
Nova Scotia
Lingan, Nova Scotia Power
Glace Bay, Nova Scotia Power
Point Alconi, Nova Scotia Power
Trenton, Nova Scotia Power
Point Tupper, Nova Scotia Power

plasma – atomic emission spectrometry (ICP-AES), and the detection limits, in µg/g, were 3.4 for Cd, 0.9 for Co, 0.9 for Cr, 1.0 for Cu, 1.2 for Fe, 0.2 for Mn, 2.0 for Ni, 2.5 for Pb, 12.6 for Tl, and 0.9 for Zn. Sediments were analyzed using gas Chromatography-mass selective detector (GC-MSD) for polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and *n*-alkanes (Mayer and Nagy 1992; Mudroch and Mudroch 1992). Naphthalene results, due to the possible loss during the freeze-drying process (Fox et al. 1991), may be low by 20 to 50%.

The sediment extraction procedures for metals are as follows. For heavy metals Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Tl and Zn, a semi-closed acid digestion was used to decompose 0.5 g of sediment utilizing a 75-mL Teflon beaker recently described (Cheam et al. 1998). Five milliliters of HF and 5 mL of HNO_3 were added to the sediment and digested on a hot plate to near dryness. Then, 0.1 M HNO_3 and 2 mL of aqua regia as well as 2 mL of 30% hydrogen peroxide were added to the residue and digested for one more hour. The solution was then diluted to 50 mL and analyzed with an ICP spectrometer. For PAHs and *n*-alkanes, the freeze-dried sediment samples were Soxhlet-extracted using 300 mL of dichloromethane (DCM) for at least 16 hours. The extracts were then reduced to 1 to 2 mL by vacuum distillation on a rotary evaporator. They were then quantitatively transferred to 15-mL graduated centrifuge tubes with DCM and brought to a volume of 1.0 mL by evaporation with nitrogen in a heated water bath. An aliquot of 100 µL was taken as subsample from each extract for capillary GC/MS quantitation of PAHs and *n*-alkanes. The remaining 900 µL of the soxhleted sediment extract was solvent exchanged to hexane and then cleaned up for PCBs quantitation.

Toxicity Tests

Detailed procedures have been described previously (Reynoldson et al. 1991, 1994). For removal of large debris and endemic species, culture water was added to the sediment, producing a slurry, which was then poured through a 250-µm mesh screen (Reynoldson et al. 1991). Sediment was then allowed to settle for 24 h. The water was decanted and used as the overlying water in the tests . However, most sediments did not pass through the sieve. As a result, the *Tubifex tubifex* test could not be performed on the 8200 Salmon Harbour Mine (or simply Salmon Harbour Mine) sample. There were a large number of endemic worms present in this sample that made it difficult to identify *T. tubifex*. Total ammonia, mg/L, was measured for each treatment with an ammonia electrode (Orion No. 95-12) on day 0 (start of test) and at the completion of each test on day 10, day 21, or day 28. For each site, an overlying water sample was taken from each replicate beaker and pH adjusted to >11 with a buffer solution of NaOH and EDTA prior to measurement. The bioassay tests were performed as follows.

Chironomus riparius

The 10-day survival and growth test was performed. The endpoints were expressed as percent survival and average growth given in mg dry weight per individual organism per replicate.

Hexagenia spp.

The 21-day survival and growth test was done, and the endpoints were expressed as above.

Hyalella azteca

The 28-day survival and growth test was done, and the endpoints were expressed as above.

Tubifex tubifex

The 28-day adult survival and reproduction test was carried out. The endpoints were expressed as (a) the number of adults surviving out of 4;

(b) the number of cocoons produced per individual adult worm and the percentage of those cocoons that hatched; and (c) the number of youngs produced per individual adult worm.

Ordination Technique

Sediment toxicity was determined by ordination of the 10 endpoints from the study sites with data from 116 reference sites. These sites were selected to represent minimally impaired conditions (Reynoldson et al. 1997a) and to have the following criteria: 1) to capture as much of biological variability in the benthic invertebrate communities of the Great Lakes as practicable; 2) to be located in depositional areas because contaminants are primarily associated with fine grained material; 3) to represent the nearshore environment as sediment remediation is considered impractical in offshore or deeper waters — primary application of the guidelines is expected to be in the International Joint Commission's "Areas of Concern", all of which are nearshore; and 4) to be unimpacted or clean (Reynoldson et al. 2000). Ordination was used to explain the variability observed among the large number of taxa with a reduced number of new variables (ordination axes). A hybrid multidimensional scaling (HMDS) method of ordination was used, i.e., semi-strong-hybrid multidimensional scaling (Belbin 1991). Multidimensional scaling methods can use either metric or non-metric rank order information. We have used a hybrid technique that incorporates both metric and non-metric scaling (Faith et al. 1987). Metric scaling methods assume that the dissimilarity measure chosen has a linear relationship with ecological distance, and non-metric scaling assumes only monotonicity and the distances between sample pairs are only maintained in rank order with their dissimilarities. The hybrid method described by Faith et al (1987) differs from these two approaches in using a prescribed dissimilarity measure that has a robust metric (linear) relationship with distance only over a certain range. A monotonic regression serves as the only direct constraint on larger dissimilarities. This hybrid attribute is of particular value when relating ordination scores to environmental characteristics. All clustering and ordination was done using PATN, a pattern analysis software package developed by CSIRO in Australia (Belbin 1993). Probability ellipses were constructed around reference sites only (90, 99 and 99.9%). Study sites inside the 90% probability ellipse were considered non-toxic. Those outside the 90% ellipse were considered toxic to various degrees.

Results and Discussion

Heavy Metals in Sediments

Table 4 gives the concentrations of heavy metals as determined by ICP (thallium and mercury were discussed in detail in Part I, but are also pertinent and given here). For the Souris River sediment, the concentrations of heavy metals were higher in the upstream samples than in the down-

Table 4. Concentrations of heavy metals in sediments[a]

Sample site	Site/Sample description	Co µg/g	Cr µg/g	Cu µg/g	Fe %	Mn µg/g	Pb µg/g	Ni µg/g	Zn µg/g	Tl µg/g	Hg µg/g
Wabamun GS, Alta.	Intake water	17.5	57.9	28.8	2.1	742	<2.5	28.8	68.1	0.52	
"	Ash lagoon effluent	9.7	39.9	20.3	1.7	180	<2.5	18.4	46.2	0.43	
Sundance GS, Alta.	Ash slurry	13.1	17.4	45.1	1.7	343	34.5	19.4	33.4	0.99	
Keephills GS, Alta.	Cooling pond screen waste	9.9	56.6	35.2	2.1	303	<2.5	27.7	108.0	0.69	
"	Ash lagoon slurry	13.5	21.9	28.3	2.1	348	<2.5	19.2	18.6	0.35	
"	Ash lagoon cenospheres	6.2	9.0	39.4	1.2	87	31.4	13.7	19.5	1.20	
Genesee GS, Alta.	Discharge	10.2	47.2	36.4	2.4	573	<2.5	21.9	95.1	0.52	
Smoky River, Alta.	u/s Sheep Creek, 5 km d/s HR Milner	7.8	35.7	19.2	1.7	221	<2.5	25.5	70.9	0.39	
"	u/s H.R. Milner GS at Hwy. 40	8.9	40.3	19.3	1.6	208	3.7	17.0	68.4	0.34	
Battle River GS, Alta.	Battle River u/s	5.3	28.4	8.6	1.6	297	<2.5	15.3	42.8	0.36	0.04
"	Battle River d/s	3.3	22.3	4.9	1.2	280	<2.5	10.2	28.6	0.47	0.04
Grand Lake GS, N.B.	Lake water	5.9	23.2	8.2	2.4	688	<2.5	12.5	34.5	0.78	0.02
Trenton GS, N.S.	Ash lagoon cenospheres	20.7	55.2	77.3	2.6	164	86.1	44.5	156.0	0.89	
Souris River, Sask.	u/s Estevan, mines and GS	15.0	89.8	35.9	3.6	464	<2.5	43.1	115.0	0.68	0.11
"	u/s Estevan, mines and GS	11.7	76.0	32.7	3.2	430	<2.5	34.8	99.9	0.68	0.10
"	d/s Estevan, mines and GS	8.1	55.3	21.1	2.2	319	<2.5	21.6	73.5	0.49	0.06
"	d/s Estevan, mines and GS	7.8	56.3	22.5	1.9	289	<2.5	20.5	67.6	0.45	0.07

(continued)

Table 4. *(concluded)*

Sample site	Site/Sample description	Co µg/g	Cr µg/g	Cu µg/g	Fe %	Mn µg/g	Pb µg/g	Ni µg/g	Zn µg/g	Tl µg/g	Hg µg/g
Bienfait Mine, Sask.	Pit water discharge	8.0	36.5	16.7	1.2	284	11.0	13.0	76.1	0.54	
Whitewood Mine, Alta.	Pit water discharge	7.4	36.5	25.8	1.5	258	5.0	16.3	158.0	0.47	
Highvale Mine, Alta.	Pit 2 drain	19.0	69.5	54.3	2.5	378	<2.5	42.5	98.1	0.87	
"	Pit 3 settling pond — outflow	18.1	76.9	44.4	3.2	398	<2.5	38.4	94.9	0.62	
Genesee Mine, Alta.	Mine drainage	17.1	77.7	54.6	3.1	369	<2.5	39.6	170.0	1.04	
Coal Valley Mine, Alta.	Tailings discharge	15.3	60.7	32.9	2.6	448	<2.5	33.8	94.7	0.47	
"	Lovett River d/s	12.9	80.0	25.9	2.4	906	<2.5	33.5	82.8	0.59	
Gregg River Mine, Alta.	Plant site water reservoir	16.8	44.8	54.3	1.1	339	8.5	37.0	196.0	0.52	
Obed Mountain Coal, Alta.	E. conveyor settling pond	8.7	39.1	24.7	1.4	417	7.7	20.3	68.4	0.25	
"	Main tailings pond (upper)	8.1	16.6	14.8	2.9	318	33.8	9.5	105.0	3.39	
"	LSP2 — coal storage drain	4.7	23.8	17.5	1.0	194	10.2	11.9	59.3	0.42	
Line Creek Mine, B.C.	Settling pond	7.4	52.4	31.5	0.9	153	9.5	22.9	199.0	1.11	
8200 Salmon Harbour Mine, NB	Lake water	26.7	94.3	36.8	5.8	1972	<2.5	45.1	132.6	0.74	0.05
Phalen Colliery, N.S.	Surface runoff brook	21.3	39.9	30.8	17.0	640	54.5	37.6	126.0	1.25	0.06
Prince Colliery, N.S.	d/s discharge	11.5	53.7	24.7	3.7	614	12.9	31.0	109.3	0.61	0.06

[a]Tl was determined by LEAFS; Hg was determined by CVAAS; other metals were determined by ICPAES.

stream samples. To verify the findings, fresh and duplicate samples from the same locations were recently collected and analyzed for heavy metals. The new results confirmed the higher concentrations in the upstream sediment compared to downstream. This was in fact true for organic compounds as well as toxicity to various organisms that will be discussed below. Also, for water samples, the upstream samples likewise contained a higher Tl content than downstream (Cheam et al. 2000). It seems, therefore, that the so-called "upstream" sediment sample (49° 07.337' latitude N., 103° 01.397' longitude W.) may in fact represent the outflow of the cooling water from the Boundary Dam generating station (Smith 1999).

It is also interesting to note that the Battle River upstream sediments also contained higher concentrations than the downstream sediments for all groups of chemicals, except perhaps Tl and Hg — we have no explanation for this. The Phalen Colliery sediment contained, by far, the highest Cd content (16.2 µg/g, all other sediments were <3.4 µg/g) and the highest Fe content (17%, the closest being 5.8%). These two concentrations were even higher than those found in five different sediment cores from Hamilton Harbour (Zeman et al. 1995) and would put the sediment in the class of "grossly polluted" according to the Ontario's sediment quality guidelines (Table 5 [Jaagumagi and Persaud 1995]). However, Cr, Pb, Mn, Ni and Zn data would place the sediment in the "marginally to significantly polluted" category only. In addition to these metals, the sediment also had high concentrations of Tl and Co (Table 4).

The 8200 Salmon Harbour Mine also had two very high levels in Fe and Mn, which would qualify the sediment as grossly polluted (Table 5). But the Cr, Ni and Zn data would classify the sediment quality as "marginally to significantly polluted". This sediment also had the highest Co concentration compared to the other sediments studied (Table 4). The Trenton generating station, on the other hand, had the highest concentrations of Cu and Pb, and would be classified as "marginally to significantly polluted" based on the Cr, Fe, Pb, Ni and Zn data (Table 5). The Prince Colliery sediment had a high Fe concentration of 3.7% (close to the "severe effect level" of 4%) and high enough concentrations of Cr, Mn and Ni to put it in the "marginally to significantly polluted" category. All other sediments also belonged to this category by virtue of at least one high concentration of an element.

All Ni data indicated that 81% of the sediments would fit in the sediment quality "marginally to significantly polluted" class. The percentages of sediments falling in this class were 77% based on Cr data, 61% on Fe data, 26% on Mn data, 16% on Pb data, and 3% on Zn data (Tables 4 and 5).

Organics in Sediments

Polycyclic aromatic hydrocarbons

The 16 polycyclic aromatic hydrocarbons (PAHs) that are priority pollutants were measured. In addition, two 252 PAH isomers, benzo[e]pyrene and perylene, were also quantified using the

Table 5. Comparison of sediment guideline levels with some high levels of metals found in some sites[a]

	Cd µg/g	Cr µg/g	Fe µg/g	Mn µg/g	Pb µg/g	Ni µg/g	Zn µg/g
Lowest effect level	0.6	26	2	460	31	16	120
Severe effect level	10	110	4	1100	250	75	820
Marginally to significantly polluted	0.6–10	26–110	2–4	460–1100	31–250	16–75	120–820
Phalen Colliery sediment	16.2	39.9	17	640	54.5	37.6	126
Salmon Harbour Mine sediment	<3.4	94.3	5.8	1972	<2.5	45	133
Trenton GS sediment	<3.4	55.2	2.6	164	86	45	156
Prince Colliery sediment	<3.4	53.7	3.7	614	12.9	31	109

[a]The guidelines define three levels: "no effect level," "lowest effect level" and "severe effect level" (Jaagumagi and Persaud 1995). Below the "no effect level," the sediment quality is termed "clean", i.e., no impact on water quality and water uses or benthic organisms are anticipated. Between the "no effect level" and "lowest effect level," the sediment quality is termed "clean to marginally polluted," i.e., the sediment has potential to affect some sensitive water uses. Between the "lowest effect level" and the "severe effect level," the sediment quality is termed "marginally to significantly polluted," i.e., some benthic organisms will be affected. Above the "severe effect level," the sediment quality is termed "grossly polluted," i.e., benthic organisms will be significantly affected by the use of the sediment.

Table 6. Concentrations (ng/g) of the 16 priority PAHs and benzo[e]pyrene and perylene

Compound	Sample No.[a] / M/z	28S	34S	105S	128S	141S[b]	209S dup1	209S dup2	211S dup1	211S dup2
	Weight (g)	41.82	59.81	43.23	19.31	28.08	12.89	12.97	38.59	29.98
	Final volume (mL)	1	1	1	1	1	1	1	1	1
Naphthalene	128	13	2	11	704	4059	61	74	18	14
Acenaphthylene	152	2	0.2	ND[c]	13	359	26	8	1	1
Acenaphthene	154	1	ND	ND	8	602	7	6	1	0.8
Fluorene	166	2	0.3	0.4	36	756	105	12	6	3
Phenanthrene	178	9	2	5	326	3399	68	89	18	10
Anthracene	178	1	ND	ND	NC[d]	739	NC	NC	4	1
Fluoranthene	202	5	1	1	32	385	262	380	14	11
Pyrene	202	6	1	7	67	599	222	298	20	17
Benzo[a]anthracene	228	2	0.4	ND	19	156	69	83	3	3
Chrysene	228	4	0.8	1	59	131	142	218	7	6
Benzo[b]fluoranthene	252	5	2	ND	26	22	103	137	7	6
Benzo[k]fluoranthene	252	2	0.4	ND	5	5	36	44	2	2
Benzo[a]pyrene	252	2	0.7	ND	14	28	30	32	2	1

(continued)

Table 6. *(concluded)*

Compound	Sample No.[a] / Weight (g) / Final volume (mL) / M/z	28S	34S	105S	128S	141S[b]	209S dup1	209S dup2	211S dup1	211S dup2
	Weight (g)	41.82	59.81	43.23	19.31	28.08	12.89	12.97	38.59	29.98
	Final volume (mL)	1	1	1	1	1	1	1	1	1
Indeno[1,2,3-cd]pyrene	276	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibenz[a,h]anthracene	278	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[ghi]perylene	276	ND	ND	ND	ND	ND	ND	ND	ND	ND
Total		54	10.8	25.4	1309	11240	1131	1381	103	76
Benzo[e]pyrene	252	2	0.6	ND	29	16	40	55	2	1
Perylene	252	26	9	ND	ND	2	16	20	9	7

[a]Sample 28S, Battle River upstream; 34S, Battle Riverr downstream; 105S, Grand Lake GS; 128S, Salmon Harbour Mine; 141S, Prince Colliery downstream discharge; 209S, Souris River upstream; 211S, Souris River downstream.

[b]Results obtained after silica gel fractionation and sulfur cleanup. Unusually high anthracene concentration was detected (also high in samples 209S dup 1 and 209S dup2).

[c]ND, not detected.

[d]NC, not confirmed.

benzo[a]pyrene response (Table 6). Most samples were found to contain small amount of the majority of these compounds. However, the concentration of total PAHs in the Prince Colliery downstream discharge sample (sample 141S) was high as it is in the same order of magnitude as that of the polluted Hamilton Harbour suspended sediments (RAP 1988; Mayer and Nagy 1992). The diversity and high levels of the PAHs in samples 209S, 128S and 141S, in particular (Table 6), compared to the other sites, seemed to suggest that these sites were affected by industrial inputs associated with coke production (Mayer and Nagy 1992). For sample 141S, the concentration of several PAHs, including naphthalene and phenanthrene, exceeded the "lowest effect level" of the Ontario's guidelines for sediment quality. The same is true for total PAHs, whose concentration of 11.2 μg/g exceeded the lowest effect level of 4 μg/g, thus putting this sediment well into the "marginally to significantly polluted" class (Jaagumagi and Persaud 1995).

n-alkanes

The determination of *n*-alkanes helped determine the types of sediments, whether they were of biological or petroleum origins. According to Bray and coworkers (Bray and Evans 1961; Cooper and Bray 1963), the types can be inferred by determining the carbon preference index (CPI) from the odd-carbon and even-carbon data in the sediments of interest. The CPI is defined for the number of carbon up to 26 as

$$CPI = 1/2\,[A/B + A/C]$$

where $A = \sum_{13}^{n-1}$ odd-carbon alkanes, $B = \sum_{14}^{n}$ even-carbon alkanes, and $C = \sum_{12}^{n-2}$ even-carbon alkanes.

The CPIs for biological systems range from about 2.5 to 5.5, whereas a CPIs of about 1 indicates crude oil or petroleum systems. In our case, the CPIs range from 0.8 to 1.7 (Table 7) with an average of 1.3 ± 0.3, which clearly indicates non-biological origins.

The Prince Colliery downstream discharge sample contained the highest total *n*-alkanes of 32 μg/g, but the smallest CPI of 0.8, which signifies an industrial system, thus corroborating with its PAHs data as discussed above. Likewise, the Souris River upstream sample, containing a fairly high *n*-alkane concentration of 7 μg/g and a low CPI of 1.5, would be of industrial sources.

Polychlorinated Biphenyls

The determination of PCBs showed that the concentrations were very low, and only very few congeners were detected. Of 40 congeners measured, only 19 were detected, namely; congener 131 found in 6 of 9 samples; congener 60 in 4 of 9 samples; congeners 101, 87 and 153 in three of nine samples; congeners 52, 40/103, 118, 129/159, 173/201 in two of nine samples; and congeners 121, 114/142, 105, 138, 182, 185, 180, 191, 170

Table 7. Concentrations (μg/g) of *n*-alkanes in sediment samples

	Sample No. [a]	28S	34S	105S	128S	141S[b]	209S dup 1	209S dup 2	211S dup 1	211S dup 2
	Weight (g)	41.82	59.81	43.23	19.31	28.08	12.89	12.97	38.59	29.98
	Final vol. (mL)	1	1	1	1	1	1	1	1	
Compound	C No.	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g
n-C12	12	0.01	ND[c]	ND	0.09	1.49	0.03	0.04	0.04	0.03
n-C13	13	0.02	ND	ND	0.09	1.74	0.04	0.05	0.03	0.03
n-C14	14	0.02	ND	ND	0.09	2.77	0.10	0.12	0.05	0.04
n-C15	15	0.03	0.01	0.01	0.09	1.10	0.20	0.23	0.08	0.06
n-C16	16	0.03	0.01	0.01	0.09	2.06	0.24	0.27	0.11	0.06
n-C17	17	0.17	0.04	0.02	0.15	2.11	0.92	1.21	0.28	0.19
n-C18	18	0.06	0.03	0.02	0.15	1.40	0.86	0.75	0.36	0.25
n-C19	19	0.08	0.04	0.03	0.21	1.87	1.09	0.86	0.41	0.32
n-C20	20	0.48	0.02	0.04	0.24	3.06	0.94	0.77	0.30	0.30
n-C21	21	0.08	0.02	0.04	0.25	2.31	0.96	0.53	0.03	0.29

(continued)

Table 7. *(concluded)*

	Sample No. [a]	28S	34S	105S	128S	141S[b]	209S dup 1	209S dup 2	211S dup 1	211S dup 2
	Weight (g)	41.82	59.81	43.23	19.31	28.08	12.89	12.97	38.59	29.98
	Final vol. (mL)	1	1	1	1	1	1	1	1	
Compound	C No.	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g
n-C22	22	0.06	0.02	0.03	0.15	2.32	0.36	0.33	0.17	0.16
n-C23	23	0.19	0.06	0.01	0.15	2.28	0.42	0.39	0.46	0.39
n-C24	24	0.08	0.03	0.01	0.07	3.16	0.20	0.24	0.20	0.16
n-C25	25	0.06	0.03	0.01	0.31	1.89	0.53	0.66	0.67	0.55
n-C26	26	0.11	0.04	ND	0.07	2.22	0.26	0.29	0.21	0.18
Total (μg/g)		1.48	0.35	0.22	2.20	31.77	7.14	6.72	3.39	3.01
Carbon preference index (Mean CPI = 1.3±0.3)		0.8	1.5	1.1	1.4	0.8	1.5	1.5	1.5	1.7

[a]Sample 28S, Battle River upstream; 34S, Battle River downstream; 105S, Grand Lake GS; 128S, Salmon Harbour Mine; 141S, Prince Colliery downstream discharge; 209S, Souris River upstream; 211S, Souris River downstream.

[b]Results were obtained after silical gel fractionation and sulfur cleanup.

[c]ND, not detected.

in one of nine samples. Overall, of the 360 congeners measured (40 congeners per sample times 9 samples), only 36 congeners or 10% were detected sparingly as above or close to the detection limit of 20 pg/g.

Sediment Toxicity

Toxicity endpoints

Reynoldson et al. (1997b) reported on sediment toxicity targets in the recently published biological sediment guidelines for the Laurentian Great Lakes. In that report, they established toxicity limits for determining toxicity of 10 test endpoints. Using the sediments from the Great Lakes reference sites, they classified sediments as non-toxic, potentially toxic and toxic, based on the percentage of survival and growth of three different organisms, namely, *Chironomus riparius*, *Hyalella azteca* and *Hexagenia spp. (Hexagenia limbata)*. As well, the survival and reproduction targets were established for the oligochaete worm *Tubifex tubifex*, based on percent survival, percent hatch, # cocoons/adult, and # youngs/adult. These guidelines are used in determining the toxicity of the sediment samples.

Table 8 shows the percent survival and the growth of the test species *Chironomus riparius* in five sediments from the various regions. It indicates that the sediments from the Battle River Power Plant (16% survival) and the Prince Colliery (40% survival) would be classified as toxic, based on the percent survival "toxic" limit of <60% (Reynoldson et al. 1997b). However, on the growth basis, all five sediment types would be classified as non-toxic since all the five growth results fell within the non-toxic range of 0.21 to 0.49 mg dry weight (note that the Battle River sediment used was a combination of the upstream and downstream sediments as each was insufficient by itself).

The sediments used would be indexed as non-toxic to *Hexagenia* spp. organisms as all the growth values fell within the non-toxic confine of 1.0 to 5.0 mg (Table 8). Furthermore, all the percent survival values were greater than the non-toxic limit of >85.

Hyalella azteca were much affected by the Prince Mine sediment as both the percent survival and the growth were below the "toxic" limits — 36.7% << 58% and 0.1 < 0.11 mg, respectively (Table 8). The high amount of ammonia of 9 ppm produced from this sediment, the highest ammonia content observed in the study, may have contributed to the observed high sediment toxicity. Of all sediments, the Prince Mine sediment also produced the highest ammonia content for every organism studied (Table 9). Additionally, an examination of the chemical data revealed that the very high content of the PAHs in the sediment (Table 6), as discussed above, might have contributed to the observed high toxicity. The sediment also contained the highest content of *n*-alkanes (Table 7). *Hyalella azteca*, on the other hand, were not as affected by the other sediments, except the Battle River sediment, which may be potentially toxic to *Hyalella* based on the percent survival of 68, which is right at the edge of the "potentially toxic" range of 58 to 67.9.

Table 8. Survival, growth and reproductioin of *Chironomus riparius*, *Hexagenia spp.*, *Hyalella azteca* and *Tubifex tubifex* in sediments

	Chironomus riparius		*Hexagenia spp.*		*Hyalella azteca*		*Tubifex tubifex*			
	% survival	Growth (mg)	% survival	Growth (mg)	% survival	Growth (mg)	% survival	Cocoons/ Adult	% Hatched	Young/ Adult
Reference values:[a]										
Non toxic	>69	0.21–0.49	>85	1.0–5.0	>68	0.24–0.76	>88	7.2–12.3	40–78	12.0–45.6
Potentially toxic	60–68.9	0.14–0.20	80–84.9	0–0.9	58–67.9	0.11–0.23	84–87.9	5.9–7.1	30.8–39.9	3.6–11.9
Toxic[f]	<60	<0.14	<80	—	<58	<0.11	<84	<5.9	<30.8	<3.6
Sediment site[b]										
Souris River, u/s	80.0	0.31	97.5	3.89	93.3	0.50	100	8.9	57.4	23.7
Souris River, d/s	89.3	0.32	98	4.29	89.3	0.64	100	8.5	27.8	13.1
Battle River GS[c]	***16.0***	0.27	100	4.54	**68**	0.38	**87.5**	5.2	62.5	5.7
Prince Colliery	***40.0***	0.38	94	1.34	***36.7***	***0.10***	95	8.7	59.6	33.9
Salmon Harbour Mine[d]	**66.7**	0.45	90	6.32	80	0.41	—	—	—	—

[a]Reynoldson et al. 1997.
[b]u/s, upstream; d/s, downstream; GS, coal-based electrical generating station.
[c]The Battle River GS sediment was a combination of both the u/s and d/s sediments as each was insufficient by itself.
[d]The Salmon Harbout Mine site was not suitable for *T. tubifex* test due to the large number of endemic worms.
Note: bold type, potentially toxic; bold type italics, toxic.

Table 9. Ammonia content (ppm) measured during the toxicity tests

Sediment site[a]	*Chironomus riparius*	*Hexagenia spp.*	*Hyalella azteca*	*Tubifex tubifex*
Souris River, u/s	Sample lost	0.03	<0.01	ND[b]
Souris River, d/s	Sample lost	0.04	<0.01	ND
Battle River GS	ND	ND	<0.01	ND
Prince Colliery	2.8	0.6	9	2.6
Salmon Harbour Mine	0.85	0.06	<0.01	

[a]u/s, upstream; d/s, downstream; GS, coal-based electrical generating station.
[b]ND, not detectable.

Table 8 also shows the toxicity results for *Tubifex tubifex*. The sediment from the Battle River Generating station would be classified as toxic since the number of cocoons/adult, 5.2, was below the toxic limit, <5.9; furthermore, the percent survival as well as the #young/adult were within the "potentially toxic" limits of 84 to 87.9 and 3.6 to 11.9, respectively. However, the chemical data (Tables 4 to 7) did not seem to corroborate with the toxicity results since the Battle River sediment contained no real high concentrations of any metals, PAHs, *n*-alkanes, or PCBs relative to other sediments. It is therefore interesting that the Battle River sediments were toxic to three out of four test species in spite of their relatively low chemical concentrations. It could be that the Battle River sediments contained more toxic organic matter than the other sediments, or they could contain other highly toxic contaminants not measured in this study.

Integration of toxicity endpoints

To integrate all the results from the toxicity endpoints and to assess the significance of the responses at the exposed sites, we have used an ordination method. Ordination reduces the variables required to identify the structure of the data. We have ordinated the results from reference sites with the coal mine/power plant sites and plotted these data in the same ordination space. If an exposed mine/power plant site was within the range of variation observed at reference sites, we would assess it as equivalent to reference, and if it was outside the range observed at reference sites, we would assess it as toxic to a varying degree. A large river quality survey conducted in the UK in 1990 provided the impetus for the development of methods to circumscribe the continuum of biological response into a series of bands that represented grades of biological quality from good to poor (Wright 1995; Wright et al. 1991). Despite the simplification, it was seen as an appropriate mechanism for obtaining a simple statement of biological quality, allowing broad comparisons in either space or time that would be useful for management purposes. We have adopted a similar approach for defining degrees of difference from the reference condition

using a multivariate approach, and based upon three probability ellipses (Fig. 1) constructed around reference sites. Sites inside the smallest ellipse (90% probability) would be considered equivalent to reference, or non-toxic; sites between the smallest and next ellipse (99% probability) would be considered possibly different, or possibly toxic; sites between the 99% probability and the largest ellipse (99.9% probability) would be considered different, or toxic; and sites located outside the 99.9% ellipse would be designated as very different, or very toxic.

Figure 1 shows the results from reference sites (open circles) and five mine/plant sites where only six end points were measured (no data for *T. tubifex*). The five sites are described earlier. The results from the six end points could be explained by two ordination axes. Two sites from SR (Souris River) showed no evidence of toxicity; one site from SHM (Salmon Harbour Mine) would be considered toxic; and two sites were very toxic (PM = Prince mine, and BRGS = Battle River generating station). The four sites for which all 10 test endpoints were available required three ordination axes to explain the variability in test response (Fig. 2, 3 and 4). Again the two sites (PM and BRGS) were identified as very toxic, and the two SR samples were non-toxic. The results from the ordination method agree well with those from the toxicity end points method. It seems therefore that the ordination technique is a powerful and effective graphical presentation to determine the toxicity of sediment.

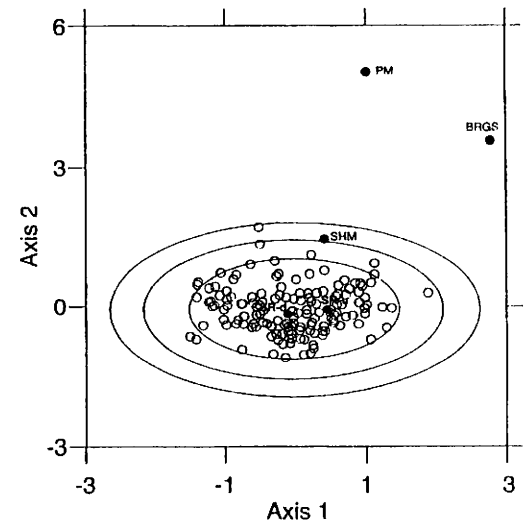

Fig. 1. Assessment of sediment toxicity by ordination of six bioassay endpoints (BRGS = Battle River generating station; PM = Prince Mine; SR-U and -D = Souris River upstream and downstream; SHM = Salmon Harbour Mine).

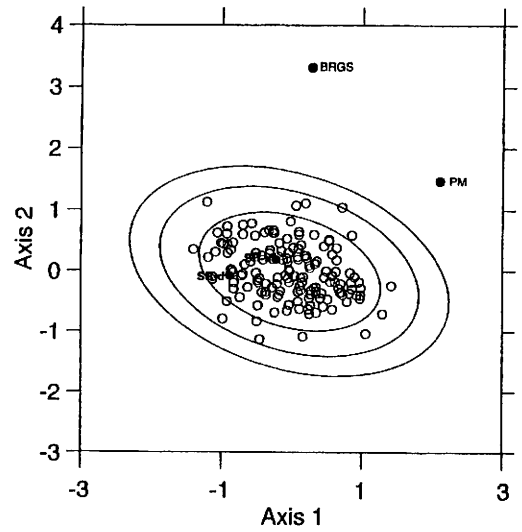

Fig. 2. Assessment of sediment toxicity by ordination of 10 bioassay endpoints (BRGS = Battle River generating station; PM = Prince Mine; SR-U and -D = Souris River upstream and downstream).

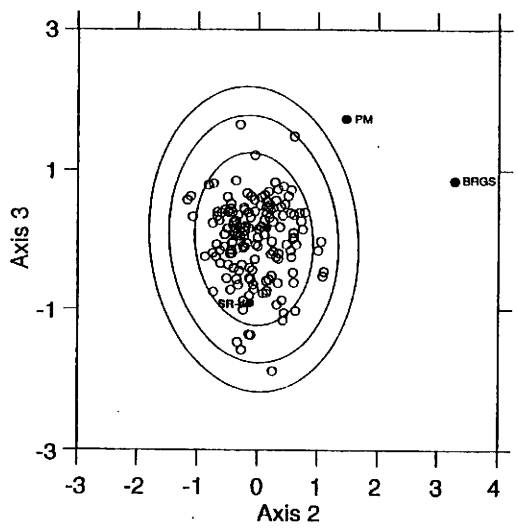

Fig. 3. Assessment of sediment toxicity by ordination of 10 bioassay endpoints (BRGS = Battle River generating station; PM = Prince Mine; SR-U and -D = Souris River upstream and downstream).

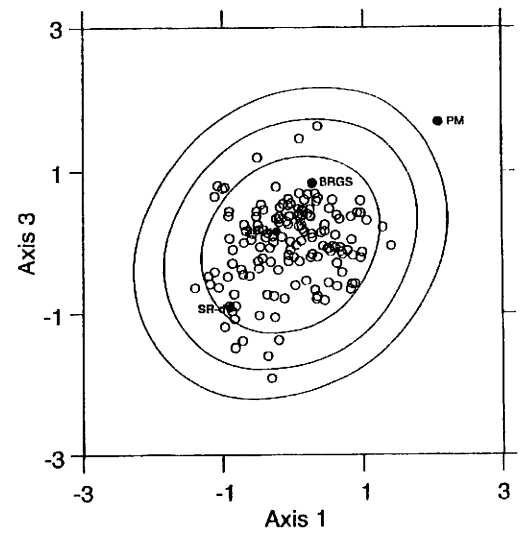

Fig. 4. Assessment of sediment toxicity by ordination of 10 bioassay endpoints (BRGS = Battle River generating station; PM = Prince Mine; SR-U and -D = Souris River upstream and downstream).

Conclusions

This initial study surveyed the local impacts of coal mines and coal-based power plants across Canada. Sediment data indicated that some sites were severely impacted by high concentrations of metals, organics and high toxicity to invertebrates.

Most of the studied sediments fell in the "marginally to significantly polluted" category of sediment quality, although two belonged to the "grossly polluted" class, based on Ontario's sediment guidelines. This was due to the extremely high concentrations of some heavy metals.

The observed diversity of PAHs and near-unity carbon preference indices indicate industrial origins of the studied sediments.

Fifty percent of the sediments tested, using the bioassay ten- endpoints toxicity results and the ordination technique, were found to be highly toxic.

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METHODS FOR THE DETERMINATION OF PAH DESORPTION KINETICS IN COAL FINES AND COAL CONTAMINATED SEDIMENTS

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ABSTRACT

Conventional batch, modified batch, conventional column, and time-resolved leaching techniques were examined utilizing various miscible organic solvent/water mixtures to determine the desorption kinetics of selected PAHs in coal fines and coal contaminated sediments.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds which consist of condensed aromatic rings, with or without substitution. They are ubiquitous environmental contaminants (1), and several have been shown to be mutagenic and/or carcinogenic (2). For these reasons, many facets of PAH sources, fates, and distributions have received considerable attention. Because they are hydrophobic and highly insoluble in water, the distribution of PAHs in aquatic systems is greatly influenced by the presence of suspended solids, especially those of an organic nature (3). Accumulated sediments, consisting of solids with bound PAHs, can be an important source or sink of PAHs to aquatic environments, depending on the rate and extent of processes which affect PAH partitioning between sorbed and free states. Several techniques have been employed to measure desorption kinetics in soils, sediments, and other solids (4,5,6), but no known reports have addressed the rates of PAH release from coal fines and coal contaminated sediments or the use of cosolvents with water to facilitate investigation of slowly desorbing materials. This work presents a comparison of experimental methods used to address the kinetics of PAH desorption in such systems.

Coal Fines and Aquatic Sediments

Coal is a mineral solid which is produced under anaerobic conditions at high temperature and pressure. Aromatic hydrocarbons make up a large percentage of the organic fraction of coal, and several PAHs have been identified among these (1,7,8). Coal fines transported to aquatic environments may have similar PAH contents, at least with respect to the higher

molecular weight, less weatherable forms. Coal piles which have either no containment or inadequate containment can contribute significant quantities of suspended coal fines to receiving waters. For example, in a study of two coal-burning power plants in New York, total solids loading during four different storm events wefe determined (9). Mass loadings ranging from 0.95 kg (for a light rainfall of 0.48 cm and a flow intensity of 0.000492 m^3/s) to 2570 kg (for a heavy rainfall of 4.06 cm and a flow intensity of 0.0202 m^3/s) were recorded. The conclusion of the study was that the majority of the solids loading in the runoff consisted of fine coal particles. Much of this suspended load becomes mixed with suspended solids from other sources, forming a coal-contaminated sediment system.

The distribution of individual PAH compounds has been used to link patterns of PAHs found in coal tars and coal tar distillates (creosotes) with those of sediment samples taken near creosote manufacturing sites (10,11). Similarly, PAH profiles and distributions in soils from sites adjacent to or otherwise impacted by industrial discharges have been determined and matched to the source materials (12,13,14). Aqueous leachate from coal piles has also been shown to contain PAHs. In three different studies in which the aqueous runoff from model coal piles was examined, naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, pyrene, chrysene, benzopyrene, and benzo(g,h,i)perylene were found in one or more samples (15,16,17). Kido et al. (8) found a similar array of compounds in waste waters from a coal depot in a steel processing mill. It is obvious from these and other studies that PAHs enter the environment from coal sources, but their rates of release to and subsequent fates in coal contaminated systems are little understood.

Coal combustion has and will continue to be a major source of steam for electric power generation and other needs. Typically, large outdoor storage piles are used, often with a minimum of 30 to 90 days worth of stock (18). Fine particles of coal are released from these piles with each rainfall, and depending on their size and the hydrodynamic properties of the receiving waters, they are widely distributed throughout the aquatic environment. The degree to which PAHs are available for biological interaction with aquatic organisms is largely a function of their state, either free or sediment-bound. PAHs, as with many hydrophobic organic compounds, may be more bioavailable when in solution (19). For this reason, the rate of release to solution of PAHs from coal-contaminated solids may directly influence their impact on aquatic organisms. Desorption rates may also be significant to considerations of porewater and groundwater chemistry, transport in streams, and effects of resuspension events.

Desorption Kinetics

Sorption equilibrium has often been assumed when the concentration of sorbing species cannot be observed to change over the time scale of interest. While this may be adequate for the purpose of some studies, it is not always sufficient for all, particularly if kinetic estimates are to be made (20). The rate of PCB desorption from river sediments has been shown to be directly related to the length of time the compounds have contacted the sediments previous to desorption (5), with lower rate constants found for contact times of 29 days versus those of five days. True equilibrium partition coefficients can only be obtained when the rates of both sorption and desorption are equal, but recent evidence shows that attaining equilibrium for desorption of hydrophobic compounds from sediments is a slower process than for adsorption (5,21). For this reason, attainment of "true equilibrium" may be required for the determination of the slowest desorption rates which may be seen in contaminated sediments.

The sorption process has been considered rapid in comparison with many other environmental processes. Batch studies have been used to estimate the kinetics of PAH adsorption and

desorption, with differing rate constants and mechanisms and hysteresis being observed (21,22,23,24). Some of the variations in results from batch studies may have resulted from experimental designs which did not allow attainment of true equilibrium. Similarly, most soil/aqueous phase models currently in use to describe hydrophobic compound sorption ignore kinetic aspects (due to ease of application and mathematical simplicity), but this may lead to unacceptable levels of accuracy (24,25).

Many works have addressed the process of desorption in sediments and soils contaminated with hydrophobic pollutants, often describing the process as two-stage, with fast and slow components (5,22,24,26,27). In a batch desorption experiment, Karickhoff (22) showed that the sorption kinetics of pyrene, phenanthrene and naphthalene followed a two-stage approach to equilibrium in both the adsorption and desorption directions. The first stage was rapid, with significant changes in amount of material adsorbed in a period of minutes, while the second stage occurred over a time scale of hours to days. The adsorbates associated with these stages were termed "labile" and "non-labile" components, respectively. The labile fraction involved about half of the total sorbate concentration. Rate constants could be calculated only for the non-labile stage, because the labile component desorbed so quickly.

For exchange of sorbate between the labile and non-labile components the following relationship was proposed by Karickhoff (22):

$$\frac{d}{dt}\left\{\frac{S_2}{(1 - X_1)}\right\} = k_d\left\{\frac{S_1}{X_1} - \frac{S_2}{(1 - X_1)}\right\} \qquad (1)$$

where S_2 = the non-labile sorbed component, S_1 = the labile component, k_d = first-order rate constant for pollutant movement into and out of S_2 and X_1 = the fraction of the total sorption capacity that is rapidly accessed. (S_1 and S_2 correspond to $[C]_1$ and $[C]_2$, respectively, in equation 3 presented later in this paper). The value of k_d was shown to increase with decreasing fraction of organic carbon in three different sediments and increasing solubility of the compounds (22).

Different mechanisms have been proposed to explain the two stage process, with labile and non-labile processes being attributed to external film transfer and intraparticle diffusion (24), "near-surface" adsorption and particle aggregation/cohesion effects (5,21), and "reversible" and "resistant" components (23), among others. In one investigation, bulk diffusion of the pollutant from the interior of the particle mass was insufficient to explain all the non-labile component sorption, and it was proposed that intraparticle sorption processes and molecular diffusion limited the rate of second stage desorption (21). For this reason, long term studies may be the only way to fully assess the desorption process.

An Overview of Applicable Desorption Methods

The elements common to all methods of determining desorption kinetics are the solids of interest with the adsorbed compound(s) and a "clean" solvent. Experimental variability is introduced in the methods by which the solids are contacted with the solvent. These range from simple batch contact periods to continuous contact schemes utilizing a flowing solvent. They are presented here in order of increasing complexity.

Simple batch tests involve the mixing of contaminated suspended solids with clean solvent for a defined period of time. Upon completion of the mixing period, the solid and liquid phases are separated and the concentration of the compound of interest is determined in one or both of the phases. If this is a non-destructive process (e.g., the system integrity is not altered), or multiple replicate vessels are prepared, another prescribed period may be allowed to pass, and a set of points thus be developed which shows the amount of compound desorbed from the solid as a function of time. A major problem with this

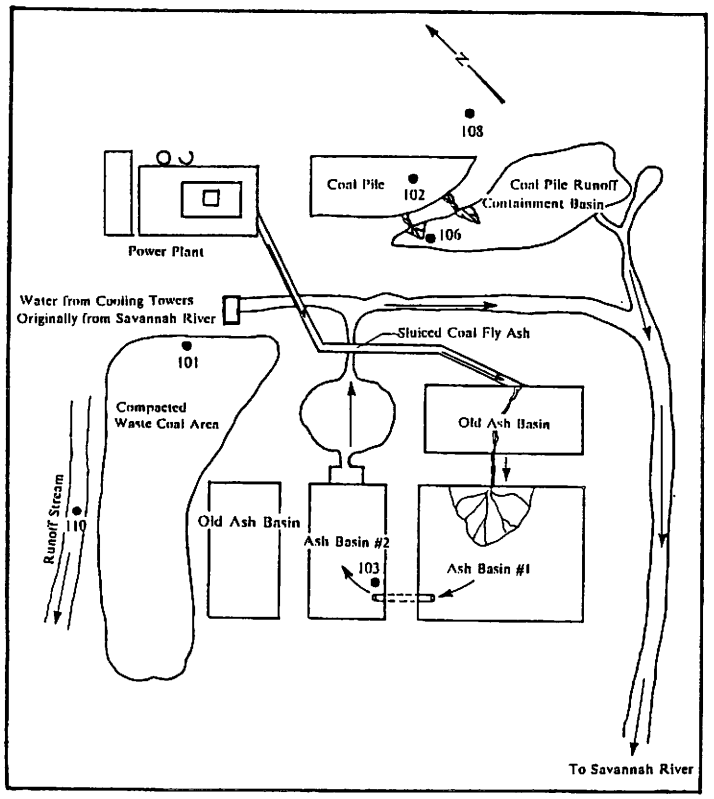


Figure 1. Site used for sample collection at the Savannah River Plant, Aiken, SC. Area D is a power production area and includes a coal combustion plant, outdoor storage piles, a runoff containment basin, ash handling basins, waste coal storage areas and runoff streams.

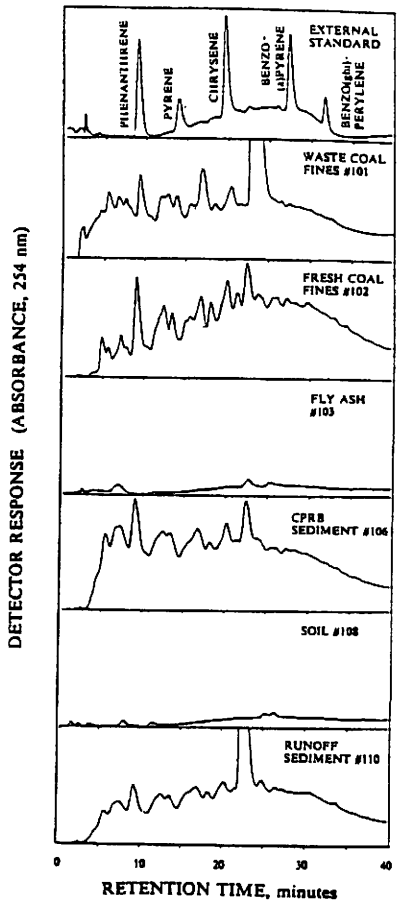
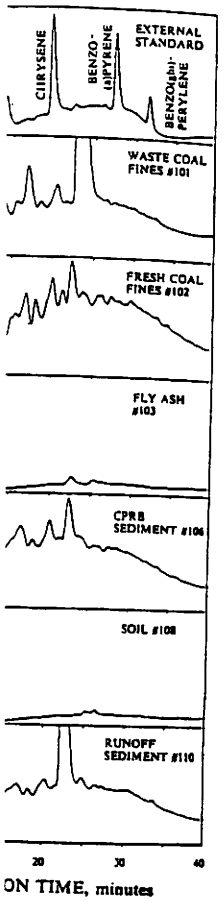


Figure 2. Sample HPLC chromatograms of solvent extracts from various solids obtained at the Savannah River Plant, Area D, Aiken, SC. Fresh coal fines, coal pile retention basin (CPRB) sediments, and waste coal runoff sediments were used in desorption kinetics experiments.



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source. Additionally, the mouth of the creek is a swamp area prone to flooding and scouring during periods of high flow of the Savannah River, so its sediments may not have been indicative of an orderly progression of deposition of Beaver Dam Creek materials. Two of the six samples were used in the desorption experiments outlined in the following sections.

All sediment samples were collected manually as grab samples and placed in solvent--rinsed glass jars. Coal samples were collected from just below the surface of the piles, while sediments were collected from the topmost 2 to 5 cm. All samples were placed in the dark immediately and refrigerated at 4°C upon return to the laboratory. The laboratory used in sample processing, extraction, and the conduct of desorption experiments was fitted with gold fluorescent lights (wavelength > 400 nm) to reduce the potential for photodegradation of PAHs. All samples were field-wet-sieved through a 500 um mesh and the fraction passing the sieve was used in analyses. Fresh coal fines were prepared by crushing the coal samples with a mortar and pestle, then collecting the fraction which passed a 500 um mesh. Estimates of organic carbon content of the samples were made by ashing the samples at 550°C overnight. A subsample of the CPRB sediment was dry-sieved through a series of sieves to determine its particle size distribution below 500 um.

Experimental Design

The optimum physical model for examining the kinetics of desorption from aquatic sediments is the continuous flow stirred tank reactor, or CFSTR, where solid particles are in intimate contact with the liquid phase and effects of physical processes such as bulk diffusion, advective transport, and dispersion are minimized or eliminated. Recent reports have given the results of kinetic studies using such a reactor, but these are dependent on gas-phase stripping of volatile hydrophobic pollutants (5,22,26). Many of the larger PAHs found associated with coal are not volatile and would not be quantitatively removed from the aqueous phase with gas stripping. Initial attempts to use a membrane for phase separation in a continuous system in a stirred cell failed due to plugging of the pores and violation of the complete mix requirement. The batch and TRL reactors represent a best reasonable alternative to the CFSTR; experimental designs utilizing these techniques are presented in following sections.

Two batch reactor configurations were used: simple batch and batch with fluid replacement (BFR). Simple batch experiments were conducted in 4000 mL Erlenmeyer flasks containing suspended sediments in double distilled water at a solids concentration of either 1000 or 10,000 mg/L. Both the solid and the liquid phases were added to the reactor at the beginning of the desorption period, and subsamples were collected from the vessel. BFR experiments utilized multiple 150 or 50-mL Teflon-capped glass centrifuge tubes as batch reactors. Solids concentration was 10,000 mg/L and all tubes were mixed on a slowly revolving tumbler (15 rpm). The time interval between sample collections (in both batch methods) was varied according to the estimated stage of the desorption process, with more frequent sample collections during the early stages of the desorption process and less frequent sampling during the later stages. Intervals were used which varied from minutes (for the very early stages) to weeks, for the later stages of desorption.

For the simple batch process, subsamples of the completely mixed solution were collected, filtered through a Gelman A/E glass fiber filter and extracted as outlined in the analytical methods section. For the BFR process, the solid and aqueous phases were separated by centrifugation, the liquid phases were carefully poured into separatory funnels for liquid-liquid extraction, the tubes were refilled with fresh solvent, and they were replaced on the tumbler. In all experiments, the mass of compounds released from the sediment was

determined as a function of time and expressed as cumulative mass released, normalized to the solids mass (dry weight basis) in the reactor.

Various system geometries were used in the early stage of experimentation, the most successful of which was a very short length, high surface area column. Long stainless steel columns similar to those used in HPLC systems (25 cm by 0.4 cm diameter) required excessive pressure and were not used. A shorter stainless steel column (1.9 cm by 1.6 cm diameter), was packed with two to four g of sediment and operated at flowrates of 0.5 to 2.0 mL per minute. This system was finally abandoned due to leaks and high pressure requirements. An all-glass filtration apparatus was fitted with a Gelman A/E glass fiber filter, slurry packed with 10 g of coal fines and exposed to dripping solvent at 1.0 mL per minute for 24 hours. A final design, selected for subsequent use in this investigation, consisted of a 47 mm stainless steel filter holder loaded with 0.5 to 3.0 g sediment, yielding a cake of 47 mm diameter by one to two mm height. This is called the TRL reactor in further discussions. Flowrates of 0.5 to 8.0 mL per minute were readily attainable with minimal pressure requirements. The effluent from all column systems was collected and liquid-liquid extracted with hexane.

Analytical Methods

Sediment samples were extracted using a modification of the method employed by Dunnivant (34), while liquid phases were liquid-liquid extracted with two aliquots of hexane. On a dry weight basis, 0.5 to 1.0 g of field-wet-sieved sediment was added to a 150-mL centrifuge tube which was then filled with acetone. The tube was placed in an ice bath and sonicated for 15 minutes at 80 percent relative output. The solution was centrifuged for 30 minutes at 4080 g (5000 rpm in a Sorvall GSA head) and the centrifugate was filtered through a Gelman A/E glass fiber filter. The centrifuge tube was rinsed with 25 mL acetone and the contents were filtered, pooling the filtrate with that of the first separation. The filtrate was transferred to a 500-mL separatory funnel, 150 mL of double distilled water and 20 mL of saturated sodium chloride solution were added, and the solution was gently mixed. Next, 20 mL of hexane were added and the funnel was shaken vigorously for three minutes, venting as required. At least 30 minutes were allowed for phase separation. The hexane layer was collected and passed through a rinsed column of anhydrous sodium sulfate. The acetone/water fraction was returned to the separatory funnel and the hexane extraction step was repeated, with the second extract being pooled with the first. The pooled extract was concentrated to one mL in a concentrator flask (placed in a 65°C water bath) under dry flowing nitrogen. Two mL of acetonitrile were rinsed along the insides of the concentrator flask and then the entire extract was concentrated further to the desired final volume. Liquid phases from desorption experiments were extracted and concentrated in a similar manner, minus the sonication, centrifugation, and filtration steps.

All extracts were analyzed using HPLC. A Waters Associates (Milford, MA) HPLC system consisting of an 840 data and chromatography control station (version 2.0) was used with two model 510 dual reciprocating pumps, a model U6k universal LC injector, a model 481 Lambda-Max LC spectrophotometer, and a system interface module, with system control provided by a DEC Professional 350 computer (Digital Equipment Corporation, Merrimack, NH). The mobile phase consisted of acetonitrile in water, programmed to run isocratically at 50 percent acetonitrile for 10 minutes followed by a gradient to 100 percent acetonitrile over the next 40 minutes, at a constant total flowrate of one mL per minute. The stationary phase used was either C18 (octadecylsilane) or a C18-based phase specially adapted for PAH analysis in a proprietary procedure (Waters Associates). Both were configured in a radial compression cartridge, eight mm I.D. by 10 cm long with a particle size of five um. Temperature of the column was controlled at 25°C +/- 1°C with an external water jacket.

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To confirm the identity of PAHs found in the solvent extracts of the CPRB sediments, a sample from a batch desorption experiment was analyzed by both HPLC and GC/MS. A Hewlett Packard Model 5890A GC fitted with a 5970B series mass selective detector and a DB-5 fused silica capillary column 19.7 m long by 0.172 mm I.D. (J&W Scientific, Folsom, CA) was used. The temperature was ramped from 40 to 250°C at 5°C per minute, held for five minutes, then ramped from 250 to 290°C at 5°C per minute where it was held until the end of the program run. Due to the complex nature of the chromatogram from uncleaned extract, a single cleanup step using a column of activated silicic acid was performed. A first fraction consisting of aliphatic compounds eluted with n-hexane was discarded, and a second PAH-containing fraction was eluted with 85:15 hexane:methylene chloride. Both National Bureau of Standards and in-house generated mass spectral libraries were used in the identification of compounds.

Both single and two stage first order models, presented in the following discussion section, were fitted to the desorption experiment data using SAS nonlinear regression procedures (Statistical Analysis System, Cary, NC). The principle of conditional error was used to determine the appropriateness of using the more complex, five parameter two stage model as opposed to the simpler, two parameter single stage, conditioned model.

Quality Assurance and Control

BFR desorption rate experiments using coal pile runoff basin sediments were conducted in duplicate to estimate the precision of the methods. Method blanks were included with each set of analyses, and system components (glassware, reagent water, analytical column etc.) were routinely checked for contamination and adsorptive removal of analytes.

Standards were prepared as per EPA Method 601, section 5.4 "Preparation of Stock Standards", with acetonitrile as the solvent. These were checked against EPA reference solutions to verify concentrations, instrument response and other complicating factors. For all analyses, a single set of "stock standards" was used and multiple sets of "dilute standards" were prepared from these. This served to help eliminate variability introduced by the use of multiple (and possibly conflicting) standard sets.

Both internal and external standards were used throughout the study. Selected samples were spiked with internal additions of one or more selected PAHs at the beginning of sample processing, but due to the complex nature of the chromatograms, this was not routinely performed. External standards were used to calibrate the analytical system and to determine recoveries in various extraction and concentration steps. Additionally, samples were prepared from water pollution quality control sample concentrates (U.S. Environmental Protection Agency, Cincinnati, OH) and analyzed according to the previously described methods. In all cases, standards were of a concentration similar to that of the PAHs in the samples.

RESULTS AND DISCUSSION

Samples and Extractions

Several sediment, ash, coal, and soil samples were collected from area D of the Savannah River Site, but after a qualitative extraction and analysis of PAH content, only two sediment samples were used for further study in desorption rate experiments. The ash and soil samples did not show detectable levels of PAHs, and because the study was sediment oriented, the coal samples were used only for methods development and evaluation of their PAH contributions to the site. HPLC chromatograms of the sonication extracts of the samples collected are shown in Figure 2. The fly ash and "clean" soil samples did not show detectable levels of PAH contamination, as was expected. The lack of PAHs in these samples supports the idea that runoff from the coal pile, not atmospheric sources, is the main input of PAHs at this site.

The two sediment samples which were used in later desorption studies were heavily contaminated with coal fines. Both were gray-black in color with a distribution of clay sized particles, sand grains, and coal particles of a wide range of size. Both had relatively high organic carbon contents: the CPRB sediment was 5.8 percent, while the waste coal runoff stream sediment was 6.9 percent organic carbon, based on loss on ignition. The high organic content was most probably related to the extent of contamination with coal fines, but it still served to indicate a matrix which proved to be highly sorptive for PAHs.

Several PAHs have been identified in the solvent extracts from these samples. Norton and Mills (35) used a methanolic-KOH-toluene solution in a two-hour Soxhlet extraction of CPRB sediments and showed the presence of acenaphthylene (102 ng/g), fluorene (79 ng/g), phenanthrene (568 ng/g), fluoranthene (494 ng/g), and benzanthracene plus chrysene (366 ng/g). Their reported levels were five to 20 times lower than those found in the present study, but this variability may have been due to either sample variability or analytical methods, or a combination of the two. Peak resolution in the HPLC chromatograms was generally poorer than those with the GC, but analytical sensitivity was somewhat greater in the former system. Peaks corresponding to the retention times of the PAHs seen using GC separation were seen above the large unresolved complex mixture (UCM) of the HPLC chromatograms. In addition, a peak for chrysene was prominent in the HPLC chromatograms. Surprisingly, no compounds with ring numbers greater than four were seen, even though high molecular weight PAHs have been identified in coal extracts. Perhaps other, more exhaustive techniques for PAH extraction from coals are required to affect the release of the larger PAHs from the solid coal matrix.

Several parent and alkylated PAHs were identified in the CPRB sediment extract analyzed via GC/MS. As in the HPLC chromatograms, unsubstituted phenanthrene was the most prevalent aromatic compound present. Naphthalene, fluoranthene, and chrysene were also clearly identified by the total ion chromatograms in the library. Mono-, di-, and tri-methylated naphthalenes as well as di- and tri-methylated phenanthrenes were strongly indicated as being present in the solvent extracts. Mass spectra were collected for qualitative purposes only, but relative peak intensities were similar to those of the HPLC chromatograms.

Evaluation of Solids Extraction Methods

In order to appropriately design desorption experiments it was important to have an estimate of the total amount of the compounds of interest which were present in the solids. A sonication extraction procedure was chosen due to its ease of use, minimal solvent requirements, and generally high efficiency. Previous work in this laboratory had shown relatively complete release of polychlorinated biphenyls (PCBs) from lake sediments during a 15 minute sonication period which utilized acetone as the leaching solvent (34). Similarly, PAHs were extracted from plant tissues using this method (36). The fundamental difference between plant tissues used in the previously mentioned study (36) and coal contaminated sediments is that, in the former group, the hydrophobic pollutants were incorporated into a preexisting solid matrix while with coal, PAHs are a major component of the parent solid. This distinction is important, as shown by the results of an experiment designed to determine necessary sonication and extraction steps discussed below.

Sonication time was varied from 10 to 60 minutes in either 10 or 15 minute increments, both with and without solvent replacement between increments. Various time periods were used to allow intraparticle transport and transport of the released compound to the bulk phase of the solution where it was ultimately quantified. The amount of phenanthrene released from a coal contaminated sediment as a function of sonication time and solvent treatment is shown in Table 2. Clearly, a 10, 20, or 30 minute sonication period either with or without solvent

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Table 2. Effects of Sonication Time, Solvent Contact Time, and Solvent Replacement on Desorption of Phenanthrene in Coal Contaminated Sediments: Mass Released, ng Phenanthrene/g Sediment

Sonication Time (minutes):	10	15	20	30	45	60
Sonication of CPRB Sediment in Methanol						
Sample Treatment:						
Continuous Sonication	1073	-	1310	1430	-	-
Sonication in 15 Minute Intervals (Discrete Samples):	-	-	-	1044	2216[a]	1624
Sonication in 15 Minute Intervals, With Solvent Replacement (One Sample, Multiple Fractions Over Time):	-	1070	-	415	729	386
Sonication in 15 Minute Intervals, With Solvent Replacement, (Same Sample as Above, Cumulative Mass):	-	1070	-	1485	2214	2600

Sonication of CPRB Sediment in Acetone

1. Duplicate sediment samples were sonicated for 30 Minutes in two 15-minute periods before and after 15 days of solvent contact. Sample values were averaged. Results: 8650

2. The same samples as in (1) above were sonicated for an additional 30 minutes in two 15-minute periods before and after an additional 41 days of solvent contact. Sample valued were again averaged. Results: 382

Total from 56 days of solvent contact and multiple sonications (1 and 2 summed): 9032

(a) Sample was left in contact with solvent overnight, after the final sonication, but before the filtration step.

replacement at intermediate points was inadequate in removing all the phenanthrene from the sediment, but solvent replacement did effect the release of greater amounts of phenanthrene.

As can be seen from the 45 minute sonication which was allowed to stand overnight, the amount released to the solvent phase was substantially greater than that of a comparable 60 minute sonication, which had a total contact time of just 60 minutes. Also, the sample which was contacted with solvent for 15 days both following and preceding a 15 minute sonication period (without solvent replacement) showed almost three times as much release as did the 60 minute sonication sample. It should be noted, however, that different solvents were used. An additional 41 days of contact with fresh solvent, again sonicated for 15 minutes both before and after the contact period, showed the release of an additional four percent of the total desorbed mass. This indicated that slow release of compound from the solid may continue for long periods, even with significant extraction efforts such as repeated sonication.

Release of PAHs from coal fines must be a slow process, possibly aggravated by tortuosity of intraparticle pathways or otherwise influenced by aggregation of solids. Coates and Elzerman (5) addressed this aspect of pollutant sorption using PCBs and sediments. They found that increasing the length of time that PCBs were in contact with sediments prior to the initiation of desorption experiments caused a direct reduction in the observed rates and amounts of desorption. While this difference was attributed to a lack of equilibrium in the sediments contacted with contaminant for shorter periods of time, it typifies the problems associated with desorption from highly sorptive solids containing large surface areas (5).

Batch Methods

The simplest way to determine desorption kinetics is to mix the contaminated solid with a clean solvent and determine the mass of contaminant released to the liquid phase as a function of time. This is usually accomplished utilizing multiple bottles, but a single large vessel with subsampling may also be used. Both techniques were used in this study. When water alone was used as the leaching solution, no quantifiable release of PAHs was observed, even after 84 days of contact in a 1000 mg/L suspension of CPRB sediments. For this reason, various water/organic solvent mixtures (acetonitrile, methanol, or acetone) were used to enhance the rates of release. Earlier studies (16,17) have shown that PAHs are leached from coal using water alone, but large masses of coal were used (7 kg or more) to obtain quantifiable amounts. Kinetic experiments in the present study by necessity were conducted on a much smaller scale, with total sediment masses on the order of one to 10 g. The use of organic cosolvents provided an avenue for bringing the quantities of PAHs desorbed into the detectable range, while also providing information on the effects of varying cosolvent strength on desorption rate constants. Data from a four-day multiple bottle batch desorption experiment using 0.10 mole fraction acetonitrile and CPRB sediments are shown in Figure 3. It is apparent from this data set that the rate of desorption slowed dramatically after only 12 hours of contact with the solvent. While the phenanthrene concentration in the liquid phase was a small fraction of the aqueous solubility (less than 0.01 percent), other organic compounds (based on the large amounts of unresolved material present in the chromatograms) were also released to the liquid phase.

A first order model was fitted to the data to provide an initial estimate of desorption rate and kinetic constants. This equation has the form

$$[C]_t = [C]_{eq}(1 - e^{-k_d t}) \qquad (2)$$

where $[C]_t$ = concentration of PAH at time t, $[C]_{eq}$ = asymptotic estimate of PAH concentration at equilibrium, and k_d = desorption rate constant, day^{-1}. This equation, a modification of the

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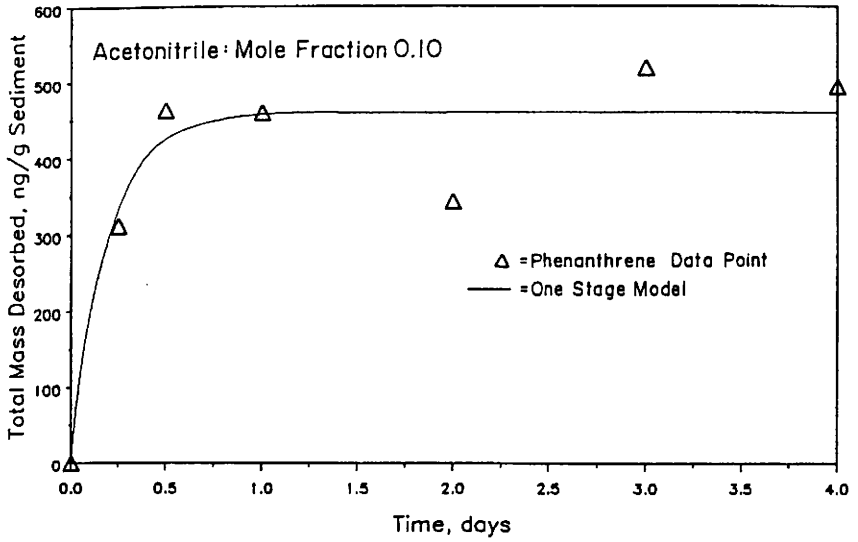

Figure 3. Phenanthrene desorption from coal pile retention basin sediments using a simple batch experimental design, a 0.10 mole fraction acetonitrile/water solvent, and multiple bottles. A single stage first order model (line) was fitted to the data (symbols).

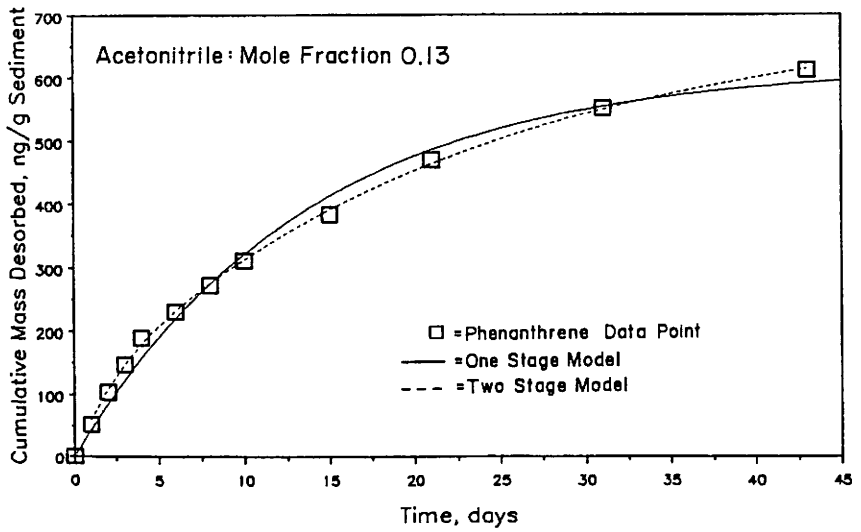

Figure 4. Phenanthrene desorption from waste coal runoff stream sediments using a BFR experimental design and a 0.13 mole fraction acetonitrile/water solvent. Both one (solid line) and two stage (dashed line) first order models were fitted to the data (symbols).

form used by Coates and Elzerman (5), describes the approach to desorption equilibrium where the cumulative mass released ($[C]_t$) asymptotically approaches a maximum value ($[C]_{eq}$). Using this equation yielded values of 460 ng/g for $[C]_{eq}$ and 5.2 day^{-1} for k_d, for the experiment mentioned above. This k_d value is relatively high in comparison to other values obtained with the same sediment and similar solvents but a longer time scale (Experiment COSOLV8, Table 3), but the model fit was poor and later data points showed a high degree of variability. No further work was done with simple batch tests because of this variability, and because, where high concentrations of the liquid phase components may accumulate, concentration gradients can decrease, thus decreasing the driving force for the desorption process.

The batch with fluid replacement (BFR) technique was used for the majority of batch experiments conducted in this investigation. In a first attempt to use the BFR technique to determine desorption kinetics in coal contaminated sediments, various mole fractions of acetonitrile in water ranging from 0.08 to 0.34 were contacted with sediments from the waste coal pile runoff stream for a four day period. The suspended solids concentration was set at 1000 mg/L. While the solution phase showed increasing amounts of phenanthrene and chrysene released with increasing cosolvent fraction, the amounts present were too low to quantify adequately and fit the rate expression to the data.

Consequently, the experiment was repeated, this time using a suspended solids concentration of 10,000 mg/L and acetonitrile mole fractions varying from 0.02 to 0.13. The decreased cosolvent fractions were used to more closely simulate aqueous conditions, and the higher solids concentration was used to increase the detectability of desorbed compounds. This second experiment was continued for 43 days, and a typical desorption curve was obtained for phenanthrene with the 0.13 cosolvent mole fraction (See Figure 4). A single rate equation was fitted to the data and estimates of k_d and [C]eq were 0.073/day and 617 ng/g, respectively. While this model appears to describe the data reasonably well, a two constant kinetic model corresponding to a two stage process fit the data better and was statistically valid, based on the principle of conditional error (Figure 4). This relationship has the form

$$[C]_t = [C]_{eq} - [C]_1 e^{-k_{d1}t} - [C]_2 e^{-k_{d2}t} \qquad (3)$$

where $[C]_t$, $[C]_{eq}$, k_d, and t are as in Equation (2) and the subscripts 1 and 2 denote fits to the first and second stages, respectively.

Karickhoff (22) described the desorption process as a two stage process wherein the first, rapid stage is controlled by rapid partitioning between the solid and liquid phases, while the second stage is kinetically controlled by other processes. Data from this investigation show that, with coal contaminated materials, release of PAHs from the solid phase also follows a two stage process, but that both stages are slow enough to be considered kinetically controlled. Equation (3) is an adaptation of the two stage model which treats the process as a combination of two kinetically controlled reactions occurring simultaneously. When t is small, C_1 and k_{d1} control the curve shape, and when t reaches a critical value (the point at which C_t begins to change less rapidly with increasing time), C_2 and k_{d2} control the curve shape. The is analogous to a physical process in which first surface, then later intraparticle, processes control the observed rate of desorption.

Model parameter estimates and fitting statistics, obtained from these data along with those of other desorption curves to be described, are given in Table 3. Data obtained with the 0.08 and 0.02 cosolvent mole fractions were not well described by a first order model, possibly due in part to their concentration levels near analytical detection limits. Further development of the relationship between cosolvent strength and desorption kinetics is presented elsewhere (37).

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Table 3. Equilibrium Concentrations and Rate Constants for Selected Experiments, Using One and Two Stage Kinetic Models

	One Stage Model		Two Stage Model				
	$[C]_{eq}$[a]	k_d[a]	$[C]_{eq}$	$[C]_1$	k_{d1}	$[C]_2$	k_{d2}
COSOLV 4: PH[b]	460	5.15	ND[c]	ND	ND	ND	ND
Batch Design, 0.10 mole fraction acetonitrile as liquid phase, 0 - 4 days experimental duration, coal pile retention basin (CPRB) sediment as solid phase							
COSOLV 8: PH	617	.074	708	104	.439	607	.043
Batch with Fluid Replacement (BFR) Design, 0.13 mole fraction acetonitrile as liquid phase, 0 - 43 days experimental duration, waste coal runoff stream (WCRS) sediment as solid phase							
BFR 5: PH	6872	.262	7357	3455	1.02	3878	.083
BFR 5: CHR[b]	2200	.068	2699	1042	.146	1608	.019
BFR Design, 1.00 mole fraction methanol as liquid phase, 0 - 84 days experimental duration, CPRB sediment as solid phase							
BFR 8: PH	9298	.928	9623	7277	1.56	2333	.153
BFR 8: CHR	3999	.710	4199	3038	1.22	1145	.116
BFR Design, 1.00 mole fraction acetone as liquid phase, 0 - 63 days experimental duration, CPRB sediment as solid phase							
COSOLV 3: PH	1771	.690	ND	ND	ND	ND	ND
Column Design, 0.10 mole fraction acetonitrile as liquid phase, 0 - 1 day experimental duration, fresh crushed coal fines as solid phase							
TRL 3D: PH	7207	.153	7816	3533	.429	4226	.052
TRL 3D: CHR	2168	.048	2400	447	.197	1953	.028
Time Resolved Leaching (TRL) Design, 1.00 mole fraction methanol as liquid phase, 0 - 86 days experimental duration, CPRB sediment as solid phase							

(a) Units of [C] = ng PAH/g sediment, units of k_d = day^{-1}.
(b) PH = phenanthrene, CHR = chrysene.
(c) ND = not determined.

Desorption curves for phenanthrene and chrysene in 100 percent methanol are shown in Figure 5. The curves shown were obtained by fitting both of the models previously described to all data (both points where duplicate data were obtained, and single data points otherwise). For both compounds, the desorption process was modeled much better by the two stage equation, as explained by the following. The principle of conditional error (PCE) was used to test the hypothesis that the improvement in fit of the double over the single stage model was solely a function of the increase in parameterization. This was rejected at the 0.01 level for all data presented, indicating that the two stage model provided a significantly better estimate of the desorption process.

Figure 6 illustrates the results using 100 percent acetone. Comparing the results for PAH desorption in the two pure solvents, 100 percent acetone universally caused higher rate constants for all models than did 100 percent methanol. The same relationship was shown for the asymptotic equilibrium concentration estimates, with the exception of the values for the second stage concentration levels.

Column Methods

Several column geometries were used, but with little success. In one 49-day experiment, double distilled water was pumped over 3 g of fresh coal fines in a small (1.9 cm by 1.6 cm diameter) stainless steel cylinder at a flow rate of 1.5 mL/min. The effluent was passed through frequently changed Waters Associates C18 Sep Pak Cartridges (Milford, MA) placed in-line as traps and discarded after hexane extraction of collected PAHs. Some phenanthrene was detected in the solvent extracts of the C18 traps, but the amounts were not quantifiable.

Based on the complex chromatograms obtained from the solvent extractions of the coal fines, it is highly likely that the C18 traps were quickly saturated with other non-PAH organic compounds, causing phenanthrene and other PAHs to pass through unadsorbed. Alternatively, the PAHs released from the coal may have existed in a nonadsorbable form. Landrum et al. (38) used C18 traps to differentiate between humic-bound and free PAHs. Those in the bound phase were nonadsorbable, while those in the free phase were adsorbed by the C18, thus affecting a separation. If PAHs that have been desorbed from a solid such as coal remain an integral part of a complex dissolved organic matrix, their ability to adsorb to a C18 phase may be inhibited.

Two desorption experiments were conducted using the all-glass filtration rig and fresh coal fines, as described in the materials and methods section. Each was conducted for 24 hours at a flow rate of 1 mL/min with hexane extractions of the collected eluents. The first, using 0.13 mole fraction methanol, failed to show detectable phenanthrene release. The second, using 0.10 mole fraction acetonitrile, showed significant release of phenanthrene in a pattern described well by first order kinetics, as shown in Figure 7. Acetonitrile is a less polar solvent than methanol, and this may have significantly affected the release kinetics for phenanthrene associated with surface sites. Some chrysene was desorbed, but the levels were too low to be quantified. Benzo(e)pyrene, added to these samples as an internal standard, was quantitatively recovered. This method was not employed further because of continuous solvent leaks, excessive pressure requirements, incomplete solvent-solids contact, and intermittent wetting-drying of the solids.

The time resolved leaching apparatus was used for most of the column work. A matrix of experimental conditions using 0.5, 1.0, 2.0 and 3.0 mL/min flowrate with 1.0, 2.0, and 4.0 g solids (WCRS sediment) was used to evaluate the effects of flowrate and solids loading on desorption rate. The solvent used was 0.10 mole fraction acetonitrile and the total leaching time for each condition was three hours. The results, in terms of phenanthrene concentrations, are shown in Table 4. Two trends were obvious. The mass-normalized

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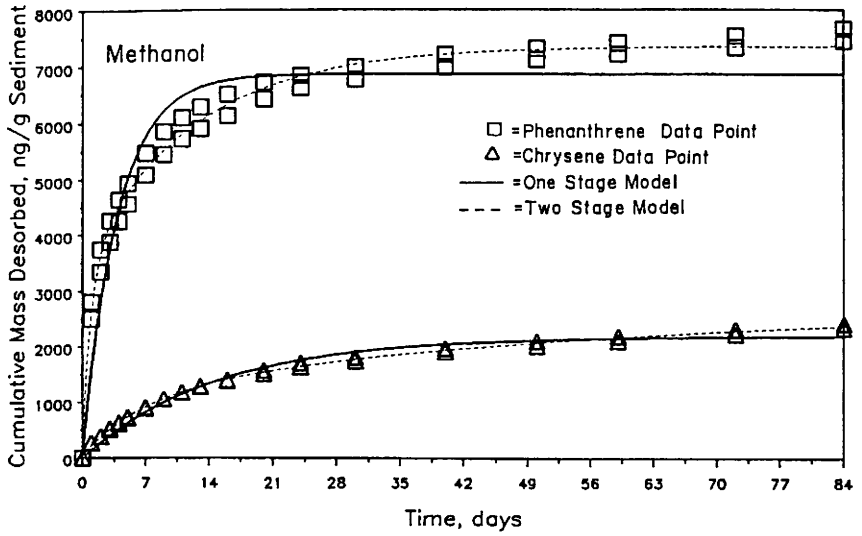

Figure 5. PAH desorption from coal pile retention basin sediments using a BFR experimental design and methanol as the solvent. Both one (solid line) and two stage (dashed line) first order models were fitted to phenanthrene (square symbols) and chrysene (triangle symbols) data.

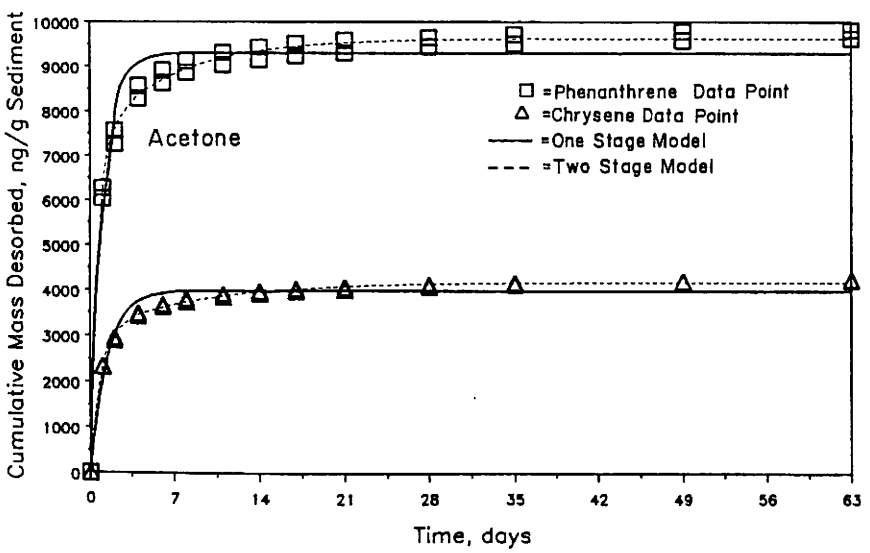

Figure 6. PAH desorption from coal pile retention basin sediments using a BFR experimental design and acetone as the solvent. Both one (solid line) and two stage (dashed line) first order models were fitted to phenanthrene (square symbols) and chrysene (triangle symbols) data.

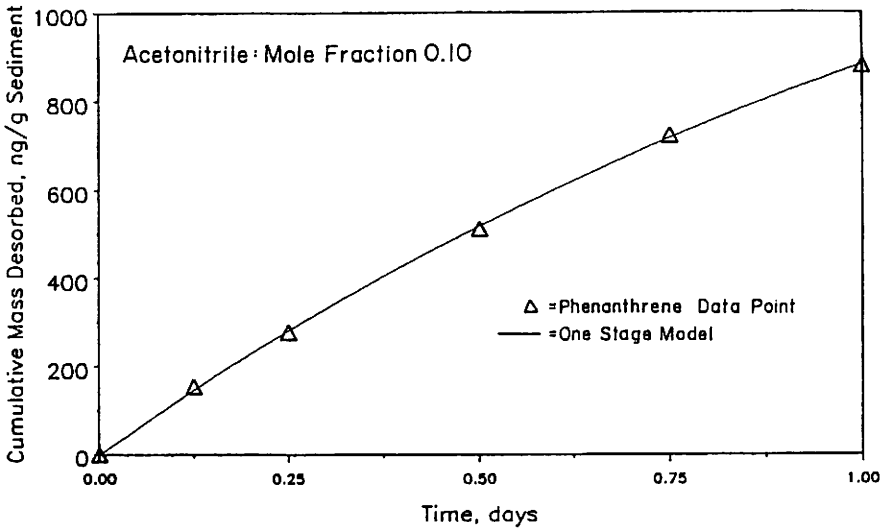

Figure 7. Phenanthrene desorption from fresh coal fines using a conventional column experimental design, 0.10 mole fraction acetonitrile/water as the solvent, and an all-glass filtration apparatus as a column. A single stage first order model (line) was fitted to the data (symbols).

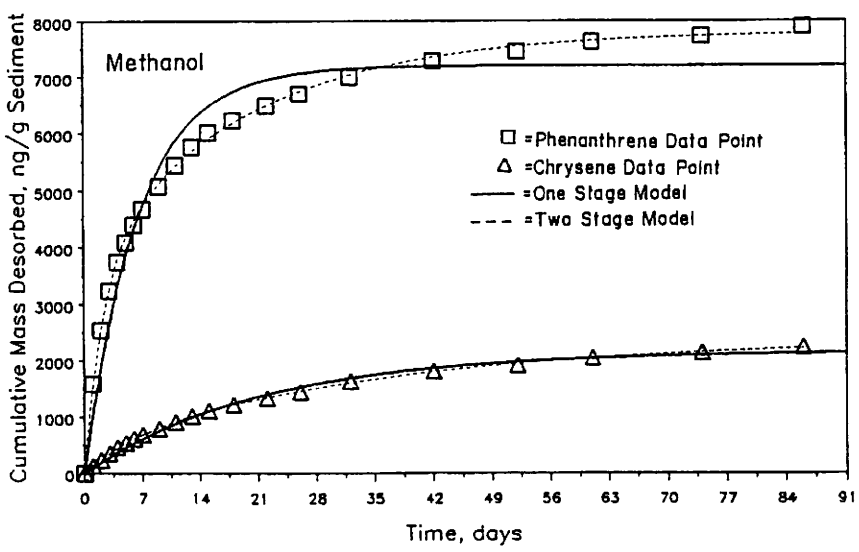

Figure 8. PAH desorption from coal pile retention basin sediments using a TRL experimental design and methanol as the solvent. Both one (solid line) and two stage (dashed line) first order models were fitted to phenanthrene (square symbols) and chrysene (triangle symbols) data.

Table 4. Effects of Flowrate and Solids Mass on Desorption Rates Observed with Coal Contaminated Sediments in a TRL Apparatus

Experiment 1: 0.10 mole fraction acetonitrile, WCRB sediments, and three-hour desorption time periods. Reported values are ng phenanthrene / g sediment for the entire time period.

Mass of Sediment, g	Flowrate, mL/min			
	0.5	1.0	2.0	3.0
1.0	16.6	50.4	94.5	ND (a)
2.0	13.7	48.8	72.7	95.2
3.0	12.9	25.3	42.8	ND

Experiment 2: 1.0 mole fraction methanol, CPRB sediments, and 50 mL leaching volumes. Reported values are ng phenanthrene / g sediment per minute of solvent contact.

Mass of Sediment, g	Flowrate, mL/min					
	0.5	1.0	2.0	4.0	6.0	8.0
0.5	ND	ND	ND	ND	50.0	ND
1.0	11.1	18.6	25.9	33.3	41.6 (b)	32.9
2.0	ND	ND	ND	ND	43.8	ND
3.0	ND	ND	ND	ND	45.9	ND
4.0	ND	ND	ND	ND	44.6	ND

(a) ND = Not determined
(b) Average of two determinations.

concentration of desorbed phenanthrene (mass phenanthrene/mass dry sediments) increased with flowrate, and decreased with increasing mass loading. As flowrate increased, so did the total volume of solvent used, a possible confounding variable. The experiment was repeated (Experiment #2) using a wider range of flowrates (0.5 to 8.0 mL/min), CPRB sediment, pure methanol, a single pass of the solvent over the solids, and a solids loading range of 0.5 to 4.3 g. The solvent volume was held constant at 50 mL while the contact time varied according to the flowrate used. These results are also presented in Table 4. With phenanthrene data normalized to both mass of solids and time (ng PAH/g solid/minute), the higher flowrates used showed a slight variation in desorbed amounts, with a maximum occurring at 6.0 mL/min, and significantly lower levels at 2.0 mL/min or less. Consequently, 6.0 mL/min was chosen for all subsequent TRL experiments. The effects of mass loading were subsequently examined at this flowrate. There was little variation across the range tested, thus 3.0 g was chosen for all subsequent TRL experiments. This loading gave the maximum solids mass which could be loaded into the TRL cell while still maintaining a high aspect ratio, or surface area to column thickness ratio.

Several experiments were run using the TRL configuration described above. Total run times varied from 100 minutes to 86 days, with any time scale over 10 hours employing a recycle of the leaching solution through the solids. Several solvent combinations were used, from 0.13 mole fraction methanol or 0.08 mole fraction acetone to pure solvents. The desorption curves obtained for phenanthrene and chrysene in CPRB sediments, as a result of pure methanol contact for 86 days, are shown in Figure 8. As with the batch desorption data, both a single and a two stage model were fitted to the data and are presented in Table 3.

Comparison of TRL and BFR Methods

A direct comparison between the results of the BFR desorption experiment in which 100 percent methanol was utilized during an 84 day contact period and the TRL data set in which 100 percent methanol was utilized during an 86 day contact period is appropriate. Each showed a well defined two-stage desorption process for both phenanthrene and chrysene; other trends were also apparent. When a single stage first order model was fitted to the data, values of $[C]_{eq}$ for both PAHs were similar using both TRL and BFR designs (Second column, Table 3). The TRL experiment employed a recirculating solvent system. The reservoir exchange frequency of this system was identical to the centrifugation/solvent exchange frequency of the BFR technique. If accumulation of organic compounds in the liquid phase affected observed desorption kinetics for one design, it should have equally affected that of the other design. The k_d values for phenanthrene and chrysene in the TRL method were smaller (60 and 70 percent, respectively) than the corresponding values in the BFR method.

The above results suggest that, while the final equilibrium concentration of PAHs may reach the same values using both techniques, rates obtained with the TRL method are slower than in the BFR method. This may have been caused by an incomplete contact of the solvent with all of the solid surfaces in the TRL cell, or mixing of the solvent in the small area of headspace at the top of the column. If desorbed PAHs mix into the volume at the top of the cell, the observed effect would be a delay in their release. An examination of dispersion within the empty TRL cell revealed that some mixing was evident, where elution of a phenanthrene spike was monitored over time. The calculated Peclet Number was 11.9, indicating that the dispersion could be modeled by two completely mixed reactors in series. It is probable that this mixing is significantly reduced in a fully loaded cell, however, and it should be noted that the "tailing" of a spike of phenanthrene injected at the beginning of the cell ended in less than 10 minutes, an insignificant time in the long term experiments.

When the parameters estimated by the two stage model from data obtained by the two methods (BFR and TRL) are compared, the BFR technique estimates lower asymptotic equilibrium values and higher desorption rates than the TRL method. These effects are less pronounced than they are with the single stage model, however. Since the two-stage model is both mechanistically and statistically a better estimation of the desorption process, the limitations previously mentioned may not be as significant. The principle of conditional error was used to test the hypothesis that data obtained from the TRL experiment and data obtained from the BFR experiment could be modeled better by a single fit than by individual fits. The hypothesis was rejected at the 0.05 level, suggesting that the two procedures are not totally interchangeable. Despite this, the two techniques estimated kinetic parameters within 43 percent of each other, a reasonably good agreement for two totally different experimental configurations. Over long periods of time, the TRL method requires exclusive use of somewhat expensive laboratory equipment, thus limiting the number of studies which may be conducted concurrently. The BFR technique, on the other hand, is limited only by the number of suitable centrifuge tubes/reactor bottles available. For short experiments, however, the time required for centrifugation is a severe limitation to the applicability of BFR techniques. TRL is ideally suited to short (one day or less) desorption experiments, while BFR is more appropriate for long-term studies.

The ability to predict the fate and distribution of PAHs in the environment is an important component of any regulatory effort regarding environmental contamination by these compounds. All too often the simplest approach, which utilizes equilibrium partitioning behavior without kinetic considerations, is used to fulfill this objective. This is due in part to the relative difficulty of obtaining estimates of kinetic parameters, especially for slow processes such as desorption of hydrophobic compounds from highly sorptive matrices such as coal fines or coal contaminated sediments. The use of organic cosolvents, in TRL and BFR reactor configurations, has been shown to be a relatively simple technique for the estimation of desorption rates, particularly where such processes are either too slow or too difficult to readily quantify under other laboratory conditions.

SUMMARY AND CONCLUSIONS

Four methods for determining the desorption kinetics of PAHs in coal contaminated sediments were presented, including simple batch, batch with fluid replacement (BFR), conventional column, and time resolved leaching (TRL). The BFR and TRL methods were both successful and their results compared reasonably well, although kinetic parameter estimates from the two methods were significantly different. The BFR technique was best suited to long-term studies while the TRL technique was best suited to short-term (one day or less) experimental periods. An evaluation of the effects of flowrate and mass loading on the initial rate of phenanthrene release was presented for the TRL experiments. Simple batch and conventional column techniques, as examined, were fraught with physical and chemical limitations and are not recommended.

Desorption curves were presented for the temporal release of the PAHs phenanthrene and chrysene from sediments from the coal pile retention basin and the waste coal runoff stream. Data from the desorption curves were fitted to both single and two stage forms of a first order kinetic relationship. For long term experiments (greater than four days) a two stage model provided a significantly better fit to the data than did a single stage model, as tested by the principle of conditional error, suggesting that a two stage model is probably more appropriate for the desorption process.

This work presents two useful methods for determining desorption kinetics of an important class of environmental contaminants in a solid system commonly found throughout the

global environment. While the two preferred methods are relatively labor intensive, they are widely applicable and may be used for a host of solid matrices and organic compound pairs. The use of organic solvents to enhance solubilization of the hydrophobic compounds may limit the direct environmental application of observed desorption rates, but may be directly applicable to some situations, such as contaminated aquifers or landfill leachates where discrete organic layers may coexist with aqueous solutions. Finally, these methods may be useful in providing reasonable estimates of desorption rates for compound-matrix combinations which in pure water are either too slow or too difficult to readily determine under other laboratory conditions.

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Local Impacts of Coal Mines and Power Plants across Canada. I. Thallium in Waters and Sediments

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A Canada-wide survey was undertaken of sites associated with coal mines and coal-fired electrical generating stations. Several water samples were found to contain very high concentrations of thallium, iron and manganese. High thallium concentrations were found in several sites in Eastern Canada, in spite of the greater coal consumption and production in the western and central regions. The data suggest that coal type (rather than quantity) and/or regional geological contributions are responsible for the high Tl concentrations observed. Our findings, coupled with others around the world, strongly indicate that Tl is an environmental pollutant. In sediments, the observed high ratios of Tl/Hg suggest there is an enrichment of Tl by at least 25% when compared to crustal concentration ratios.

Key words: **coal mine, power plant, thallium, thallium enrichment, mercury, waters and sediments**

Introduction

Coal is Canada's most abundant fossil fuel. Its annual production and consumption exceed 78 and 55 million tonnes, respectively (Table 1, The Coal Association of Canada 1997). Across Canada there are 35 active coal mines and 25 coal-fired generating stations (Tables 2 and 3). Coal is also important to the Canadian economy and its exports are worth $2 billion (Natural Resources Canada 1994).

However, the effects of coal production and consumption may be detrimental to the environment. For example, Smith and Carson (1977) reported that the air emissions from the 415 American coal-burning power plants in highly populated regions form the largest collective source of thallium (Tl) discharged atmospherically. Four states around the Great Lakes (including Ohio), along with Texas, have the highest coal-fired generating capacity in excess of 15,000 megawatts of electrical power. Indeed, we recently found that the concentration of dissolved Tl in the Great Lakes waters, particularly Lake Erie, is higher than that of cadmium (Cd). These two facts led us to suspect that high concentrations of Tl and other metals, as well as organics, may be found surrounding coal

Table 1. Production, consumption, import and export of coal in Canada (in tonnes)

Province	Production	Consumption	Import	Export
British Columbia	27,892,747	200,817	—	27,278,581
Alberta	36,343,416	26,264,343	—	9,181,069
Saskatchewan	11,652,553	10,018,189	—	—
Manitoba	—	263,829	185,572	—
Ontario	—	13,877,042	11,393,496	—
Quebec	—	732,265	750,265	—
New Brunswick	170,958	1,326,676	1,150,622	—
Nova Scotia	2,632,994	3,051,199	—	49,924
Total	78,692,668	55,734,360	13,479,955	36,509,574

mines and coal-based power plants, with consequent environmental effects. This part of the study describes a Canada-wide survey of local impacts of coal mines and power plants in terms of thallium and other metals in waters, as well as thallium and mercury in sediments (part 2 will deal with metals, organics and toxicity in sediments).

Materials and Methods

Mines and Power Plants in Canada

The study was designed to include all Canadian active coal mines and coal-burning electrical power plants (generating stations), the locations of the principal ones being shown in Fig. 1 and 2. These mines have a saleable production of coal ranging from 0.27 million tonnes by NB Coal Limited to 12.7 million tonnes by Highvale (The Coal Association of Canada 1998). Alberta and other western provinces have more plants and mines than the eastern and central provinces combined. Most of the sites were accessible and therefore sampled, and the remaining sites were either closed or inaccessible, as access permission was not provided (by two companies).

The following companies provided permission to collect water and sediment samples from their sites: Alberta Power Limited, Cape Breton Development Corporation, Edmonton Power, Luscar Ltd., Manalta Coal Ltd./Prairie Coal Ltd. Mines, Manitoba Hydro, NB Coal Limited, New Brunswick Power Corporation, Nova Scotia Power, Ontario Hydro, Quinsam Coal Corporation, SaskPower, Smoky River Coal Limited, and TransAlta.

Sampling Protocols

At each sampling location (a mine or a generating station), there are at least three sampling sites: water intake such as upstream of a river,

Table 2. List of all active coal mines in Canada and their owners

Principal mines and their owners
(1997 data from the The Coal Association of Canada)

British Columbia
- Quinsam, Quinsam Coal Corporation
- Bullmoose, Teck Corporation
- Quintette, Teck Corporation
- Fording River, Fording Coal Ltd.
- Greenhills, Fording Coal Ltd.
- Line Creek, Line Creek Resources Ltd.
- Elkview, Teck Corporation
- Coal Mountain, Fording Coal Ltd.

Alberta
- Smokey River, Smokey River Coal Ltd.
- Obed, Luscar Ltd.
- Highvale, TransAlta Utilities Corporation
- Whitewood, TransAlta Utilities Corporation
- Luscar, Luscar Ltd.
- Gregg River, Manalta Coal Ltd.
- Coal Valley, Luscar Ltd.
- Genesee, Edmonton Power & Fording Coal Ltd.
- Vesta, Alberta Power Ltd.
- Paintearth, Luscar Ltd.
- Montgomery, Manalta Coal Ltd.
- Sheerness, Luscar Ltd.

Saskatchewan
- Poplar River, Manalta Coal Ltd.
- Utility, SaskPower
- Boundary Dam, Luscar Ltd.
- Costello, Manalta Coal Ltd.
- Shand, Luscar Ltd.
- Bienfait, Luscar Ltd.

New Brunswick
- NB Coal (Minto), NB Coal Ltd.

Nova Scotia
- Prince, Cape Breton Development Corporation
- Phalen, Cape Breton Development Corporation

Minor mines
(Natural Resources Canada 1998)

Alberta
- Dodds
- Egg Lake

Nova Scotia
- Stellarton
- Thomas Brogan
- Evans
- Thorbourn

Table 3. List of coal-based electrical generating stations and their owners

Alberta	
	Sundance, TransAlta Utilities Corporation
	Wabamun, TransAlta Utilities Corporation
	Keephills, TransAlta Utilities Corporatioin
	Battle River, Alberta Power Ltd.
	H.R. Milner, Alberta Power Ltd.
	Sheerness, Alberta Power Ltd. and TransAlta Utilities Corporation
	Genesee, Edmonton Power
Saskatchewan	
	Boundary Dam, Saskpower
	Poplar River, Saskpower
	Shand, Saskpower
Manitoba	
	Brandon, Manitoba Hydro
	Selkirk, Manitoba Hydro
Ontario	
	Nanticoke, Ontario Hydro
	Lakeview, Ontario Hydro
	Lambton, Ontario Hydro
	Thunder Bay, Ontario Hydro
	Atikokan, Ontario Hydro
New Brunswick	
	Belledune, New Brunswick Power
	Dalhousie, New Brunswick Power
	Grand Lake, New Brunswick Power
Nova Scotia	
	Lingan, Nova Scotia Power
	Glace Bay, Nova Scotia Power
	Point Alconi, Nova Scotia Power
	Trenton, Nova Scotia Power
	Point Tupper, Nova Scotia Power

water discharge after the intake has gone through all necessary processes, and water at the tailing/disposal site such as downstream or pond. Additional samples such as those from settling lagoons, nearby lakes and rivers are also included if available.

Bottle washing

All containers were washed as follows: rinsed with hot tap water and emptied well, soaked with 30% nitric acid for at least 1 week, rinsed with Milli-Q water six times, and soaked with 0.2% nitric acid (high purity) for a minimum of 1 week before use. Sub-boiled Seastar acid was used to preserve samples.

Water sampling

Van Dorn bottles were used whenever possible. If the Van Dorn bottle was inappropriate, a "scoop" technique was used, where a "sampling bottle" (250-mL bottle) was scooped to an arm-length depth under the

Fig. 1. Coal-fired electrical generating stations in Canada.

Fig. 2. Principal coal mines in Canada.

water surface. A sample bottle was rinsed three times with the actual sample first before it was filled up to top. Standard precautions were followed, such as avoiding touching the bottle rim throughout sample collection and handling, tightening bottle caps to avoid cross contamination due to possible leakage during transportation, bagging blanks separately from samples, storing samples in ice chest immediately, collecting sediments last and bagging them completely separated from water samples. A total of 279 different samples were collected.

Sediment sampling

Several sites for initial examination were selected in this study. Thirty- two sediment samples were collected, 17 from power plant sites and 15 from mine sites. A mini-ponar sampler (1 to 2 L) or an Eckman sampler was used to collect sediment samples. All containers, bags, spoons and other utensils used were plastic. All sediment samples were collected after water collection.

Collection of blanks and duplicate samples

The collection of blanks using a Van Dorn bottle was done as follows. On site and just before collecting the first upstream water sample, the Van Dorn bottle was well rinsed with 1 L of ultrapure water. The last part of the rinsing water was collected into a small bottle marked "blank before". The upstream water sample was then collected in duplicate by rinsing and then filling two separate small bottles to the rim. The "blank after" was obtained by rinsing the Van Dorn bottle with 1 L of ultrapure water, the last part of which was saved as blank.

The collection of blanks using a "scooping" technique was similarly processed as above. On site and just before collecting the first upstream water sample, a 250-mL sampling bottle was rinsed three times with 20 to 30 mL of ultrapure water and the fourth rinse was saved as "blank before". The upstream water sample was then collected in duplicate by scooping the 250-mL bottle into an arm-length depth and by rinsing then filling two separate small bottles to the rim. The "blank after" was obtained as above by collecting the fourth rinse. In total, about 7% of the samples were blank samples . More than 40% of the samples were measured for pH before acidification to give an idea of the sample acidity. Most samples had a pH between 7 and 8. Duplicate samples for discharge and downstream sites were collected as above.

Separate bagging

Samples for blanks, upstream, discharge, downstream and sediment were bagged separately to avoid cross-contamination.

Sample Collection, Handling and Preservation

Water samples were refrigerated immediately after collection and maintained at 4°C. When in our laboratory, the samples were allowed to settle in a 4°C room overnight or over the weekend. The clear samples, i.e., those without visible particulates, were preserved by acidifying the whole bottle content to 0.2 % HNO_3. From the samples with visible particulates settled at the bottom of the bottle, 20 mL of the clear upper layer was pipetted (called decantate) into a clean container and preserved at 0.2% HNO_3. The samples with suspended materials were centrifuged and the decantate acidified. Those samples, which were cloudy due to suspension or naturally colored due to humic substances, were centrifuged and acidified as above. Samples with high-salt content, as evidenced by severe peak height suppression during analysis for thallium, were diluted 10 times or more until the suppressive effect was manageable.

Sediment samples were refrigerated at 4°C until use. Plastic bottles of 250 mL in size were used for the wet sediments, which were freeze-dried, crushed, sieved and subsampled for the determination of Tl and Hg.

Analytical Methods and Analytes

Trace metals in waters were determined using the inductively coupled plasma–atomic emission spectrometry (ICP-AES). The detection limits (in mg/L) were 0.034 for Cd, 0.009 for Co, 0.009 for Cr, 0.01 for Cu, 0.012 for Fe, 0.002 for Mn, 0.02 for Ni, 0.025 for Pb, 0.126 for Tl and 0.009 for Zn. Thallium, undetected in both substrates by ICP-AES, was determined by the LEAFS (laser-excited atomic fluorescence spectrometric) methods recently developed by Cheam et al. (1996; 1998). The method for water analysis had a detection limit of 0.03 ng/L for thallium and that for sediment 0.5 ng/g of Tl. Mercury in sediments was determined by the cold vapor atomic absorption spectrometry, and the detection limit was 2 ng/L of mercury for aqueous solutions.

The sediment extraction procedures for metals were as follows. For thallium, a weight of 0.1 g of sediment was used and dissolved via the simple cold dissolution procedure; it used 2.5 mL of concentrated nitric acid and 2.5 mL of concentrated hydrofluoric acid, followed by a dilution (Cheam et al. 1998). For mercury, 0.2 g of sediment was weighed into a microwave Teflon bottle followed by the addition of 5 mL of HNO_3. The mixture was left to stand over the weekend and was microwaved. Three-and-a-half mL of the digested solution was pipetted into a volumetric flask, diluted to 100 mL, preserved by BrCl, and analyzed by a cold vapor atomic absorption method.

Results and Discussion

Thallium and Other Metals in Water

Metals determined by ICP included Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Tl and Zn. Seventy-nine percent of the total data showed "less than" values, and of the 21% reportable positive results, more than half were Fe and Mn results. For the Highvale Mine, the "pit 2 drain" site contained up to 70 mg/L of Fe and positive results for other metals, except Pb and Tl. The

"pit 3 settling pond" inflow had 40 mg/L of Fe compared to only 0.01 mg/L for the outflow. For other metals, the inflow concentration was also greater than the outflow, indicating an effective removal mechanism of metals in the settling pond. It was interesting to note that the Fe concentration of the local groundwater (well water) contained a high Fe concentration of 20 mg/L. The three sites had positive, but relatively low results — < less than 1 mg/L, for Mn and most other metals.

The impoundment #5 discharge of the Paintearth Mine contained a very high Fe concentration of 122 mg/L. This mine is located by the Paintearth Creek, whose upstream Fe concentration was fairly high at 1.5 mg/L, and downstream concentration at 7 mg/L. Also the mine's runoff discharge contained 10 mg/L of Fe. The coal pile runoff of the Lingan generating station had a high Fe content of 72 mg/L and 4 mg/L of Mn, but the wastewater discharge to lagoon and ash lagoon return contained less than 1 mg/L of Fe and 2 mg/L of Mn, respectively. Other sites containing more than 1 mg/L of Fe included the spoil pond 5-5 of the Boundary Dam generating station, the ash lagoon slurry of the Keephills generating station and the settling pond discharge MSA of the Line Creek Mine. The sites at the Belldune generating station had high Mn concentrations, the treated discharge containing 73 mg/L, the equalization pit 55 mg/L and the coal pile runoff 14 mg/L of Mn. On the other hand, Fe concentrations in these sites were less than 1 mg/L. These sites also contained positive results of Ni and Co.

Besides Fe and Mn, nickel had only 24% of its data as reportable positive results and cobalt had 22%. Other metals had lower percentages: Cr 18%, Zn 16%, Cu 11%, Pb 6%, Cd 1% and Tl 0%. Since Tl is a very toxic element and of particular importance, according to the statement by Smith and Carson (1977) that the air emissions from coal power plants form the largest collective source of Tl discharge into the environment, Tl was also measured by the LEAFS method and is discussed below. For all the metals measured, the upstream metal concentrations were found to be smaller than the downstream, discharge or pond concentrations 95% of the time.

Table 4 shows Tl results in western coal mine waters. Samples with brown-black deposits and brown decantate such as those from the Highvale and Paintearth mines tended to have higher Tl concentrations than other samples. For three such samples from the Highvale mine, centrifugation did not help bring down Tl concentration of the decantates. It appears that decantation (careful pipetting of 20 mL of the solution above the deposit) was representative of the water samples. Also, samples from settling pond, pit water, downstream and discharge usually had concentrations (1100 to 1300 ng/L) higher than those from upstream or water intakes (low ng/L). The eastern mines, including the abandoned ones, showed high Tl concentrations of about 700 ng/L (Table 5). Although these concentrations were not as high as those observed in the eastern power plant sites (discussed below), they might have come from the same Tl sources.

Table 4. Thallium concentrations in ng/L in waters from western coal mines

Western mines	Site/sample description	Tl concentration
Whitewood Mine (TransAlta Utility Corp.)	Pit water discharge (some black deposit, clear decantate), decanted[a]	6.64
Highvale Mine (Manalta Coal)	Pit 2 drain (brown deposit, ~ clear dark brown decantate), decanted	463.6
	Duplicate, centrifuged[b]	518.5
	Pit 3 (some brown deposit, ~ clear dark brown decantate), decanted	106.9
	Duplicate, centrifuged	109.3
	Beaver Creek (clear)	2.92
	Pit 3 settling pond — outflow (clear)	0.32
	Pit 3 settling pond — inflow (black deposit, clear dark brown decantate) decanted	846.1
	Duplicate, centrifuged	1326.2
	Well water (local groundwater) (visible particulates[c], clear decantate), decanted	5.47
Genesee Mine	Mine drainage (some brown deposit, clear decantate), decanted	7.52
Coal Valley Mine	Tailings discharge (visible particulates, clear decantate), decanted	7.20
Luscar — Sterco (Luscar Ltd.)	Lovett River intake (clear)	2.82
	Duplicate, centrifuged	2.43
	Coal Creek impoundment (clear)	2.70
	Lovett River downstream (clear)	8.64
	Duplicate	4.21
	25 ? east mine drain (visible particulates, clear decantate), decanted	16.4
	Centre Creek — treated water (clear)	16.6
	Reservoir — well water (clear)	1.74

(continued)

Table 4. *(continued)*

Western mines	Site/sample description	Tl concentration
Gregg River Mine (Manalta Coal)	HI pit — plant makeup (clear)	16.3
	Plant site water reservoir (clear)	63.9
	Refuse = tailings (black coal-like deposit, clear decantate), decanted	9.49
	Well water — tap (clear)	3.67
Cardinal River Mine (Luscar Ltd.)	West Jarvis Creek intake (clear)	4.13
	Luscar Creek downstream plant (visible particulates, clear decantate)	6.54
	Duplicate, decanted	5.92
Cardinal River Mine (Luscar Ltd.)	Tailings (black coal-like deposit, clear decantate), decanted	17.1
	Well water (clear)	1.46
	Luscar Creek, downstream Cardinal and Gregg mines (clear)	3.56
Whitehorse Creek	At Mountain Park (clear)	1.78
	Downstream Mountain Park (clear)	1.33
	Downstream Cadomin — abandoned, but active quarry (clear)	2.39
Gregg River	Downstream Gregg River Mine, at Hwy 40 (clear)	2.59
Obed Mountain Coal (Luscar Ltd.)	E. conveyor settling pond (visible particulates, clear decantate), decanted	3.61
	Main tailings pond (lower) (visible particulates, clear decantate), decanted	0.91
	Reservoir (treated water) (visible particulates, clear decantate), decanted	7.97
	Main tailings pond (upper) (dark brown deposit, clear decantate), decanted	2.24
	Duplicate, decanted	2.95
	LSP2 — coal storage drain (for rail shipment) (clear)	19.1
Smoky River Coal (Smoky River Coal)	Sheep Creek upstream Smoky River (clear)	2.42

(continued)

Table 4. *(continued)*

Western mines	Site/sample description	Tl concentration
Line Creek Mine (Manalta Coal)	Settling pond discharge — MSA north ponds (clear)	5.26
	Line Creek upstream — 0200335 (clear)	0.66
	Duplicate	0.20
	South pit water (dark brown deposit, clear decantate), decanted	217.4
	Line Creek downstream (clear)	6.92
	Duplicate	5.37
	Wash water after thickener (visible particulates, clear decantate), decanted	38.5
	Tap water not treated (clear)	9.07
Elk River	At Sparwood downstream from four mines (clear)	2.51
Crowsnest Creek	Crowsnest Pass (downstream coal mountain mine) (clear)	9.09
Sheerness Mine (Luscar Ltd.)	Pit water (visible particulates, light decantate), decanted	10.6
Montgomery Mine (Manalta Coal)	Pit water (visible particulates, light decantate), decanted	1.84
	Settling pond discharge (visible particulates, light decantate), decanted	4.55
Carolside reservoir	Downstream mines and GS (visible particulates, light decantate), decanted	4.19
Paintearth Mine (Luscar Ltd.)	Surface runoff discharge (very brown, brown decantate), decanted	811.2
	Section 7 Lake (pit and surface runoff) (dk brown, lt brown decantate),decanted decanted	63.0
	Impoundment #5 discharge (black deposit, visible brown decantate), decanted	1119.1
	Paintearth Creek downstream (very brown deposit, light brown decantate), decanted	257.3
	Paintearth Creek upstream (brown deposit, very light brown decantate), decanted	35.7
	Blank before	0.73
	Blank after	0.93

(continued)

Table 4. *(continued)*

Western mines	Site/sample description	Tl concentration
Vesta Mine	North drainage (brown deposit, very light brown decantate), decanted	53.5
(Manalta Coal)	Vesta east — Pond 3 (brown deposit, clear decantate), decanted	51.7
Crowsnest River	Upstream Chinook coal plant, Coleman, Alberta (clear)	4.29
(Chinook Coal)	Decommissioned in 1978 (clear)	4.72
(Manalta Coal)	Blank before (clear)	0.14
	Blank after (clear)	0.72
	Downstream Chinook coal plant (clear)	3.96
	Duplicate	4.72
	Downstream Coleman and Frank slide (clear)	5.07
	Downstream Leitch Colliery (clear)	2.95
Hell's Gate	Groundwater (clear)	2.58
Athabasca River	Hwy. 93 south of Jasper (clear)	1.03
Poplar River North Mine	Settling pond NSP1 (clear)	2.81
(Prairie Coal Ltd.)	Upstream East Poplar River (clear)	0.92
	Duplicate	1.19
	East Poplar River — upstream blank (clear)	0
	Duplicate	0
	East Poplar River — downstream (clear)	3.79
Utility Mine (Prairie Coal Ltd.)	Settling pond E-4	34.9
	Pond near coal storage pile	6.86
	Dewatering discharge into BD reservoir	8.05

(continued)

Table 4. *(concluded)*

Western mines	Site/sample description	Tl concentration
Boundary Dam mine	Settling pond/holding pond	17.7
(Estervan Coal Corp.)		
Bienfait Mine	Dewatering discharge from west side of mine	50.7
(Estervan Coal Corp.)	Discharge from mine areas of section 4-2-6-W2M (V-notch weir)	12.8
Costello Mine expansion	Dewatering discharge from proposed mine	1.26
(Prairie Coal Ltd.)		
Old Mac Mine — abandoned	Old coal spoil pond (Old Mac Mine)	0.31
Quinsam Mine	Blank before (clear)	1.13
(Quinsam Coal Corporation)	Blank after (clear) on Quinsam River flowing towards mine (clear)	0.19
	Duplicate	0.68
	Settling pond (clear)	5.69
	Duplicate	6.27
	Downstream from the mine on Quinsam River before going into the small lake (clear)	0.35
	Duplicate	0.53
	Downstream outlet of the small lake (clear)	1.47
	Duplicate	1.07

[a] Decanted refers to 20 mL pipetted from the top of bottle, which was left to settle in the cold room overnight or longer.
[b] Centrifuged refers to sample being centrifuged as compared to decanted.
[c] Visible particulates are particulates at bottom of bottle.

Table 5. Thallium concentrations in ng/L in waters from eastern coal mines

Eastern mines	Site/sample description	Tl concentration
8200 Salmon Harbour Mine (New Brunswick Coal)	Pit water (visible particulates, clear decantate), decanted[a]	53.3
	Duplicate, decanted	35.2
	Lagoon discharge (visible particulates, [b]clear decantate), decanted	9.33
	Duplicate, decanted	6.55
	Lake water (visible particulates, clear decantate), decanted	7.72
	Duplicate, decanted	7.43
Phalen Colliery, Nova Scotia (Cape Breton Development)	Mine water discharge (high Na) (brown clear decantate), decanted	424.0
	Town water (from tap at security) (clear)	4.13
	Surface runoff brook (visible particulates, clear decantate), decanted	169.2
Victoria Junction coal Preparation plant, Nova Scotia (Cape Breton Development)	V.J. tailings basin — old final discharge KL1 (clear)	18.9
	V.J. tailings basin KL3 (clear)	1.47
	V.J. final discharge WWT3 — treated water (clear)	121.1
	North and south process wells — for wash and town water (clear)	0.64
	Surface water pond WWT1 (brown, clear brown decantate), decanted	404.3
Prince Colliery, Nova Scotia (Cape Breton Development)	Process water — reservoir and well combined (clear)	1.95
	Mine discharge and coal pile runoff (light clear decantate), decanted	698.3
	Treated lagoon discharge (clear)	565.0
	Downstream discharge (clear)	552.5
	Duplicate	514.0

(continued)

Table 5. *(concluded)*

Eastern mines	Site/sample description	Tl concentration
Abandoned coal mines[c]		
Gardiner Mine	Mine discharge (clear brown decantate)	0.15
Pioneer Coal	At Sydney Airport	100.9
	Duplicate	107.2
Brogan Brothers	At Point Aconi 5th seep	83.8
Brogan Brothers	At Point. Aconi 11th seep	76.5
Prince	At Edwards Pond	660.6
Prince	Duplicate	718.5

[a] Decanted refers to 20 mL pipetted from the top of bottle, which was left to settle in the cold room overnight or longer.

[b] Visible particulates are particulates at bottom of bottle; particulates in decantate may give high results if decantate is not diluted — filtration or digestion may be needed for more accurate results if dilution is not done.

[c] Samples were subsampled by Henry Wong, NWRI, Environment Canada.

The majority of results for the generating stations in western provinces were low (Table 6). The blank values ranging from 0 to 6 ng/L were considered acceptable as the clean-room practices (clean hood, special clean clothes or gloves) were not followed since it was deemed unnecessary to use them in this study. The results for discharge water, ash lagoon, ash slurry or downstream were higher than for other locations, but even the highest results — 97 ng/L for Long Creek below Boundary Dam reservoir, or 140 to150 ng/L for Keephills ash lagoon slurry — were low when compared to the high results of some sites to be discussed below.

Samples collected from the eastern power plants sites in New Brunswick and Nova Scotia generally contained higher Tl content than their western or central counterparts (Table 7). For example, the ash lagoon discharges of Grand Lake and Trenton power plants contained some 12,000 ng/L and 24,000 ng/L of Tl, respectively. The other generating stations, such as Belledune, Lingan, Point Aconi and Point Tupper, also had elevated Tl concentrations of up to 5000 ng/L. These levels could be the result of the local geological contribution in the eastern provinces, or the type of coal used. The Belledune generating station, for example, reportedly had been using 75% Columbian coal and 25% Salmon Harbour coal. The Tl concentrations in the central (Ontario) sites were relatively low, the highest being only 175 ng/L (Table 7) and the mean value 38 ng/L. The western sites had a mean value of 47 ng/L (range between 0 and 1326 ng/L), whereas the eastern sites' mean value was 1376 ng/L (range between 0 and 23,605 ng/L). Even if we include the Tl concentrations in lakes around the Inco smelters in Sudbury, Ontario, which we recently measured, the mean value for the central region would still be small. Also, several water samples collected from the province of Quebec were found to contain small Tl concentrations.

Even though the Great Lakes are surrounded by the biggest consumers of coal used in coal-fired generating stations in both the U.S. (Fig. 3) and Canada (Table 8), the concentrations of Tl in the Great Lakes waters (Cheam et al. 1995) were much lower than those found in waters from the eastern generating stations (Table 7). The numerous power plants and mine sites in Western and Central Canada also contained smaller Tl concentrations than their eastern counterparts. These two facts tend to indicate that it is not the amount but the type of coal used and/or the local geochemical contributions that caused some of the higher Tl concentrations observed in the eastern provinces. Chou and Uthe in 1995 had observed high Tl content in Belledune Harbour and although the source of Tl was obscure, they suspected that the nearby fertilizer plant and the lead smelter, as well as the power plant, were the sources of thallium. Zitko et al. (1975) reported very high Tl concentrations (up to 88,300 ng/L) in the South Tomogonops River, Little River and South Little River in northeastern New Brunswick. South Tomogonops and South Little rivers received discharges from base-metal mining operations. Wong (personal communication) had found very high Tl content in some local sediment samples, such as those from Upsalquitch Lake.

Table 6. Thallium concentrations in ng/L in waters from western generating stations (GS)[a]

Western GS	Site/sample description	Tl concentration
Wabamun GS (TransAlta Utility)	Intake water (clear)	0.15
	Duplicate	0.61
	Blank before (clear)	0.90
	Blank after (clear)	0.05
	Ash lagoon effluent (clear)	5.87
	Duplicate	4.57
	Ash slurry (some black deposit, clear decantate), decanted[b]	8.44
	Duplicate, centrifuged[c]	11.4
	Discharge water (clear)	2.53
Wabamun Lake	At Wabamun downstream Wabamun GS (clear)	1.78
Sundance GS (TransAlta Utility)	North Saskatchewan River intake (clear)	2.27
	Duplicate	2.01
	Blank before (clear)	1.02
	Blank after (clear)	0.27
	Pond discharge (clear)	5.83
Keephills GS (TransAlta Utility)	River makeup (clear)	1.40
	Duplicate	3.29
	Blank (clear)	0.04
	Cooling pond discharge (clear)	4.32
	Duplicate	4.36
	Ash recirculation water (clear)	8.46
	Ash lagoon slurry (some black deposit, clear decantate), decanted	140.2
	Duplicate	150.6

(continued)

Table 6. *(continued)*

Western GS	Site/sample description	Tl concentration
Genesee GS (Edmonton Power)	Intake water (clear)	7.27
	Duplicate	7.06
	Blank before (clear)	3.97
	Blank after (clear)	1.32
	Discharge water (clear)	15.1
	Duplicate	12.4
North Saskatchewan River	Downstream Keephills and Sundance GS. (clear)	15.1
H.R. Milner GS (Alberta Power Ltd.)	Wastewater — discharge (visible particulates,[d] clear decantate), decanted	9.25
	Smoky River intake (clear)	1.15
	Final discharge (visible particulates, clear lt brown decantate), decanted	4.09
	Duplicate	6.90
	Duplicate, centrifuged	2.26
H.R. Milner GS	Smoky River downstream discharge (clear)	2.69
Smoky River	Upstream Sheep Creek (clear)	3.17
	Duplicate	2.89
	Upstream H.R. Milner GS at Hwy. 40 (clear)	1.89
	Duplicate	3.40
	Blank before (clear)	0.03
	Blank after (clear)	0.01

(continued)

Table 6. *(continued)*

Western GS	Site/sample description	Tl concentration
Sheerness GS (Alberta Power Ltd.)	Intake water (visible particulates, clear decantate), decanted	5.13
	Discharge water (visible particulates, clear decantate), decanted	8.30
	Duplicate, decanted	8.65
	Duplicate, centrifuged	17.5
	Duplicate, centrifuged	8.41
	Cooling water lagoon (clear)	9.47
	Duplicate	6.43
Battle River GS (Alberta Power Ltd.)	Battle River upstream (visible particulates, clear decantate), decanted	7.87
	Duplicate, decantated	7.11
	Intake water (visible particulates, clear decantate), decanted	1.81
	Ash lagoon — input (some black deposit, clear decantate), decanted	37.9
	Ash lagoon — discharge (some dark deposit, clear decantate), decanted	18.6
	Discharge water (visible particulates, clear decantate), decanted	6.64
	Duplicate, decanted	2.62
	Spillway downstream (visible particulates, clear decantate), decanted	14.1
	Battle River downstream (clear)	3.53
	Duplicate	6.68
	Blank before (clear)	2.46
	Blank after (clear)	5.78

(continued)

Table 6. *(concluded)*

Western GS	Site/sample description	Tl concentration
Boundary Dam GS (Saskpower)	Spoil pond 5-5 (SERM Station No. 72579) (clear)	36.2
	Spoil pond 32-5 (SERM Station No. 72524) (clear)	30.5
	Long Creek inlet (BDC1-SERM208) — upstream Boundary Dam Reservoir (clear)	3.12
	Cooling water inlet (BDC2-SERM72506) (clear)	21.5
	Cooling water discharge canal: return to reservoir (BDC1-SERM44886) (clear)	24.7
	Long Creek below Boundary Dam reservoir (BDC3-SERM235) (clear)	97.5
	Upstream Souris River near Boundary Dam GS (clear)	4.48
	Duplicate (clear)	2.98
	Blank before (clear)	0.04
	Blank after (clear)	0.11
	Downstream Souris River at Nopney's Crossing	1.54
Poplar River GS (Saskpower)	Auxiliary cooling water (ACW) canal discharging to Cookson reservoir	0.19
	Downstream East Poplar River (SERM 541)	5.21
Shand GS zero discharge plant) (Saskpower)	Raw water sample	35.7
Estevan GS (inactive) (Saskpower)	Discharge into drainage ditch No. 7	65.0
	Ash lagoon No. 5 (SE corner)	6.32
Selkirk GS (Manitoba Hydro)	Red River intake	16.5
	Well intake	15.7
	Selkirk discharge	63.9

[a] GS, coal-fired electrical generating station.
[b] Decanted refers to 20 mL pipetted from the top of bottle, which has been left to settle in the cold room overnight or longer.
[c] Decanted refers to 20 mL pipetted from the top of bottle, which has been left to settle in the cold room overnight or longer.
[d] Visible particulates are particulates at bottom of bottle.

Table 7. Thallium concentrations in ng/L in waters from Eastern and Central Ontario generation stations (GS)[a]

	Site/sample description	Tl concentration
Belldune GS[b] (New Brunswick Power)	Coal pile runoff (brown-black deposit, clear decantate), decanted[c]	744.1
	Equalization pit (plant waters) (dark deposit, clear decantate), decanted	2376.6
	Treated discharge (visible particulates, clear decantate), decanted	4000.5
	Ash leachate pond discharge (clear)	5087.1
Grand Lake GS (New Brunswick Power)	Ash lagoon discharge (clear)	11989.0
	Duplicate	11453.0
	Lake (visible particulates, clear decantate), decanted	159.1
	Intake water (visible particulates, clear decantate), decanted	25.4
	Duplicate, decanted	23.3
Lingan GS (Nova Scotia Power)	Ash lagoon return (visible particulates, clear decantate), decanted	4426.1
	Wastewater discharge to lagoon (black deposit, clear decantate), decanted	885.4
	Pretreatment wastewater (visible black deposit, clear decantate), decanted	2660.0
	Coal pile runoff (visible particulates, clear yellowish decantate), decanted	417.5
Point Aconi GS (Nova Scotia Power)	Ash leachate pond discharge (pH 12) (clear)	398.1
	Coal pile runoff (visible particulates, clear brownish decantate), decanted	569.2
	Wastewater discharge (Lingan sample #96-150) (clear)	558.0
	Well water — intake water (clear)	0.53
Point Tupper GS (Nova Scotia Power)	Wastewater — pretreatment (visible particulates, clear decantate), decanted	33.7
	Coal berm runoff pond (brown-yellow clear, clear decantate), decanted	212.1
	Final wastewater discharge — treated (clear)	373.6
	Landrie Lake water (visible particulates, clear decantate), decanted	1.94
	Ash leachate pond discharge (clear)	1034.6
Trenton GS (Nova Scotia Power)	Coal leachate pond (visible particulates, clear decantate), decanted	1076.0
	Ash lagoon discharge (clear)	23605.0

(continued)

Table 7. *(concluded)*

	Site/sample description	Tl concentration
	Intake water — treated town water (clear)	0.86
	Pit B discharge — previously collected by Trenton — (clear)	982.0
Lambton Hydro GS (Ontario Hydro)	Coal pile runoff creek at Sarnia	55.6
	Duplicate	70.3
	Water intake channel at Sarnia	3.18
	Duplicate	3.18
Lakewiew GS (Ontario Hydro)	Intake channel at Toronto	6.06
	North coal runoff pond	112.1
	Blank at Toronto	0.00
	Ash lagoon filtration effluent at Toronto	175.3
Nanticoke GS (Ontario Hydro)	Outfall channel	18.2
	Intake channel	11.8
	Ash lagoon	41.5
	Coal pile runoff pond	50.1
Antikokan GS (Ontario Hydro)	Intake line	1.25
	Discharge/Sn. Lake	28.1
Thunder Bay GS (Ontario Hydro)	Intake canal	7.16
	Discharge canal	14.0
	Downstream Mission River	9.39

[a] GS, coal-fired electrical generating station.
[b] Belledune GS uses 75% Columbian coal and 25% Salmon Harbour mine coal.
[c] Decanted refers to 20 mL pipetted from the top of bottle, which has been left to settle in the cold room overnight of longer.
[d] Visible particulates are particulates at bottom of bottle. Particulates in decantate may show very high results if decantate is not diluted; filtration or digestion may be needed for more accurate results if dilution is not done.

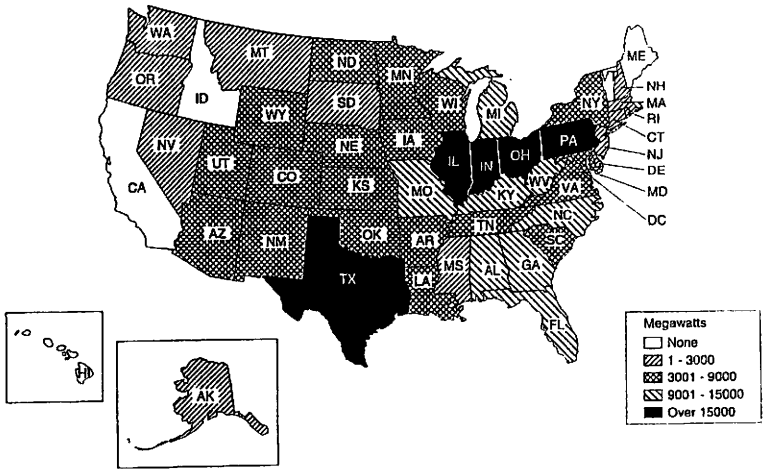

Fig. 3. Coal-fired generating capacity by state in USA (as of December 31, 1993).

These high Tl concentrations found in Canada (24,000 ng/L near a power plant and 88,300 ng/L in a river draining a base-metal mining) are by no means alone as there are numerous other high concentrations found around the world, which include the hot springs of New Zealand (7000 ng/L of Tl), a table mineral water in Germany (3500 ng/L), a cement plant wastewater in Germany (20,000 ng/L), an oil drill wastewater in the U.S. (672,000 ng/L), a smelter waste in Germany (800,000 ng/L), a mining waste in Germany (23,000 ng/L), an irrigation canal in China (96,000 ng/L), petroleum refineries in Canada (310,000 ng/L), wastewater in the U.S. (2,400,000 ng/L), and a tailings pond effluent in Canada (1,620,000 ng/L) (Schoer 1984; IPCS 1996). It is obvious that Tl, being a highly toxic element, is a global environmental concern.

Thallium and Mercury in Sediments

Table 9 gives the concentrations of Tl and Hg as determined respectively by LEAFS and CVAAS. The concentrations of thallium were in general similar to other Tl concentrations reported around the globe for sediments (Cheam 1999; Cheam et al. 1998), except one very high concentration found in the Obed Mountain Coal main tailings pond sample, which had a concentration of 3.39 μg/g. As a comparison, the highest concentration of Tl reported in the world's sediment reference materials was 2.9 μg/g, which was a certified value for a Chinese stream sediment (Govindaraju 1994). Of interest also, the highest concentration found in the Great Lakes reference materials was 2.6 μg/g; this sediment was from Hamilton Harbour (Cheam et al. 1998). Other fairly high concentrations, ~1 μg/g of Tl, were found in the Sundance generating station ash slurry

Table 8. Canadian coal-based electrical generation capacity in megawatts

Generating station	Owner	Total capacity (MW)
Sundance	TransAlta Utilities Corp.	1987
Wabamun	TransAlta Utilities Corp.	569
Keephills	TransAlta Utilities Corp.	754
Battle River	Alberta Power Ltd.	735
H. R. Milner	Alberta Power Ltd.	140
Sheerness	Alberta Power Ltd. and TransAlta Utilities Corp.	766
Genesee	Edmonton Power	400
Boundary Dam	SaskPower	875
Poplar River	SaskPower	592
Shand	SaskPower	272
Brandon	Manitoba Hydro	237
Selkirk	Manitoba Hydro	132
Thunder Bay	Ontario Hydro	423
Nanticoke	Ontario Hydro	4096
Lakeview	Ontario Hydro	2400
Lambton	Ontario Hydro	2040
Atikokan	Ontario Hydro	230
Belledune	New Brunswick Power	440
Dalhousie	New Brunswick Power	286
Grand Lake	New Brunswick Power	82
Lingan	Nova Scotia Power	602
Glace Bay	Nova Scotia Power	116
Trenton	Nova Scotia Power	350
Point Aconi	Nova Scotia Power	165
Point Tupper	Nova Scotia Power	150

sample, in the Keephills generating station ash lagoon cenospheres sample, in the Genesee Mine drainage sample, the Line Creek Mine settling pond, and Phalen Colliery surface runoff brook. Most of the Tl concentrations were, however, below 1 μg/g.

Mercury is likely the most studied element among the toxic metals because of the well-known bioaccumulation of the highly toxic compound methyl mercury, not because of its high concentration. In fact, mercury concentration in the environment is usually quite low compared to other toxic metals, and this study confirms it. Table 9 shows the concentrations of Hg were lower than Tl. The concentration differential between Tl and Hg is similar to the one found by Lentz in 1993 for the concentrations found in a massive sulfide deposit at Bathurst, New Brunswick. Also this differential occurs in most of the world's sediment reference materials (Cheam 1999). Similarly, the Earth's crust content is between 450 to 600 ppb of Tl, compared to only 200 ppb for Cd and 80 ppb for Hg (CRC

Table 9. Concentrations of thallium and mercury in sediments

Sample site	Site/sample description	Tl[a] μg/g	Hg[b] μg/gg
Wabamun GS, Alberta	Intake water	0.52	
Wabamum GS, Alberta	Ash lagoon effluent	0.43	
Sundance GS, Alberta	Ash slurry	0.99	
Keephills GS, Alberta	Cooling pond screen waste	0.69	
Keephills GS, Alberta	Ash lagoon slurry	0.35	
Keephills GS, Alberta	Ash lagoon venospheres	1.20	
Genesee GS, Alberta	Discharge	0.52	
Smoky River, Alberta	Upstream Sheep Creek, 5 km d/s HR Milner	0.39	
Smoky River, Alberta	Upstream H.R. Milner GS at Hwy 40	0.34	
Battle River GS, Alberta	Battle River upstream	0.36	0.04
Battle River GS, Alberta	Battle River downstream	0.47	0.04
Grand Lake GS, N.B.	Lake	0.78	0.02
Trenton GS, N.S.	Ash lagoon cenospheres	0.89	
Souris River, Saskatchewan	Upstream Estevan, mines and GS	0.68	0.11
Souris River, Saskatchewan	Upstream Estevan, mines and GS	0.68	0.10
Souris River, Saskatchewan	Downstream Estevan, mines and GS	0.49	0.06
Souris River, Saskatchewan	Downstream Estevan, mines and GS	0.45	0.07
Bienfait Mine, Saskatchewan	Pit water discharge	0.54	
Whitewood Mine, Alberta	Pit water discharge	0.47	
Highvale Mine, Alberta	Pit 2 drain	0.87	
Highvale Mine, Alberta	Pit 3 settling pond — Outflow	0.62	
Genesee Mine, Alberta	Mine drainage	1.04	
Coal Valley Mine, Alberta	Tailings discharge	0.47	
Coal Valley Mine, Alberta	Lovett River downstream	0.59	
Gregg River Mine, Alberta	Plant site water reservoir	0.52	
Obed Mountain Coal, Alberta	East conveyor settling pond	0.25	
Obed Mountain Coal, Alberta	Main tailings pond (upper)	3.39	
Obed Mountain Coal, Alberta	LSP2 — coal storage drain	0.42	
Line Creek Mine, B.C.	Settling pond	1.11	
8200 Salmon Harbour Mine, N.B.	Lake water	0.74	0.05
Phalen Colliery, N.S.	Surface runoff brook	1.25	0.06
Prince Colliery, N.S.	Downstream discharge	0.61	0.06

[a] Tl was determined by LEAFS.
[b] Hg was determined by CVAAS. Other metals were determined by ICPAES.

handbook 1992–93; Korenman 1963). The crustal rock concentrations of Tl are also higher than those of Hg and Cd — 530 ppb of Tl versus 150 ppb for Cd, and 67 ppb for Hg (Winter 1998). These crustal concentrations give the Tl/Hg ratios of 5.6 to 7.9, whereas the ratios for the 10 samples investigated range from 6 to 39, with a mean value of 13 and a median value of 10. The ratio values seem to suggest there is an enrichment of Tl by at least 25%, or even as high as 117%, which indicates Tl input from other sources.

Conclusions

For metals in water samples, 95% of the upstream concentrations were smaller than the downstream, discharge or pond concentrations.

Some very high thallium concentrations were found in the eastern region near power plants. Since the western and central regions produced and consumed more coal than the eastern region, it was concluded that the coal type, not its amount and/or the regional geological contributions, were responsible for the observed high levels.

In addition to Canada, other countries also saw some very high thallium levels reported, which implies that thallium is a global environmental pollutant.

The high ratios of Tl/Hg observed in sediments, compared to crustal concentration ratios, seem to suggest a Tl enrichment by at least 25%.

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DEVELOPMENT AND APPLICATION OF METHODS FOR ASSESSING THE BIOAVAILABILITY OF CONTAMINANTS ASSOCIATED WITH SEDIMENTS: I. TOXICITY AND THE SEDIMENT QUALITY TRIAD

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Introduction

Three areas of ongoing research at the MSC are outlined in this paper: (1) Development of Methods for Assessing Sediment Toxicity Using Laboratory Exposures, (2) Use of Benthic Invertebrate Communities Assessments and the Sediment Quality Triad to Evaluate Contaminated Sediment, and (3) Development of Sediment Quality Guidelines to Assess Contaminated Sediments. A companion paper for this workshop by Besser et al. (1997) discusses development and application of: (1) bioaccumulation tests and (2) Sediment Toxicity Identification (TIE) procedures.

Sediment is a major repository for many of the more persistent chemicals that are introduced into surface waters and provides habitat for many aquatic organisms. In the aquatic environment, most anthropogenic chemicals and waste materials including toxic organic and inorganic chemicals eventually accumulate in sediment. Mounting evidences exists of environmental degradation in areas where EPA Water Quality Criteria are not exceeded, yet organisms in or near sediments are adversely affected (EPA 1994a). Although certain chemicals are highly sorbed to sediment, these compounds may still be available to the biota. Contaminated sediments may be directly toxic to aquatic life or can be a source of contaminants for bioaccumulation in the food chain. EPA recently completed a National Sediment Inventory and reported that 26% of the samples in a national database were categorized as having a high probability of causing adverse effects and an additional 49% of the samples were categorized as having an intermediate probability of causing adverse effects (EPA 1996a). Concentrations of contaminants in sediment may be several orders of magnitude higher than in the overlying water; however, bulk sediment concentrations are not always strongly correlated to bioavailability. Because relationships between concentrations of contaminants in sediment and their bioavailability are poorly understood, determining effects of contaminants in sediment on aquatic organisms requires controlled toxicity and bioaccumulation tests (Ingersoll et al. 1997a).

Development of Methods for Assessing Sediment Toxicity Using Laboratory Exposures

Over the past decade, research on freshwater sediments has focused on developing testing procedures for conducting 10-d toxicity tests with the amphipod *Hyalella azteca* and the midges *Chironomus tentans* and *C. riparius* (Ingersoll et al. 1995). Toxicity endpoints measured in these tests are survival for *H. azteca* and survival and growth for *C. tentans* and *C. riparius*. Methods have also been developed for conducting 28-d bioaccumulation tests with the oligochaete *Lumbriculus variegatus*, including

determination of bioaccumulation kinetics for different compound classes (Besser et al. 1997). These methods have been applied to a variety of sediments to address issues ranging from site assessments to bioavailability of organic and inorganic contaminants using field-collected and laboratory-spiked samples. Survival and growth of controls routinely meet or exceed test acceptability criteria. Results of laboratory bioaccumulation studies with *L. variegatus* have been confirmed with comparisons to residues (PCBs, PAHs, DDT) present in field-collected field populations of oligochaetes.

Researchers at MSC have been working with other groups in developing a variety of standard methods for assessing the toxicity of contaminants associated with marine and freshwater sediments using amphipods, midges, polychaetes, oligochaetes, mayflies, or cladocerans (Ingersoll 1991; USEPA 1994a,b; ASTM 1996a-f; Environment Canada 1996a,b). These standard methods suggest several potential endpoints that can be monitored in sediment tests including survival, growth, behavior, or reproduction. Usually, survival of test organisms in 10- to 14-d exposure is the endpoint most typically reported. These short-term exposures which monitor only effects on survival can be used to identify high levels of contamination; however, these exposures may not be able to discriminate among marginally contaminated sediments (Kemble et al. 1994).

Additional research is being conducted with the EPA to develop methods for assessing sublethal effects of contaminants associated with sediments in 42-day exposures with the amphipod *H. azteca* (Ingersoll et al. 1997b) and the midge *C. tentans* (Benoit et al. 1997). Endpoints monitored in these tests include survival, growth, and reproduction of *H. azteca* and survival, growth, emergence, reproduction, and egg viability of *C. tentans*. These methods are currently undergoing round-robin testing to evaluate inter-laboratory precision and to develop test acceptability requirements.

Use of Benthic Invertebrate Communities Assessments and the Sediment Quality Triad (Triad) to Evaluate Contaminated Sediment

The Triad is a weight-of-evidence approach used to assess sediments and incorporates measures of: (1) sediment chemistry, (2) sediment toxicity, and (3) benthic community composition (Chapman et al. 1987). We have used the Triad approach to assess sediment contamination at a variety of locations including the Clark Fork River in Montana (Canfield et al. 1994), the Great Lakes (Canfield et al. 1996), and the upper Mississippi River (Canfield et al. 1997; USEPA 1996b). The following section describes the results of a recent Triad evaluation conducted on the upper Mississippi River in cooperation with USGS (Moody and Meade 1992) and EPA.

The USGS has been monitoring the upper Mississippi River (UMR) since 1987 to document the fate and transport of contaminated sediments. The UMR is that part of the river upstream of the confluence with the Ohio River at Cairo, Illinois and consists of a series of 26 navigational pools created by a lock and dam system extending from Minneapolis, Minnesota to St. Louis, Missouri. The navigational pools are shallow lake-like areas which trap and store large quantities of fine grained sediments during normal river flows. Concern with the redistribution of the river sediments arose after the flood of 1993. A project was designed to evaluate the current status of sediments in the UMR by: (1) measuring the concentrations of contaminants in sediments of the UMR, (2) evaluating the toxicity of sediments collected from the river, (3) determining the bioaccumulation of contaminants from UMR sediments using both field-collected and laboratory-exposed oligochaetes, (4) and determining the benthic community structure in fine-grain sediments from within the river.

In the summer of 1994, sediment samples and benthic organisms were collected from 24 of the

navigational pools in the river and from one pool in the Saint Croix River. Two types of sediment samples were collected from the pools. One sediment sample was a composite sample of 15 to 20 sediment grabs along one to five transects across the downstream one-third of each pool (B samples). The other sediment sample was a composite sample from one station along one transect within each pool (C samples). These latter stations were selected based on historical chemistry data and the potential for the sample to contain a large number of oligochaetes. Samples were not collected from the main navigation channels. Whole-sediment toxicity tests were conducted for 28 days with the amphipod *H. azteca* measuring effects on survival, growth and sexual maturation. Toxicity tests were conducted with both the B and C sediment samples. Bioaccumulation of contaminants from sediments was evaluated using field-collected oligochaetes and 28 day bioaccumulation studies conducted in the laboratory with the oligochaete *L. variegatus*. Bioaccumulation tests were conducted with C sediment samples from 13 of the 24 possible individual C sediment samples. Benthic community assessments were conducted on all 24 of the C samples. In addition, the Triad approach was used to assess the overall status of the UMR by integrating data from sediment chemistry, laboratory toxicity tests, and benthic community measurements.

Survival of *H. azteca* in laboratory exposures to sediments collected from the UMR was significantly reduced in only one sediment sample relative to both a control and reference sediment. Growth of amphipods was also reduced in only one sediment sample. Sexual maturation was not significantly reduced in any treatments. Significant correlations were not observed between survival, growth, or sexual maturation and any of the physical or chemical sediment characteristics. Using sediment chemistry and the Effect Range Medium (ERM), 96% of the samples were classified as non-toxic (i.e., measured chemical concentrations rarely exceeded ERMs). Classifications using ERMs and sediment chemistry were consistent with the biological results from the *H. azteca* toxicity tests. Winger and Lasier (1997) evaluated sediment toxicity with *H. azteca* in the lower Mississippi River from Cairo, Illinois to New Orleans, Louisiana and observed toxicity in only one set of samples (upstream from Memphis, Tennessee).

In the bioaccumulation tests, concentrations of contaminants were relatively low in oligochaetes collected from the pools and in oligochaetes exposed to the sediments in the laboratory. Organochlorine pesticides were generally below detection in sediment and tissue samples. Only aliphatic and polycyclic aromatic hydrocarbons (PAHs) and total polychlorinated biphenyls were frequently measured above detection limits in oligochaete tissue and in sediment samples. Concentrations for a specific contaminant in laboratory-exposed and field-collected oligochaetes were similar within a station. About 90% of the paired PAH concentrations in laboratory-exposed and field-collected oligochaetes were within a factor of three of one another. Concentrations of PAHs in oligochaetes collected from the pools or exposed in the laboratory to sediments from the UMR averaged about 1000 times less than tissue concentrations measured in oligochaetes from other sites within the U.S.

The benthic community was dominated (>80%) by oligochaetes and chironomids in 14 of the 23 sediment samples from the UMR and the one sediment sample from Saint Croix River. Total abundance values of benthic invertebrates in these samples ranged from 250/m2 to 22,389/m2 and were comparable to previously reported values for the UMR. The frequency of chironomid mouthpart deformities was only 3% which is consistent with the incidence of mouthpart deformities from uncontaminated sediments. Correlations between benthic measures, sediment chemistry, or other abiotic parameters exhibited few strong or significant correlations indicating benthic communities are most likely controlled by factors independent of contaminant concentrations in sediment.

Results of the Triad analysis indicated that 88% of the samples from the UMR were classified as not impacted based on sediment chemistry, laboratory toxicity, and benthic measures. These results are consistent with the bioaccumulation study in which concentrations of contaminants in tissue were less

than other sites across the United States that have been studied (Ingersoll et al. 1995). In addition, pools in about the lower third of the river had lower sediment contaminant concentrations, less accumulation of contaminants in tissue, and greater taxa richness. The results of this study indicate that the UMR is not severely contaminated relative to other sites that have been studied. Reductions in productivity of the river would not likely be related to chemical contamination but rather other perturbations such as channelization, sedimentation from surface runoff, or long-term changes in the natural flow conditions of the river due to lock and dam construction. This study only conducted a partial assessment of the UMR sediments and included no assessment of river water. Also this study was a one-time assessment and did not evaluate temporal or spatial variability of sediment contamination within the pools. Any future research on, or management of, the Upper Mississippi River should evaluate the limitations of this study.

Development of Sediment Quality Guidelines (SQGs) to Assess Contaminated Sediments

Procedures are described in EPA (1996c) and in Ingersoll et al. (1996) for calculating and evaluating sediment quality guidelines (SQGs) using laboratory data on the toxicity of contaminants associated with field-collected sediment to the amphipod *H. azteca* and the midge *C. riparius*. SQGs are defined as the concentrations of individual contaminants in sediment below which toxicity is rarely observed and above which toxicity is frequently observed. These SQGs were used to classify toxicity data for Great Lake sediment samples tested as part of the EPA Great Lakes National Program Office (GLNPO) Assessment and Remediation of Contaminated Sediments (ARCS) Program (Ingersoll et al. 1996).

Three types of SQGs were calculated for *H. azteca* and for *C. riparius*: (1) Effect Range Low (ERL) and Effect Range Median (ERM), (2) Threshold Effect Level (TEL) and Probable Effect Level (PEL), and (3) No Effect Concentration (NEC; analogous to Apparent Effect Thresholds). The SQGs were calculated using: (1) dry-weight concentrations, (2) dry-weight concentrations normalized to total organic carbon concentrations (for non-ionic organics), or (3) dry-weight concentrations normalized to acid volatile sulfide concentrations (for divalent metals). SQGs were calculated primarily for total metals, simultaneously extracted metals, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons. The ranges of concentrations in sediment were too narrow in the database to adequately evaluate SQGs for butyltins, methyl mercury, polychlorinated dioxins and furans, or chlorinated pesticides.

Historically, the predictive ability of SQGs has been evaluated by determining the frequency of exceeding individual SQGs in independent datasets. In addition to evaluating the frequency of exceeding SQGs, we also evaluated the predictive ability of SQGs using a toxic quotient approach. A toxic quotient for ERMs was calculated for each sample by summing the concentration of each chemical divided by the ERM for that chemical. The mean ERM quotient was then calculated by dividing the sum ERM quotient by the total number of ERMs evaluated.

Good correspondence was observed between the proportion of ERMs exceeded and the mean ERM quotient. The frequency of samples classified as toxic was highest at a proportion of ERMs exceeded of >0.4 or at a mean ERM quotient of >2. About 60 to 80% of the sediment samples in the database were correctly classified as toxic or not toxic depending on type of SQG evaluated. ERMs and ERLs were generally as reliable as paired PELs and TELs at classifying both toxic and non-toxic samples in the database. Reliability of the SQGs in terms of correctly classifying sediment samples was similar between ERMs and NECs; however, ERMs minimized Type I error (false positives) relative to ERLs and minimized Type II error (false negatives) relative to NECs. Correct classification of samples was improved by using only the most reliable individual SQGs for chemicals (i.e., those with a higher

percentage of correct classification).

Calculating SQGs using dry-weight concentrations vs SQGs calculated using sediment concentrations normalized to TOC concentrations for PAHs and total PCBs resulted in similar correct classification of toxicity and similar Type I and Type II error. The range of TOC concentrations in the database was relatively narrow compared to the ranges of contaminant concentrations. Therefore, normalizing dry-weight concentrations to a relatively narrow range of TOC concentrations had little influence on relative concentrations of contaminants among samples.

The SQGs were calculated from toxicity tests with field-collected samples. If a chemical concentration exceeds an SQG generated using data from these tests with field-collected samples, it does not necessarily mean the chemical caused the observed effect. Rather, the SQG is the concentration of a chemical that is associated with the effect. Field-collected sediments typically contain complex mixtures of contaminants. Additional information is needed to identify the specific contaminants that were actually responsible for the toxicity. Confirmation of sediment toxicity due to individual or groups of contaminants can be determined by using Toxicity Identification Evaluation (TIE) procedures or by conducting toxicity tests with spiked sediments (Besser et al. 1997). Once the probable cause(s) of sediment toxicity has been identified, better decisions can be made regarding remediation options.

Future Directions

Research is continuing in the areas of: (1) chronic sediment toxicity methods, (2) field validation of laboratory toxicity and bioaccumulation tests, and (3) Toxicity Identification and Evaluations (TIE). Additional research is also needed to evaluate factors controlling the partitioning or sorption of a compound between water, colloids, and sediment including: aqueous solubility, pH, redox, affinity for sediment organic carbon and dissolved organic carbon, grain size of the sediment, sediment mineral constituents (oxides of iron, manganese, and aluminum), and the quantity of acid volatile sulfides in sediment. Additional research is also needed on aspects of fluid mechanics to quantify the physical processes of colloidal growth and transport and physical mass-transfer processes over a wide spectrum of solute-solid interfaces.

Future collaborative efforts involving all four USGS Divisions could lead to the development of methods for assessing the bioavailability, geochemistry, sources, and distribution of contaminants associated with sediments. The goal of this research would be to assimilate the biological, hydrological, and geological information necessary for the assessment and management of contaminated sediments. The end result of this research would be an improved understanding of the importance of contaminants in sediment relative to other factors influencing ecosystems.

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Polynuclear Aromatic Hydrocarbons: Properties and Environmental Fate

An EXAMS Model Simulation

Hiroshi Awata, Stephanie Bates, David Knaub, Rob Popelka

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Introduction

The purpose of this paper is to analyze the effect of structure on the environmental fate of a group of compounds. Polynuclear aromatic hydrocarbons (PAHs) are a class of compounds found throughout the environment in the air, in the soil and in the water. They are found naturally in crude oil, creosote, coal tar, and coal. They are man-made during incomplete combustion of hydrocarbons like coal, oil, gas, tobacco, and during forest fires (2). There are more than 100 different compounds that make up this particular class. PAHs generally exist as colorless, pale yellow or white solids (2). Because they do not dissolve easily in water and generally do not burn, they can persist in the environment for months to years. Many different strains of microorganisms have the ability to degrade PAHs. *Pseudimonas*, *Flavobacterium*, *Alcaligenes*, *Arthrobacter*, *Micrococcus* and *Bacillus* have been shown to metabolize naphthalene (3). It is difficult to isolate and analyze PAHs in the laboratory, due to the fact that they exist naturally as mixtures of many compounds. Samples can be analyzed using a gas chromatograph with a high-resolution mass-spec detector. This provides a positive qualitative identification for the constituents in the sample. High-performance liquid chromatography coupled with UV/Vis detection can also be used. The advantage of this technique lies in the strong and characteristic absorption by the conjugated systems found in the PAHs.

Structure and Physical Properties

Naphthalene, the smallest of the PAHs, contains two rings (structure- *see Appendix A-1*). It is a white, crystalline solid that can be found in the form of scales, balls, powder or cakes. It has the strong aromatic odor that is associated with mothballs. Synonyms for naphthalene include mothballs, white tar, tar camphor, and albo carbon. Some properties of naphthalene are found in *Table 1*.

Anthracene (structure *see Appendix A-1*) is common in the natural environment. This chemical has several nicknames such as anthracin, green oil and paranaphthalene. It has a crystalline structure, and is pale yellow in color. It exhibits a weak aromatic odor. It is a combustible solid, with a flash point of 121.1 C (6). Anthracene is a relatively small PAH. Some larger PAHs can have nine or more rings. Some of the physical and chemical properties of anthracene are listed in *Table 1*.

Phenanthrene is an isomer of anthracene. Instead of three rings in a line, as in the latter, phenanthrene has one of its rings removed from the line (structure *see Appendix A-1*). As a result, many of the physical properties of the two are very similar (*see Table 1*). The major differences lie in the melting point and the properties directly related to solubility. Phenanthrene is purified as brown to white monoclinic crystals, and also has the characteristic faint aromatic smell.

Table 1. Physical Properties[a]

	Naphthalene	Anthracene	Phenanthrene	Benzo(a)pyrene
CAS number	91-20-3	12-12-027	85-01-8	50-32-8
Molecular Weight (g/mole)	128.16	178.23*	178.23	252.3*
Melting Point (°C)	80.28	216.4*	100.5	179*
Boiling Point (°C)	217.95	340*	338	310-312*
Solubility (aqueous, mg/L)	30	0.065*	1.28	3.8E-3*
Vapor Pressure (Torr)	0.082	5,63E-6*	1.250E-04	5.25E-9*
Henry's Constant (atm-m3/mol)	4.27E-04	1.8E-6*	2.800E-04	5.53E-07
Log Kow	3.36**	4.456**	4.46*	6.2**
Molar Volume (cm3/mole)	148	197	199	263
Heat of Vaporization (kJ/mol)	43.2	52.4	52.7	71.7
Molecular Volume (Angstroms^3)	126.9	170.3	169.5	228.6
Molecular Surface Area (Angstroms^2)	155.8	202.2	198	225.6

[a]all data obtained from JINNO DATABASE (10) unless otherwise noted

*data obtained from Mackay 1992

**data obtained from Schwarzenbach 1993

^data obtained from the Fisher MSDS

Benzo[a]pyrene (3,4-benzpyrene) is the largest of the four compounds, with five rings (see *Appendix A-1*). It also has the faint aromatic odor. Pure benzo[a]pyrene is pale yellow, and is found as monoclinic or orthorhombic crystals (The Merck Index 1989). These can be separated from a mixture of PAHs using various standard separation techniques, and recrystalized from benzene and methanol. Benzo[a]pyrene is the only one of the four compounds that is a known human carcinogen. Some properties of benzo[a]pyrene are found in *Table1*.

Commercial Uses

PAHs are formed by incomplete combustion of hydrocarbons, and can be isolated from the processing of fossil fuels. Many of these compounds have no use other than research. There are some, however, that are important in the making of pharmaceuticals, dyes, plastics, and pesticides.

Naphthalene is the most abundant distillate of coal tar. Its most common use is as a household fumigant against moths (hence the name mothballs). Naphthalene is an important hydrocarbon raw material used in the manufacture of pthalic anhydride (used in dye making), of celluloid and hydronapthalenes (used in lubricants), and of motor fuels. At one time, it was used as an insecticide and vermicide. However, this use is decreasing due to the low toxicity of the vapor. Naphthalene is also of some use as an antiseptic and as a soil fumigant (4). Commercial production of this chemical is a result of crystallization from the intermediate fraction of condensed coal and tar from the heavier fraction of cracked petroleum (4). The demand for naphthalene in the United States in 1986 was 250 million pounds, in 1987 255 million pounds, and in 1991 approximately 270 million pounds (20).

Anthracene, like many PAHs is used in the production of fast dyes as well as fibers and plastics. It is one of the most important feedstocks for the production of anthraquinone. Anthracene can also be used in insecticides and for a wood preservative (17). This compound is widely abundant. It is found in any type of coal or tar. It is possible to isolate PAHs from roofing material via flash chromatography. Flash chromatography is used for purification of organic as well as inorganic compounds. It is a phase separation between a stationary phase and a rapid organic solvent. The process takes less that 15 minutes to complete once the solvent is determined (16). It is also relatively inexpensive.

Like anthracene, phenanthrene is used in the production of dyes. It is also used in the manufacture of explosives, and is an important starting material for phenanthrene based drugs. This leads directly to use in biochemical research for the pharmaceutical industry. In New York State, a mixture of phenanthrene and anthracene tar is used to coat water storage tanks to prevent rust (17).

Benzo[a]pyrene, or B[a]p is not produced commercially in the US. B[a]p is not allowed for commercial use in Canada and US (15). Thus large scale manufacturing processes are not available. It is formed when gasoline, garbage or any plant or animal materials are burned. So B[a]p is usually present in soot and smoke. It is also found in the coal tar pitch industry, and is used to join electrical parts together. It is also found in creosote, a chemical used as a preservative for wood. B[a]p is used extensively as a positive control in a variety of laboratory mutagenic and carcinogenic short-term tests.

Entry into the Environment

A contaminant can enter into the environment via air, water, and soil. The fate of the compound will depend on its stability, the medium to which it is released, and the pathways that are available to degrade it (3). Information about the chemical and physical transformations in each environmental compartment will help to determine where the compound will accumulate.

Naphthalene enters into the atmosphere through emissions and exhaust produced by its presence in fuel oil and gasoline. Another major contributor of naphthalene (in the atmosphere) is the aluminum smelting industry (4). It accounted for about 21% of the total atmospheric emissions measured in Canada in 1991 (4). Entry into the soil and water compartments arises mainly due to discharges and spills during the storage, transportation and disposal of fuel oil and coal tar (20). The Toxic Release Inventory database reports that 39,024,998 pounds of production-related naphthalene wastes were generated for the year 1995, and a total of 2,659,941pounds of naphthalene released in the United States, mostly to the air.

Anthracene is released into the environment from a variety of sources. It can be released via non-point sources as well as industrial effluents from the dye and pesticide manufacture. As seen in the Toxic Release Inventory most of the anthracene released was to the air. According to this index in 1995 a total of 5488 pounds of anthracene was released from industry in the United States. Of that amount 5475 pounds was released to the air while the remaining was released to ground and water. The total waste produced from the production of anthracene was 22938 pounds in 1995 (12). Its natural sources are coal and tar, and can be released by the incomplete combustion of organic compounds. Therefore it is a constituent of the exhaust from automobiles, lawn mowers, and charcoal grills. It can also seep into the ground and surface water from coal piles (6).

There are three major industries that produce phenanthrene are:

- Petroleum refining and petroleum related products
- Steel
- Carbon and graphite products

The most recent data from the TRI (1995) indicates that the total amount of production related phenanthrene produced was almost one and one half million pounds, most of which was treated on-site by recycling and burning for energy. The total amount of releases and transfers was almost 150,000 pounds, most of which was released to the air. Only a small amount of phenanthrene was deposited on land, and even less was released to the water. Phenanthrene is also a by-product of incomplete combustion, and is released to the air in internal combustion exhaust. There is also a significant amount of phenanthrene released by forest fires.

The largest sources of B[a]p in the air are open burning and home heating with wood and coal. Factories that produce coal tar also contribute small amounts of B[a]p to the air. It is estimated that greater than 100 metric tons per year (18) of the total emissions of B[a]p to the atmosphere are a result of coal fired residential furnaces, coke production, forest fires, and burning coal refuse banks. More than 10 metric tons of B[a]p is released from coal-fired industrial boilers, residential fireplaces, iron and steel sintering, commercial incinerators, open burning of auto components and leaves, trucks and automobiles, and tire wear (18). The toxic release inventory does not list B[a]p probably because it is not produced in the United States.

Human Health Effects and Toxicity

There are several factors that will determine whether exposure to PAHs will pose health effects and how severe those effects will be. It will depend on the dose of the contaminant, the length of the exposure, the route of the exposure, and individual characteristics such as age and sex. The U.S. Department of Health and Human Services has determined PAHs to be possible human carcinogens. PAHs enter the body quickly and go to the fat containing tissues.

There is little data available for the toxic effects of naphthalene on humans. Short-term low exposure to naphthalene may cause eye and skin irritation (3). At slightly higher levels (above 10 ppm), headaches, fatigue and nausea occur. If naphthalene is ingested it has the potential to cause hemolytic anemia, a condition that involves the breakdown of red blood cells (3). Naphthalene poses more of a threat to African-Americans and people of

Mediterranean descent due the higher incidence of problems with the enzymes that produce red blood cells (11). Acute effects can be detected 2 to 4 days after exposure. Long term effects of exposure to levels of naphthalene greater than 10 ppm may lead to chronic effects. Naphthalene is a suspected human carcinogen, and has been proven to cause damage to the kidneys and to the liver. Chronic exposure can lead to reproductive defects including fetal damage and decreasing fertility. Higher incidences of lung and skin tumors have been reported for people who have been occupationally exposed to naphthalene and other PAHs (4).

Several studies have been conducted using animal subjects. Rabbits exposed to high levels of naphthalene developed cataracts (3). A case study involving marine invertebrates found that short-term exposure to naphthalene proved to be moderately toxic (3). Acute toxic effects can include low growth or even death in birds, animals, fish and plants. Toxic thresholds for naphthalene include a LC50 of 240ug/L for embryos of largemouth bass (4).

Naphthalene is listed by RCRA as a toxic hazardous waste (U165), however it is not currently regulated in drinking water. It is on the list of proposed additions. The Code of Federal Regulations (CFR) lists naphthalene as a constituent of a number of specific and non-specific hazardous wastes. Among these are F025, F034, K087, and K145. The Occupational Safety and Health Administration (OSHA) has issued regulations regarding permissible exposure limits for naphthalene. These limits are: 10 ppm time weighted average and 15 ppm as short term exposure limits (11). Naphthalene is also regulated under the Clean Air Act (CAA), the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), the Federal Insecticide, the Fungicide, and Rodenticide Act, the Clean Water Act, the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA) and the Resource Conservation and Recovery Act (RCRA) (11).

Anthracene exposure can cause skin and eye irritation, which can be aggravated by sunlight. Repeated exposure may cause alteration of skin pigments as well as cancerous growth, although there is no carcinogenic data for anthracene. Inhaled anthracene can cause bronchitis like symptoms (6). There is limited information on human reproductive implications. Anthracene may cause genetic mutations in cells (6).

Anthracene is not currently considered a toxic substance, and does not appear on the RCRA hazardous waste lists. It is also not specified as a constituent of specific or non-specific industrial wastes by the CFR. Additionally, there is no drinking water limit for anthracene.

Phenanthrene is also a skin and eye irritant, with increasing effects in sunlight due to photosensitization. There is currently no data available for human oral and inhalation exposure. It is however, a suspected carcinogen, although there is no data for humans. There have been several studies of carcinogenic effects in animals. Out of fourteen studies listed by the Integrated Risk Information System (IRIS), only one yielded a positive result. A group of 30 mice were given a single dermal application of 1.8 mg in benzene, followed by twice weekly applications of tetradecanoylphorbol acetate (TPA, a promoter) for 35 weeks (Scribner, 1973). They found a 40% tumor incidence compared to 0% in the control group. There are some uncertainties in this study. It is unclear whether the TPA dose was 3mg total or 3mg/ application. Also it was unclear whether the control group received benzene. This is particularly noteworthy since benzene is a known human carcinogen.

Phenanthrene is not currently listed by RCRA as hazardous, and is not listed in the CFR

as a constituent of any specific or non-specific industrial processes. There is also no drinking water standard for phenanthrene, and it can be land disposed. However, much of the recoverable phenanthrene is either used for on-site energy production (incineration) or recycled by simple separation and purification techniques.

The general population may be exposed to dust, soil, and other particles that contain B [a]p. Many water supplies throughout the United States contain low levels (.55ppb) of the compound (18). Food grown in contaminated soil or air may contain B[a]p. B[a]p has been found in various types of cereals, vegetables, fruits, and meats. High temperature cooking processes, like charcoal grilling or charring, can increase the amount of B[a]p found in food. It is also a component of tobacco products, and is one of the cancer causing agents in cigarette smoke.

The greatest chance of high level exposure to B[a]p is likely to occur in the workplace. People who work in coal tar production plants, coking plants, asphalt production plants, coal gasification sites, and smoke houses receive higher doses than the general population.

B[a]p is a known precursor to cancer causing metabolites in laboratory animals (Casarett 1995). Various studies have determined that B[a]p is toxic (8). B[a]p is converted by cytochrome P450 to a variety of oxides that react with DNA, making them highly mutagenic. The U.S. Department of Health and Human Services has determined that B[a]p may reasonably be anticipated to be a carcinogen to humans as well as animals. It is reported that mice fed high levels of B[a]p during pregnancy had trouble reproducing as did their offspring (1). The newborn animals of pregnant mice fed B[a]p had other harmful effects including birth defects and low body weight. It is possible that similar effects could happen to humans exposed to B[a]p.

Even though B[a]p is a known carcinogen, OSHA does not ban its use in the workplace. They set rules governing the exposure limits of employees. B[a]p is regulated along with substances known as "coal tar pitch volatiles." Exposure is limited to two tenths of a milligram of coal tar pitch volatiles per cubic millimeter of air (11). The Institute for Occupational Safety and Health (NIOSH) does not have a specific workplace limit for B[a] p, either.

Environmental Fate

In the environment, PAHs are found adsorbed to particulate matter in the atmosphere. The two mechanisms by which they are transformed are ozone-induced oxidation and hydroxylation. The photo-oxidation half-life in the atmosphere is between 1704-132000 hours (4).

A mixture of PAHs released in the water would be expected to sorb to particulate matter and dissolved organic matter. The degree of sorption depends on the mechanism, which is determined by the identity of the sorbate. They would also tend to bioaccumulate in aquatic organisms, due to their relative non-polarity. The bioaccumulation is only a problem for organisms that lack microsomal oxidase (17). This enzyme allows for the breakdown of PAHs to more water-soluble products for excretion. The fraction not sorbed would be subject to photolysis and subsequent breakdown. The reported half-lives for aquatic fate vary due to the nature of the system (17). This includes stratification of the water column, flow of water, quantity of natural organic matter and many other characteristics.

Volatilization biodegradation, and adsorption to particulate matter and sediment are all processes, which affect the fate of naphthalene in the water compartment. When a petroleum product enters into the water column, the lighter hydrocarbons spread out along the surface of the water and then evaporate. The volatilization half-life of naphthalene is .4 – 3.2 hours (4). The naphthalene that does not evaporate sorbs to the particulate matter or is transformed into a water in oil emulsion.

Again, volatilization plays an important role in the fate of naphthalene in the soil. Degradation through microbial activity also occurs but the extent is dependent upon the temperature, the soil type, and the presence of the proper organisms. The low molecular weight PAHs, like naphthalene, are expected to volatize or biodegrade within 3 to 4 months (4).

Anthracene released to the ground would sorb to the soil. It would be a minimal problem for groundwater contamination. Anthracene would be subject to biodegradation in the ground. It would not hydrolyze due to the lack of functional groups. The half-life for biodegradation of terrestrial released anthracene is about 100 to 150 days (17). The strong adsorption to particulate matter makes it less bioavailable.

Most of the anthracene released to the atmosphere would volatilize or sorb to particulate matter. It would be subject to photolysis immediately. It has a very short half-life associated with atmospheric fate. It is on the order of hours to days depending on the degree of adsorption. Non-adsorbed compound will have a shorter half-life than adsorbed compound. It is broken down via ozonation and hydroxide radical photolysis (17).

If a release of phenanthrene were to occur to the soil, most of the compound would sorb to the soil. It is not expected to volatilize to a great extent. Biodegredation is expected to be the major removal porcess from the soil, given the right conditions. The low solubility of phenanthrene would limit removal by leaching to ground water.

An atmospheric release of phenanthrene would also lead mostly to sorption. Photolysis occurs rapidly with a half-life of about 49 hours. Phenanthrene not converted by photolysis would be subject to wet and dry deposition. The small amount of the compound that is not sorbed would be found in the vapor phase, where it can react with photochemically produced hydroxyl radicals with a half-life in days (19).

A release of phenanthrene to the water would also be governed by sorption. Most of the compound released should be removed from the water by sorbing to the particulate matter and dissolved organic matter. The degree of sorption depends upon the sorption mechanism, which depends on the type of sorbant.

B[a]p released to the atmosphere would likely be associated with particulate matter and may be subject to moderately long distance transport. The degree of transport depends on the particle size distribution and climactic conditions, which determines the rate of wet and dry deposition. B[a]p released to soil would absorb very strongly to the soil and would not leach to the groundwater. It would not hydrolyze, and evaporation from soils and surfaces may not be significant due to its higher molecular weight. B[a]p released to water, also would absorb very strongly to sediments and particular matter. It would not hydrolyze, but would be expected to bio-concentrate in aquatic organisms without metabolism. B[a]p would undergo significant photo-degradation near the surface of waters. Adsorption to

sediments and particulates may significantly retard biodegradation, photo-degradation, and evaporation (18).

Biodegradation tests of B[a]p in soils have resulted in a wide range of reported half-lives: 2 days (Mackay 1992) to 1.9 year (Mackay 1992). Based on these values and the apparent lack of a significant competing fate process, biodegradation may be an important process in soils. B[a]p also has been shown to be susceptible to metabolic activity in some natural waters lacking carbon or another energy source (18). However, in most waters and in sediments it has been shown to be stable towards biodegradation.

Analysis of Exams Data

The four compounds that we examined differed in molecular weights and isomerization. Using the Exams model it was possible to compare how the compounds differed in the environment on the basis of the physical properties listed in *Table 1*. For each of the four compounds only the molecular weight, vapor pressure, solubility, Henry's Law constant and octanol-water partition coefficients were added to insure unity in the analysis by the model. Several trends were noticed in the fate of the molecules as a function of size and isomerization. The results of the Exams model are listed in *Appendix 2*.

The results from Tables 15 and 17 show the distribution of the chemicals at steady state in the pond environment with a stream load of 0.0001 kilograms per hour. Under these conditions the majority (> 75%) of all four chemicals released into the pond would end up in the benthic sediment. Naphthalene has a relatively high aqueous solubility in comparison to the other compounds; therefore, almost 25% of the quantity released to the pond remained dissolved in the water column. With the increased size of the compound there is a decreased solubility. The trend for the distribution in the sediment can also be seen with the increased log of K_{ow} for each compound as well as the increasing molecular weight. K_{ow} is inversely proportional to the aqueous solubility. As the K_{ow} increases its tendency to adsorb to particulate matter increases. It is a characteristic of PAHs to bind tightly to sediments. These compounds are do not have polar functional groups to allow them to dissolve in water. Larger compounds have more surface area to bind to the particulate matter, so these compounds would end up in the sediment. As seen in both tables the increasing molecular weight gives a higher percentage of compounds being located in the benthic sediment.

Most of the PAHs that remain in the water column end up dissolved. In the case of naphthalene, anthracene and phenanthrene, over 95% of the quantity remains dissolved. Benzo(a)pyrene has a lower dissolution percentage due to its reduced aqueous solubility and elevated K_{ow}. A larger fraction of the B[a]p is sorbed to the sediment or bio-accumulated in the biota. The trend is increasing size decreases the fraction of PAH that will be found in solution.

Most of the PAHs that remain in the benthic sediment are sorbed to the sediment. The amount that ends up dissolved or in biota is minute. The trend is increasing size increases the fraction of PAH sorbed to the sediment. Naphthalene is the only one of our compounds that has a significant dissolved fraction. Once again this is due to its small size and higher aqueous solubility.

Table 18 gives an analysis of the steady state fate of the organic chemical. The model

reports PAHs are subjected to either surface water-borne export or volatilization. The amount, which is volatized, is increased as the size of the compound decreases. Naphthalene, the smallest compound, experiences volatilization of approximately 89% of the load whereas B[a]P, the largest compound, experiences volatilization of roughly only 1% of the load. The bent isomer of anthracene (phenanthrene) experiences slightly more volatilization when compared to the straight chain version. This is possibly due to a lower heat of vaporization in anthracene. The Van der Waals forces are slightly weaker in phenanthrene, and causes an increase in the vapor pressure by about two orders of magnitude. As the vapor pressure increases, the amount volatilized also increases. Conversely, as the amount of the load that undergoes surface water-borne export increases, the size of the compound also increases. When analyzing the results for the isomers, it can been seen that phenanthrene experiences half as much surface water export in comparison to anthracene.

Table 20 in the Exams model provides an exposure analysis summary. It summarizes the exposure and fate data found in Tables 15 and 17. It also provides an estimate of the persistence of each compound in the environment and the length of time to achieve greater than 95% cleanup. The clean-up times of the four compounds are:

- Naphthalene – 8 months
- Phenanthrene – 30 months
- Anthrecene – 53 months
- B[a]P – The model indicated that after 84 years, there was no loss of the initial chemical burden. Therefore, there is little chance to achieve total clean-up

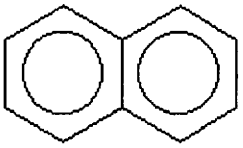
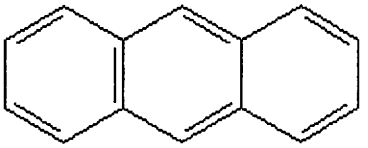
Conclusions

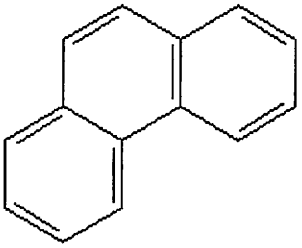
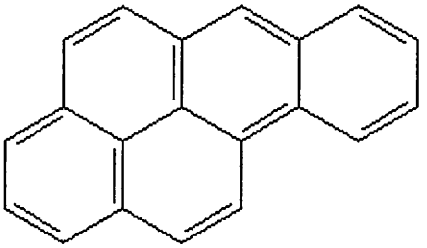
PAHs represent a group of compounds that tend to follow trends. We analyzed our four compounds for the trends in environmental fate in the case of accidental release. The trends expressed by the EXAMS model represent the same trends that were predicted by the literature.

Size plays a major role in the fate of PAHs. It affects the most important fate parameters like solubility, vapor pressure, K_H, and Kow. Although none of the PAHs dissolve to a great extent, increasing size of the compound decreases the aqueous solubility. Larger molecules encounter a greater difficulty in being totally associated with water molecules. This is indeed the trend observed in the model. Increasing size increases the sorption. Larger molecules have more surface area to sorb to the sediment or particulate matter. We also observed this trend in PAHs. Finally, increasing size decreases the amount of volatilization. Larger molecules are more difficult to vaporize, due to stronger intermolecular forces between the PAH molecules.

We did however noticed an anomaly in the general trend. We analyzed our compounds with the assumption that the trends would follow the following order: naphthalene, anthracene, phenanthrene, and B[a]p. According to the EXAMS model, the fate of phenanthrene was more similar to naphthalene than anthracene. This could be due to differences in the amount of intermolecular interactions in the two isomers.

Appendix A-1 Structures

	
NAPHTHALENE	ANTHRACENE

	
PHENANTHRENE	BENZO[A]PYRENE

Appendix A-2 Exams Data

Table 15

	Water Column				
Compound	**Mass (%)**	**Total (mg/L)**	**Dissolved (mg/L)**	**Sediments (mg/kg)**	**Biota (ug/g)**
Naphthalene	24.73	4.14E-04	4.12E-04	3.87E-02	0.201
Anthracene	2.6	1.22E-03	1.18E-03	1.36	5.57
Phenanthrene	2.54	5.87E-04	5.66E-04	0.668	2.73
Benzo(a)pyrene	0.14	3.72E-03	1.25E-03	79.5	224

	Benthic Sediment				
Compound	**Mass (%)**	**Total (mg/kg)**	**Dissolved (mg/L)**	**Sediments (mg/kg)**	**Biota (ug/g)**
Naphthalene	75.27	3.73E-02	3.96E-04	3.71E-02	0.192
Anthracene	97.4	1.35	1.17E-03	1.35	5.55
Phenanthrene	97.46	0.666	5.64E-04	0.666	2.73
Benzo(a)pyrene	99.86	80.7	1.25E-03	80.7	228

Table 17

	Water Column			
Compound	**Total (mg/L)**	**Dissolved (mg/L)**	**Sediments (mg/kg)**	**Biota (ug/g)**
Naphthalene	4.13E-04	4.12E-04	3.87E-02	0.201
Anthracene	1.22E-03	1.18E-03	1.36	5.57
Phenanthrene	5.87E-04	5.66E-04	0.668	2.73
Benzo(a)pyrene	3.72E-03	1.25E-03	79.5	224

	Benthic Sediment			
Compound	**Total (mg/kg)**	**Dissolved mg/L**	**Sediments**	**Biota (ug/g)**

			(mg/kg)	
Naphthalene	3.73E-02	3.96E-04	3.71E-02	0.192
Anthracene	1.35	1.17E-03	1.35	5.55
Phenanthrene	0.666	5.64E-04	0.666	2.73
Benzo(a)pyrene	80.7	1.25E-03	80.7	228

Table 18

	Surface Water-Borne Export		
Compound	Mass Flux (kg/d)	% Load	Half-life (days)
Naphthalene	2.64E-04	11.02	87.68
Anthracene	2.37E-02	32.44	27.44
Phenanthrene	3.75E-04	15.64	852.4
Benzo(a)pyrene	0.8685	99.08	43.55

	Volatilization		
Compound	Mass Flux (kg/d)	% Load	Half-life (days)
Naphthalene	2.14E-03	88.98	10.86
Anthracene	4.93E-02	67.55	13.18
Phenanthrene	2.02E-03	84.36	158
Benzo(a)pyrene	5.46E-03	0.62	6934

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NATIONAL CENTER FOR ENVIRONMENTAL RESEARCH
Office of Research and Development
U.S. Environmental Protection Agency

Science to Achieve Results (STAR) Program

Final Report: Ecological Assessment of the Phototoxic Polycyclic Aromatic Hydrocarbon Fluoranthene in Freshwater Systems

EPA Grant Number: R823873
Title: Ecological Assessment of the Phototoxic Polycyclic Aromatic Hydrocarbon Fluoranthene in Freshwater Systems
Investigators: J. T. Oris, S. I. Guttman, G. A. Burton
Institution: Miami University, Wright State University
EPA Project Officer: Dale Manty
Project Period: October 1, 1995–September 30, 1998
Research Category: Environmental Biology

Executive Summary

Project Description and Objectives of Research:

The overall objective of the project was to determine the environmental hazard of phototoxic polycyclic aromatic hydrocarbons (PAH) to freshwater fish and invertebrates. Previous investigations and research had defined several important aspects of the photo-induced toxicity of PAH. However, there were many environmental factors that still required examination as predictions of photo-induced toxicity had not been rigorously validated in the field. In addition, the importance of differential genetic sensitivity within a population of PAH exposed organisms had not been thoroughly evaluated. If the photo-induced toxicity of PAH to freshwater organisms was determined to be a potential hazard under natural conditions, then the assessment of PAH must include considerations of factors regulating this phenomenon. Because hazard was determined by levels of toxicity, exposure, and genetic variability, the factors involved in the expression of toxicity and the various routes of exposure and bioaccumulation were examined. Effects due to dissolved organic carbon, particulate inorganic matter and primary reproduction were examined in lab, microcosm and *in situ* field experiments.

Some of the weaknesses of only using the surrogate toxicity assay in stream assessments are avoided by conducting *in situ* community surveys such as used by the Ohio Environmental Protection Agency or recommended by the U.S. EPA (Rapid Bioassessment Protocols I-III). Various fish and macroinvertebrate community metrics exist which have effectively quantified stream degradation. It is sometimes difficult, however, to separate natural stress causation factors (such as habitat) from anthropogenic stress. In addition, when community degradation is detected, it is "after the fact"; therefore, the stream ecosystem is not protected from initial degradation by biomonitoring.

Given the different attributes of the surrogate toxicity assay and the *in situ* community survey

approaches, it is apparent that combining them into an integrative assessment, which includes key physical and chemical concentration data should provide a more valid product. This approach was effectively used in marine sediment quality assessments, and was recommended by the U.S. EPA as an effective tool for evaluating sediment quality. A weakness, however, in the previously used integrative approaches was that toxicity was only measured directly in the laboratory and not *in situ*.

A limited number of *in situ* exposures have been conducted to assess water column toxicity (Burton, et al., 1996). These assays utilized adult fish, phytoplankton, adult amphipods, and protozoans. Some *in situ* evaluations were based on ecosystems dosing of experimental ponds or streams, followed by monitoring of community structure. This approach has many advantages, however, these systems were difficult to replicate and required extensive resources. The portion of this U.S. EPA project conducted by Wright State University addressed photo-induced toxicity in the laboratory, mesocosms, and *in situ* and provided important information on controlling factors, effects, and field assessment techniques.

Summary of Findings:

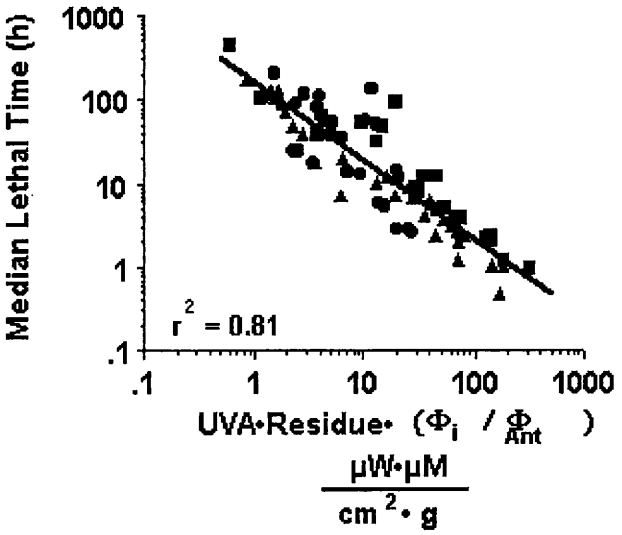
Environmental Factors. Environmental factors, such as organic carbon content, clay content, humic acid concentration, light condition, primary production activity and etc. have strong effects on photo-induced toxicity of PAHs in aquatic environments. In order to understand the levels of effects of these environmental factors on photo-induced toxicity of PAHs, microcosm testing was conducted in the laboratory. Environmental factors, organic carbon content in sediment, clay content (turbidity), humic acid concentration and primary production activity were examined individually and combined for effect on PAH toxicity. The results showed that when organic carbon content of sediment, turbidity of water and humic acid concentration in water increased, toxicity decreased accordingly. For example, the mortality of 4-d old fathead minnow at 200 mg/kg of sediment was 100 percent, 70 percent and 30 percent for 0 percent, 3.5 percent and 7.0 percent of organic carbon of sediments, respectively. While, when humic acid was added at 2.5 mg/L, the mortality was decreased dramatically to 30 percent, 20 percent and 10 percent, respectively. Fish (Pimephales promelas) are particularly sensitive to the effect of these factors. For the benthic organisms (Hyalella azteca), the effects of these factors are less obvious. Therefore, it was assumed that these factors could either prevent releasing PAHs from the sediment to water or reduce concentration of PAHs in water. Clay content significantly reduced fluoranthene concentration in water. This could reduce the exposure and consequently reduce toxicity. However, if organisms live in and feed on contaminated sediment, these factors will not prevent them from exposure of contaminants. For example, PAH toxicity towards Hyalella azteca was not reduced very significantly, 100 percent to 90 percent mortality, when the organic carbon content was increased from 0 percent to 7 percent. It also was found that the effects of these factors on reducing toxicity of PAHs were additive. Focusing a reciprocity model that incorporates the product of UV intensity and PAH body residue, good predictions of time to death can be estimated for *in situ* toxicity. The relationship estimated for this model was based on the following factors:

UVA = intensity of radiation in range 320-400nm (μW/cm^2)
Body Residue = concentration of PAH in organism tissue (μM/g)
Relative Photodynamic Action (RPA) = Quantum yield of phototoxicity reactions relative to anthracene

These factors were multiplied (unweighted) to form an index of phototoxic dose received by the organism. For multiple PAHs, the concentration of each PAH multiplied by its RPA was summed for a total phototoxic dose measurement. The figure below includes data from minnows, amphipods, zooplankton, and oligochaete exposures in the presence of humic materials, montmorillonite, kaolinite, algae, and MTBE. The top, right-most data point in the graph is from an *in situ* toxicity test conducted at Lake Tahoe, CA. This model provides reasonable predictions of time to death for a broad range of

organisms under numerous environmental conditions and mixed PAH exposures.

Log(LT50) = 2.212 - 0.9294 (Log(UVA•Residue•RPA))



Pure chemical and mixture studies were conducted with the amphipod, Hyalella azteca, and the fathead minnow, Pimephales promelas. Anthracene and fluoranthene were tested at multiple concentrations both singly and in combination. Results showed additive interaction effects in acute exposures in the presence of UV. Exposures of H. azteca and the oligochaete, Lumbriculus variegatus were conducted *in situ*, at a site contaminated with PAHs. The organisms showed slight effects in 4 week exposures. Amphibian effects were studied by collecting field samples of the leopard frog, Rana pipiens and exposing eggs and larvae to multiple concentrations of fluoranthene. No hatching effects were observed, however, effects on larvae were noted as low as 5 μg/L in the presence of sunlight. Effects were dependent on UV intensity, with no effects observed under simulated natural light.

Seven sediments were spiked with 300 mg/kg fluoranthene and weathered outdoors for either 0, 3, 16, 28, 32, 64 or 90 days. For the 90-day weathering treatments, each sediment was weathered both in a refrigerator at 4°C (90-d F) and outside or not in a refrigerator (90-d). The sediment treatments included a reference sediment, kaolin, sand, Acton Lake sediment at 0 percent, 3.5 percent and 7 percent TOC, Little Scioto River sediment at 8 percent TOC, and West Bearskin sediment at 11.7 percent TOC. After weathering, toxicity tests ranging from 3-168 hours were initiated with 4-d Pimephales promelas. Fish exposed to reference sediments from 3-168 hours yielded ~93 percent survival. There seems to be a possible trend between toxicity and TOC levels or particle size. Sediments with little to no TOC (e.g., Sand, Acton Lake at 0 percent and 3.5 percent TOC) yielded the lowest survival. Exposure to sand resulted in 0 percent survival for all weathering treatments by 48 days of exposure, except following 90-d F weathering (~67 percent survival).

The partitioning and effects of fluoranthene also were studied in the laboratory using radioactive fluoranthene (FLU). The concentrations of FLU in three types of media where measured using C^{14} activity. The media included sediments, water and tissue (e.g., the oligocheate worm, Lumbriculus variegatus and the fish, Pimephales promelas). For sediments, FLU levels remained near 1.0 μg/g for both Acton Lake 3.5 and 7 percent TOC (i.e., > 0.98 μg/g) after 168 hours. However, sand, kaolin and Acton Lake at 0 percent TOC (clay) did not retain FLU as readily as the sediment treatments with higher TOC and the concentrations decreased for all three low TOC sediments over time. The opposite was the case for FLU measures in overlying water. FLU concentration was lowest for water overlying sediments with the highest TOC (e.g., Acton Lake at 3.5 and 7 percent TOC) (< 0.05 ng/mL). For sand, kaolin and

Acton Lake at 0 percent TOC, FLU concentrations peaked at about 3 hours, and decreased steadily by 144 hours. The lowest FLU concentrations were 0.191, 0.109 and 0.172 ng/mL for sand, kaolin and Acton Lake at 0 percent TOC, respectively. FLU concentrations in both fish and worm tissues were highest when exposure was to sediments with low TOC. Tissue concentrations were very low for fish (< 0.075 µg/g) and worm (< 0.29 µg/g) tissue exposed to Acton Lake at 3.5 and 7 percent TOC, following 96 hours of exposure. For fish tissue, concentrations from Acton Lake at 0 percent TOC rose steadily over an exposure duration of 48 hours, peaking at 1.235 µg/g. The highest concentrations in fish tissues exposed to sand and kaolin were 1.215 and 1.133 µg/g respectively, both peaking at 24 hours. There was no fish survival after 48 hours of exposure for sand, kaolin and Acton Lake at 0 percent TOC. Worm tissue concentrations increased steadily over time until 24 hours for kaolin (3.12 µg/g), and until 48 hours for sand (3.29 µg/g) and Acton Lake 0 percent TOC (3.45 µg/g). Worm survival was 0 percent for Kaolin after 24 hours, and for sand and Acton Lake 0 percent TOC after 48 hours.

The effect of weathering and fluoranthene toxicity was studied using different sediment types. Test treatments were: water only, water, sand, Acton lake sediment (0, 3.5, and 7 percent TOC), kaolin, montmorillonite, Little Scioto River sediment (8 percent TOC), and West Bearskin sediment (11.7 percent TOC). All treatments except the PAH contaminated Little Scioto River sediments were spiked with fluoranthene (300 mg/kg) and weathered outdoors during the summer for 0, 3, 16, 28, 32, 64, and 90 days. For the 90 day treatments, sediments were compared to split samples maintained at 4°C for 90 days. After weathering, toxicity tests were conducted for 3 to 168 hours of exposure with P. promelas (4 days old). Survival in reference sediments was good (> 90 percent). Survival increased with increased time of weathering. Survival also was higher in sediments containing higher levels of TOC. Longer exposure times increased mortality.

Hyalella azteca and Pimephales promelas were exposed to three types of sediments, at three *in situ* exposure treatments within mesocosms. The field mesocosm exposures were compared with laboratory microcosm exposure of PAH contaminated sediment (Little Scioto River) and the sediments (ACTON) spiked with fluoranthene. The amphipod and fathead minnow where exposed in the mesocosms in *in situ* chambers in three locations: near surface, near sediment, and on the sediment surface. Survival was determined after 4 and 7 days of exposure. Survival was relatively good in the reference sediments. The turbidity treatment showed a slight increase in amphipod mortality after 7 days, primarily in the spiked and Little Scioto—near sediment treatments. The fathead minnow, conversely showed greater mortality in the near surface treatments containing PAHs. However, a second experiment showed slightly different trends. The amphipods and fish were adversely affected in only the spike, near surface treatment. No significant differences were observed in the humic acid treatments, with all surviving relatively well. A population of 200 fathead minnows was placed unconfined in each of the treatments, throughout the baseline, turbidity, and humic acid treatments. So, unlike the *in situ* chamber exposures, these fish were exposed to all treatments which provided a combined exposure period of 37 days. Dry weight measures of these fish showed an average wet weight of 0.6 g vs. spiked and Little Scioto mesocosm weights of 0.29 and 0.30, respectively. These results suggest that exposure periods of > 7 days would have detected greater effects from PAHs and perhaps more treatment interactions with turbidity and humic acids. This is supported by the results of the weathering experiment and in-lab experiments.

in situ test exposures were conducted in the Little Scioto River, which is heavily contaminated with polycyclic aromatic hydrocarbons, including high concentrations of fluoranthene. Experiments were conducted at seven locations on the river from upstream reference sites to the mouth of the river, 9.5 miles downstream. Sediment chemistry analysis was conducted on these samples and showed a gradient of PAH contamination existed from river mile 6.5 to the mouth. Based on chemical data, five locations were selected as *in situ* testing sites. The upstream reference site was at Pleasant Hill Road (level of PAHs is <0.02 ng/L and not detectable), which is 2.5 miles upstream from the input of contaminants.

The highest contamination site was at St. Hwy 95, 2 miles downstream from the input source. The intermediate contaminant site was at Keener Pike, 4 miles from the input. The less contaminated sites were at St. Hwy 203 an Green Camp Road, 6 and 8 miles from the source, respectively. The concentrations of total PAHs (16 priority) in the sediment at these sites are 3,631.1, 583.6, 110.1 and 33.9 mg/mg for St. Hwy 95, Keener Pike, HW203 and Green Camp Rd., respectively. During base flow these testing locations had a thick layer of fine sediment (rich in organics and clay), a shallow stream (25-40 cm), clear water (1.8-5.2 NTU), and slow flow (0.01-0.15 m/sec).

in situ exposures were conducted for 2, 4, and 7 days using 4-day old Pimephales promelas and 2-week old Hyalella azteca. The *in situ* chamber design in which organisms were exposed to sediment through mesh often underestimated toxicity, particularly for benthic organisms that could not be fully exposed to the contaminated sediments. A new chamber design was used to allow the organisms inside to be exposed directly to sediments and also allowed 50 percent of ultraviolet wavelengths of sunlight to penetrate the chambers. This partially improved the correlation between mortality and contaminant concentration. In order to compare the toxicity evaluation conducted *in situ* an in the laboratory, acute toxicity tests were conducted at WSU for 2, 4, and 7 days. Results showed that toxicity responses differed between laboratory and field exposures. For severely contaminated sites, toxicity in the laboratory was higher than that *in situ*. However, at less contaminated sites, toxicity in the laboratory was lower than *in situ*.

At these less contaminated sites, follow-up experiments were conducted to better understand the toxicity contribution from different environmental compartments. A chamber was designed which allowed organism exposures to only water or only sediment. It was found that the major contribution of toxicity was from sediments, with a minor component from overlying waters. According to chemistry analysis, the concentration of PAHs in soluble phase was not detectable (<0.02 ng/L), therefore, the toxicity contribution could be from the suspended solids in water column. Light was shown to be a major inducer of acute toxicity in Little Scioto River. Non-photo-induced toxicity in Little Scioto River only comprises a small portion of the total toxicity.

Toxicity responses differed between laboratory and field exposures. For traditional laboratory testing, the sediment toxicity was correlated with the concentration of contaminants, however, the toxicity assessed *in situ* exposure were not concentration dependent. Several different *in situ* exposures also were tested. The toxicity of the contaminants in the real environment was strongly influenced by all the aspects of environmental factors and stressors.

Conclusions from Environmental Factors Studies. The combination of laboratory, field mesocosm, and field confined chamber exposures provided unique information documenting the effects of PAHs on freshwater organisms. Differences observed between the three types of experiments appear to be related to exposure differences, such as: (1) length of exposure; (2) turbidity, humic acid, and organic carbon levels; (3) location of the organism (near surface vs. sediment); and (4) weathering/PAH fate issues. Therefore, caution should be used in reaching broad- based conclusions on PAH threshold levels since the toxicity and fate of compounds are linked closely to so many physicochemical factors and spatial-temporal exposure issues. It is apparent that organic carbon, turbidity, weathering, and sediment contact have dominant roles in determining whether PAHs will adversely affect aquatic biota. Focusing a reciprocity model that incorporates the product of UV intensity and PAH body residue, relatively good predictions of *in situ* toxicity can be made. However, the complex dynamics and unknowns associated with these factors at most sites will make extremely accurate predictions (modeling) of effects difficult a priori, but these predictions will help risk assessors determine the relative likelihood that adverse conditions exist.

Genetics. The ability of a species to survive and adapt to changing environmental conditions may be

increased by it possessing a greater pool of genetic variability that can respond to varying selection forces. Under natural conditions (e.g., absence of anthropogenic influence), the allelic frequencies of a population should fluctuate with time according to stochastic and environmental selection pressures while maintaining a certain level of genetic variability. However, severe perturbations, such as pollution, may reduce genetic variability of populations and thereby increase their susceptibility to the effects of further environmental changes. The plasticity of enzyme formation, maintained by genetic diversity, may increase the chance of survival for a species by allowing for adaptation to natural and human-induced environmental changes. The loss of genetic diversity may, therefore, weaken the stability of the species. The technique most commonly used to quantify genetic structure in populations employs electrophoretic analysis of selected enzymes to determine allele and genotype frequencies for specific gene loci. These data are used to describe the genetic structure of populations and to compare the genetic diversity among populations.

Our published data suggest that individuals with certain allozymes are more sensitive than others to the toxic effects of environmental contaminants. Electrophoretic assessment of genetic structure (allozyme diversity) in fishes thus appears to be sensitive to changes in water quality. It is a potentially useful tool both to monitor the health of existing aquatic populations and, by using laboratory bioassays, to predict the potential impact of byproducts on natural populations.

The purpose of the genetic study described here was to examine the effect of genotype at variable enzyme loci on the photo-induced toxicity of fluoranthene contaminated sediment to Hyalella azteca and Pimephales promelas. In addition, we wanted to determine the effect of genotype at variable enzyme loci on the photo-induced toxicity of sediment from a field site with known PAH contamination to juvenile Hyalella azteca and Pimephales promelas.

Genetically-based tolerance of contaminant exposure has been found in populations in contaminated areas, and has been developed in laboratory cultures. Such tolerance can develop only when appropriate genetic variability exists in the stressed population. Enzyme electrophoresis has been used to elucidate relationships between variation at enzyme loci and differential survivorship in laboratory exposures. To test for the presence of genotype-survivorship relationships one-month-old fathead minnows (Pimephales promelas) were exposed to fluoranthene-contaminated sediment (1.24 mg/gm organic carbon) during a 96 h exposure. Of the 909 minnows exposed to fluoranthene, 684 (75 percent) minnows died during the exposure. Horizontal starch-gel electrophoresis was used to determine genotypes at six variable enzyme loci (ß-GAL*, GPI-1*, GPI-2*, IDHP-1*, MDH-2*, and PGM*). Statistical analyses were used to evaluate the relationships between the genetic data and weight, length and time-to-death (TTD) of fish using an accelerated failure time regression model (LIFEREG). The GPI-1*, MDH-2*, and PGM* loci were found to be significantly related to TTD. Multi-locus heterozygosity also was related to TTD. Lower heterozygosity was related to a longer TTD and a greater chance of survival. Fish weight was strongly related to TTD and survival. Larger fish had a longer TTD and a greater chance of survival. Mean fish weight differed significantly among genotypes at each locus. This resulted in large differences between LIFEREG regression models that factored weight out and those models that did not separate weight from the genotypes or multi-locus heterozygosity. The results of the study indicated that differential survival to fluoranthene was genetically related. The frequencies of several genotypes were significantly different in the survivors of the fluoranthene exposure compared with those in the initial population.

A second study examined genotypic responses of Hyalella azteca to the toxicity of sediment contaminated by the PAH fluoranthene (310 µg/goc). We monitored time to death of 696 Hyalella azteca, which were exposed to UV and sediment spiked with fluoranthene. The survival distribution functions (SDFs) within genotypes at each of three variable allozyme loci [acid phosphatase (ACP*), glucose-6-phosphate isomerase (GPI*) and phosphoglucomutase (PGM*)] were compared using a log-

rank test. Results showed significant differences among SDFs at all three loci. No association of heterozygosity with time to death was observed. The homozygote ACP*-CC was associated with decreased survivorship when compared with ACP*-AA, ACP*-BB and ACP*-AB. However, GPI*-AA was associated with increased survivorship when compared with GPI*-BB, GPI*-CC and GPI*-BC. Significant differences in resistance also were observed for PGM*-BB vs either PGM*-AC or PGM*-BC. These results indicate that differential resistance to PAH phototoxicity was genetically related resulting in the significant alteration in frequencies of several genotypes in the population.

During July 1999 populations of both H. azteca and P. promelas were caged in the Little Scioto River for 4 days in clear plastic cages developed by WSU. One control site (replicates exposed to sunlight and under bridge) and one contaminated site (replicates exposed to sunlight and under bridge) were utilized. A total of 2000 Hyalella and 600 Pimephales were used. None died! It was subsequently determined that the plastic cages did not allow penetration of sufficient UV light. Nw cages were designed in September 1999; these were tested utilizing a smaller number of H. azteca and P. promelas in unshaded exposures for a 7d period. hile few deaths occurred in the control exposures, most of the Hyalella and Pimephales at the contaminated site died. ample size of Pimephales was too small to provide useful experimental data and,therefore, the exposure will be repeated in summer 2000. The data for Hyalella could be valuable; we will analyze genetic data on Hyalella during spring 2000.

Conclusions from Genetics Studies. Acute exposures of H. azteca and P. promelas to fluoranthene-contaminated sediment and UV light results in differential resistance to PAH phototoxicity. Differential resistance was genetically related resulting in the significant alteration in frequencies of several genotypes in the population of each species.
Since multi-locus heterozygosity was significantly associated with survivorship in P. promelas but not in H. azteca, it appears that selection acts at the level of the individual locus.

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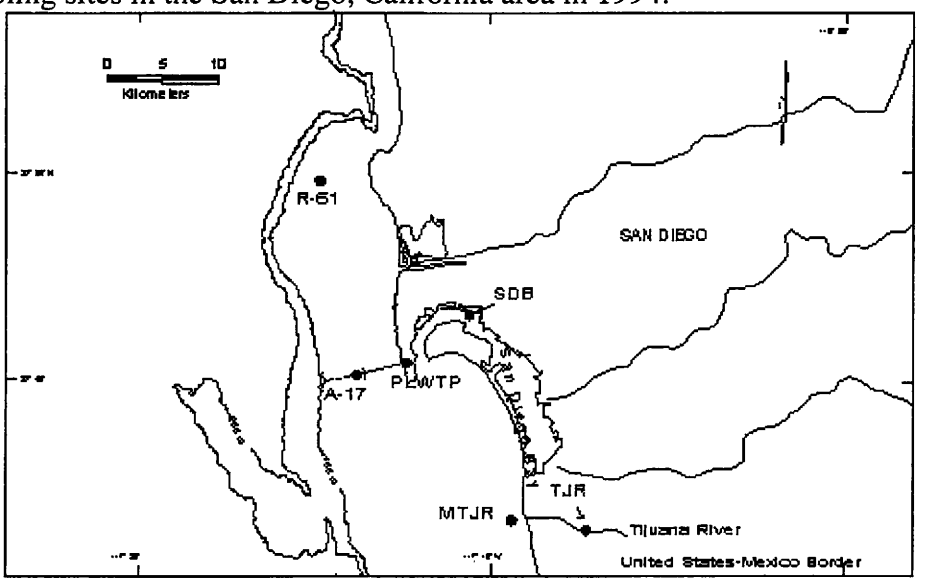
Compositional Indicies of Polycyclic Aromatic Hydrocarbon Sources off San Diego, California

Eddy Y. Zeng, Cherrie L. Vista

The main sources of anthropogenic hydrocarbon compounds to the marine ecosystem off Southern California are 1) municipal and industrial waste discharge, 2) surface runoff, 3) inadvertent spills, and 4) aerial deposition. Only the hydrocarbons in the first two sources can be easily measured and regulated.

FIGURE 1.

Location of sampling sites in the San Diego, California area in 1994.



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In addition to these, *in situ* biochemical processes also produce significant amounts of hydrocarbons (Wakeham *et al.* 1980, Gassmann 1982, and references therein) of marine origin. The mixing of hydrocarbons from various sources yields a complicated assemblage that may not be readily recognized. Degradation of organic compounds primarily partitioned on particulates may occur in the water column before deposition. These factors affect efforts to evaluate the impact of wastewater discharges on the coastal marine environment.

The four major municipal wastewater dischargers in Southern California (City of Los Angeles Hyperion Treatment Plant, County Sanitation Districts of Los Angeles County (CSDLAC), County Sanitation Districts of Orange County, and City of San Diego Point Loma Wastewater Treatment Plant (PLWTP)) have made great efforts to implement improved wastewater treatment technologies. As a consequence, the mass emission rates for a variety of contaminants from their sewage outfalls have steadily declined over the last 25 years (SCCWRP 1995). However, the discharge of a large quantity of numerous contaminants over the years has resulted in notable stresses in coastal marine sediments around the Southern California Bight (Bergen *et al.* 1995). Due to the slow degradation of many chemicals, contaminated sediments continue to impact the benthic community.

The compositional patterns of polycyclic aromatic hydrocarbon (PAH) and aliphatic hydrocarbon (AH) assemblages have been used to discern the origins of hydrocarbon compounds found in the aquatic environment (Sporstøl *et al.* 1983, Colombo *et al.* 1989, and references therein). PAHs are sensitive

indicators of petrogenic and pyrogenic inputs of hydrocarbons while n-alkanes are useful in identifying biogenic- or petrogenic-products. In general, PAHs from petrogenic-related sources are abundant in alkylated homologues relative to their parent compounds, while combustion of fossil fuels yields PAHs generally devoid of alkylated homologues.

These observations prompted the introduction of two useful indicators: 1) alkyl homologue distributions (AHDs) of naphthalene, phenanthrene/anthracene, and fluoranthene/pyrene, etc.; and 2) parent compound distributions (PCDs) (Lake *et al.* 1979). Other individual ratios generally involving two PAH compounds (e.g., phenanthrene/anthracene (P/A), methylphenanthrene/phenanthrene (MP/P), fluoranthene/pyrene (FL/PYR), and benz[a]anthracene/chrysene (BZ[a]A/CHR)) have also been applied to source recognition. Similarly, several molecular indices derived from n-alkane components have been shown to be sensitive in differentiating biogenic and petrogenic inputs of hydrocarbons (Colombo *et al.* 1989, and references therein).

At present, little is known about the contributions of organic contaminants from various sources to the coastal marine environment off San Diego. To gain insight into this, we conducted a comprehensive study of their contributions during the fiscal year 1993/94. The objectives of this study were to identify the possible origins or sources of hydrocarbons in the coastal region off San Diego and to evaluate the extent of organic contamination exerted by the point and nonpoint inputs. In addition, to further understand the lateral transport of urban pollutants into the ocean, we also measured linear alkylbenzenes (LABs). The methods for data analysis utilized in this study for PAHs and AHs were similar to those employed by Sporstøl *et al.* (1983) and Colombo *et al.* (1989). In particular, we evaluated the molecular compositions and indices associated with the PAH and n-alkane assemblages in each sample. For LABs, the concentrations of the LAB compounds with 10 to 14 carbons in the alkyl chain were quantified. We also evaluated the LAB chemical compositions and the ratios of internal to external isomers (I/E ratio; Takada and Ishiwatari 1990) of phenyldodecanes in each sample. The data were used to further assess the input levels of these sewage-derived organic contaminants and their fate in the coastal marine environment. The results from this study are presented in three separate articles in this annual report. This first part in the series reports the results from PAHs.

STUDY SITE

The coast off San Diego begins at the United States-Mexico border and extends northwest approximately to Point La Jolla (Figure 1). A major municipal wastewater treatment facility, PLWTP, discharged treated sewage (advanced primary treatment) into the ocean in the area through a submarine outfall at a water depth of 60 m. An extension of the sewage outfall to a depth of 100 m began operation in November, 1993.

The Tijuana River (TJR) drains an area of 4,480 km2, of which 27% lies in Mexico and 73% lies in the United States (Brownlie and Taylor 1981), and emerges into the ocean on the southern San Diego coast. Although discharges from TJR only accounted for 2% of total gauged runoff to the Southern California Bight in 1987 and 6% in 1988, it contained the highest concentrations of suspended solids, Cd, Cr, Cu, Ni, Pb, Zn, and total PCBs (Aroclor 1242 + Aroclor 1254) and second highest concentration of total DDTs (DDT and metabolites) among the eight largest creeks and rivers in Southern California (SCCWRP 1992).

San Diego Bay (SDB) is a southeast-northwest embayment; its widths vary from 1 to 4 km and its length is over 18 km with a maximum water depth of 21 m (Lenihan *et al.* 1990). Due to the highly elevated level of contamination in SDB, the National Benthic Surveillance Project (NBSP) under the National Oceanic and Atmospheric Administration National Status and Trends Program had established five sampling stations in the vicinity from 1984 to 1993 to monitor the distributions of contaminants in fish and sediments (Van Rhyn and Gauthier 1992).

Four stations were selected in the present study (Figure 1): A-17 (32o40.28' N/117o17.03' W), R-61 (32o49.64' N/117o19.67' W), SDB (32o43.53' N/117o10.86'W), and MTJR (32o32.94' N/117o08.81' W). In addition, effluent was collected from PLWTP and runoff was collected from TJR at Dairy Mart Road, about 6 km upstream from the ocean.

A-17 is located between the Y-shaped arms of the old PLWTP outfall with a water depth of 60 m. The reference station R-61, about 20 mi away from A-17 and at a water depth of 60 m, is near the northern San Diego coast off La Jolla and has little sediment contamination (SCCWRP 1993a). Station SDB in San Diego Bay is located at East Harbor Island at a depth of 7 m, close to a station used by NBSP (32o43.2' N/117o11.3' W; McCain *et al.* 1992). Station MTJR near the mouth of TJR is about 500 m from the coastline at a water depth of 16 m.

MATERIALS AND METHODS

Supplies used in the measurements of total organic carbon (TOC) and total nitrogen (TN) have been described previously (SCCWRP 1993b). GF/C 47-mm glass fiber filters (1.2 µm pore size) were obtained from Whatman International Ltd. (Maidstone, England) and baked at 420oC for at least 4 h prior to use. A custom mixture of 12 PAHs was prepared by AccuStandard, Inc. (New Haven, CT) with 2000 µg/mL of individual PAHs in methylene chloride. An additional sixteen PAHs in a mixture were obtained from Ultra Scientific, Inc. (North Kingstown, RI). Internal (nitrobenzene-d5, 2-fluorobiphenyl, and p-terphenyl-d14) and surrogate (naphthalene-d8, acenaphthalene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12) standards were purchased from AccuStandard, Inc. and Ultra Scientific, Inc., respectively. A PAH reference standard (SRM 1491) was acquired from the National Institute of Standards and Technology (NIST; Gaitherburg, MD). Ultra resi-analyzed grade hexane and methylene chloride were obtained from J.T. Baker Inc. (Phillipsburg, NJ) and used as supplied. All the standards were prepared in hexane.

Sample Collection

Sediment traps were deployed at 1 m and 5 m from the sea floor at both A-17 and R-61 in December 1993 and May 1994; they were retrieved 30 days after deployment. Surface sediments from A-17, R-61, SDB, and MTJR, microlayer samples from A-17 and R-61, effluent from PLWTP, and runoff from TJR were collected in January and June 1994.

The sediment traps used were designed to collect sinking particulates and are described in detail elsewhere (Hendricks and Eganhouse 1992). Three moorings were deployed at each of the A-17 and R-61 sites. Three and nine traps were used at the 1-m and 5-m depths, respectively. This sampling design was intended to obtain sufficient particulates for chemical analyses. All the traps deployed in December 1993 were recovered, while all three traps deployed at A-17 1-m, six traps at A-17 5-m, and one trap at R-61 5-m in May 1994 were lost. Upon retrieval, the traps were disassembled and water over the particles was decanted slowly. The sample bottles were capped with Teflon-lined caps.

Sediments were collected using a modified 0.1 m2 Van Veen grab (Stubbs *et al.* 1987). Subsamples of the top 2 cm sediments were transferred into precleaned glass jars. Procedures for microlayer sample collection and handling were detailed previously (Cross *et al.* 1987). The upper 50 µm surface water samples were collected into precleaned 1-L amber glass bottles. Twenty-four-hour composite effluent samples were obtained from PLWTP and stored in precleaned 1-gal amber bottles. TJR runoff was collected by immersing a 1-gal glass bottle into the middle of the stream from a bridge. All the samples collected were immediately cooled with ice. Upon returning to the laboratory, the sediment and sediment trap samples were stored at -20oC and microlayer, effluent, and runoff samples were stored at 4oC until further treatment.

Sample Extraction

Sediments and Sediment Trap Particulates.
A weighed subsample was transferred into a 250-mL centrifuge bottle. The bottle was centrifuged at approximately 50 x g for 5 min and the top water layer was decanted. The sample was mixed with ~30 g of anhydrous sodium sulfate, spiked with surrogate standards, and extracted successively three times with methylene chloride (100 mL each) using a roller table. The combined extract was concentrated and solvent-exchanged to hexane using a rotary evaporator at 30oC and 650 mm Hg vacuum pressure. After sulfur removal with activated copper granules (overnight in the dark), the extract was further concentrated to ~250 µL under gentle nitrogen flow. The extract was applied to a 1:2 alumina/silica gel glass column for separation of different fractions. The first fraction, containing AHs, was eluted with 15 mL of dry hexane. The second fraction, containing PAHs and LABs, was collected by eluting 5 mL dry hexane and 30 mL of a 30/70 mixture of methylene chloride and hexane through the alumina/silica gel column. Each fraction was concentrated to ~ 0.5 mL using the rotary evaporator and transferred to a half-dram vial. The pear-shaped flask was rinsed with additional hexane and the solvent was also transferred to the half-dram vial. The final volume of the extract was adjusted to 500 µL under gentle nitrogen flow. Appropriate amounts of the internal standards were added to the extract prior to instrumental analysis.

Effluent, Runoff, and Microlayer.
Particulates in each sample were separated with precleaned, preweighed GF/C filters. Sample bottles were shaken vigorously before filtration. A measured amount of the sample was gradually poured into the all-glass filtration assembly and filtered under vacuum. The filter was replaced when the flow dropped to approximately half of the initial speed. Each filter was transferred to a precleaned glass petri dish. The filters were cut in pieces with a clean, stainless steel blade and combined in a glass centrifuge bottle. The rest of the extraction procedure was the same as used for sediments and sediment trap particulates.

The filtrates were extracted three times with methylene chloride using the liquid-liquid extraction technique (Zeng and Khan 1995). The combined extract was concentrated and fractionated in the same fashion for the sediments and sediment trap particulates.

Total Suspended Solid (TSS), Moisture, TOC, and TN Measurements
An appropriate amount of an aqueous sample was filtered with a preweighed GF/C glass fiber filter. The loaded filter was placed in a petri dish and dried overnight at 60oC to constant weight. The difference in the weights of the filter before and after filtration with a specific sample volume was defined as the TSS concentration (in mg/L).

Moisture content was determined for sediments and sediment trap particulates. Approximately 10-15 g of sample were transferred to a tared aluminum pan and weighed with an electronic balance (accuracy ~0.5 mg). The sample was dried at 60oC for 24 h, cooled in a dessicator, and weighed. The weight loss was defined as moisture content.

For sediments and sediment trap particulates, the TOC and TN contents were measured using a procedure in SCCWRP (1993b). For aqueous samples, particulates were filtered with GF/C filters. The loaded filters were treated in a same fashion as for sediment and sediment trap particulates. Analysis of blank glass fiber filters indicated no detectable TOC or TN.

Gas Chromatography/Mass Spectrometry (GC/MS) Analysis and Quantitation
Measurements of PAHs were made using an HP 5890 II GC with a 5970 mass selective detector (MSD); the experimental conditions are described in Zeng and Khan (1995).

Quantitation of PAH concentrations was performed using the internal calibration method. The internal standards were either prepared with the calibration standards or added to the final sample extracts. Twenty-six PAH compounds were measured in this study (Table 1). åC1-naphthalene consisted of 1-methylnaphthalene and 2-methylnaphthalene. C2-naphthalenes were quantified using the relative response factor of 2,6-dimethylnaphthalene; C3-naphthalenes using 2,3,6-trimethylnaphthalene; and C1-phenanthrenes using either 2-methylphenanthrene or 1-methylphenan-threne, depending on the closeness of their retention times.

Procedural performance and matrix effects were monitored by recoveries of surrogate standards prepared with calibration standards or spiked to samples prior to extraction. The mean ± 1 SD (n=31) for the recoveries of the surrogate standards in field samples were as follows: naphthalene-d8 - 33.8 ± 12.6, acenaphthalene-d10 - 69.2 ± 14.5, phenanthrene-d10 - 82.0 ± 14.4, chrysene-d12 - 84.8 ± 24.4, and perylene-d12 - 98.6 ± 31.8. Instrumental performance was checked for each batch of samples (less than 10) by analyzing the NIST SRM 1491 solution. The measured values were within ±20% of the certified values given by NIST for more than 80% of the PAH compounds (or times).

Concentrations of PAH compounds were expressed based on either particle dry weight for solid samples or volume for aqueous samples; they were not corrected for the recoveries of the surrogate standards. The detection limits (Table 1) were set slightly higher than the method detection limits determined using the procedure given previously (Clesceri *et al.* 1989). These detection limits were based on 1 g dry weight or 1 L volume for a sample. The actual detection limits for a sample with a different weight or volume were corrected accordingly.

RESULTS

Total Suspended Solids

Total suspended solid (TSS) concentration showed more than a 20-fold variation in PLWTP effluent, TJR runoff, and microlayer samples from four locations (Table 2).

TSS concentration was 56 and 27.5 mg/L in the PLWTP effluent samples collected in January and June 1994, respectively. In TJR runoff TSS was 88 mg/L in January 1994 and 15 mg/L in June 1994.

Microlayer samples showed a wide range of TSS concentrations at the same sampling site at different times or at different sites at the same time. TSS ranged from 11.5 mg/L (A-17 in June 1994) to 258 mg/L (A-17 in January 1994) with a mean value of 100 (±88) mg/L.

TOC and TN

Particulates were higher in TOC and TN in PLWTP effluent than TJR runoff (Table 3). PLWTP effluent particulate TOC, TN, and C/N (TOC/TN) ratios were 34.4, 6.3, and 5.5% in the January sample and 35.7, 6.3, and 5.7% in the June sample, respectively. In TJR runoff particulates, TOC, TN, and C/N were 10.2, 2.18, and 4.7% in January and 8.15 %, 1.58, and 5.16% in June 1994. The difference probably results from mixing of raw sewage with other wastes or particles with less TOC and TN contents in TJR runoff.

Similar to the TSS results, TOC and TN in microlayer particulates varied widely from sample to sample, ranging from 1.55 % (A-17 in January 1994) to 20.7 % (R-61 in June 1994) for TOC and from 0.108 % (A-17 from January) to 2.06 % (R-61 from June) for TN. C/N varied in a relatively narrower range, from 3.6 (R-61 from January 1994) to 17 (A-17 from June 1994) (Table 3).

The A-17 and R-61 sediments contained fairly similar TOC and TN (TOC<1% and TN<0.1%), typical of relatively uncontaminated marine sediments. Sediments collected from MTJR contained the lowest

TOC (0.374 % in January 1994 and 0.120 % in June 1994) and also relatively low TN. Overall, the SDB sediment samples contained the highest TOC and TN concentrations (0.82 % in January and 0.83 % in June for TOC; 0.069 % in January and 0.082 % in June for TN) among all the samples (Table 3).

The TOC concentrations in sediment trap particulates varied from 1.89 to 3.22 % with a mean of 2.58 (±0.44) % and TN ranged from 0.180 to 0.352 % with a mean of 0.264 (±0.06) %. In general, R-61 trap particulates contained higher TOC and TN than those from A-17 (Table 3).

Spatial and Temporal Distributions of PAHs

PLWTP Effluent.

A large difference in particulate PAH concentration was observed between the effluent samples collected in January 1994 (5,920 ng/g) and in June 1994 (17,500 ng/g) (Table 4). In the present study, different subsamples were used in measuring TSS and organic compounds, due to the concern that some organic compounds might be lost if the same subsample processed for TSS measurement was also analyzed for organic compounds. Sample heterogeneity may be partially responsible for the large difference in the TSS concentrations (Table 2), resulting in elevated particle-based PAH concentrations in the effluent collected in June 1994. If the aqueous volumes were used, the particulate PAH concentrations were 332 ng/L in the January sample and 481 ng/L in the June sample (Table 4). The PAH concentrations on a whole effluent basis were similar in both samples (1,780 ng/L in January vs. 1,550 ng/L in June).

TJR Runoff.

The runoff samples were collected during low flows. The runoff filtrate collected in June 1994 carried higher PAH concentration relative to that collected in January 1994 (Table 4). This difference likely resulted from the different sample volumes used for analyses, as was in the case of the PLWTP effluent. The total PAH concentrations based on the aqueous volume were similar in the particulate and aqueous portions of the January sample, but much higher in the filtrates than in the particulates of the June sample (Table 4). Again, this discrepancy was partially due to the large differences in TSS (Table 2).

Microlayer.

In processing the microlayer samples collected in January 1994 (the first batch in the present study), black ribbon filter papers were used to hold anhydrous sodium sulfate for removal of water content from extracts. Excessive, mostly unresolved peaks were found in the chromatograms of these samples, as well as in those of procedural blanks (pure solvent going through the extraction processes). GC/MS analyses indicated that ion fragments typical of hydrocarbon compounds (e.g., m/z 59, 71, 85, 99, etc.) were dominant. Due to the possible interference with sample quantitation, the analytical results for these samples were abandoned. Baked glass wool replaced the filter papers in the subsequent extraction of the other samples. The same interfering peaks did not appear in procedural blanks and samples.

No PAHs were detected in the microlayer filtrates at A-17 and R-61 and only a few PAHs were present in the microlayer particles (Table 4). The dry weight based concentrations of particulate PAHs were 1,770 ng/g in A-17 and 381 ng/g in R-61 sample. However, the concentrations based on the aqueous sample volume were similar in both samples (20.4 ng/L in A-17 and 44.2 ng/L in R-61). This drastic difference was clearly a result of the distinct concentrations of TSS in these two samples (11.5 mg/L in A-17 vs. 116 mg/L in R-61; Table 2).

The MTJR microlayer particulate sample contained a PAH concentration of 2,830 ng/g (dry weight); the filtrate sample had non detectable PAH content. The total PAH concentration based on the aqueous sample volume was similar in the MTJR microlayer (79.2 ng/L) and TJR runoff (80.1 ng/L) in June 1994.

The SDB microlayer particulates were highly enriched with PAHs (68,600 ng/g dry weight or 798,000 ng/g TOC based). On the other hand, the microlayer filtrates had a fairly low PAH concentration (42.2 ng/L) and only two PAH compounds, fluoranthene and pyrene, were detected. The total PAH concentration based on volume was 1,480 ng/L.

Sediments.
The magnitude of sediment PAH contamination followed the order of SDB>A-17>R-61>MTJR. The PAH concentrations in A-17 sediments were 257 ng/g dry weight in January 1994 and 122 ng/g dry weight in June 1994; the temporal decline was possibly related to the initiation of the PLWTP outfall extension in November 1993. Similar trend was observed in R-61 sediment samples (23.9 vs. 7.1 ng/g dry weight).

Extremely low levels of PAHs were found in the sediment at MTJR, 16.5 ng/g dry wt. in January and these were nondetectable in June 1994. The PAH concentrations in SDB sediments were comparable in January (983 ng/g) and June (898 ng/g) 1994 (Table 4).

Sediment Trap Particulates.
The A-17 sediment trap particulates contained slightly higher PAH concentrations than the R-61 particulates, but the difference was not as significant as in the case of sediments. The samples collected in January also contained slightly higher PAH concentrations than those collected in June. The PAH concentration decreased from the 1-m depth to 5-m depth at A-17, but increased at R-61. However, the variation at R-61 was not significant. Due to the higher TOC contents in sediment trap particulates than in sediments (Table 3), the TOC normalized PAH concentrations were higher in A-17 sediments than in sediment trap particulates, although the dry weight based concentrations were similar.

PAH Compositions
High molecular weight PAHs were relatively more abundant in the PLWTP effluent particulates than in the filtrates (| Figure 2a | Figure 2b |). Both effluent filtrates and particulates contained mostly 2,3-ring PAHs and extremely low concentrations of fluoranthene/pyrene (Table 4). The particulates from TJR runoff contained only one PAH component (pyrene), while the filtrates were enriched with low molecular weight PAHs (| Figure 3a | Figure 3b | ; Table 4).

The number of PAH compounds detected was normally small for microlayer samples except for the SDB sample, which contained a large number of PAHs (Figure 3d). PAHs with more than three benzene rings were dominant in this sample (Table 4).

A common feature in the sediments and sediment trap particulates was the low percentage (from 0 to 15%) of the 2,3-ring PAHs, as opposed to the dominance (from 90 to 100%) of these low molecular weight PAHs in the PLWTP effluent (Table 4). There was a substantial difference in PAH compositions between the PLWTP effluent and A-17 sediment and sediment trap particulate samples (Figure 2). Although not shown, PAH compositions in R-61 sediments and sediment trap particles were similar to those in A-17 samples.

The alkyl homologue distributions (AHDs) of naphthalene and parent compound distributions (PCDs) for a selected and representative group of samples varied somewhat between samples (Figure 4 and Figure 5). Due to the generally low PAH concentrations in our samples, other AHD series (e.g., phenanthrene/anthracene, fluoranthene/pyrene, etc.) could not be determined accurately. Therefore, any conclusions regarding PAH origins derived from AHDs only refer to low molecular weight PAHs.

Vertical Fluxes of Organic Materials at A-17 and R-61

The fluxes of particulates, TOC, TN, and total PAHs at A-17 and R-61 varied spatially and temporally (Table 5). The flux of particulates at each depth was the average of multi-trap measurements. Fluxes of TOC, TN, and PAHs were calculated directly from the concentrations of TOC, TN, and PAHs (Table 4 and Table 5) and the fluxes of particulates. PAH concentrations were possibly underestimated in these samples, due to insufficient sample amounts for the PAH measurements in the May - June 1994 sediment trap particulates.

The maximum flux of particulates was 255.2 g/m2 d at the A-17 1-m traps deployed between December 21, 1993 and January 20, 1994. The A-17 1-m traps were lost in the second sampling during May - June 1994, hence no temporal comparison could be made at this depth. A substantial decline in fluxes of particulates between January and June was obvious at all other traps. They decreased from 89.4 to 22.0 g m-2 d-1 for the A-17 5-m traps, from 87.8 to 34.7 g m-2 d-1 for the R-61 1-m traps, and from 55.8 to 14.6 g m-2 d-1 for the R-61 5-m traps. Since TOC, TN, and PAH contents were only slightly higher in the sediment trap particulates collected in June 1994 than those collected in January 1994 (Table 4 and Table 5), the temporal variation in the fluxes of TOC, TN, and PAHs followed the same pattern as did the fluxes of particulates. For the samples collected in the winter of 1993/94, the PAH fluxes varied from 82.9 to 24.1 µg m-2 d-1 at A-17 and from 12.7 to 9.1 µg m-2 d-1 at R-61 in going from 1-m to 5-m traps (Table 5).

DISCUSSION

PAH Origins:Compositional Indices

The PAH assemblages in the samples analyzed in the present study can be divided into two distinct groups based on their PAH compositional patterns. The first group includes PLWTP effluent, TJR runoff, and MTJR microlayer particulates which were dominated by low molecular weight PAHs, i.e., high proportion of 2,3-ring PAHs (38-100%, Table 4). The PAH compositions in the second group of samples were characterized by the predominance of 4,5-ring PAH compounds, generally considered combustion-related products. This type of PAH assemblages has been observed in most marine sediments around the world (Laflamme and Hites 1978) and is believed to derive mainly from incomplete combustion of fossil fuels.

Alkylated naphthalenes were more abundant than the parent compound in both the PLWTP effluent filtrate and particulate samples, although the patterns were slightly different (Figure 4a and Figure 4b). The AHD pattern of the filtrate sample was similar to that of a crude oil sample (Sporstøl *et al.* 1983), while the relative abundance of alkyl substituted naphthalenes in the particulate sample showed an almost linear increase with increasing alkyl carbon number. Nevertheless, the relatively high abundance of alkylated naphthalenes suggested that PAHs (especially those with low molecular weights) received by the PLWTP were mostly petroleum-related.

Among the sediment and sediment trap samples from A-17 and R-61, only the A-17 1-m sediment trap sample collected in January 1994 contained a recognizable AHD pattern (Figure 4c-e; R-61 samples not shown), which was similar to those in the PLWTP effluent samples, i.e., low molecular PAHs were likely derived from petroleum related sources. On the other hand, PCDs determined in these samples (Figure 5c - d - e; R-61 samples not shown) were similar to those found in the sediments from Narragansett Bay (Rhode Island) believed to be contaminated by combustion-generated PAHs (Lake *et al.* 1979). Biodegradation and desorption of low molecular weight PAHs during transport and deposition was a possible mechanism for the PAH compositional difference in the effluent and sediment (and sediment trap) samples. However, the TOC normalized PAH concentrations in sediments (47,600 ng/g in January and 23,800 ng/g in June; Table 4) were comparable to those in the PLWTP effluent particulates (17,200 ng/g in January and 49,000 ng/g in June; Table 4). If the PLWTP outfall was a sole source for PAH inputs, biodegradation of sewage-derived PAHs would yield a much lower TOC normalized concentration of total PAHs. In addition, dilution of the effluent particulates by particles

from other sources may also be possible. Apparently, PAH assemblages in the water column particles and sediments at A-17 and R-61 originated from both combustion and petroleum related sources. For the microlayer samples collected at A-17 and R-61, only a few mid range molecular weight PAHs were detected in the particulates. Thus, no AHDs and PCDs could be accurately determined. As also discussed in the following section, nonpoint source inputs, presumably produced by combustion-related processes, may have exerted a greater impact on the microlayer than the PLWTP outfall.

Both AHD and PCD (Figure 4f and Figure 5f) in the TJR runoff filtrate sample collected in June 1994 suggested a petrogenic source for PAHs. As noted previously (SCCWRP 1992), a large percentage of the TJR discharge has reportedly been raw sewage and industrial and agricultural wastes, whose composition may be comparable to that of the wastes received by the PLWTP. In addition, only 3% of the drainage land of TJR on the U.S. side is urban and suburban (Brownlie and Taylor 1981). Therefore, combustion-derived PAHs that normally dominate urban riverine runoff (Hoffman *et al.* 1984, Prahl *et al.* 1984, Anderson and Gossett 1987) should not be the major components in TJR runoff.

Unlike the other microlayer samples, the MTJR microlayer particulates contained high concentrations of low molecular weight PAHs (Figure 3c), indicating a predominant petrogenic origin for PAH compounds. This observation was collaborated by the patterns of AHD and PCD in this sample (Figure 4g and Figure 5g). By contrast, the MTJR sediment displayed low proportion of 2,3-ring PAHs (Table 4); its AHD and PCD patterns were indicative of predominant pyrogenically produced PAHs, showing little or no effect from the TJR runoff.

The relative abundance of four to six-ring PAHs in SDB sediments ranged from 89 to 94% (Figure 3e and Table 4), similar to the result (~90% were four to six-ring PAHs) of McCain *et al.* (1992). This may indicate a consistent source, predominantly combustion-related, of PAH inputs into the study site. However, the AHD (Figure 4i) showed possible petrogenic PAH inputs, at least for low molecular weight PAHs. On the other hand, the PCD (Figure 5i) in the sample was similar to those in sediments contaminated with pyrogenic PAHs (Lake *et al.* 1979). Apparently, PAHs in this sediment may have derived from both petroleum and combustion sources. The microlayer particulate sample was clearly contaminated with PAHs of combustion origin, as indicated by the similar PCD patterns (Figure 5j) and reported by Lake *et al.* (1979) for sediments containing predominant combustion-derived PAHs. The AHD in this sample (Figure 4j) also pointed to a similar conclusion. The microlayer filtrate sample contained extremely low PAH concentrations and therefore neither AHD nor PCD was determined. The only PAHs detected in the filtrate sample were fluoranthene and pyrene, indicating a combustion-related origin for PAHs.

A major source of PAH inputs into the SDB site may be a large storm runoff outfall draining the San Diego International Airport, engine exhausts from boats and ships, and accidental oil spills. Without detailed analyses of samples collected from these sources, it is impossible to quantify their individual contributions of PAHs from each of these sources. Since the proportion of 2,3-ring PAHs in the SDB sediment and microlayer samples were all less than 20% (Table 4), PAHs from combustion sources appeared to prevail. This might effectively disqualify oil spills from contributing significant amounts of PAHs. Automobile exhausts, probably similar to boat engine exhausts, were known to contain both petroleum residues and incomplete combustion products (Simoneit 1985, Takada *et al.* 1990).

It may be concluded from the above discussions that PAHs in the PLWTP effluent and TJR runoff were predominantly derived from petroleum-related sources. Sediments and water-column particulates near the PLWTP outfall received PAHs mostly from combustion sources, with minor inputs of low molecular weight PAHs from petrogenic sources, probably the PLWTP outfall and natural oil seepage. Despite heavy shipping activities in San Diego Bay, oil spills did not appear to be the significant source for the PAH contamination in the sediment and microlayer. Instead, combustion-related sources, e.g., engine

exhausts and urban surface runoff, seemed to contribute significant amounts of PAHs to San Diego Bay.

To corroborate the above conclusions, we calculated ratios of MP/P, P/A, FL/PYR, and BZ[a]A/CHR in the same samples (Figure 6). These ratios have been used extensively to distinguish petrogenic and pyrogenic sources of PAHs (Colombo *et al.* 1989). In general, petroleum-contaminated samples contain higher MP/P, FL/PYR, and P/A and lower BZ[a]A/CHR than combustion contaminated samples (Colombo *et al.* 1989).

For MP/P, the highest ratios were found in the PLWTP effluent particulates and TJR runoff filtrates. In addition, the PLWTP effluent filtrates also showed a fairly high MP/P ratio. Nondetectable methylphenanthrene in MTJR microlayer particles and sediments yielded a zero MP/P ratio for these samples. SDB microlayer particulates also had a small MP/P ratio. Similarly, the highest value of P/A ratio occurred in the PLWTP effluent particulates. Since anthracene was not detectable in the PLWTP effluent filtrates, TJR runoff filtrates, and MTJR microlayer particulates, a very high P/A ratio would be expected for these samples. The SDB microlayer particles and sediments had the smallest P/A ratios. For BZ[a]A/CHR, both benz[a]anthracene and chrysene were not detectable in the PLWTP effluent (both filtrates and particulates) and TJR runoff filtrates. Benz[a]anthracene was not found in the MTJR microlayer particulates. Since benz[a]anthracene and chrysene are normally abundant in samples contaminated with combustion-derived PAHs, the low levels of these compounds indicated a predominantly petroleum-related origin. As a comparison, the A-17 and MTJR sediments and A-17 sediment trap particulates displayed relatively large BZ[a]A/CHR ratios. The trend of the BZ[a]A/CHR ratios was consistent with those observed for MP/P and P/A. These results are generally in agreement with the conclusions drawn above based on the patterns of AHDs and PCDs.

By contrast, the FL/PYR ratio did not show any consistent trend among the samples examined. In particular, the PLWTP effluent particulate and TJR runoff filtrate samples had relatively low FL/PYR ratios, while the SDB microlayer particulate and sediment samples possessed high FL/PYR ratios. As observed by Colombo *et al.* (1989), the range of the FL/PYR ratio did not vary much (0.5 to 0.9) for a variety of sediments.

It should be noted that the generally low levels of PAHs found in the sample media limit the applicability of compositional indices in the identification of PAH origins. Many other factors, such as solubility, extent of biodegradation, etc., may also contribute to the alteration of PAH assemblages after they are released into the environment. In this sense, the above compositional analyses are qualitative at best. If possible, other molecular indices should be combined to enhance the confidence of source identification. For instance, n-alkanes have also been found useful for source identification (Colombo *et al.* 1989).

C/N ratios also have been used to determine the sources of organic matter. Typically, high C/N ratios indicate terrestrial origins, while marine *in situ* processes generate organic materials with low C/N values. PLWTP effluent and TJR runoff particulates had C/N ratios around 5 (Table 3). In addition, sediment trap particulates at A-17 and R-61 also had a narrow range of C/N ratios around 10. By contrast, the range of C/N ratios was quite broad for microlayer particulates and sediments. For microlayer samples, this may underscore the dynamic nature of the sea surface microlayer, as also observed in the TSS data. For sediments, this may mean that the usefulness of the C/N ratio as a source indicator for organic matter inputs is limited.

Assessment of PAH Inputs from Point and Non-point Sources

There are two major point sources of PAHs in the study area: PLWTP sewage outfall and TJR. Nonpoint sources may include aerial fallout, inadvertent oil spills, and marine oil seepage. PAH inputs from PLWTP and TJR may be estimated from this study and relevant information in the literature.

Contributions from nonpoint sources, however, are difficult to quantify; only a qualitative assessment can be made.

From the PAH concentrations in the PLWTP effluent (Table 4) and the average effluent flow of 172 mgd (6.5 ´ 108 L) in 1994 (City of San Diego 1994), the average mass emission of total PAHs from the PLWTP outfall is estimated to be 395 kg in 1994. An estimate of the PAH mass emission from TJR is somewhat difficult, as the samples were collected during low flows and the total water discharge in 1994 is unavailable. If a long-term annual mean flow of 42.9 ´ 106 m3 from 1955 to 1988 (SCCWRP 1992) is used, the average mass emission of PAHs during 1994 was roughly 2.2 kg. This estimate may still be in the same order of magnitude even if data during storm events were applied, since PAH concentrations might be slightly lower during storms as in the case of oil and grease measured in Los Angeles River runoff (SCCWRP 1973).

Eganhouse and Gossett (1991) estimated the mass emission of a similar suite of total PAHs to be 110.5 metric tons (MT) for the Joint Water Pollution Control Plant (JWPCP) of the CSDLAC in 1979. If a mass emission ratio of 3.4:1 for aromatic hydrocarbons determined in the effluents of JWPCP and PLWTP in 1979 (Eganhouse and Kaplan 1982) was used to correct for PAHs, the PAH mass emission from PLWTP was approximately 32.5 mt in 1979. Thus, it appears that PAH emissions from the PLWTP outfall have been reduced by a large factor over the last 15 years, probably attributable to dramatic source reduction from petrochemical inputs and improved treatment processes. For comparison, our results suggest that the PAH contribution from TJR appeared to be insignificant.

Since the microlayer reflects recent inputs of contaminants, the microlayer data may be useful in identifying the in-situ sources of contaminants. The percentages of fluoranthene + pyrene relative to total PAHs were 100% and 67% in the A-17 and R-61 microlayer, respectively; these were much higher than those found in the PLWTP effluent (Table 4). Since fluoranthene and pyrene are generally considered as combustion-related PAHs (Hites *et al.* 1980, Prahl *et al.* 1984), the dominance of fluoranthene + pyrene in the A-17 and R-61 microlayer suggests that aerial fallout might have a greater impact on the sea surface microlayer than the inputs from the PLWTP outfall, even though A-17 is close to the outfall. However, without the knowledge of atmospheric PAH deposition rates in the area, the relative importance of the contributions from the PLWTP outfall and aerial deposition cannot be quantified.

By contrast, the PAH compositions were similar in MTJR microlayer and TJR runoff (both contained relatively high portions of 2,3-ring PAHs), underscoring the impact of TJR. The higher PAH concentration (2,830 ng/g) in MTJR microlayer particulates, compared to those in TJR runoff (158 and 104 ng/g) (Table 4), confirmed a significant enrichment of PAHs in the sea microlayer (Hardy *et al.* 1990, Kucklick and Bidleman 1994). It seems that PAHs remaining in the area after being discharged are possibly localized mostly in the sea surface microlayer. This speculation is consistent with the extremely low PAH concentrations in the sediment at the same sampling location (Table 4) and enhanced TOC content in the microlayer particulates (Table 3).

Baker *et al.* (1995) estimated that 3% of sewage particles rose to the surface in a laboratory experiment within 24 h, while 22% settled onto the bottom and 75% remained in suspension. If these results are applicable in the coastal marine environment, then the water column dynamics must be evaluated before a better understanding of the point and nonpoint inputs can be obtained.

The fluxes of particulates at A-17 (both 1-m and 5-m depths) were greater than those at R-61 (Table 5). In addition, the particulate fluxes at both A-17 and R-61 were greater in January 1994 than in June 1994. Fluxes of particulates, TOC, TN, and PAHs at the 5-m depth of A-17 were similar to those at the 5-m depth of R-61 measured in June 1994. As mentioned previously, discharge from the PLWTP sewage

outfall extension began in November 1993, which increases the distance between the discharge site and station A-17. All these suggest that the PLWTP sewage outfall was an important source of particulates and organic matter in the surrounding water column. It should be noted that the particulates may also carry materials from nonpoint sources into the sediment traps (more discussions below), thus amplifying organic matter fluxes.

Water Column Dynamics

Sedimentation processes in the water column can be extremely complex. As noted previously by Eganhouse and Gossett (1991), petroleum-generated PAHs, enriched on the surfaces of sewage-derived particles, were more vulnerable to biodegradation and/or desorption in the water column during deposition. Therefore, sinking organic materials may undergo rapid degradation or desorption (especially for low molecular PAH compounds), leading to depleted TOC and PAH concentrations in sediments compared to water column particulates. On the other hand, resuspension of selective fractions of sediment particulates may magnify or compromise this effect.

From the results obtained in the present study, several observations can be summarized: (1) PAH compositions in the sediments and sediment trap particulates were similar, but substantially different from those of the PLWTP effluent (e.g., 0 to 17% of the PAHs were 2,3-ring PAHs in sediments and trap particulates, compared to 90 to 100% in the PLWTP effluent); (2) A-17 sediment trap particulates contained higher TOC, TN, and PAH concentrations (dry weight) than the respective sediments, but the TOC normalized PAH concentrations were higher in sediments than in the sediment trap particulates; (3) R-61 sediment trap particulates contained higher TOC, TN, and PAH concentrations (both dry weight and TOC normalized) than the respective sediments; (4) there was a trend of increasing TOC and TN contents from 1-m trap to 5-m trap particulates for both A-17 and R-61; (5) PAH concentrations (both dry weight and TOC normalized) decreased from 1-m trap to 5-m trap at A-17, but they were similar in the 1-m and 5-m traps at R-61. These observations may have reflected the water-column dynamics related to a number of processes, e.g., mixing and transport of organic matter from point and nonpoint sources, bottom sediment resuspension, and biochemical degradation.

Observation (1) implies that sources other than the PLWTP outfall contribute significantly to the PAH presence in the water column and sediment, or that degradation and/or desorption of PAHs may occur rapidly in the water column. The following information supports the first mechanism. The sediment PAH concentrations (dry weight-based) in A-17 sediments and trap particulates were about 20 to 150 times lower than those found in the PLWTP effluent particulates, while the TOC-normalized concentrations in these samples were comparable (Table 4). If PAHs in the water column or sediments were solely from the PLWTP effluent, degradation or desorption would yield lower TOC normalized concentrations of PAHs in the water column particulates and sediments, assuming TOC is the main component for partitioning of PAH in particles. On the other hand, the similar PAH compositions in A-17 and R-61 sediments and sediment trap particulates (Figure 2) may underscore the influence on the depth dependence of particle fluxes from sediment resuspension by near-bottom currents (Table 5) (Hendricks and Eganhouse 1992). Resuspension of sediment particulates occurs over a short vertical distance magnifying the flux of sinking particles near the bottom.

Observation (2) suggests that at station A-17, the sediment traps collected sinking sewage-derived, high-density particulates. Organic materials settling with particulates from the upper water column may undergo rapid degradation, resulting in depleted TOC and TN concentrations in the sediments (Hendricks and Eganhouse 1992). The higher TOC normalized PAH concentrations in the sediments were mainly a result of much lower TOC contents in the sediments than in the sediment trap particulates. This might indicate that PAHs degraded much slower than sewage-derived organic carbon, due to the rapid deposition associated with the high-density particulates. Observation (3) probably pointed to a long-range transport mechanism that carried the sewage-derived organic matter to remote

locations, such as R-61. Low-density sediment particulates highly enriched with PAHs (Prahl and Carpenter 1983, Saliot *et al.* 1985) (presumably also enriched with TOC and TN) may tend to stay in suspension and are transported by currents to adjacent areas. These particulates may eventually aggregate with each other or with high-density particulates from other sources and finally sink to the sea floor. Since the sedimentation process is relatively slow for low-density particles, organic materials may experience biodegradation, fractionation, and transformation.

Observation (4) further supports the hypotheses of rapid degradation for organic materials during sedimentation or that the settling particles normally contain low contents of organic matter. Prahl and Carpenter (1983) suggested that combustion-derived PAHs did not preferentially stay in finer grained sediment particles of greater surface area; therefore, they were not easily subject to biodegradation or desorption from the particles. Hence, observation (5) might be due to a combination of slow degradation of sinking combustion-derived PAHs and resuspension of low-density particles enriched with PAHs from the bottom sediments.

CONCLUSIONS

The magnitude of PAH contamination in the coastal marine environment off San Diego has declined significantly over the last decade or so, apparently attributable to improved waste treatment techniques and source control. For instance, the mass emission rate of PAHs from the PLWTP outfall in 1994 (~395 kg/yr), estimated from the present study, was approximately 1.2% of that in 1979. Sediment PAH contamination at a specific site in San Diego Bay also declined to one third of the level as measured almost a decade ago.

Partially due to the decline of PAH emission from the PLWTP outfall as noted above, PAHs found in the sea surface microlayer, sediments, and water column particulates near the PLWTP outfall were predominantly derived from nonpoint sources. The sea surface microlayer near the mouth of TJR appeared to accumulate enhanced amounts of PAHs, TOC, and TN, probably discharged from the river, although they were in extremely low abundance in the sediments at the same location. Surprisingly, PAHs detected in the microlayer and sediments in San Diego Bay were mainly derived from combustion sources rather than oil spills, despite the heavy shipping activities in the area.

Low-density particles enhanced with organic materials may tend to stay in suspension or continue to be resuspended from the sea floor. Sewage-derived organic materials settling along with high density particulates may undergo rapid degradation in the water column. These hypotheses could explain the trend of increasing TOC, TN, and PAH concentrations from bottom sediments to water column particulates. However, this needs to be corroborated by additional parameters. Sediment resuspension caused by near-bottom currents may result in similar PAH compositions in water column particulates and sediments. Settling of resuspended particulates may enhance the flux of particles, as well as the fluxes of organic materials, near the sea floor.

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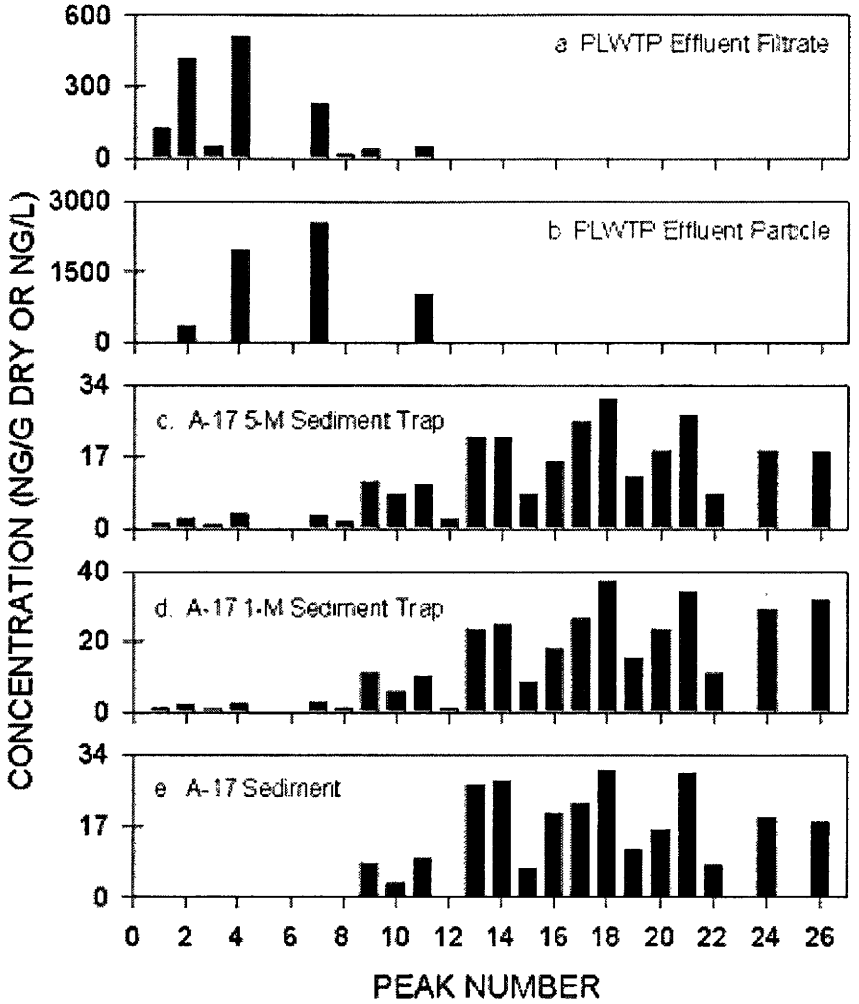
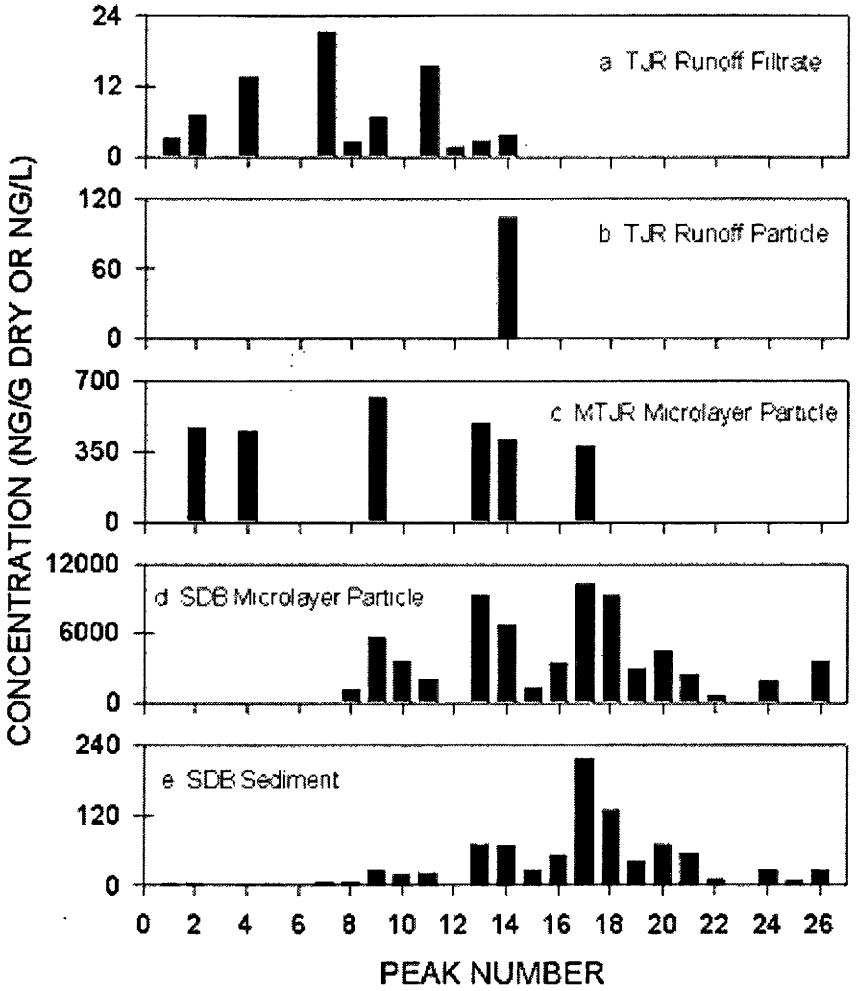
FIGURES

FIGURE 2.
Polycyclic aromatic hydrocarbon (PAH) compositions in the Point Loma Wastewater Treatment Plant (PLWTP; City of San Diego) effluent, A-17 (near old PLWTP outfall) sediments, and A-17 sediment trap particulates collected in January 1994. Peak numbers are defined in Table 1.



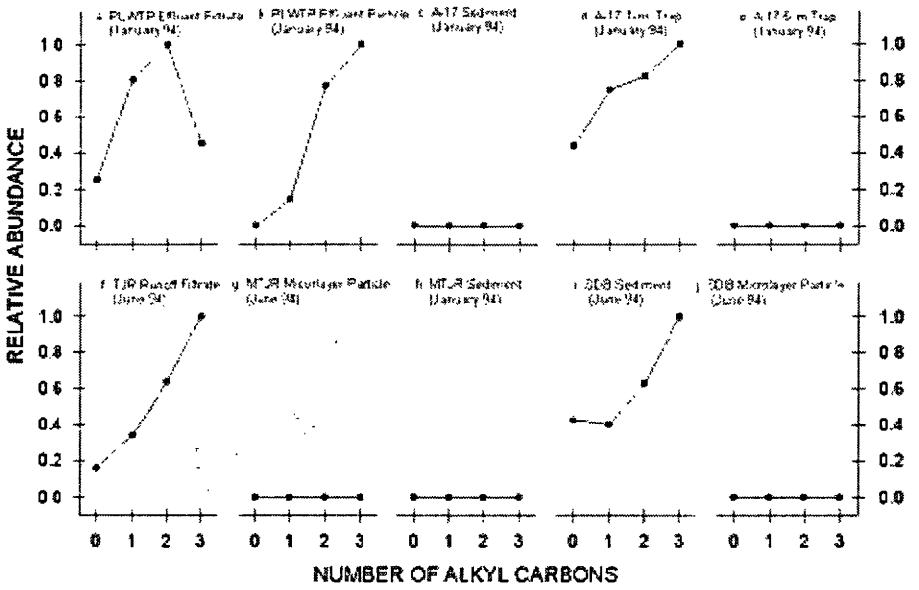
Return to PAH Compositions **FIGURE 3.**
Polycyclic aromatic hydrocarbon (PAH) compositions in the Tijuana River (TJR) runoff, mouth of Tijuana River (MTJR) microlayer particles, San Diego Bay (SDB) microlayer particles, and SDB sediment collected off San Diego, California in June 1994. Peak numbers are defined in Table 1.



Return to PAH Compositions

FIGURE 4.

Alkyl homologue distributions (AHDs) of naphthalene in selected samples collected off San Diego, California.



| Return to PAH Compositions | Return to Vertical Fluxes | Return to PAH Origins |

FIGURE 5.

Parent compound distributions (PCDs) in selected samples collected off San Diego, California.

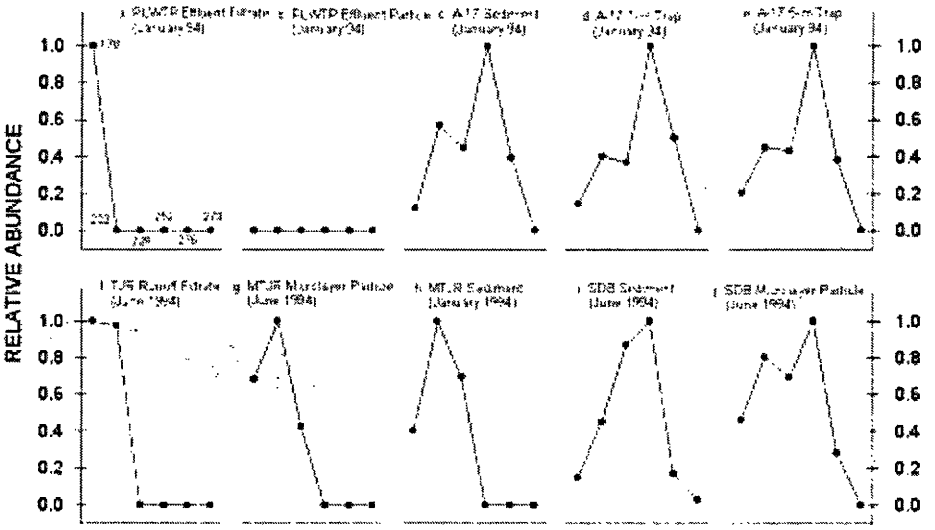
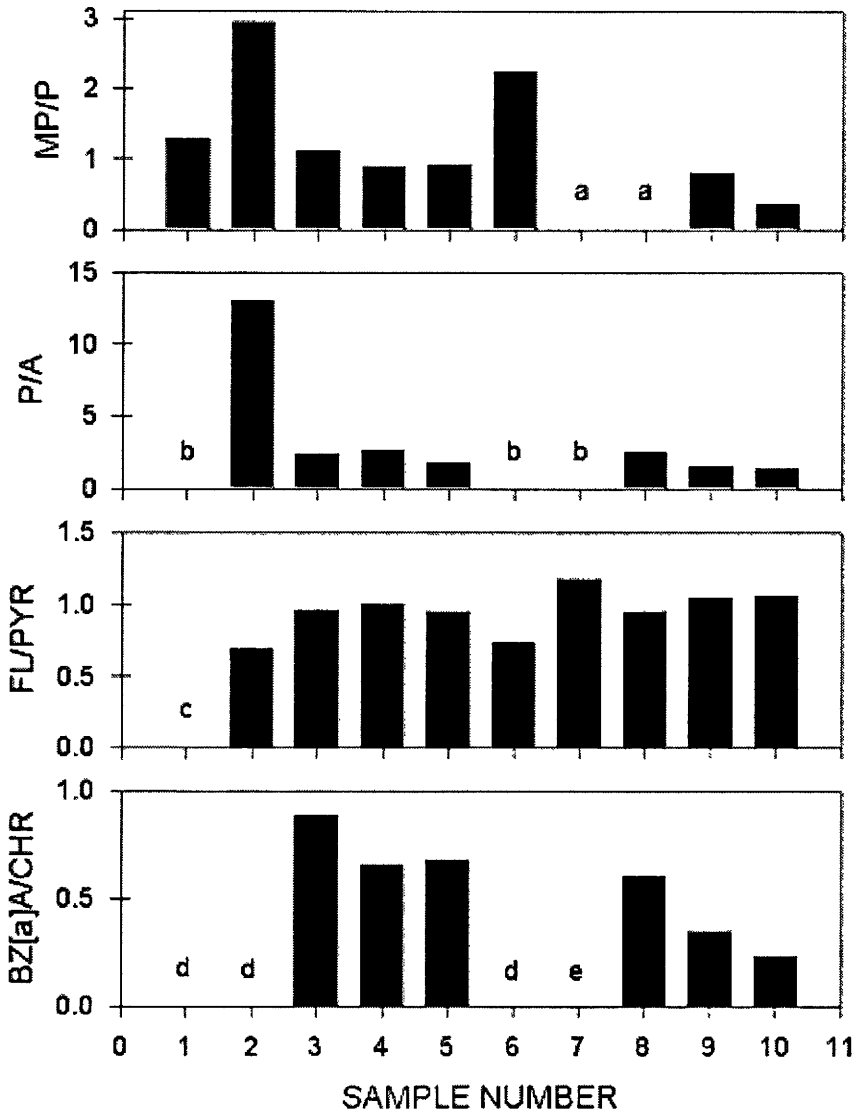


FIGURE 19. Parent compound distributions (PCDs) determined from PLTP effluent, A-17 sediment and sediment trap, and R-61 sediment, sediment trap, and microlayer

FILE: PCD-1.SPW

Return to PAH Origins

FIGURE 6.
Ratios of methylphenanthrene/phenanthrene (MP/P), phenanthrene/anthracene (P/A), fluoranthene/pyrene (FL/PYR), and benzo[a]anthracene/chrysene (BZ[a]A/CHR) in selected samples collected off San Diego, California. The sample number follows the same order as used in Figures 4 and



5.
- **a** Concentrations of methylphenanthrenes were below detection limits.
- **b** Concentrations of anthracene were below detection limits.
- **c** Concentrations of both fluoranthene and pyrene were below detection limits.
- **d** Concentrations of both benz[a]anthracene and chrysene were below detection limits.
- **e** Concentration of benz[a]anthracene was below detection limit.

Retrun to Discussion

TABLES

TABLE 1.
Polycyclic aromatic hydrocarbon (PAH) analysis in samples collected off San Diego, California, in 1994. The method detection limits (MDLs) were based on 1 g of solid or 1 L of aqueous samples.
Return to GCMS

			MDL	
Peak No.	**PAH Compound**	**Molecular Ion for Quantitation (m/z)**	**Solid (ng/g)**	**Aqueous (ng/L)**
1	Naphthalene	128	40	35
2	Total C1-Naphthalene	142	40	35
3	Biphenyl	154	40	35
4	Total C2-Naphthalene	156	40	35
5	Acenaphthylene	152	40	35
6	Acenaphthene	154	40	35
7	Total C3-Naphthalene	170	40	35
8	Fluorene	166	40	35
9	Phenanthrene	178	40	35
10	Anthracene	178	40	35
11	Total C1-Phenanthrene	192	40	35
12	3,6-Dimethylphenanthrene	206	40	35
13	Fluoranthene	202	40	35
14	Pyrene	202	40	35
15	2,3-Benzofluorene	216	40	35
16	Benzo[a]anthracene	228	40	35
17	Chrysene	228	40	35
18	Benzo[b]fluoranthene	252	40	35
19	Benzo[k]fluoranthene	252	40	35
20	Benzo[e]pyrene	252	40	35
21	Benzo[a]pyrene	252	40	35
22	Perylene	252	40	35
23	9,10-Diphenylanthracene	330	200	200
24	Indeno[1,2,3-cd]pyrene	276	200	200
25	Dibenzo[a,h]anthracene	278	200	200
26	Benzo[g,h,i]perylene	276	200	200

m/z = mass to charge ration

TABLE 2.
Concentrations of total suspended solids (TSS) in samples collected off San Diego, California, in 1994.
| Return to Total Suspended Solids | Return to TJR Runoff | Return to Microlayer |

	TSS (mg/L)

	Jan-94		Jun-94	
Sample Type	**Mean**	**SD**	**Mean**	**SD**
PLWTP Effluent	56	4a	27.5	3.5
TJR Runoff	88	22b	15	1.4
	Microlayer			
A-17	258	20	11.5	2.1
R-61	80.5	1	116	6
MTJR	198	3	28	3
SDB	87	12	21	5

a Three measurements. **b** Eleven measurements.

TABLE 3.
Concentrations of total organic carbon (TOC), total nitrogen (TN), and TOC/TN (C/N) ratio in samples (particulate portions only for effluent, runoff, and microlayer samples) collected off San Diego, California, in 1994.

| Return to TOC and TN | Return to Sediment Trap Particles |

	TOC (%)				TN (%)				C/N			
	Jan 94		Jun 94		Jan 94		Jun-94		Jan-94		Jun-94	
Sample Type	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**
PLWTP Effluent	34.4	3.5[a]	35.7	6.9	6.3	2.1	6.3	2.4	5.5	1.6	5.7	1.2
TJR Runoff	10.2	2.5[b]	8.15	0.2	2.18	0.83	1.58	0.09	4.7	1.7	5.16	0.18
	Microlayer											
A-17	1.55	0.74	12.9	1.1	0.108	0.092	0.77	0.24	14.4	8.5	17	7
R-61	1.63	0.13	20.7	0.8	0.45	0.17	2.06	0.31	3.6	1.2	10	1.1
MTJR	4.94	0.1	9.9	7.4	0.73	0.2	0.72	0.69	6.8	1.8	14	5
SDB	6.9	6.5	8.6	3.1	1.31	0.53	1.1	0.6	5.3	3.1	7.8	1.4
	Sediments											
A-17	0.539	0.009	0.513		0.063	0.001	0.042		8.6	0.1	12.2	
R-61	0.841	0.006	0.554		0.063	0.002	0.019		13.3	0.5	29.2	
MTJR	0.374	0.008	0.12		0.046	0.002	0.045		8.1	0.2	2.67	
SDB	0.82	0.1	0.829		0.082	0.004	0.069		10	0.7	12	
Sediment Trap Particulates												
A-17 (1 m)	1.89	0.03[d]	**[c]		0.18	0.01	**[d]		10.5	0.6	**[d]	
A-17 (5 m)	2.23	0.07[e]	2.94		0.211	0.004		0.32	10.6	0.2	9.16	
R-61 (1 m)	2.46	0.05[d]	2.56		0.244	0.012		0.259	10.1	0.3	9.87	
R-61 (5 m)	2.73	0.04[d]	3.22		0.28	0.011		0.352	9.8	0.4	9.14	

a Three measurements.**b** Eleven measurements. **c** Traps were lost. **d** Five measurements. **e** Six

measurements.**SD** = Standard deviation.

TABLE 4.
Concentrations of polycyclic aromatic hydrocarbons (PAHs) and percentages of 2,3-ring PAHs and fluoranthene+pyrene relative to total PAHs.
| Return to PLWTP Effluent | Return to TJR Runoff | Return to Microlayer | Return to Sediments | Return to PAH Compositions | Return to Vertical Fluxes | Return to PAH Origins |

	Sample Size[a]		Total PAHs (dry wt based)[b]		Total PAHs (TOC based)[c]		%2,3-ring PAHs[d]		% FL+PYR[e]	
Sample Type	**Jan-94**	**Jun-94**	**Jan-94**	**Jun-94**	**Jan-94**	**Jun-94**	**Jan-94**	**Jun-94**	**Jan-94**	**Jun-94**
	PLWTP Effluent									
Filtrates	2.4	10	1450	1070	—	—	100	99	0	1
Particulates	0.134	0.275	5920 (332)	17500 (481)	17200	49000	100	90	0	5
	TJR Runoff									
Filtrates	10	30	10.8	78.5	—	—	38	92	62	8
Particulates	0.888	0.45	158 (13.9)	104 (1.6)	1550	1280	0	0	100	100
	Microlayer									
A-17 Filtrates	NA	5	NA	ND	—	—	NA	ND	NA	ND
A-17 Particulates	NA	0.0575	NA	1770 (20.4)	NA	13700	NA	0	NA	100
R-61 Filtrates	NA	5	NA	ND	—	—	NA	ND	NA	ND
R-61 Particulates	NA	0.58	NA	381 (44.2)	NA	1840	NA	33	NA	67
MTJR Filtrates	NA	5	NA	ND	—	—	NA	ND	NA	ND
MTJR Particulates	NA	0.14	NA	2830 (79.2)	NA	28500	NA	55	NA	32
SDB Filtrates	NA	5	NA	42.2	—	—	NA	0	NA	100
SDB Particulates	NA	0.105	NA	68600 (1440)	NA	798000	NA	18	NA	23
	Sediments									
A-17	41.1	42	257	122	47600	23800	8	15	21	21
R-61	39.3	40.6	23.9	7.1	2840	1270	6	0	25	44
MTJR	41.9	44.1	16.5	ND	4690	ND	13	ND	43	ND
SDB	34.1	38.3	983	898	120000	108000	6	11	11	15
	Sediment Trap Particulates									
A-17 (1 m)	47.6	**[h]	325	**	17200	**	13	**	15	**
A-17 (5 m)	46.8	4.58	270	224	12100	7650	17	13	16	22

R-61 (1 m)	5.61	6.96	145	120	5900	4690	7	6	29	29
R-61 (5 m)	9.6	6.96	163	130	5960	4030	7	12	23	31

a In g (gram) for solid (particulates and sediments) and L (liter) for aqueous samples (filtrates). **b** In ng/g dry weight for solid samples and ng/L for aqueous samples; the numbers in parentheses are concentrations based on the aqueous volumes, in ng/L. **c** In ng/g TOC for solid samples; TOC was not measured for aqueous samples. **d** Percent of the concentrations from naphthalene to 3,6-dimethylphenanthrene (see Table 1) relative to total PAHs. **e** Percent of the concentrations of fluoranthene and pyrene relative to total PAHs.**f** NA=not analyzed; see text for reasons. **g** ND=not detectable. **h** A-17 1-m traps were not recovered in June 1994.

TABLE 5.
Fluxes of particulates, total organic carbon (TOC), total nitrogen (TN), and total polycyclic aromatic hydrocarbons (PAHs) at A-17 and R-61 (outfall and reference) off San Diego, California, in 1993-1994.
Return to Vertical Fluxes

Site	Collection Date	Level off Bottom (m)	Particulates (g/m2/d)	TOC (g/m2/d)	TN (g/m2/d)	Total PAHs (µg/m2/d)
A-17	**12/21/93-1/20/94**	1 (3 traps)	255.2	4.82	0.459	82.9
		5 (9 traps)	89.4	1.99	0.189	24.1
	5/30/94-6/29/94	1 (trap lost)	—	—	—	—
		5 (3 traps)	22	0.65	0.07	4.9
R-61	**12/21/93-1/20/94**	1 (3 traps)	87.8	2.16	0.214	12.7
		5 (9 traps)	55.8	1.52	0.156	9.1
	5/30/94-6/29/94	1 (3 traps)	34.7	0.89	0.09	4.2
		5 (8 traps)	14.6	0.47	0.051	1.9

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An analysis in support of sediment quality thresholds for polycyclic aromatic hydrocarbons (PAHs) to protect estuarine fish

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ABSTRACT

1. Under the US Endangered Species Act and the Essential Fish Habitat provisions of the Sustainable Fisheries Act, it is the responsibility of the National Marine Fisheries Service (NMFS) to safeguard the health of fish in estuarine and coastal waters.
2. This includes assessment of the impacts of exposure to toxic chemicals on fish and their critical habitat.
3. This analysis was conducted to assist NMFS resource managers in determining when fish are exposed to potentially harmful concentrations of one of the most common environmental contaminants, polycyclic aromatic hydrocarbons (PAHs).
4. Effects thresholds were estimated primarily through segmented regression of site-specific sediment PAH concentrations and associated disease prevalences in a resident fish species, English sole, *Pleuronectes vetulus*.
5. The analyses and supporting data encompass several endpoints, including DNA damage, liver lesions, and impacts on growth and reproduction.
6. In general, liver lesion prevalences, DNA adduct levels, and impacts on growth and reproduction were minimal at sediment PAH concentrations at or below 1000 ppb. Above 1000 ppb, there appears to be a substantial increase in the risk of contaminant-related injury to English sole.
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KEY WORDS: polycyclic aromatic hydrocarbons; English sole; sediment quality criteria

INTRODUCTION

Under the US Endangered Species Act (ESA) and the Essential Fish Habitat provisions of the Sustainable Fisheries Act (SFA) it is the responsibility of the National Marine Fisheries Service (NMFS) to safeguard the health of fish in estuarine and coastal waters. This includes assessment of the impacts of exposure to toxic chemicals on fish and their critical habitat. Under the ESA, the responsibilities are very specific:

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endangered fish must be protected against any activities that may kill or injure them, or interfere with breeding, spawning, rearing, migrating, feeding, or sheltering (NOAA, 2000). Similarly, under the SFA, the NMFS is charged with managing threats to essential fish habitat, defined as 'those waters and substrate necessary to fish for spawning, breeding, feeding, or growth to maturity' (USDOC, 1996).

Although sediment and water quality standards for both marine and fresh waters are in place in many parts of the United States, these standards are generally designed to protect aquatic life in general, and are based on a limited number of model taxa (USEPA, 1986a). As such, they may not be adequately protective of listed species, or of specific commercially important marine fish covered under the Essential Fish Habitat provisions of the SFA. Moreover, they are often based on laboratory bioassays where mortality is the main endpoint. As a result, they may not be protective against sublethal effects on individuals, which are important under the ESA.

Since the mid-1990s, over 20 United States Pacific Coast salmon and steelhead trout stocks have been listed as threatened or endangered by the NMFS (NMFS, 2000), and the American Fisheries Society has identified 62 marine fish stocks that it considers vulnerable to extinction (Musick *et al.*, 2000). Consequently, the degree to which current water and sediment quality regulations are protective of fish species that are potentially at risk has become a major concern for the NMFS and other agencies that act as trustees for marine and estuarine resources. Our ESA responsibilities, in particular, require us to carefully examine existing practices and regulations, in order to answer questions such as: What are acceptable levels of contaminants in marine and estuarine sediments for minimal biological and ecological damage? What levels are safe for protection of threatened or endangered species? What are realistic target levels for sediment contaminants in remediation projects?

The analysis described in this paper was conducted to assist resource managers in the NMFS in determining when fish are exposed to potentially harmful concentrations of one of the most common environmental contaminants, polycyclic aromatic hydrocarbons (PAHs). PAHs are frequently detected in sediments of Puget Sound and other industrialized embayments worldwide. The majority of PAHs associated with sediments in Puget Sound as well as at other coastal urban sites originate from petroleum and combustion products (Varanasi *et al.*, 1992; MacDonald and Crecelius, 1994). Sources include industrial discharges, creosote from treated wood, municipal run-off, and atmospheric emissions from incineration and automobile emissions. PAHs are also introduced into marine systems through accidental spills of fuel oil, crude oil, and other petroleum products, and from non-point sources.

PAHs, particularly the higher molecular weight compounds, tend to adsorb to organic or inorganic matter in sediments, where they can be trapped in long-term reservoirs. Although only a portion of sediment-adsorbed PAHs are readily bioavailable to marine organisms, there is substantial uptake of these compounds by resident benthic fish through the diet, through exposure to contaminated water in the benthic boundary layer, and through direct contact with sediment. Benthic invertebrate prey are a particularly important source of PAH exposure for marine fishes, as PAHs are bioaccumulated in many invertebrate species (Varanasi *et al.*, 1989, 1992; Meador *et al.*, 1995).

A notable feature of PAHs is that they are metabolized extensively in vertebrates, including fishes, unlike many chlorinated hydrocarbons, which bioaccumulate in tissues. Cellular metabolism of PAHs (Varanasi *et al.*, 1989) results in conversion of these hydrophobic compounds into polar, water-soluble forms that can be readily excreted from the organism. Consequently, although PAHs and their metabolites in invertebrate prey are passed on to consuming fish species (James *et al.*, 1991, McElroy *et al.*, 1991), and PAH–DNA adducts accumulate in the liver of fish chronically exposed to sediment-associated PAHs (Reichert *et al.*, 1998), parent PAHs generally do not bioaccumulate in fish or other vertebrates.

In spite of the fact that they do not bioaccumulate in tissues, PAHs are capable of causing a variety of deleterious effects in exposed animals. While metabolism serves mainly as a pathway of detoxication for PAHs, some of the metabolites that are intermediates in this process possess carcinogenic, mutagenic and

cytotoxic activity. Laboratory tests with rodents, as well as epidemiological studies, have established that certain PAHs, including benzo[*a*]pyrene, benz[*a*]anthracene, dibenz[*a,h*]anthracene, benzofluoranthene, and ideno(1,2,3-*c,d*)pyrene, are chemical carcinogens (NTP, 1999). Some PAHs are also known to be immunotoxic and to have adverse effects on reproduction and development (Klaasen, 1997). Over the past 20 years, a number of studies have been conducted on effects of PAHs on marine fish and other marine biota. These studies show that PAHs exhibit many of the same toxic effects in fish as they do in mammals. For example, liver cancer and related lesions have been documented in several species of wild fish as a result of environmental exposure to PAHs (Moore and Myers, 1994).

Sediment quality standards for PAHs have been established in the State of Washington (WAC, 1995), and national standards are under development by the EPA (USEPA, 2000). However, current sediment quality assessments rely heavily on methods based on bioaccumulation of contaminants in target organisms, such as determination of biota-sediment accumulation factors (BSAFs) or critical body residues (see Meador *et al.*, 2002a,b). Consequently, PAH toxicity estimates are frequently based on bioassays with benthic invertebrates, which bioaccumulate PAHs. While these methods are relevant for protection of the prey base for marine and estuarine fish, they may not be suitable for assessing the direct impacts of sediment PAHs on fish because fish metabolize PAHs, and may differ from invertebrates in their sensitivity to PAHs. This analysis attempts to relate sediment PAH concentrations to sublethal biological effects in resident populations of a representative marine benthic fish, English sole (*Pleuronectes vetulus*). The goal is to arrive at a realistic estimate of threshold sediment PAH concentrations that are associated with reductions in fish health.

Of the fish in Puget Sound, English sole is one of the most extensively studied species in pollution monitoring programmes. Several features make it suitable as a sentinel species for studies of the effects of environmental pollution. It is widely distributed along the Pacific coast of the USA, in both urban and non-urban environments. Because of its benthic life history as a juvenile and as an adult, it is particularly likely to take up sediment-associated contaminants. In addition, with the exception of a winter spawning migration, English sole within Puget Sound are relatively sedentary, and show high fidelity to the sites where they are resident (Day, 1976). Consequently, biological effects observed in English sole are generally an accurate reflection of PAH exposure at the sites where they are collected. A large body of data has been generated about the effects of PAHs on this species, in both field and laboratory studies. These data show that English sole from PAH-contaminated embayments are highly susceptible to the development of liver cancer and related lesions (Myers *et al.*, 1994, 1998a), and also appear to be prone to a number of other adverse health effects, including reproductive abnormalities, immune dysfunction, and alterations in growth and development (Arkoosh *et al.*, 1996; Johnson *et al.*, 1998a).

Liver disease, including cancer, is one of the best-documented effects of PAH contamination on English sole in Puget Sound (Myers *et al.*, 1987, 1990, 1994, 1998a,b; O'Neill *et al.*, 1998; PSWQAT, 2000) and other embayments along the west coast (Myers *et al.*, 1994, 1998a). In general, the prevalence of liver disease increases with increasing urbanization (Myers *et al.*, 1998a; O'Neill *et al.*, 1998). Typically, between 25% and 40% of adult English sole sampled from urban embayments, such as Elliott Bay and Commencement Bay, exhibit neoplastic, preneoplastic, or unique degenerative liver lesions, as compared with 3–8% of adult sole from non-urban and moderately urbanized sites. In several independent statistical analyses of field data from different studies (Rhodes *et al.*, 1987, Landahl *et al.*, 1990, Myers *et al.*, 1990, 1994, 1998a,b), exposure to PAHs was identified as the major risk factor for neoplasms and related liver lesions in English sole. A cause-and-effect relationship between PAHs and toxicopathic liver lesions in English sole is supported by induction of degenerative, proliferative, and preneoplastic lesions, identical to those observed in field-collected fish, when sole are exposed in the laboratory to model carcinogenic PAHs such as benzo[a]pyrene (BaP) and to extracts of sediments from PAH contaminated sites (e.g. Eagle Harbor) in Puget Sound (Schiewe *et al.*, 1991) where lesions are observed.

In addition to toxicopathic liver disease, English sole residing in contaminated areas in Puget Sound also suffer from various types of reproductive impairment. Field studies show that female English sole from areas with high concentrations of PAHs in sediment are less likely to enter vitellogenesis and have lower plasma concentrations of the female reproductive hormone, 17β-estradiol, than sole with low levels of contaminant exposure (Johnson *et al.*, 1988, 1997, 1999). At minimally contaminated sites within Puget Sound (sediment total PAH concentrations <500 ppb dry wt), approximately 80–90% of adult females undergo gonadal development (Johnson *et al.*, 1988, 1991, 1999; Sol *et al.*, 1999), while at more highly contaminated sites (e.g., the Duwamish and Hylebos Waterways and Eagle Harbor) the percentage declines to 40–60%. In statistical analyses of these data, exposure to PAHs emerges as a major risk factor for inhibited ovarian development in adult sole. English sole from PAH-contaminated areas also display increased ovarian atresia and reduced egg production (Johnson *et al.*, 1988, 1997). Results of these field studies are supported by laboratory experiments showing that pretreatment of gravid female English sole with extracts of contaminated sediment or crude oil containing high levels of PAHs decreased levels of endogenous estradiol (Stein *et al.*, 1991; Johnson *et al.*, 1995). More recent experiments suggest that exposure to benzo[*a*]pyrene or PAH-contaminated sediment may suppress estradiol-induced vitellogenin production in English sole (Anulacion *et al.*, 1997).

Studies also suggest that English sole from PAH-contaminated areas that do successfully enter vitellogenesis may experience inhibited spawning ability and reduced egg viability. When gravid English sole from four Puget Sound sites (Port Susan, Sinclair Inlet, the Duwamish Waterway, and Eagle Harbor) were brought into the laboratory and artificially induced to spawn, spawning success was significantly lower in fish from the two most contaminated sites, Eagle Harbor and the Duwamish Waterway (Casillas *et al.*, 1991). Moreover, exposure to PAHs in the water column (e.g., fluoranthene at 0.075–7.5 mg of PAH lit^{-1} of seawater) caused larvae to become disoriented and to exhibit signs of narcosis, with mortality at the higher concentrations (Eddy *et al.*, 1993).

Exposure to PCBs may also contribute to reproductive problems in female English sole, as PCBs often co-occur with PAHs at contaminated sites, and are known reproductive toxicants (Brouwer *et al.*, 1995). In several studies (Johnson *et al.*, 1997, 1999; Casillas *et al.*, 1991), exposure to PCBs and other organ ochlorine compounds was highly correlated with reduced larval viability, reduced egg size, and precocious sexual maturation in female English sole. However, PAH exposure was more highly correlated than PCB exposure with inhibited gonadal development, inhibited spawning, and reduced egg quality: reproductive problems especially prevalent in sole from Eagle Harbor, a site with high concentrations of PAHs, but minimal PCB contamination (Johnson *et al.*, 1988; Casillas *et al.*, 1991).

Effects of PAHs on reproduction have not been studied as extensively in male as in female English sole. There is evidence, however, that males may also be susceptible to PAH-related reproductive dysfunction. Preliminary studies suggest that although testicular development in male sole from PAH-contaminated sites is relatively normal, plasma concentrations of 11-ketotestosterone and testosterone are reduced in fish with particularly high concentrations of PAH metabolites in bile, a measure of PAH exposure (Sol *et al.*, 1999). In other fish species, PAH exposure has been associated with reduced sperm production and reduced sperm quality (Nagler and Cyr, 1997), but these parameters have not been measured in English sole.

English sole growth also appears to be affected by exposure to PAHs. Recent laboratory studies (Kubin, 1997; Rice *et al.*, 2000) show reduced growth in juvenile English sole exposed to PAHs through contaminated sediment or diet. These effects have not yet been corroborated in wild populations of English sole, but if they do occur, they could impact sole populations by reducing fecundity or altering the time to sexual maturity (Brandt *et al.*, 1992). Slow growth rates have also been associated with increased juvenile mortality in several fish species (Peterson and Wroblewski, 1984; Lorenzen, 1996; McGurk, 1996).

ANALYSIS

The purpose of the following analysis was to use existing data on PAH effects in English sole to determine sediment PAH concentrations at which biological injury is likely to occur. We selected English sole as the target species because of its sensitivity to PAHs, its presence at sites within Puget Sound where resource damage assessment and restoration efforts are planned or underway, and because there is substantial information on health effects of PAHs in this species from field studies, which have been corroborated, in large part, by laboratory studies. Our initial focus was on liver lesions in English sole, because of the abundance of data available for this health effect, and the preponderance of evidence for a cause and effect relationship between PAHs and the development of liver cancer in English sole. However, we also include data on DNA damage, reproductive effects and impaired growth.

For this analysis, biological effects were linked directly to sediment PAH concentrations at sites where test animals were resident, rather than to contaminant body burdens. This was done primarily because PAHs are metabolized in fish and do not bioaccumulate (Varanasi *et al.*, 1989), but also because the large volume of field data available on site-specific sediment PAH concentrations and associated biological effects in English sole made such an analysis feasible. Additionally, the sediment-based analysis is more directly applicable to the development of appropriate sediment quality guidelines for the protection of estuarine fish. An advantage of using field data for the analyses is that threshold estimates are based on health effects measured in a native organism collected from its natural environment. As such, there are fewer questions as to the environmental relevance of this approach, compared to laboratory bioassays. The effects considered reflect long-term exposure, potentially over the life of the organism, and incorporate exposure through all routes of uptake, including diet, water, and directly from sediment through skin contact or ingestion. In laboratory exposure studies, exposure generally lasts for only a limited period of time, and uptake is typically restricted to a single route of exposure, such as diet, or direct contact with sediments. A disadvantage of the field-based approach is that it may not adequately account for biological effects resulting from exposure to other contaminants or contaminant mixtures present in sediments. However, this can be mitigated to some extent by choosing endpoints, such as liver cancer and related lesions, for which PAHs are known to be a strong causative factor.

Liver disease

National Benthic Surveillance Project (NBSP) data set: Using data collected over the past 10 years from a variety of field studies in Puget Sound and on the West Coast (Myers *et al.*, 1998a; Brown *et al.*, 1998; McCain *et al.*, 2000), we statistically determined threshold PAH concentrations at which liver lesion prevalences begin to increase. The hockey stick regression model (Horness *et al.*, 1998) was employed in these analyses. Hockey stick regression is one of a number of standard dose-response models (Gad and Weil, 1991), and has been used in a variety of epidemiological and toxicological studies (e.g. Hammer *et al.*, 1974; Cox *et al.*, 1989; Gordon and Fogelson, 1993). The model consists of two linear segments whose 'blade and handle' shape resembles a hockey stick (Yanagimoto and Yamamoto, 1979). In the present application (Figure 1), the lower segment was assigned a slope of zero to represent a constant low-level background effect. The upper segment was defined as a linear function with a positive slope. The upper segment represents a dose–response relationship above a threshold that is estimated by the point of intersection of the two segments, as follows:

$$\text{Effect} = \text{background for } SC < SC_T$$
$$\text{Effect} = \text{background} + \beta(SC - SC_T) \quad \text{for } SC > SC_T$$

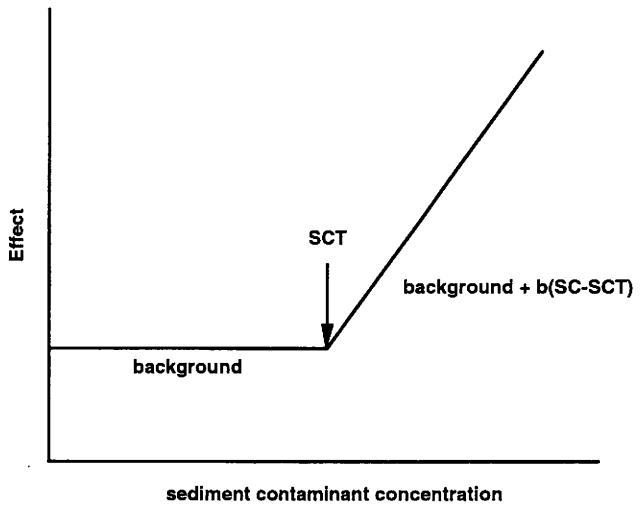

Figure 1. Generalized hockey-stick regression model relating biological effect to sediment contaminant concentration. SC = sediment contaminant concentration, SCT = threshold sediment contaminant concentration at which the biological effect begins to increase above background level.

where SC is the sediment contaminant concentration, SC_T the threshold sediment contaminant concentration.[1]

SC_T (threshold contaminant concentration), background (the spontaneous background effect) and β (the slope of the curve) are the estimated parameters. Effect and SC (sediment contaminant concentration) are the dependent and independent variables, respectively.

We realize that the risk analysis models used in epidemiology typically assume that cancer induction is a non-threshold phenomenon, and our choice of a threshold model for this exercise is not meant to imply that a true threshold exists in the process of carcinogenesis in English sole. Rather, the model was chosen for pragmatic reasons, to facilitate our identification of exposure levels at which statistically detectable and biologically relevant increases in lesion prevalence would be expected to occur in wild fish populations. The application of a threshold model is supported by the fact that, for most carcinogens, repair processes and compensatory mechanisms exist that can counteract the effects of carcinogens at low levels of exposure, even though one molecule of a carcinogen could theoretically induce an initiated cell, leaving no latitude for a threshold. Based on a similar rationale, the application of a threshold approach for regulating exposure to some carcinogens has been suggested for human health risk management (Lutz, 1998; Butterworth and Bogdanffy, 1999; Gaylor *et al.*, 1999).

The model was used to relate sediment PAH concentrations to prevalences of the four most common toxicopathic hepatic lesion types found in English sole. These four types were (1) neoplasms; (2) preneoplastic foci of cellular alteration (FCA), which are thought to be precursors of neoplasms; (3) specific degeneration/necrosis (SDN), a degenerative lesion associated with exposure to PAHs; and (4) non-neoplastic proliferative lesions, such as hyperlasia of hepatocytes or bile ducts. Additionally, a composite category was examined consisting of the presence of one or more of any of the first three lesions (neoplasms, FCA, and SDN) in an individual fish. Lesion prevalences were based on examination of between 30 and 60 fish per site. Collection site locations are described in detail in Horness *et al.* (1998) and

[1] The notation SC_T (threshold sediment contaminant concentration) is used in this paper to be consistent with Horness *et al.* (1998), but in application this is equivalent to SET (sediment effect concentration) used in Meador *et al.* (2002a,b) which are in this volume.

Myers *et al.* (1994). Because age is a significant risk factor for preneoplastic and neoplastic lesions in English sole, all fish less than 2 years of age were excluded from prevalence calculations. This exclusion is based on data indicating that fish below this age have not had sufficient time to develop these types of hepatic lesions even at high exposure levels (Myers *et al.*, 1998b).

To characterize the level of contamination present at a given site, surficial sediment samples were collected from the area in which the fish were captured and analysed for toxic contaminants (Sloan *et al.*, 1993) including both low and high molecular weight PAHs (Table 1). The correlation between the low and high molecular weight analytes was too high to consider them as separate factors ($r^2 = 0.94$). Moreover, there is only limited direct information to link a specific subset of PAHs to the effects that have been observed. Consequently, total sediment PAH content (the sum of all analytes shown in Table 1) was used as the contaminant category of interest for this analysis. It should be noted that the sediment samples used in this study contained not only lower molecular weight compounds associated with oil and other petroleum products, but significant concentrations of higher molecular weight PAHs which are typical of industrial urban sites (Brown *et al.*, 1998). Consequently, sediment PAH effects thresholds generated with these data may not be fully applicable at sites where sediments contain primarily low molecular weight PAHs, whose carcinogenic potency is generally not as great as that of high molecular weight PAHs (NTP, 1999).

As contaminant concentration data are generally log-normally distributed, the PAH concentrations were log-transformed prior to the regression. Thus, log (sediment PAH concentration) was used for the independent variable SC. Lesion prevalence was used for the dependent variable (Effect). The model was fitted using a non-linear regression parameter estimation routine from the SAS statistical package JMP. Confidence intervals were computed at an α of 0.1, rather than the standard 0.05, to increase the statistical power to detect a threshold and decrease the likelihood of a type II error (false negatives) without greatly increasing the likelihood of type I errors (false positives) (Peterman, 1990).

Table 1. Polycyclic aromatic hydrocarbons (PAHs) measured in sediment samples included in determination of PAH effect thresholds for liver lesions in English sole for NBSP studies (Brown *et al.*, 1998; McCain *et al.*, 2000) and PSAMP studies (PSWQAT, 2000; Myers and O'Neill, in preparation)

NBSP List	EPA List
Low molecular weight (2–3 rings)	
Naphthalene	naphthalene
2-Methylnaphthalene	2-Methylnaphthalene
Acenaphthene	acenaphthene
Fluorene	fluorene
Phenanthrene	phenanthrene
Anthracene	anthracene
Biphenyl	acenaphthalene
1-Methylnaphthalene	
2,6-Dimethylnaphthalene	
1-Methylphenanthrene	
High molecular weight (4–6 rings)	
Fluoranthene	Fluoranthene
Pyrene	Pyrene
Benz[*a*]anthracene	Benz[*a*]anthracene
Chrysene	Chrysene
Benzo[*a*]pyrene	Benzo[*a*]pyrene
Perylene	Benzo(*g*,*h*)perylene
Dibenzo[*a*,*h*]anthracene	Dibenzo(*a*,*h*)anthracene
Benzo[*e*]pyrene	Benzofluoranthene
	Ideno(1,2,3-*c*,*d*)pyrene

Depending on the specific type of lesion, threshold effect estimates ranged from 54 to 2800 ppb (ng g^{-1} dry wt.) (Figures 2(a–d); see Table 2 for regression parameters). All threshold estimates were statistically significant ($\alpha = 0.1$) except for that for FCA for which no lower confidence bound was found. At 2800 ppb (90% CI = 11–5500 ppb), neoplasms exhibited the highest PAH threshold. FCA exhibited the lowest threshold (54 ppb; CI = 0–870 ppb) and the lack of a lower confidence limit suggests that FCA prevalence in English sole may be directly proportional to sediment PAH content over the entire range of contaminant concentration rather than operating through a threshold relationship. The calculated threshold concentration for SDN, the most common toxicopathic lesion in English sole, was 940 ppb (CI = 600–1400 ppb).

DNA damage

The threshold analysis for DNA damage was done in the same manner as the analyses for liver lesions, but using the mean concentration of aromatic compound–DNA adducts in liver of English sole from the sampling sites as the outcome variable (i.e. Effect). As with liver lesions, our application of a threshold model for this analysis does not imply that DNA adduct formation itself is a threshold phenomenon. Our objective was to use the model to assist us in identifying the PAH exposure level where increases in mean DNA adduct levels in liver could first be detected in English sole populations. Mean DNA adduct levels were based on analyses of liver tissue from 3 to 10 fish per site. The threshold effect estimate was 290 ppb (ng/g dry wt.), with a 90% CI of 6–1380 ppb (Figure 3; see Table 2 for regression parameters). This threshold estimate is at the lower end of the range of threshold estimates for liver lesions, which is toxicologically consistent with the hypothesis that this type of DNA damage is a precursor to more overt pathological conditions in the liver, and a necessary step in the development of certain types of neoplasms (Farber and Sarma, 1987). A threshold in this range is also supported by a laboratory study (French *et al.*, 1996) in which exposure to sediments contaminated with 1200 ng g^{-1} dry wt. PAH resulted in DNA adduct concentrations in English sole liver of 15–20 adducts mol^{-1} nucleotides, in comparison with 5–6 adducts mol^{-1} nucleotides in fish exposed to sediments containing 20 ng g^{-1} PAH. The threshold model predicts adduct levels of 28 adducts/mol nucleotides at 1200 ng g^{-1} dry wt. PAH, and 5 adducts/mol nucleotides and 5 ng g^{-1} dry wt. PAH. The laboratory study, however, did not include any exposure treatments between 20 ng/g and 1200 ng g^{-1} PAH. Additional data on DNA adduct levels in sole exposed to sediments with PAH concentrations in the 100–1000 ppb range would be necessary to provide laboratory validation of the threshold estimate.

DNA adducts represent a tissue-level alteration or injury that is caused by PAH exposure, is correlated with other health effects such as liver disease, and can develop with relatively short-term exposure of days to weeks (Reichert *et al.*, 1998). In addition, hepatic DNA adducts in fish are persistent and accumulate with chronic exposure to sediment-associated PAHs (French *et al.*, 1996; Reichert *et al.*, 1998). As such, DNA adducts can be used as an indicator of PAH exposure and effects for estimating the likelihood of PAH-induced injury in species that are short-term residents of urban estuaries, such as anadromous salmonids.

Reproductive dysfunction

Although we do not have sufficient data to statistically determine precise thresholds for other effects in English sole, available information indicates that additional types of impairment begin to occur at sediment

Figure 2. Hockey-stick regressions of hepatic lesion prevalence in English sole versus total polycyclic aromatic hydrocarbons (PAH) in bottom sediment in ng/g dry wt. (ppb) for (a) neoplasms (Neo); (b) foci of cellular alteration (FCA); (c) specific degenerative/necrosis (SDN); lesions; (d) proliferative lesions (Prolif); (e) and either Neo, FCA, or SDN (any lesion). Arrows indicate threshold concentrations. Shaded grey bar represents the 90% confidence interval. No lower confidence found was found for the FCA threshold estimate. $n = 29$. Data from Horness *et al.* (1998).

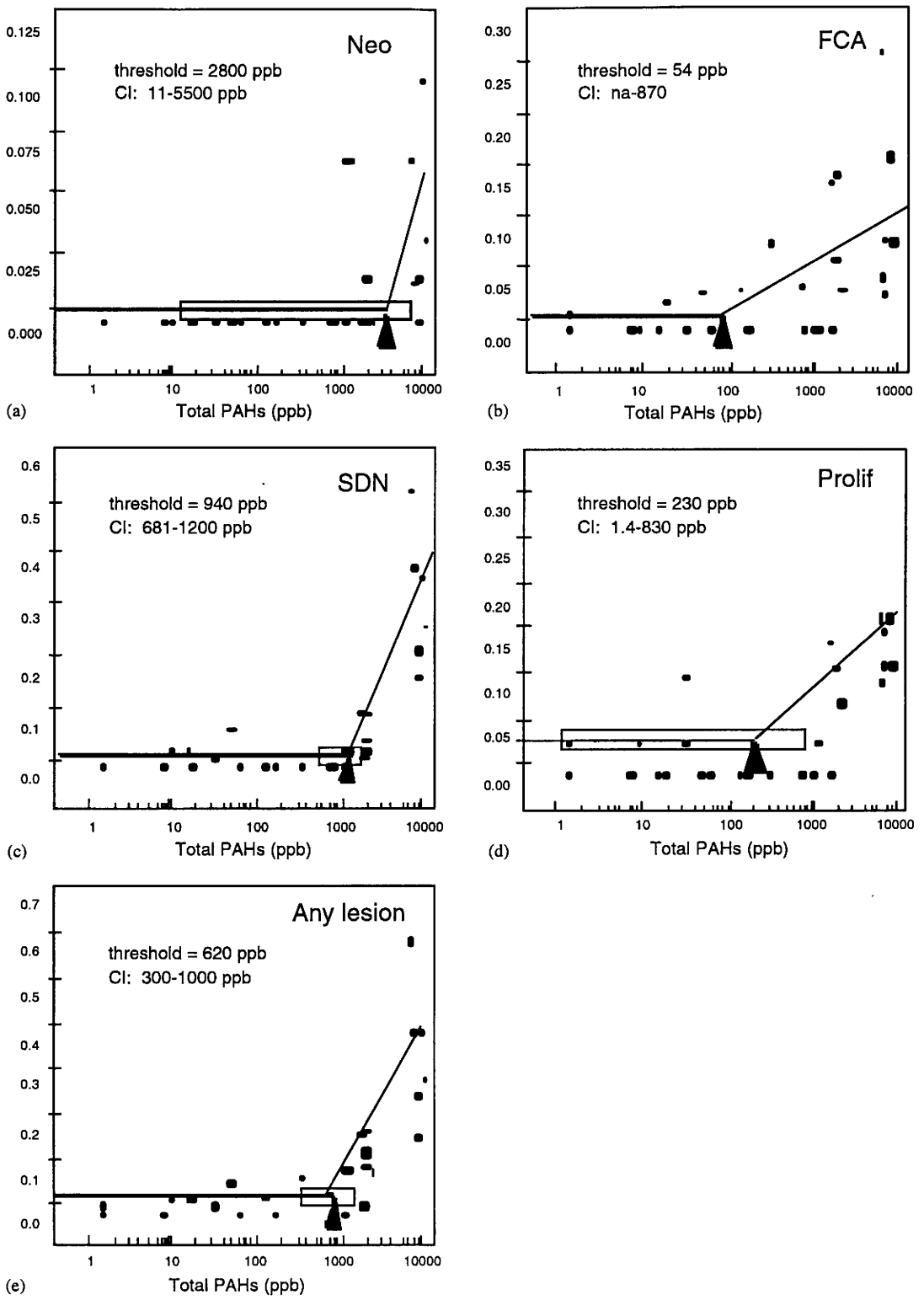
Neo
threshold = 2800 ppb
CI: 11-5500 ppb
0.125
0.100
0.075
0.050
0.025
0.000
1
10
100
1000
10000
(a)
Total PAHs (ppb)
FCA
threshold = 54 ppb
CI: na-870
0.30
0.25
0.20
0.15
0.10
0.05
0.00
(b)
SDN
threshold = 940 ppb
CI: 681-1200 ppb
0.6
0.5
0.4
0.3
0.2
0.1
0.0
(c)
Prolif
threshold = 230 ppb
CI: 1.4-830 ppb
0.35
(d)
Any lesion
threshold = 620 ppb
CI: 300-1000 ppb
0.7
(e)

Table 2. Parameter estimates for hockey stick regression of the relationship of sediment polycyclic aromatic hydrocarbon (PAH) concentration (dry weight) with hepatic lesions and reproductive abnormalities in English sole. Adapted from Horness *et al.* (1998).

	Hockey stick regression parameter estimates				Back-transformed threshold estimates	
Effect[a]	Threshold[b] (log ppb)[c]	Threshold confidence limits (log ppb)[c]	Background[d]	Rate of increase (β)[e]	Threshold (ppb)[c]	Threshold confidence limits (ppb)[c]
DNA damage	2.46	0.75–3.09	4.5	38	288	6–1318
Liver lesions						
Neo	3.45	1.04–3.75	0.004	0.10	2800	11–5500
FCA	1.74 (ns)[f]	na[g]–2.94 (ns)[f]	0.008	0.04	54 (ns)[f]	na[g]–870
SDN	2.97	2.75–3.16	0.013	0.37	940	600–1400
Prolif	2.37	0.14–2.92	0.024	0.09	230	1.4–830
Any lesion	2.79	2.48–3.01	0.024	0.31	620	300–1000
Reproductive abnormalities						
Inhibited gonadal growth	3.6	nd[h]	0.15	0.31	4000	nd[h]
Inhibited spawning	2.8	nd[h]	0.12	0.26	630	nd[h]
Infertile eggs	2.8	nd[h]	0.38	0.19	630	nd[h]
Abnormal larvae	2.8 (ns)[f]	nd[h]	0.25	0.12 (ns)[f]	630 (ns)[f]	nd[h]

[a] For all liver lesions, inhibited gonadal growth, and inhibited spawning, effect endpoints are sampling site prevalences. For DNA damage, endpoint is mean concentration of PAH–DNA adducts in liver of fish from the sampling site. For infertile eggs and abnormal larvae, endpoints are the average proportion of spawned eggs that were infertile or proportion of larvae that were abnormal in females from Puget Sound sampling crossed with reference males. Neo = neoplasms, FCA = foci of cellular alteration, SDN = specific degeneration/necrosis, Prolif = proliferative lesions, any lesion = Neo or FCA or SDN, immature = failing to undergo gonadal development, Non-spawning = failing to spawn; Infertile eggs = proportion of spawned eggs that not fertilized, Abnormal larvae = proportion of hatched larvae with developmental abnormalities.

[b] For liver lesions, thresholds are estimated from hockey-stick regression; for reproductive abnormalities, threshold = the geometric mean of the highest sediment PAH concentrations where the effect level was at background and the lowest sediment PAH concentration where an increase in effect level was seen.

[c] Measurement units in ppb = sediment PAH concentration in ng/g dry wt. sediment.

[d] For all liver lesion categories, Immature and Non-spawning, units for background values are prevalence in frequency of occurrence; for infertile eggs and abnormal larvae, units are proportion of eggs or larvae affected. For DNA adducts, units are number of adducts per nmol of bases. For liver lesions and DNA adducts, background was estimated using hockey-stick regression; for reproductive abnormalities, background = the effect prevalence or proportion at the reference sites with the lowest sediment PAH concentration (see Johnson *et al.*, 1988, 1991, 1999; Casillas *et al.*, 1991; Sol *et al.*, 1998).

[e] Rate of increase computed as the increase per unit increase in log (PAH concentration in ppb). For reproductive abnormalities, threshold and background effect level estimates from field data were substituted into the hockey-stick regression model for computation of β.

[f] ns = not significant; the confidence interval does not lie entirely within the data range, or for β, does not exclude 0. The threshold estimate for Abnormal larvae was not calculated through regression, but is considered non-significant because of the lack of a significant positive correlation between sediment PAH concentration and proportion of abnormal larvae.

[g] na = not available: the confidence interval is unbounded in this direction.

[h] nd = not determined: sufficient data were not available for calculation of this parameter.

[h] nd = not determined: sufficient data were not available for calculation of this parameter.

PAH concentrations similar to those associated with liver lesion occurrence and DNA damage. For example, in Figure 4, prevalences of several types of reproductive impairment observed in female English sole (Johnson *et al.*. 1988, 1999; Casillas *et al.*, 1991) are plotted against sediment PAH concentrations at the sites where fish were collected in Puget Sound. All fishes utilized in these analyses were of reproductive size and age, at least 3 years of age or 30 cm in length, which is when female English sole typically reach maturity (Garrison and Miller, 1982; Johnson *et al.*, 1991). The plots indicate that spawning failure and egg infertility begin to increase above background levels at sediment PAH concentrations between 250 and 1600 ppb, while the proportion of sole failing to undergo ovarian maturation begins to increase at

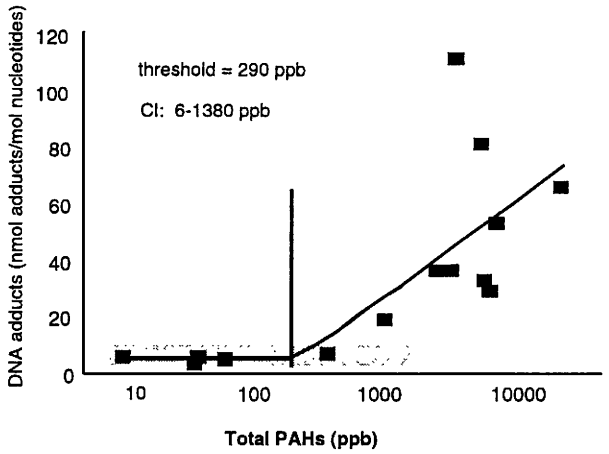

Figure 3. Hockey-stick regression of PAH–DNA adducts (nmol adducts per mol nucleotides) in liver of English sole versus total polycyclic aromatic hydrocarbons (PAHs) in bottom sediments in ng/g dry wt. (ppb) for selected sampling sites in Puget Sound, Washington. Threshold concentration is indicated by vertical line. Shaded gray bar represents the 90% confidence interval. Data from Stein *et al.* (1992); French *et al.* (1996); Collier *et al.* (1998); French (unpublished data).

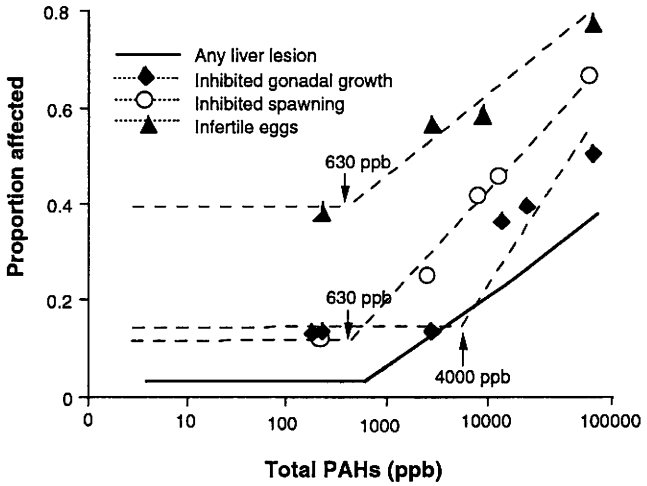

Figure 4. Measures of reproductive function in female English sole plotted against sediment total PAH concentrations at sites in Puget Sound where sole were collected. For inhibited gonadal growth and inhibited spawning, data points represent the proportion of females at the sampling site that exhibited these conditions. For infertile eggs, the data points represent the average proportion of spawned eggs that were infertile in crosses with sperm from reference males for females from the sampling sites. Data are from Johnson *et al.* (1988, 1999); Casillas *et al.* (1991); Collier *et al.* (1998). The dotted lines indicate the hypothetical hockey-stick regression models for reproductive endpoints. The horizontal portion of the curve represents background values for these endpoints, estimated from field data at the reference site with the lowest sediment PAH concentration. Threshold concentrations (indicated by arrows) are the geometric mean of the highest sediment PAH concentration where effect values were at the background level, and the lowest concentration where an increased effect level was observed. The upper portion of the curve is the fitted hockey-stick regression model. Estimated threshold and background effect levels were substituted into the model, rather than calculated through regression analysis as for liver lesions. The solid black line represents the fitted hockey-stick regression model and effects threshold estimate for any lesion in English sole (neoplasms, foci of cellular alteration, or specific degenerative necrosis; Horness *et al.*, 1998).

concentrations between 1600 and 10 000 ppb. If we estimate the effect thresholds by taking the geometric mean of these two points, this yields an effect threshold of 4000 ppb for inhibition of ovarian development, and a threshold of 630 ppb for all other reproductive endpoints.

Exposure–response relationships for reproductive endpoints at sediment PAH concentrations above the threshold levels were estimated using the formula for fitting the upper (sloped) segment of the hockey-stick regression:

$$\text{Effect} = \text{background} + \beta(\text{SC} - \text{SC}_\text{T})$$

Estimated threshold and background effect levels were substituted into the model, rather than calculated through regression analysis as for liver lesions and DNA adducts. Background effect levels were assumed to be identical to those found at reference sites with the lowest sediment PAH concentrations (see Johnson *et al.*, 1988, 1991, 1999; Casillas *et al.*, 1991; Sol *et al.*, 1999), so that background = 0.15 for proportion failing to mature; 0.12 for proportion failing to spawn; 0.25 for proportion of abnormal larvae; and 0.38 for proportion of infertile eggs. The estimated SC_T's used for this analysis were 4000 ppb for failing to mature and 630 ppb for all other endpoints, as described above. Parameter estimates derived from the regression analysis are shown in Table 2, and plotted regression curves are shown in Figure 4. The horizontal portion of the curve represents background values for these endpoints, estimated from field data, while the upper portion is the fitted hockey stick regression model.

The results show that the proportion of sole that failed to mature, the proportion that failed to spawn and the proportion of eggs spawned that were infertile were all significantly correlated with increasing sediment PAH concentration, as indicated by positive estimates for β with confidence intervals that excluded zero. However, the proportion of abnormal larvae produced showed no clear relationship with sediment PAH level; the confidence interval for β included zero, indicating that the slope of the line describing the relationship between sediment PAH concentration and the proportion of abnormal larvae was not statistically different from zero. Consequently, this endpoint was excluded from further analyses of PAH effect thresholds and exposure–response relationships.

While more data would be needed to calculate sediment concentration thresholds and confidence intervals (SC_T's and CI's) for the reproductive endpoints, this analysis currently provides the best available threshold estimates to compare to the SC_T's for liver lesions in English sole. The results also suggest that these types of reproductive impairment are found at sediment PAH concentrations similar to those associated with the development of hepatic lesions.

Growth reduction

Data from two recent laboratory exposure studies suggest that declines in growth of juvenile English sole also occur from exposure to PAHs (Kubin, 1997; Rice *et al.*, 2000). Although neither of these experiments were designed specifically to identify effects thresholds or model dose response relationships, the results provide information on PAH exposure levels associated with growth impairment in sole. Kubin (1997) exposed juvenile English sole to sediments contaminated with PAHs at concentrations of approximately 4000, 2000 and <50 ppb dry wt. for 6 months.[2] For the first 3 months, growth rates were similar for all treatments (1.0–1.1% per day for weight, and 0.36–0.38% per day for length). However, during the next 3 months, growth rates were significantly lower in the high exposure group; relative to control fish, a 19% reduction in growth rate, measured by either weight or length, was observed. The fish exposed to sediments with moderate PAH concentrations showed no significant decrease in growth rate relative to control fish. These data suggest a threshold for growth effects in the 2000–4000 ppb range. Actual threshold effect concentrations could be lower, as in this experiment, uptake of PAHs was from sediment and water only,

[2] Sediment PAH concentrations for this study were determined using the HPLC/PDA screening system of Krahn *et al.* (1991), which provides an estimate of PAH concentration by measurement of fluorescent aromatic compounds (FACs) in sediments. Total PAH concentrations, as determined by GC/MS, were estimated based on data from Krahn *et al.* (1988), in which parallel sediment samples from a variety of urban and non-urban sites along the US West Coast were analysed using both methods.

and in the natural environment, substantial exposure would also occur through the diet, with ingestion of invertebrate prey species residing in contaminated sediment.

A study by Rice *et al.* (2000) confirmed both the effect of PAHs on growth of juvenile English sole and the importance of dietary exposure. The findings showed significantly reduced weight in juvenile English sole fed polychaete worms reared on sediments containing 3000–4000 ppb dry wt. of PAHs, after an exposure period of only 12 days. The growth rate was markedly lower (0.05-0.1% per day) in exposed fish than in control fish (1.1–1.2% per day). If sole had been exposed to PAHs through uptake from both sediment and diet, as they are in the natural environment, and for a more extended period, it is reasonable to assume that effects on growth could be observed at lower sediment PAH levels, more comparable to the SCT for liver lesions. If, for example, a safety factor (Mount, 1977) of 2 were applied to the 3000 ppb sediment, PAH level associated with growth reductions in Rice *et al.* (2000), to account for additional PAH uptake through sediment and the water column, this would yield a threshold concentration of 1500 ppb, which is comparable to threshold concentrations associated with liver lesions, DNA damage, and certain reproductive effects.

The central finding from these data is that English sole exposed to PAHs in sediments at concentrations where toxicopathic lesions are observed are also likely to experience negative impacts on growth and reproduction. All three types of effects represent significant injury to the health of affected fish. The impacts on growth and reproduction are particularly likely to affect the productivity of stocks from contaminated sites because of their potential to reduce fecundity and age of sexual maturation.

SOURCES OF UNCERTAINTY IN THRESHOLD ESTIMATES

Although we believe that the present analysis provides good guidance on approximate sediment PAH concentrations associated with injury in English sole, several variables that could influence exposure–response relationships cannot be fully accounted for in this analysis of current data. Among the more important factors are fish age, length of exposure, relative proportions of high and low molecular weight PAHs in sediments, exposure to other contaminants, and species sensitivity, if the analysis is to be used to extrapolate to effects on other species.

The present analysis adjusts for fish age only in a very basic manner. Very young fish were excluded, as well as sites where the majority of fish collected were sub-adults. Because the analysis was done on a site basis rather than on individual fish basis, it was not possible to fully adjust for the increasing risk of disease development with age. Moreover, the number of animals lost to disease is not known, and is not incorporated into the analysis. Because of these limitations, the analysis may underestimate the lifetime cancer risk to English sole of a particular PAH exposure concentration.

The suite of PAHs used to calculate total PAH concentrations for the development of effects thresholds in this analysis differs somewhat from the group of 16 priority PAHs recommended by EPA (USEPA, 1986b; Table 1). Recalculation of the thresholds with this alternate group of PAHs could yield different threshold estimates. However, preliminary analyses of sediment PAH thresholds for liver lesions in English sole have been performed using data from Washington State's Puget Sound Ambient Monitoring Program, in which total PAHs are calculated based on EPA's set of 16 compounds. Liver lesion thresholds, calculated as described in Horness *et al.* (1998), ranged from 500 to 2000 ppb dry wt total PAH in sediment (O'Neill *et al.*, 1998; Myers and O'Neill, in preparation). The threshold for SDN, for example, was 540 ppb dry wt total PAHs (Figure 5). These thresholds are very similar to those derived for English sole using our NBSP data set. These results suggest that the thresholds we have determined are not highly dependent on the exact suite of individual PAHs used to calculate total PAHs, assuming that commonly occurring carcinogenic and mutagenic PAHs are included.

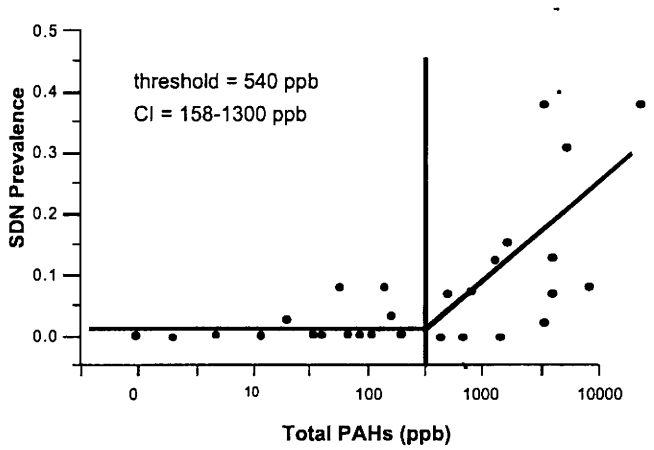

Figure 5. Hockey-stick regressions of hepatic lesion prevalence in English sole versus total polycyclic aromatic hydrocarbons (TPAH) in bottom sediment in ng/g dry wt. (ppb) for specific degeneration/necrosis (SDN), based on data collected as part of the State of Washington's Ambient Monitoring Program. Threshold concentration is indicated by vertical line. Data from O'Neill *et al.* (1998), Myers and O'Neill (in preparation). Total PAHs include the 16 priority PAHs delineated by the United States Environmental Protection Agency (USEPA, 1986; also see Table 1).

A more serious concern is the fact that the applicability of these thresholds to estuarine environments where the suite of PAHs present differs substantially from those typically present at industrialized urban sites (e.g. sites with a preponderance of lower molecular weight petrogenic PAHs) is not known. One way in which this question could be explored would be to express sediment PAH concentrations in terms of BaP equivalents, giving heavier weight to the high molecular weight, carcinogenic and mutagenic PAHs that are thought to be primarily responsible for the development of liver disease in English sole (Myers *et al.*, 1998). However, the extent to which high and low molecular weight PAHs contribute to other biological effects, such as reduced growth and reproductive dysfunction, is less clear, so for these endpoints, such an analysis may be less appropriate. Additional analyses with a variety of data sets would be needed to better establish the applicability of these threshold estimates in other estuarine environments.

The co-occurrence of other contaminants along with PAHs at sites where English sole were collected is not incorporated into the analysis. While the correlations between PAH exposure and the endpoints we measured in this study are statistically valid and well-supported by other scientific evidence, sediments at the sites included in the analysis contain a variety of other compounds (e.g. PCBs, chlorinated pesticides, and heavy metals; see Malins *et al.* (1982); Brown *et al.* (1998); Coller *et al.* (1998); Meador *et al.* (1994) for more detailed information) that are promotors of carcinogenesis, or reproductive toxicants. These compounds could act either additively or synergistically with PAHs to produce the observed health impacts. Their presence could alter disease prevalence, and they are likely an important factor contributing to variability in response among fish populations at different sampling sites. Incorporating the effects of co-occurring chemicals into PAH threshold estimates is beyond the scope of the present analysis. However, the potential of interactive effects among co-occurring compounds is an area that warrants additional research because it does introduce uncertainty in the sediment threshold values.

The present analysis establishes PAH sediment thresholds for protection of a single species, English sole. Their application to other estuarine fish is not known. Species differences in sensitivity to the effects of PAHs are well-documented (Collier *et al.*, 1992, 1993; Johnson *et al.*, 1992, 1998a; Anulacion *et al.*, 1998; Myers *et al.*, 1998a), so variation in PAH effects thresholds would be expected. However, previous research with English sole suggests it is relatively sensitive to PAH-associated injury (Collier *et al.*, 1992; Anulacion

et al., 1998; Johnson *et al.*, 1998b; Myers *et al.*, 1998a), so sediment thresholds developed for this species may be protective of other fish as well. We have conducted limited preliminary analyses with other bottomfish species, which suggest that sediment PAH thresholds for some categories of non-neoplastic proliferative and degenerative lesions are similar to those for English sole (Lomax *et al.*, 1994). For example, sediment PAH threshold concentrations associated with the development of hydropic vacuolation were determined for winter flounder collected as part of the NBSP on the east coast of the United States (Johnson *et al.*, 1992, 1994). Hydropic vacuolation is a toxicopathic liver lesion that does not occur in English sole, but is commonly associated with PAH exposure in other species, including winter flounder, starry flounder, white croaker, and rock sole (Moore and Myers, 1994; Stehr *et al.*, 1998; Myers *et al.*, 1998a). The threshold for this lesion, estimated according to Horness *et al.* (1998), was 298 ppb total PAH (Figure 6), well within the range of values observed for liver lesions in English sole. While these results suggest that a variety of bottomfish species may exhibit adverse health effects at PAH concentrations similar to those that affect English sole, a more thorough investigation of species differences in PAH sensitivity is needed.

The applicability of the standards developed for English sole to pelagic species, including anadromous salmonids, is more difficult to assess. Because these species often spend less time in contaminated estuarine sites, have less contact with sediments, and do not rely as heavily on benthic invertebrates as prey items, their exposure may be considerably less in comparison to bottomfish at sites of comparable sediment PAH concentration. Levels of DNA adducts in liver of juvenile salmonids collected from the Hylebos Waterway, for example, were approximately 10 nmol per mol DNA bases, while adduct levels in English sole from this waterway ranged from 30 to over 100 nmol per mol DNA bases (Collier *et al.*, 1998). As yet we do not have sufficient data to estimate threshold sediment PAH concentrations associated with reduced growth or suppressed immune function in juvenile salmonids. However, we can say that these effects have been observed in fish collected from sites with sediment total PAH levels in the 5000–10000 ppb range (Arkoosh *et al.*, 1998; Casillas *et al.*, 1995, 1998). Similarly, Heinz *et al.* (1999) report increased mortality in pink salmon embryos exposed to oiled gravel with total PAH concentrations in the 3800–4600 ppb range. Consequently, an effect threshold is likely at or below this level. This raises some concern about whether some current sediment quality criteria for PAHs, which allow total PAH concentrations in the 20000 ppb range or above (WAC, 1995; USACE, 1998) are adequately protective of listed salmonids.

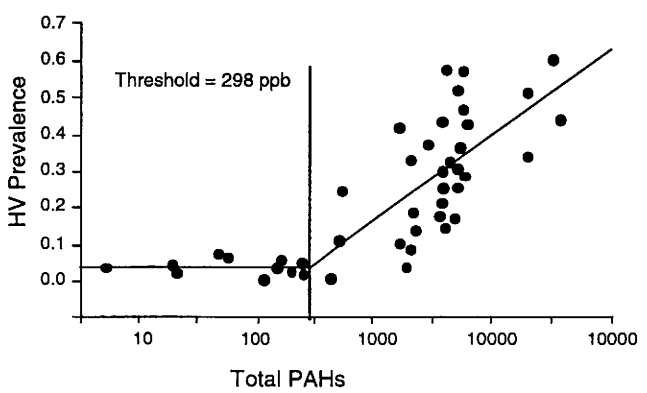

Figure 6. Hockey-stick regression of hydropic vacuolation (HV) prevalence in winter flounder versus total polycyclic aromatic hydrocarbons (TPAHs) in bottom sediment in ng/g dry wt. (ppb). Data were collected as part of NOAA's National Benthic Surveillance Program for the Northeast Coast of the United States (Johnson *et al.*, 1992, 1993; Harmon *et al.*, 1998). Threshold concentration is indicated by vertical line. Adapted from Lomax *et al.* (1994).

SEDIMENT QUALITY THRESHOLD GUIDANCE

In order to assess the likely degree of injury experienced by English sole exposed to sediments with different sediment PAH concentrations, expected prevalences of liver lesions and reproductive abnormalities were calculated using the regression equations from Table 2 for total PAH concentrations ranging from 50–100 000 ppb (ng dry wt.$^{-1}$). As illustrated in Table 3, liver lesion prevalences, as well as levels of other detrimental effects in English sole, were generally close to levels characteristic of fish from uncontaminated sites at sediment PAH concentrations below 1000 ppb. This concentration approximates the upper confidence levels of the thresholds for DNA damage and the occurrence of one or more hepatic lesions, and is close to the estimated threshold of 630 ppb for several reproductive effects. Above 1000 ppb, increases are observed in several categories of liver lesions, and reductions are observed in spawning ability and egg quality. On this weight of evidence basis, the sediment PAH threshold below which no significant carcinogenic or adverse reproductive effects in English sole are observed is estimated to be 1000 ppb (ng g^{-1} dry wt.), With sediment PAH concentrations at or below this level, sole should exhibit only minimal liver injury, and little or no disruption of growth or reproductive function, and relatively low levels of DNA

Table 3. Estimated effect levels associated with increasing sediment PAH concentration for selected liver lesions and indicators of reproductive function in English sole.

PAH (ppb dry wt.)	Neoplasm prevalence	FCA prevalence	SDN prevalence	Proliferative lesion prevalence	Any lesion prevalence
Liver lesions					
50	0.00	0.01	0.00	0.02	0.00
100	0.00	0.02	0.00	0.02	0.00
1000	**0.00**	**0.06**	**0.01**	**0.08**	**0.09**
2000	0.00	0.07	0.12	0.11	0.18
3000	0.01	0.08	0.20	0.13	0.24
5000	0.03	0.09	0.27	0.14	0.31
10000	0.06	0.10	0.38	0.17	0.40
100000	0.16	0.14	0.75	0.26	0.71
Reproductive indicators					
PAH (ppb dry wt.)	Inhibited gonadal development prevalence	Inhibited spawning prevalence	Infertile proportion eggs of eggs spawned		DNA Damage (nmol adducts per mol nucleotides)
50	0.15	0.12	0.38		5
100	0.15	0.12	0.38		5
1000	**0.15**	**0.17**	**0.42**		**25**
2000	0.15	0.25	0.48		36
3000	0.15	0.30	0.51		43
5000	0.18	0.35	0.55		51
10 000	0.27	0.43	0.61		63
100 000	0.58	0.69	0.80		100

For all liver lesions, inhibited gonadal development, and inhibited spawning, the effect level is the proportion of fish estimated to be affected at the indicated sediment PAH concentration; for infertile eggs, the effect level is the proportion of eggs produced by an individual female that are estimated to be unfertile. Effect levels for liver lesions were calculated with hockey-stick regression. For reproductive indicators, effect levels at the sampling sites where PAH concentrations were lowest were used to estimate background effect levels (i.e. effect levels at PAH concentrations below 5000 ppb for inhibited gonadal development, and below 1000 ppb for inhibited spawning and infertile eggs).

adducts. While this threshold is well below current sediment quality criteria for PAHs as set by the Washington State Department of Ecology (7400 ng g^{-1} for low molecular weight AHs, and 19 200 ng g^{-1} for high molecular weight AHs (WAC, 1995), assuming a sediment TOC content of 2%, a fairly typical value for Puget Sound sediment (Michelsen and Bragdon-Cook, 1993)), it is not overly conservative. Based on threshold values calculated for non-neoplastic liver lesions and DNA damage in English sole, a lower value could be justified. Moreover, the 1000 ng g^{-1} dry wt. guideline does not incorporate a safety factor, as risk analyses often do, to account for uncertainty in this threshold estimate due to factors such as variations in sensitivity of fish species, or PAH analytes measures, or in ratios of low to high molecular weight PAHs in sediments. We recommend the 1000 ppb threshold as a practical value for making management decisions, as it would be protective of estuarine fish populations, but not unworkable from the perspective of sediment remediation and management.

Above the threshold effects concentration of 1000 ppb, the proportion of animals affected and the number of adverse effects observed increases. The degree of increase is modeled by the upper arm of the hockey stick regression, which can be used to estimate the likely degree of injury at various sediment PAH concentrations (Table 3). At 5000 ppb, for example, levels of hepatic DNA adducts would be approximately 10-fold the levels found in fish from uncontaminated reference sites, about 30% of the population is predicted to have some form of liver disease, and the number of fish failing to spawn would increase from about 12% to over 35%. At PAH concentrations of 10 000 ppb, DNA adducts levels would have increased 12–13-fold, 50% of the sole would be expected to have liver disease, nearly 30% of the females would show inhibition of gonadal growth, and over 40% would show inhibition of spawning. This type of information, in combination with data on contaminant effects on other indigenous species, could be used to estimate the loss of productivity or ecosystem services due to PAH contamination at impacted sites.

CONCLUSIONS

Based on the analyses above, we determined threshold sediment PAH concentrations for toxicopathic liver lesions in English sole ranging from 54 to 2800 ng g^{-1} dry wt, and a threshold for DNA adducts in liver of 300 ng g^{-1} dry wt. Although we do not have sufficient data to statistically determine precise thresholds for other types of injury to English sole, available data indicate that several other types of impairment, including inhibited gonadal growth, inhibited spawning, reduced egg viability, and reduced growth, begin to occur at sediment PAH concentrations in a similar range. Based on these data, a sediment quality guideline of 1000 ppb total PAH (ng g^{-1} dry wt.) is suggested to protect estuarine fish against several important health effects, including selected degenerative liver lesions, spawning inhibition, and reduced egg viability. With sediment PAH concentrations at or below 1000 ppb, liver lesion prevalences, DNA adduct levels, and growth and reproductive indicators are generally similar to levels observed in English sole from reference sites with minimal sediment PAH contamination, and English sole exhibit little or no toxicopathic injury. Above 1000 ppb, there appears to be a substantial increase in the risk of liver disease and reproductive impairment, as well as potential effects on growth. As sediment PAH concentrations increase, the proportion of animals affected and the number of adverse effects observed steadily increases. These relationships can be used to help assess the likely degree of injury to marine resources at various sediment PAH concentrations.

Unfortunately, achieving PAH thresholds in estuarine sediments in the United States would be a substantial task, as sediment contamination at this level is widespread. For example, in a recent EPA report on contaminated sediments in the Untied States, sediments from nearly 6000 stations throughout the country were examined for PAHs, and of these 36% were within the range where adverse effects were considered probable or possible, with concentrations exceeding the 1000 ppb recommended threshold (USEPA, 1997). Moreover, active sources of PAH input, such as urban runoff and atmospheric deposition,

continue to contribute to environmental releases. However, our data suggest that failure to achieve such standards will result in impaired productivity of our fish stocks, which, in combination with other stressors, such as overharvest and habitat destruction, could put additional species in danger of extinction.

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Hazard Assessment

Short Communication

FOUR INDEPENDENT APPROACHES TO DEVELOPING SEDIMENT QUALITY CRITERIA YIELD SIMILAR VALUES FOR MODEL CONTAMINANTS

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Abstract—Separate approaches to determining marine sediment quality criteria yielded similar values for three contaminants. These values, including concentrations at or below which biological effects have been shown to be minimal and lowest concentrations at which biological effects have been shown to occur, range from (dry weight sediment): lead, 50 to 300 μg/g (ppm); polyaromatic hydrocarbons, 2.0 to 12.0 μg/g; polychlorinated biphenyls, 0.06 to 0.13 μg/g.

Keywords—Sediment quality criteria Lead Polyaromatic hydrocarbons Polychlorinated biphenyls

INTRODUCTION

At the Seventh Annual Meeting of the Society of Environmental Toxicology and Chemistry (November, 1986), a platform session was organized by C. Cowan (Battelle) entitled "Sediment Quality Criteria Development in Support of Environmental Protection." During the course of this session we each presented information on our respective approaches to developing sediment quality criteria. Each of these approaches, although pursued independently, involved relating bulk sediment chemistry to biological effects (field and/or laboratory). After the presentations, we realized that these values were surprisingly similar. These similarities are noteworthy and are reported herein.

METHODS

The sediment quality triad [1] provides a broad-scale approach to developing sediment quality criteria. The triad is based on the assumption that the biological responses observed in sediment bioassays and in situ studies are a function of the concentration of certain chemicals sorbed to the study-area sediment. The triad values were based on bulk sediment chemistry, sediment bioassay, and bottomfish abnormality data for Puget Sound (Washington State).

The Screening Level Concentration (SLC) approach [2] estimates the highest concentration of a particular sediment contaminant that can be tolerated by approximately 95% of benthic infaunal species. Calculations are based on a graphic plot and cumulative frequency distribution of species presence versus concentration of particular chemical contaminants. The SLC values are based on synoptic bulk sediment chemistry and benthic infaunal community data for parts of Puget Sound, and the New York and Southern California Bights.

The Apparent Effects Threshold (AET) approach (R. Barrick, H. Beller, T. Ginn and S. Becker. Apparent effects thresholds (AET): Evaluation as a tool for sediment quality management, in preparation) identifies concentrations of con-

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taminants that are associated exclusively with sediments that exhibit statistically significant biological effects (relative to reference conditions). The AET values were based on synoptic bulk sediment chemistry, sediment bioassay, and benthic infaunal community data for Puget Sound, and used different data sets than the triad.

Laboratory sediment bioassay tests were conducted with the phoxocephalid amphipod, *Rhepoxynius abronius*, to determine the toxicity of creosote-contaminated sediment from Eagle Harbor, Washington State [3]. Test sediment was mixed with reference sediment from Yaquina Bay, Oregon, and the 10-d LC50 of Eagle Harbor sediment was calculated by probit analysis to be 660 μg/g, wet weight. Thirteen polyaromatic hydrocarbons (PAHs) were analyzed in the sediment mixtures and the concentration at the 10-d LC50 was calculated by interpolation. A no-effect concentration for acute toxicity of total PAH was estimated as the 10-d LC01, from probit analysis.

RESULTS AND DISCUSSION

A number of studies are currently underway that attempt to develop sediment quality criteria. Four of these approaches, the triad, SLC, AET, and laboratory studies, are based on laboratory and/or field biological effects data.

Comparative values are presented in Table 1 for three model contaminants using the above four approaches, and are compared to concentrations of these contaminants shown to be toxic by Chapman et al. [4] in San Francisco Bay. The data from San Francisco Bay are not included in calculations of the other values, and hence represent a comparison between predicted and actual values. Biological effects represented by Table 1 values encompass a wide range of endpoints, including liver tumors in bottomfish; lethal, sublethal, and genotoxic laboratory bioassay responses; and significant changes in benthic infaunal community composition.

The partitioning of sediment contaminants into dissolved and particulate-bound fractions complicates development of sediment quality criteria. However, the similarities reported herein suggest that we may be able, within a reasonably tight range (e.g., less than an order of magnitude), to converge on appropriate sediment quality criteria which can be widely applied and which are supported by the burden of available biological effects data. We plan further independent and cooperative studies to determine the ultimate applicability of these approaches and values, including the relative significance of different sediment characteristics, biological responses, and methods of calculating the criteria.

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Table 1. Comparison of values obtained for three contaminants by four separate approaches to developing sediment quality criteria, and bioeffects data from San Francisco Bay

Chemical contaminants	No or minimal biological effects at or below these values[a]			Significant biological effects at or above these values[a]	Significant biological effects determined in San Francisco Bay at these minimum values[a]
	Triad	SLC[b]	Laboratory studies	AET	
Pb	50	—[c]	—	300	130
PAH[d]	3.8	7.6	2.0	5.2; 12.0	9.5
PCBs[e]	0.1	0.06	—	0.13	0.16

[a]All concentrations expressed as μg/g dry weight of sediment.
[b]Dry weight concentrations calculated from organic carbon normalized values assuming 2% organic carbon content.
[c]No data.
[d]Polyaromatic hydrocarbons. Triad = nine 4–6-ring PAHs; SLC = estimate for ten 4–6-ring PAHs; laboratory studies = thirteen 1–6-ring PAHs; AET = first value is for six 2–3-ring PAHs, second value is for ten 4–6-ring PAHs. San Francisco Bay = eighteen 1–6-ring PAHs.
[e]Total polychlorinated biphenyls.