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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] / 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
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

Compound	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	
	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)

Compound	C No.	28S	34S	105S	128S	141S[b]	209S dup 1	209S dup 2	211S dup 1	211S dup 2
	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	
		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.

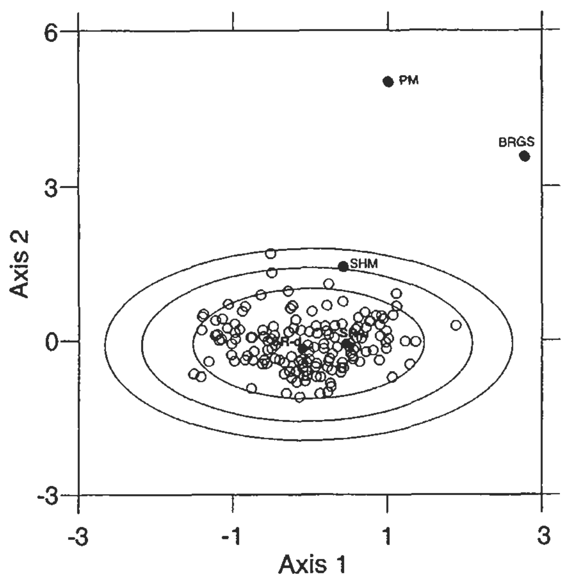

Fig. 1. Assessment of sediment toxicity by ordination of six bioassay endpoints (BRGS = Battle River generating station; PM = Prince Mine; SR-U and -D = Souris River upstream and downstream; SHM = Salmon Harbour Mine).

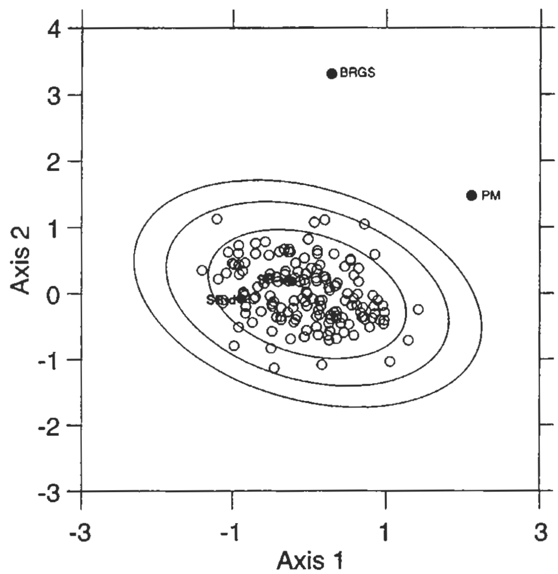

Fig. 2. Assessment of sediment toxicity by ordination of 10 bioassay endpoints (BRGS = Battle River generating station; PM = Prince Mine; SR-U and -D = Souris River upstream and downstream).

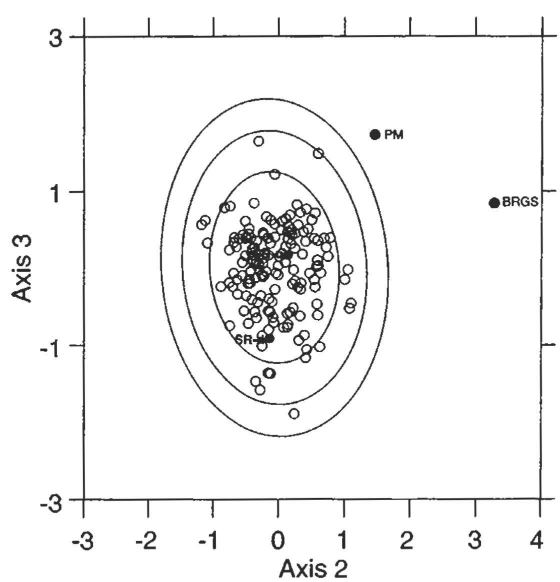

Fig. 3. Assessment of sediment toxicity by ordination of 10 bioassay endpoints (BRGS = Battle River generating station; PM = Prince Mine; SR-U and -D = Souris River upstream and downstream).

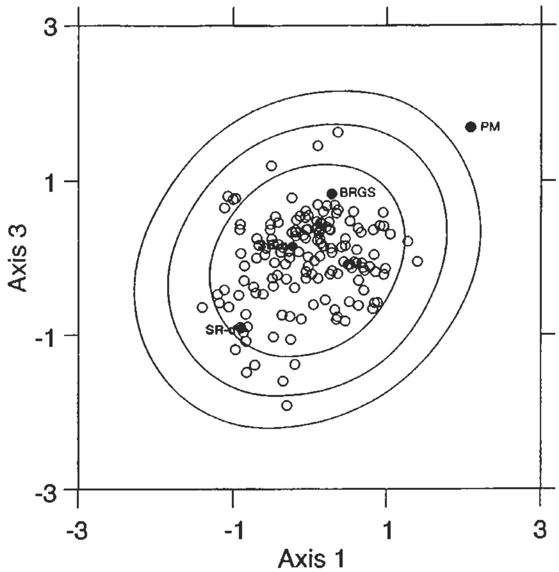

Fig. 4. Assessment of sediment toxicity by ordination of 10 bioassay endpoints (BRGS = Battle River generating station; PM = Prince Mine; SR-U and -D = Souris River upstream and downstream).

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- end-points toxicity results and the ordination technique, were found to be highly toxic.

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