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BOTTOM SEDIMENTS COLLECTED FROM THE
UPPER ATZ BASCA
RIVER, SEPTEMBER, 1993

E.C. Brownlee and R.W. Crossley

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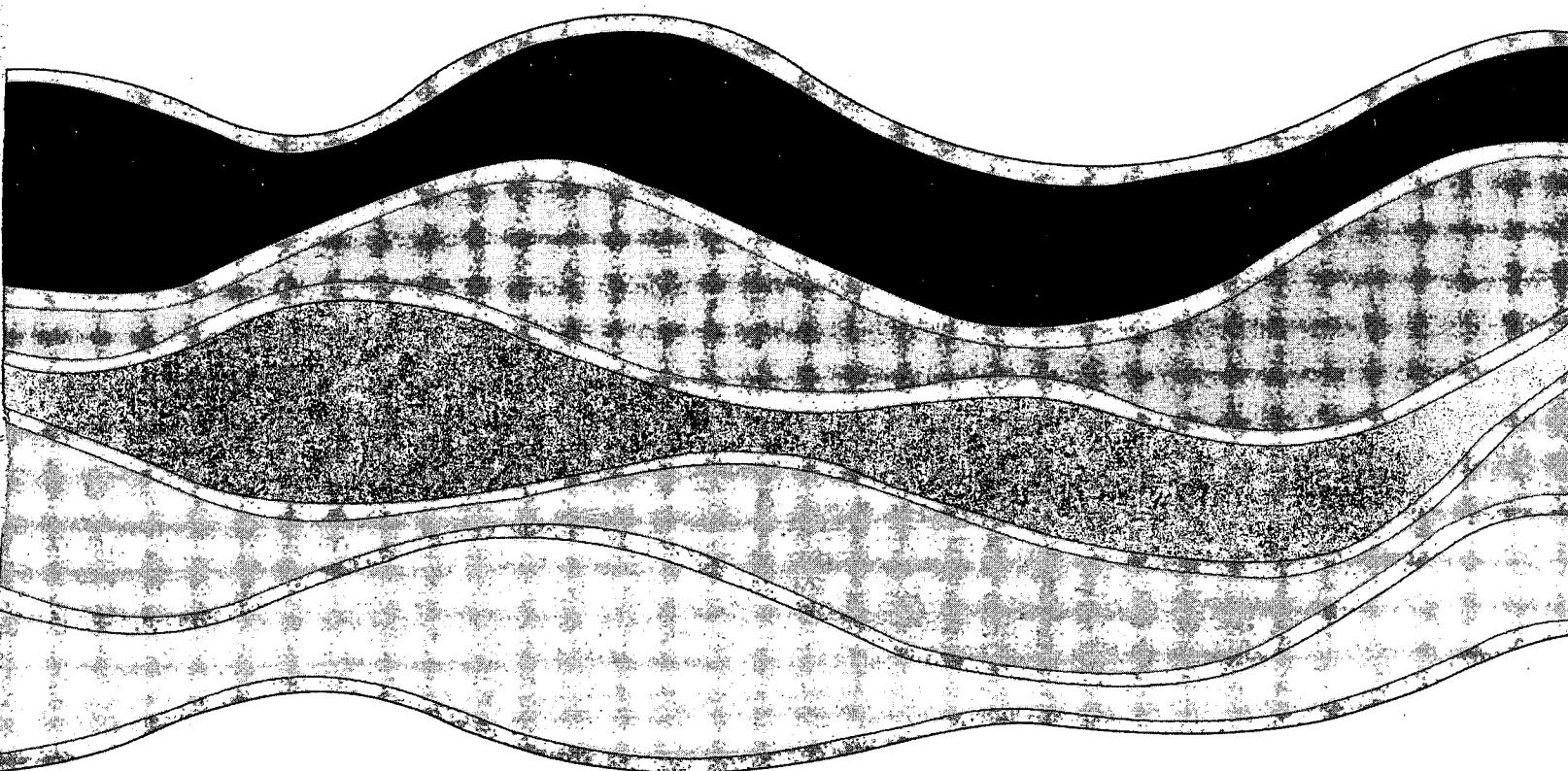
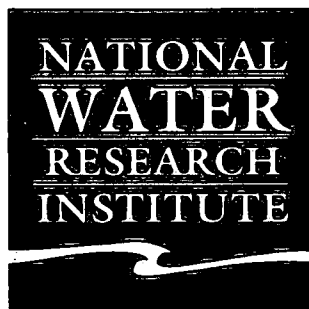
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**POLYCYCLIC AROMATIC HYDROCARBON
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BOTTOM SEDIMENTS COLLECTED FROM THE
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Polycyclic Aromatic Hydrocarbon Analysis of a Set of Bottom Sediments Collected
from the Upper Athabasca River, September, 1993

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Aquatic Ecosystem Protection Branch Technical Note

AEPB-TN-96-02

Management Perspective

As part of a Northern River Basins Study project on sediment toxicity, in September of 1993 a set of bottom sediments was collected from the upper Athabasca River from upstream from the bleached kraft mill at Hinton to approximately 200 km downstream. Contaminant analysis of these sediments was carried out as part of a triad approach to examine the toxicity of these sediments. This Technical Note presents the results of analysis of these sediments for polycyclic aromatic hydrocarbons.

Introduction

In September of 1993, bottom sediments were collected from seven sites on the upper Athabasca River from upstream from Hinton to Windfall, a distance of about 200 km (Figure 1). This was part of a project using the "triad" approach to examine the toxicity of bottom sediments from the river: (1) laboratory toxicity testing, (2) benthic community analysis, and (3) contaminant analysis.

This report contains the results of polycyclic aromatic hydrocarbon (PAH) analysis of these sediments. Other contaminant analyses (polychlorinated dioxins/furans, polychlorinated biphenyls, chlorinated phenolics, resin acids, organochlorine pesticides, toxaphene, and metals) were done by commercial laboratories and these results can be found in Northern River Basins Study (NRBS) data reports. Toxicity and benthic community analysis results can be found in NRBS reports (Day and Reynoldson 1995, Saffran 1995).

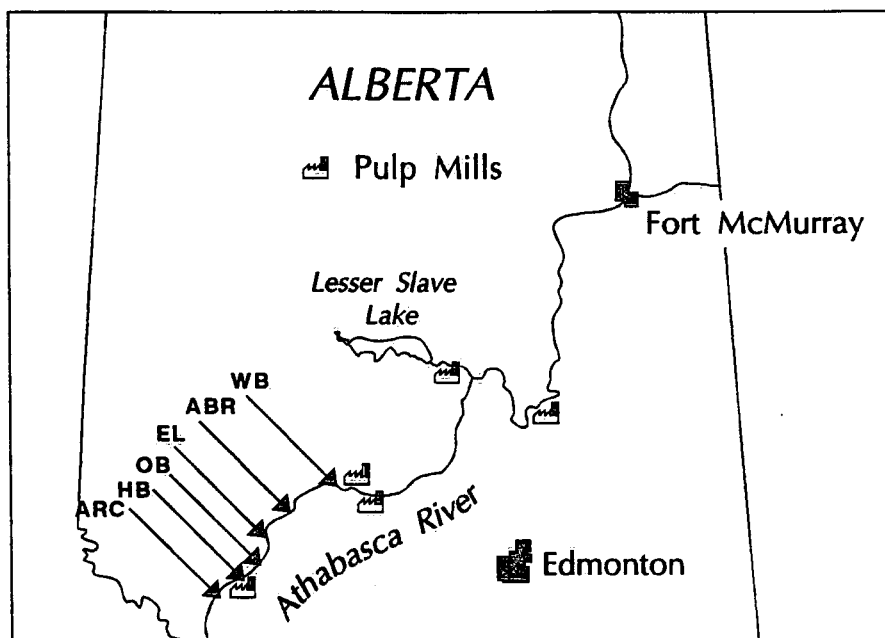


Figure 1. Location of sampling sites and pulp mills along the Athabasca River.

Sample Set

<u>Site No.</u>	<u>Date</u>	<u>Site Location (see Figure 1 above)</u>
ARC	Sep 15/93	200 m above Maskuta Creek along right side of AR
ARC2	Sep 15/93	just downstream of ARC site
HB	Sep 15/93	ca. 1 km below Weldwood Haul Bridge near right bank
OB	Sep 16/93	ca. 1 km below Obed bridge along right side
EL	Sep 16/93	ca. 2 km below bridge at Emerson Lake along left side
ABR	Sep 17/93	u/s Berland River about 1.5 km above bridge
WB	Sep 17/93	ca. 2 km below Windfall bridge along right side

Samples were frozen and shipped to NWRI, Burlington for processing.

Methods

SAMPLE PREPARATION

The samples were processed at the NWRI Sedimentology Laboratory (J. Dalton). Three replicates from each site were freeze-dried, combined and homogenized. At this point, subsamples were taken for particle size and carbon (organic and total) analysis (Gauthier 1994).

SEDIMENT PROPERTIES

<u>Sample</u>	<u>% Organic C</u>	<u>% Sand</u>	<u>% Silt</u>	<u>% Clay</u>
ARC	0.43	10.5	74.9	14.6
ARC2	0.32	34.7	51.8	13.5
HB	0.49	25.1	59.1	15.8
OB	1.05	29.1	53.7	17.2
EL	0.54	21.2	58.4	20.4
ABR	0.48	36.0	44.7	19.3
WB	0.87	0.0	67.4	32.6

SOLVENT EXTRACTION OF SEDIMENTS

A 1 cm layer of combusted (450°C) sodium sulfate was placed in a glass Soxhlet extraction thimble. Sediment sample (10.0 g) was added to the top of the sodium sulfate layer. Diphenyl-d10 (0.100 mL of 1.00 µg/mL in toluene) was added to the top of the sediment. The blank consisted of sodium sulfate without sample. The thimble was placed in a Soxhlet apparatus charged with 350 mL of glass-distilled dichloromethane (DCM). The sediment sample was extracted for 16 h at a rate of 5-6 cycles per hour. The DCM extracts were reduced to 5-10 mL on a rotary evaporator, transferred with a 1 mL DCM rinse to a 15 mL centrifuge tube, reduced to 1-2 mL under a stream of ultra high purity argon, isooctane (2 mL) was added and the volume reduced to ca. 1 mL under argon.

EXTRACT CLEANUP

A glass wool plug was placed in the bottom of a 1.1 x 25 cm glass column with stopcock. A 1 cm layer of combusted sodium sulfate was placed on top of this. Silica gel (5 g of Supelco LC-SI silica gel, 40 µm particle size, activated for 8 h at 140°C) was slurry-packed into the column and topped with a 1 cm layer of combusted sodium sulfate. Pentane (25 mL) was passed through the column and the extract (in 1 mL isooctane) was loaded onto the column using 2 x 1 mL pentane rinses. Three fractions were collected: 15 mL pentane (fraction 1), 15 mL pentane-DCM (50:50 v/v, fraction 2), and 15 mL DCM (fraction 3). PAHs and alkyl-PAHs elute in fraction 2, with trace amounts of light PAHs in fraction 1 and heavier PAHs in fraction 3.

Fraction 2 samples were reduced to 1-2 mL under an argon stream, dibenzofuran-d8 internal standard (0.20 mL of 500 ng/mL in toluene) was added and the volume reduced to 0.2 mL under an argon stream in a micro Kuderna-Danish evaporator.

The samples were analyzed by gas chromatography-mass spectrometry (GC-MS) in selected ion monitoring mode (SIM).

GC-MS ANALYSIS

Gas chromatographic conditions: Hewlett-Packard model 5890 chromatograph, 30 m x 0.25 mm DB-5 capillary column, 0.25 μ m film thickness, programmed from 80-245°C at 3°C/min. then from 245-280°C at 4°C/min. with a ten minute hold, constant flow programming mode, splitless injection, 1 μ L sample size. Mass spectrometric conditions: Hewlett-Packard model 5971 mass spectrometer operating in electron impact mode at 70 eV. Data acquisition: Chemstation software, one target and one qualifier ion per window (listed below). The target compound list consisted of the standard list of 16 "EPA" PAHs; nine alkylated naphthalenes, phenanthrenes and anthracenes for which we have standards; four additional PAHs (dibenzothiophene, retene, benzo[e]pyrene and perylene); diphenyl-d10 recovery standard; and dibenzofuran-d8 internal standard. A tenth alkylated PAH (1,5-dimethylnaphthalene) was included in the standards but could not be quantitated because of a strong, interfering peak about 0.06 min. earlier in retention time. Five levels of calibration standards were run (20, 50, 100, 200 and 500 ng/mL). Results were calculated using the Chemstation software. Qualifier ion ratio limits were set at \pm 20% relative.

Results and Discussion

The results are summarized in Table 2.

QUALITY ASSURANCE

Traces (< 1 ng/g) of three compounds, naphthalene, phenanthrene and fluoranthene were detected in the blank. This was < 1% of concentrations of naphthalene and phenanthrene and < 10% of concentrations of fluoranthene measured in the samples. Recoveries for diphenyl-d10 ranged from 58-107% and averaged 82%. In a number of cases, qualifier ion ratios were not satisfied, generally at lower concentrations. The calibration standards covered the concentration range from about 0.5 to 10 ng/g. As can be seen in Table 2, many of the results exceed this by 10-100 times so the response factors used are extrapolated from lower concentrations. In most cases where higher concentrations were encountered the calibration curves were linear and so this should only result in a relatively small error in the results. Detection/quantification limits were not established, but at a level equivalent to 1.0 ng/g, a standard gave the expected values within \pm 20% and qualifier ion ratios were met for most analytes. The detection limit for dibenzo[a,h]anthracene is higher because the target ion used does not give maximum sensitivity.

Table 1. Compound list and the target and qualifier ions monitored in SIM.

Compound	Target Ion m/z	Qualifier Ion m/z
Naphthalene	128	102
Naphthalene, 2-methyl	142	115
Naphthalene, 1-methyl	142	115
Naphthalene, 2,7-dimethyl	156	141
Naphthalene, 1,3-dimethyl	156	141
Acenaphthylene	152	151
Naphthalene, 1,8-dimethyl	156	141
Acenaphthene	154	153
Naphthalene, 2,3,5-trimethyl	170	155
Fluorene	166	165
Dibenzothiophene	184	139
Phenanthrene	178	176
Anthracene	178	176
Anthracene, 2-methyl	192	191
Phenanthrene, 1-methyl	192	191
Anthracene, 9-methyl	192	191
Fluoranthene	202	200
Pyrene	202	200
Retene	219	234
Benzo[a]anthracene	228	226
Chrysene+Triphenylene	228	226
Benzo[b]fluoranthene	252	126
Benzo[k]fluoranthene	252	126
Benzo[e]pyrene	252	126
Benzo[a]pyrene	252	126
Perylene	252	126
Indeno[1,2,3-cd]pyrene	276	138
Dibenzo[a,h]anthracene	276	138
Benzo[ghi]perylene	276	138
Diphenyl-d10 (Recovery Std)	164	162
Dibenzofuran-d8 (Internal Std)	176	NA

REPORTING

Results in Table 2 are given to one decimal place (0.1 ng/g) for concentrations of < 10 ng/g. Higher concentrations are reported to two significant figures.

Three sums are given in Table 2. Low molecular weight PAHs include naphthalene, acenaphthylene, acenaphthene and fluorene. High molecular weight PAHs include phenanthrene/anthracene and higher, but do not include dibenzothiophene, retene or perylene. Alkyl PAHs are alkyl naphthalenes, phenanthrenes and anthracenes.

SUMMARY

There are no obvious upstream/downstream or intersite patterns to the results for individual compounds or for the sum parameters of low mol wt PAHs, high mol wt PAHs or alkyl PAHs. Concentrations were not elevated downstream from the pulp mill between sites ARC and HB. Highest concentrations were found in sediments from OB, the site with the highest TOC, and site WB, the site with the highest percent clay.

References

- Day, K. and T.B. Reynoldson. 1995. Ecotoxicology of depositional sediments Athabasca River May and September, 1993. Northern River Basins Study Project Report No. 59. Northern River Basins Study, Edmonton, AB.
- Gauthier, M. (1994). Northern Rivers Basin September 1993 Bottom Sediments. NWRI Technical Note No. AER-TN-94-18.
- Saffran, K. 1995. Aquatic macroinvertebrate identifications Athabasca River May and September, 1993. Northern River Basins Study Project Report No. 59. Northern River Basins Study, Edmonton, AB.

Table 2. Concentration of PAHs, recoveries, and sum of low and high mol wt PAHs and alkyl PAHs.

Compound	Blank	PAH Concentration (ng/g)						
		ARC	ARC2	HB	OB	EL	ABR	WB
Naphthalene	0.7 #	140	170	71	300	73	100	270
Naphthalene, 2-methyl		250	320	120	630	130	210	550
Naphthalene, 1-methyl		130	160	67	320	75	110	310
Naphthalene, 2,7-dimethyl		200	250	110	570	140	170	460
Naphthalene, 1,3-dimethyl		340	440	180	920	240	270	880
Acenaphthylene		0.4 #	0.4 #	0.4 #	0.6 #	0.3	0.3 #	0.4 #
Naphthalene, 1,8-dimethyl		2.7 #	4.3 #	0.7 #	6.5 #	2.1 #	2.6 #	6.5
Acenaphthene		14	21	10	31	11	11	32
Naphthalene, 2,3,5-trimethyl		180	520	140	370	170	170	160 #
Fluorene		140	310	160	360	200	130	570
Dibenzothiophene		75	160	72	180	120	71	250
Phenanthrene	0.3 #	320	760	340	890	510	350	1200
Anthracene		12	12	16	11	23	9.8	5.2
Anthracene, 2-methyl		1.6	0.8 #	2.4 #	1.1 #	3.3	1.1 #	0.7 #
Phenanthrene, 1-methyl		1.1 #		1.2 #	37 #		19 #	38 #
Anthracene, 9-methyl				0.2		0.3 #		0.2 #
Fluoranthene	0.3 #	5.0	7.7	11	19	8.4	12	13
Pyrene		10	15	11	22	14	13	20
Retene		35	26	22	220	38	52	45
Benzo[a]anthracene		0.5 #	0.4 #	2.1	2.6 #	1.2 #	3.7	1.7
Chrysene+Triphenylene		16 #	21	27 #	47 #	27 #	24	30
Benzo[b]fluoranthene		8.2	11	11	18	11	14	13
Benzo[k]fluoranthene				0.4 #	0.2 #	0.1 #		0.3 #
Benzo[e]pyrene		7.8	10	10	17	10	12	12
Benzo[a]pyrene		0.6 #	0.8 #	2.3 #	2.6 #	1.3	1.7 #	2.2 #
Perylene		23	22	25	46	30	32	39
Indeno[1,2,3-cd]pyrene		0.6 #	0.8 #	1.8 #	1.9 #	1.3 #	1.3 #	2.5 #
Dibenzo[a,h]anthracene			2.3 #	2.3 #	3.6 #	3.2 #	3.1 #	4.0 #
Benzo[ghi]perylene		2.8	3.4	4.6	6.8	4.8	4.8	7.9
Diphenyl-d10 (Recovery %)	94	76	77	58	107	65	81	94
Low mol wt PAH	0.7	290	510	240	700	280	240	870
High mol wt PAH	0.6	380	850	440	1000	620	450	1300
Alkyl PAH	0.0	1100	1700	620	2900	770	960	2400

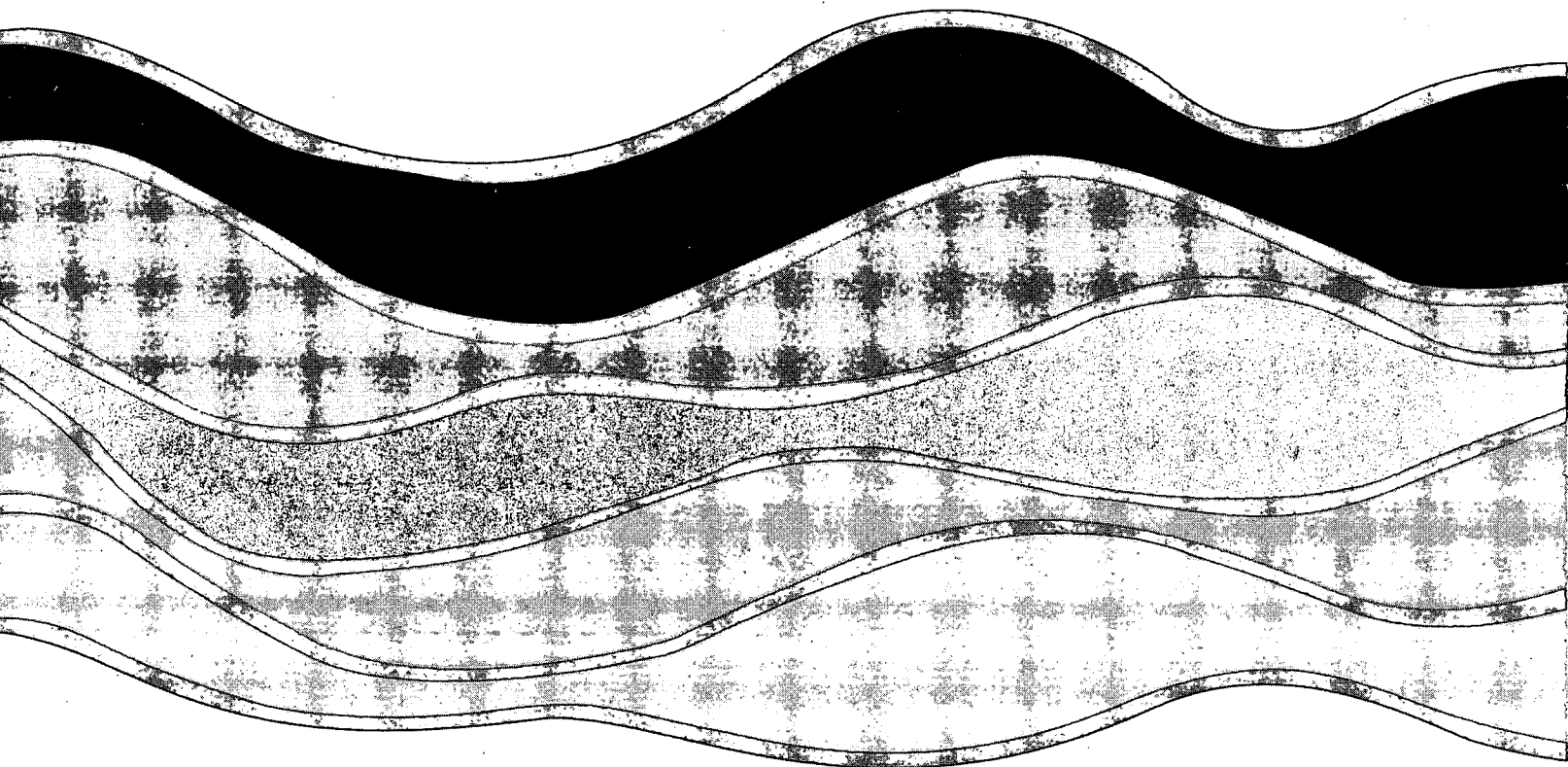
Qualifier ion ratios not satisfied.

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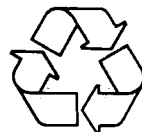
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