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Polycyclic aromatic hydrocarbons in surficial sediments and caged mussels of the St. Marys River, 1985

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Abstract

During 1985, a biological monitoring study was conducted in the St. Marys River to determine the availability and source areas of polycyclic aromatic hydrocarbons (PAHs) and the relative importance of water and sediment to tissue contaminant concentrations. Clean unionid mussels (*Elliptio complanata*) were exposed in cages for three weeks at 14 stations and surficial sediments were obtained at 12 of these. The highest concentrations of total PAHs as well as many individual compounds were found in sediments and mussels from the Algoma Steel Slip above St. Marys Falls and in sediments below the discharge of the Edison Sault Electric Co. Canal. Although concentrations were lower below the Falls, elevated levels persisted downstream along the Ontario shore into Lake George. PAHs were also accumulated by mussels exposed along the Michigan shoreline, but at lower levels than along the Ontario shore. From 23 to 63 percent of the PAHs in sediments and 6 to 27 percent of those in mussels were comprised of compounds with mutagenic and/or carcinogenic properties. The predominance of higher molecular weight PAHs in both sediments and mussels as well as lower molecular weight PAHs and nitrogen- and sulfur-containing PAHs in certain areas, indicates that high temperature combustion of fossil fuels is the major source of PAHs, augmented by localized spills of fossil fuels and coke oven by-products.

Mussels contained fewer PAHs (up to 18 vs. 25) at lower concentrations ($\mu g\ kg^{-1}$ vs. $mg\ kg^{-1}$) than the associated surficial sediments. Also, mussels suspended at mid-depth in the water column accumulated similar concentrations to those exposed to sediments, indicating that the major exposure pathway is via the water filtered by these organisms, and hence, is due primarily to external industrial inputs.

1. Introduction

The St. Marys River, connecting Lake Superior with Lake Huron, is a large river supporting a diverse aquatic flora and fauna (Kauss, 1991). At the same time it provides drinking and process water for, and receives wastes from, a sizeable urban and industrial area centred at the twin cities of Sault Ste. Marie, Ontario and Michigan, in the upper part of the river (Fig. 1).

The major Sault Ste. Marie point source dischargers (and their 1985 average daily discharge rates) include the Michigan Publicly Owned Treatment Works ($\sim 11 \times 10^3\ m^3\ d^{-1}$). On the Ontario side of the river, sources include: the east end Water Pollution Control Plant ($50.3 \times 10^3\ m^3\ d^{-1}$); St. Marys Paper Inc. ($28.2 \times 10^3\ m^3\ d^{-1}$), a producer of groundwood specialties (e.g., coated newsprint) from stoneground hardwood and purchased Kraft pulp; and Algoma Steel

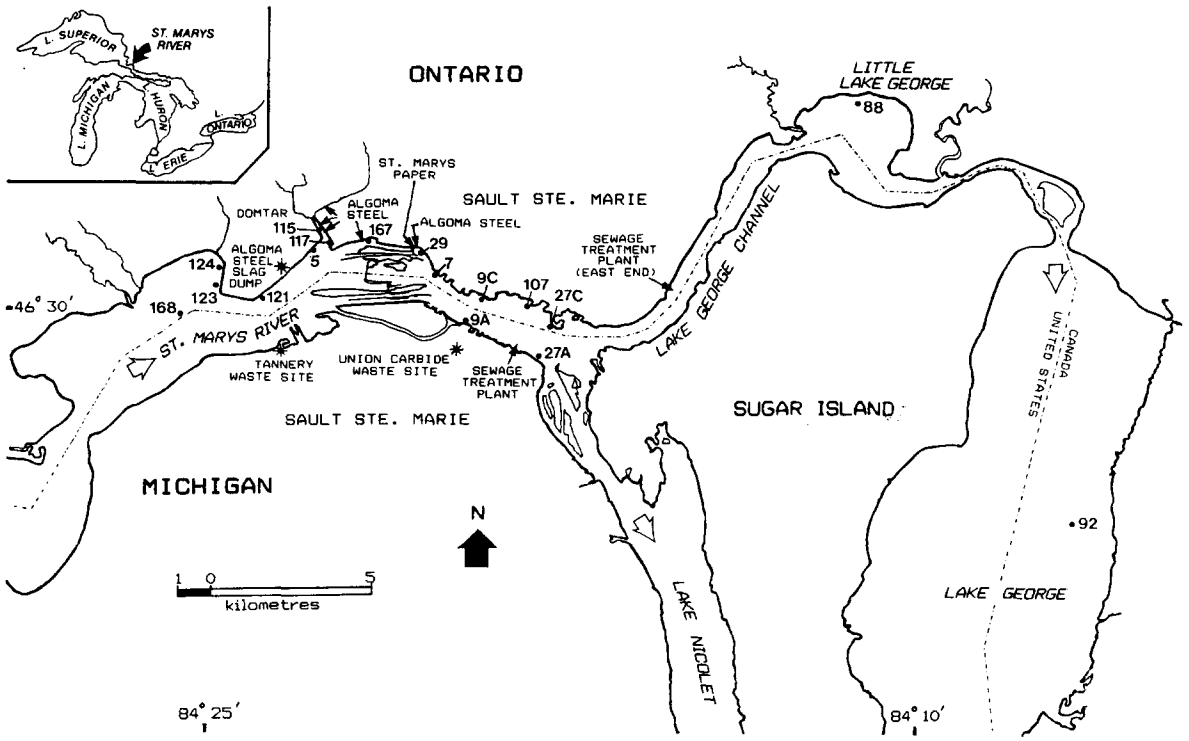

Fig. 1. 1985 St. Marys River biomonitoring and sediment sampling stations. Arrows indicate location of major industrial and municipal discharges.

Corp. Ltd. (506.3×10^3 m^3 d^{-1}), which manufactures iron and steel from iron concentrates/pellets, limestone and coke (the latter produced on-site from coal) (OME, 1986; 1987a). Cumulatively, the discharge from these facilities was about 0.3 percent of the average daily flow rate of the St. Marys River during 1985 ($21{,}440 \times 10^3$ m^3 d^{-1}).

Inputs of contaminants from the above sources and from storm sewers, combined sewer overflows, shipping traffic, and power generation have resulted in degraded water and sediment quality, mainly along the Ontario shoreline. This has led to classification of the St. Marys River as an 'Area of Concern' by the International Joint Commission (IJC, 1985), i.e. as an area where desirable water uses are restricted due to exceedences of Great Lakes Water Quality Agreement (IJC, 1978), and provincial (OME, 1984) objectives for such contaminants as ammonia, cyanide, phenols, iron, zinc, oil and grease, and bacteria.

On November 4, 1986, Algoma Steel was served with an Amending Control Order by the Ontario Ministry of the Environment requiring measures to ensure that emissions to air and water do not adversely affect the environment. Examples of such reductions and their effective dates are: decreases of daily loadings of phenols to 22.7 kg d^{-1} by 1989 and of oil and grease to 1023 kg d^{-1} by 1990. For comparison, 1985 average daily loadings of phenols and oil and grease were 102 kg d^{-1} and 1880 kg d^{-1}, respectively (OME, 1987a).

Monitoring of effluent, water, and sediment quality by the OME and other agencies during the recent binational Upper Great Lakes Connecting Channels Study of 1985/86 and the Municipal-Industrial Strategy for Abatement (MISA) pilot site study of Algoma Steel during 1986/87 focused on many of the above-listed contaminants in order to assess current impacts and temporal trends. Samples of potable water from the Sault

Ste. Marie, Ontario municipal water treatment plant contained the highest total polycyclic aromatic hydrocarbon (PAH) concentrations of any Ontario city tested in 1980 (Williams *et al.*, 1982). (The intake at that time was located in the power plant headrace downstream of some Algoma Steel discharges, but has since been moved to Gros Cap in Lake Superior.) Consequently, the above studies also emphasized determining the concentrations, distribution, and biological availability of PAHs in the river, as well as the magnitude of source inputs.

PAHs are a diverse and large group of hydrocarbons containing two or more fused benzene rings, with or without substituent groups. Parent and substituted PAHs are present in fossil fuels (coal, crude oil) and some petroleum products such as used crankcase oil. Consequently, they can reach the environment through spills or as a result of the incomplete and sometimes uncontrolled combustion of organic matter. Other potential sources of PAHs include: gasification and liquifaction of coal; incineration of wastes; burning of wood; and the production of coke,

Table 1. Polycyclic aromatic hydrocarbons analyzed for in sediments and mussel tissues.

Compound	Abbreviation	Quantification ion (secondary ion)	Mutagenicity	Carcinogencity
Naphthalene	N	128	–	–
*Acenaphthylene	Acy	152	–	–
*Acenaphthene	Ac	154	+	–
*Fluorene	F	166 (166)	–	–
*Phenanthrene	Ph	178	–	–
*Anthracene	An	178	–	–
*Fluoranthene	Ft	202 (101)		–
*Pyrene	P	202 (101)	–	–
*Chrysene	C	228 (114)	+	±
*Benzo(a)anthracene	B(a)An	228 (114)	+	+
*Benzo(b)fluoranthene	B(b)Ft	252 (126)		+ +
*Benzo(k)fluoranthene	B(k)Ft	252 (126)		–
Benzo(j)fluoranthene	B(j)Ft	252 (126)		+ +
Benzo(e)pyrene	B(e)P	252 (126)	+	±
*Perylene	Per	252 (126)		–
Dimethylbenz(a)anthracene	DMB(a)An	256 (241)		+ + + +
*Benzo(a)pyrene	B(a)P	252 (126)	+	+ + +
*Indeno(1,2,3-c,d)pyrene	IP	276 (138)		+
*Dibenzo(a,h)anthracene	DB(ah)An	278 (139)	+	+ + +
*Benzo(g,h,i)perylene	B(ghi)Per	276 (138)		–
Anthanthrene	Ant	276 (138)		
Benzo(b)chrysene	B(b)C	278 (139)		
Coronene	Co	300 (150)		–
Quinoline	Q	129 (102)	+	+
Carbazole	Car	167 (166)		–
Acridine	Acr	179 (89)	+	–
Benz(a)acridine	B(a)Acr	229 (114)	+	
Benzothiophene	Bt	134 (89)		
Dibenzothiophene	DBt	184 (92)		

Notes: 1) Compounds prefixed by '*' are on USEPA Priority Pollutants List (Keith & Telliard, 1979).
2) Information on mutagenic and carcinogenic properties is from Verschueren (1983); Oehme (1985); and from U.S. National Academy of Sciences, reported in National Research Council (1983).
3) Carcinogencity ranking is: '–', not carcinogenic; '±' uncertain or weakly carcinogenic; '+', carcinogenic; '+ +', '+ + +', '+ + + +', strongly carcinogenic.

carbon black, coal tar pitch, asphalt, and creosote. Through atmospheric transport, PAHs are widely distributed in the environment (Lunde & Bjorseth, 1977), and are found at low levels even in remote areas (Hites & Gschwend, 1982). However, concentrations of these compounds are usually elevated near urban and industrial centres, where PAHs can reach surface waters via direct discharges (industrial and municipal), urban runoff, spills, and seepage. For example, in the Great Lakes basin, elevated sediment concentrations of such PAHs as fluoranthene (> 10 mg kg^{-1}) and benzo(a)pyrene (> 1 mg kg^{-1}) have been found in localized areas of: Lake Superior (near Duluth); western Lake Erie (Black River and Cleveland Harbour); eastern Lake Erie (Buffalo River); and western Lake Ontario (Hamilton Harbour). It is noteworthy that all of these areas have coke manufacturing facilities (Baumann & Whittle, 1988).

The low water solubility of many PAHs results in their tendency to partition out of the aqueous phase and to adsorb onto particulate matter, with eventual deposition in the sediments of aquatic systems. The resulting elevated concentrations can mean increased exposure risk to resident benthic biota. This high escaping tendency (or fugacity) from the aqueous phase also results in the potential for PAHs to accumulate in the lipids of aquatic organisms, particularly if these compounds are only slowly depurated and not readily metabolized (Mackay, 1982; Gobas *et al.*, 1987). PAHs can be metabolized by fish and some invertebrates that possess inducible enzyme systems (Frank *et al.*, 1986; Maccubbin *et al.*, 1988; Vandermeulen & Penrose, 1978), thereby increasing the rate of elimination and decreasing the bioconcentration factor (BCF) of the parent compound. This may make the analysis of parent PAH levels in fish a poor indicator of their environmental exposure (Eadie *et al.*, 1982a).

Several PAHs are of environmental concern because they are mutagenic or their metabolites are carcinogenic (see Table 1). PAHs and their reduced derivatives have been recommended for further research and possible regulatory attention (Passino & Smith, 1987) as well as for effluent monitoring (OME, 1987b). In fact, the detection of tumors (neoplasms) in some resident bottom-feeding fish species has been correlated with high concentrations of such PAHs in sediments (Fabacher *et al.*, 1988; Baumann *et al.*, 1982), high total body burdens of PAHs (Baumann *et al.*, 1982), high PAH concentrations in stomach contents (Maccubbin *et al.*, 1985) or elevated concentrations of aromatic compound metabolites in their bile (Krahn *et al.*, 1986).

The objectives of the study reported here were to:

i) Determine the distribution, biological availability and major source area(s) of PAHs in the St. Marys River.
ii) Determine the relative importance of PAH-contaminated sediments and water on tissue contaminant levels.

The organism used was the freshwater mussel, *Elliptio complanata* Lightfoot (Fam. Unionidae; Subf. Ambleminae). This bivalve filter-feeding mussel has been used as a biomonitor of organochlorine contaminants by OME in Ontario lakes (Suns *et al.*, 1980) and rivers (Curry, 1977/78) as well as in Great Lakes Connecting Channels such as the Niagara River (Niagara River Toxics Committee, 1984) and the St. Clair and Detroit Rivers (Kauss & Hamdy, 1985; EC-OME, 1986). Studies in New York State (Heit *et al.*, 1980) and in the St. Marys River (Kauss, 1986) showed that *E. complanata* was also suitable for monitoring the biological availability of PAHs.

2. Materials and methods

2.1. Field

Sampling stations were selected on the basis of past water and sediment quality data, their proximity to major industrial outfalls, and to permit both cross-channel and upstream-downstream comparisons (Fig. 1). Stations were located in the nearshore, away from major shipping channels, in 0.7 m to 10 m of water (Table 2).

Table 2. Physical and chemical characteristics of St. Marys River waters, 1985.

Station	Water depth m	Mid(M) or bottom(B)	Current speed $m\ s^{-1}$	Temperature °C	Dissolved oxygen $mg\ l^{-1}$	pH	Conductivity $\mu S\ cm^{-1}$@25°C	Suspended solids $mg\ l^{-1}$	Calcium $mg\ l^{-1}$	Magnesium $mg\ l^{-1}$	Hardness $mg\ l^{-1}$
124	0.7	B	0.00/0.00	15/12	10.1*/10.8*	8.1/8.3	115/106	5.06/1.90T	15.6/15.3	2.96/2.76	51/50
123	1.5	B	0.00/0.02	16/12	10.0*/10.8*	7.8/7.8	123/112	1.11T/0.09T	16.6/16.7	2.54/2.71	52/53
121	1.7	B	0.00/0.03	15/12	10.2*/10.8*	7.8/7.8	91/91	1.62T/1.63T	13.4/14.3	2.53/2.67	44/46
115	5.0	M	0.07/0.05	20/16	6.0/6.8	–	–	–	–	–	–
		B	0.03/0.03	20/16	0.0/0.0	7.6/8.2	152/188	7.58/6.44	22.0/20.5	3.12/3.13	68/64
117	6.0	M	0.23/0.19	19/17	7.2/8.0	–	–	–	–	–	–
		B	0.09/0.08	16/13	4.7/5.8	6.7/7.3	115/141	11.49/5.89	18.5/18.0	3.67/3.92	62/61
167	3.0	M	0.05/0.24	17/14	9.7*/10.4*	–	–	–	–	–	–
		B	0.04/0.11	17/14	9.4/10.1	8.3/8.4	129/117	2.09/1.60T	17.3/15.1	3.05/2.84	56/50
29	2.0	B	0.04/0.08	15/12	9.9/10.5	7.7/7.7	91/91	0.91T/0.77T	13.1/13.8	2.64/2.70	44/46
9C	2.0	B	0.00/0.04	15/12	9.5/10.3	7.7/7.7	92/92	0.62T/0.27T	13.3/13.7	2.66/2.74	44/46
107	2.0	M	0.04/0.04	15/12	10.2*/10.4	–	–	–	–	–	–
		B	0.04/0.04	15/12	7.7/8.6	7.7/7.7	91/91	1.13T/3.90	13.6/14.1	2.64/2.80	44/47
27C	1.4	B	0.07/0.13	15/12	9.7/10.0	7.3/7.8	92/89	0.50T/0.95T	13.4/13.8	2.68/2.68	44/46
9A	10.0	B	0.04/0.07	15/12	6.8/8.2	7.8/7.8	91/88	1.73T/0.90T	13.2/13.6	2.68/2.66	44/45
27A	2.0	B	0.04/0.06	15/12	9.4/10.0	7.6/7.6	91/89	5.05/0.48T	13.2/13.6	2.72/2.73	44/45
88	2.0	B	0.05/0.04	20/12	9.0/10.5	7.6/7.6	88/91	1.48T/1.03T	13.2/13.5	2.68/2.70	44/45
92	2.0	B	0.00/0.02	20/12	9.0/10.5	7.6/7.3	85/91	29.5/5.36	12.9/13.7	2.47/2.71	42/46
Balsam Lake	1.5	B	0.00/0.00	23/14	9.2/5.2	8.4/5.6	130/123	2.51/0.75	20.2/14.9	2.56/2.08	61/46

Notes: 1) Station numbers correspond to locations on Fig. 1.
2) St. Marys River data is from two samplings in 1985: Oct. 3/Oct. 24;
Balsam L. data are maximum/minimum of five samplings spanning May 29–Sept. 10, 1984.
3) '–' indicates no sample or no analytical result.
'T' indicates tentative value.
'*' indicates saturated oxygen level.

2.1.1. Caged mussels

E. complanata specimens of a restricted size class (6.5 to 7.2 cm, maximum shell length) were diver-collected from Balsam Lake in central Ontario. Mussels were transported to the study area in bags of lake water within 48 h of collection.

At each of 17 stations, five mussels were placed in a hexane-rinsed wire cage (about 30 cm × 36 cm × 10 cm) fabricated from 1.5 cm open-mesh galvanized wire. Cages were anchored to the bottom with a weight or tethered to a shoreline structure so that mussels were in contact with the sediments. In addition, mussels were also suspended at mid-depth at four of these stations, numbers 115, 117, 167 and 107 (Fig. 1).

After exposure for three weeks (October 3–24, 1985), mussels were retrieved from 14 of the stations and immediately put on ice. [Cages could not be recovered from three of the stations (see Fig. 1), due either to strong currents (Stn. 168), burial by rubble (Stn. 5) or suspected vandalism (Stn. 7). Mortality of mussels was very low, with 98 percent of recovered individuals being alive after their exposure. Three died, one at Station 123 and two at Station 9A.] Within 24 h, mussels were shucked, rinsed, and the drained soft tissues wrapped in hexane(glass-distilled)-rinsed aluminum foil and frozen. Soft tissues were weighed and growth rings of the shells counted to determine age. A random sub-sample of mussels from Balsam Lake was also processed in this manner immediately after collection to provide data on contaminant levels prior to exposure in the St. Marys River. Mussel tissues were kept frozen (– 20 °C) until analyzed.

During deployment and retrieval of the caged mussels, field measurements were obtained of conductivity, water temperature, dissolved oxygen, pH, and current speed. Water samples (unfiltered) were also collected for laboratory analysis of hardness, calcium, magnesium, and suspended solids, using a 1-l glass bottle (OME, 1985).

2.1.2. Bottom sediments

Bottom sediments were also collected in 1985 during the period September 24 to October 4, as part of a larger study of sediment quality and benthic invertebrates (Burt *et al.*, 1988). However, samples could not be obtained at 2 of the above 14 stations (Stns. 167 and 29), due to the fast current and unavailability of sediment (Fig. 1).

At each of the 12 sampled stations, the top 3 cm of at least three Shipek grabs (each of 0.04 m^2 surface area) were composited and homogenized. A subsample of this composite was frozen (– 20 °C) in a 0.5-l wide-mouth solvent-rinsed amber jar with foil-lined cap until analyzed.

2.2. Analytical

Calcium (as Ca^{2+}) and magnesium (as Mg^{2+}) in water samples were determined by automated atomic absorption spectroscopy in the presence of lanthanum chloride. Hardness (as calcium carbonate) was determined using a semi-automated titrimetric procedure employing EDTA and Erichrome Black T indicator. Suspended solids concentration was obtained gravimetrically after drying the filtrate at 103 °C (OME, 1983).

The surficial sediment sample and the entire soft tissues of each of three mussels from each station were analyzed for 29 PAHs (Table 1). This list includes the 17 PAHs on the U.S. Environmental Protection Agency's (USEPA) Priority Pollutants List.

Wet mussel tissue (6.5 to 10.8 g) was spiked with two deuterated surrogate standards [d_{10}-anthracene and d_{12}-benzo(a)pyrene] and then refluxed for 3 h with 5 percent potassium hydroxide in methanol. The cooled sample was diluted with organic-free water, acidified, and then extracted with three portions of hexane. The combined hexane extracts were dried over sodium sulphate (Na_2SO_4) and then concentrated by rotary evaporation, with solvent exchange into iso-octane. After concentration by evaporation, half of the sample was submitted for clean-up (alumina column) and eluted with benzene. The eluate was again concentrated by evaporation and spiked with an internal standard (d_{10}-phenanthrene) prior to gas chromatography (GC)/ mass spectrometry-selected ion monitoring (MS–SIM)

analysis using a Finnegan 4500 system. GC analysis employed a 30 m × 0.25 mm ID DB5 column, helium carrier gas @20 cm s^{-1}, with an oven temperature profile of: 60 °C for 2 min; 60 °C–210 °C @ 10 °C min^{-1}; 210 °C–315 °C @ 16 °C min^{-1}; hold for 20 min. On-column injection was used. MS–SIM analysis in electron impact mode included an ionization voltage of 70eV, 0.5 A filament emission, 1500 V electron multipler and stepped-ion MID scan.

For sediments, a weighed portion (10 to 20 g) of wet sample was spiked with the above surrogate standards and then Soxhlet extracted for 16 h with benzene. Na_2SO_4 and concentrated hydrochloric acid were added to ensure good solvent-sample contact. The extract was then concentrated by rotary evaporation followed by solvent exchange into iso-octane. The final volume was submitted for clean-up as described above for mussel tissue and spiked with the internal standard. GC analysis employed the same column and carrier gas as utilized for mussel extracts. However, the oven temperature profile was; 80 °C for 2 min; 80 °C–210 °C @ 10 °C min^{-1}; 210 °C–290 °C @ 16 °C min^{-1}; hold for 10 min. A splitless injection mode was used. MS conditions were identical to those described above, but the electron multiplier was operated at 2000 V. This was followed by analysis under the following conditions to provide additional sensitivity for the higher molecular weight PAHs: GC using the above-noted column and carrier gas and a temperature profile of 120 °C for 2 min, followed by 120 °C–220 °C @ 10 °C min^{-1}, 220 °C–310 °C @ 16 °C min^{-1} and hold for 12 min; MS was as described above for mussels.

A direct couple GC/MS interface was used with a transfer area of 250 °C.

In addition to the isotopically-labelled surrogate standards added to both mussel tissue and sediment matrices, quality control measures included method blanks and analysis of the U.S. National Bureau of Standards Urban Dust Reference Material (SRM-1649).

Confirmation of the identity of individual PAHs required: the presence of appropriate secondary ions (Table 1) in the mass spectrum; a signal to noise ratio of at least 3 to 1; and retention time within 2 percent of reference standard.

Quantification of PAH compounds was achieved by comparing MS responses of selected ions (Table 1) to those of high purity external standards. [Pure crystals of benzo(j)fluoranthene, benzo(b)chrysene, and anthanthrene were not readily available, so the available solution was used only for retention time confirmation and an isomeric compound was used for quantification.] Calculations were based on the sample dry weight, and no correction was made for deuterated surrogates' spike recoveries.

3. Results and discussion

3.1. Water quality

Measurements of basic physical conditions and water chemistry were restricted to the beginning and end of the mussels' 3 week exposure period. Nevertheless, it is evident from the range of values (Table 2) that, with the exception of the Algoma Slip, the spatial and temporal variability of factors such as dissolved oxygen (6.8–10.8 mg O_2 l^{-1}), conductivity (85–129 μS cm^{-1}), calcium (12.9–17.3 mg l^{-1}) and hardness (44–56 mg l^{-1}) was not great. Also, these concentrations as well as the range of pH (6.7–8.3) were within applicable provincial (OME, 1984) and/or Agreement (IJC, 1978) objectives for the protection of aquatic life.

In contrast, somewhat higher temperatures (up to 20 °C) were noted in waters of the Algoma Slip, which receive effluents from Algoma Steel (Fig. 1) and in the shallow areas of Little Lake George and Lake George (Stns. 88 and 92). Algoma Slip Stations 115 and 117 also tended to have somewhat higher conductivities (115–188 μS cm^{-1}), calcium (18.0–22.0 mg l^{-1}), magnesium (3.12–3.92 mg l^{-1}), hardness (61–68 mg l^{-1}) and lower dissolved oxygen levels (0.0–8.0 mg l^{-1}), particularly near the bottom.

Current speed varied spatially and temporally, ranging from the still waters of Leigh Bay (0.0 m s^{-1}) to the more rapid flow (0.24 m s^{-1}) down-

stream of an Algoma Steel discharge in the Great Lakes Power Corp. headrace (Stn. 167).

Suspended solids concentrations were quite changeable, varying up to 20-fold at the same station (e.g., 27A). However, the majority (60 percent) of values were below 2.0 mg l^{-1}, reflecting

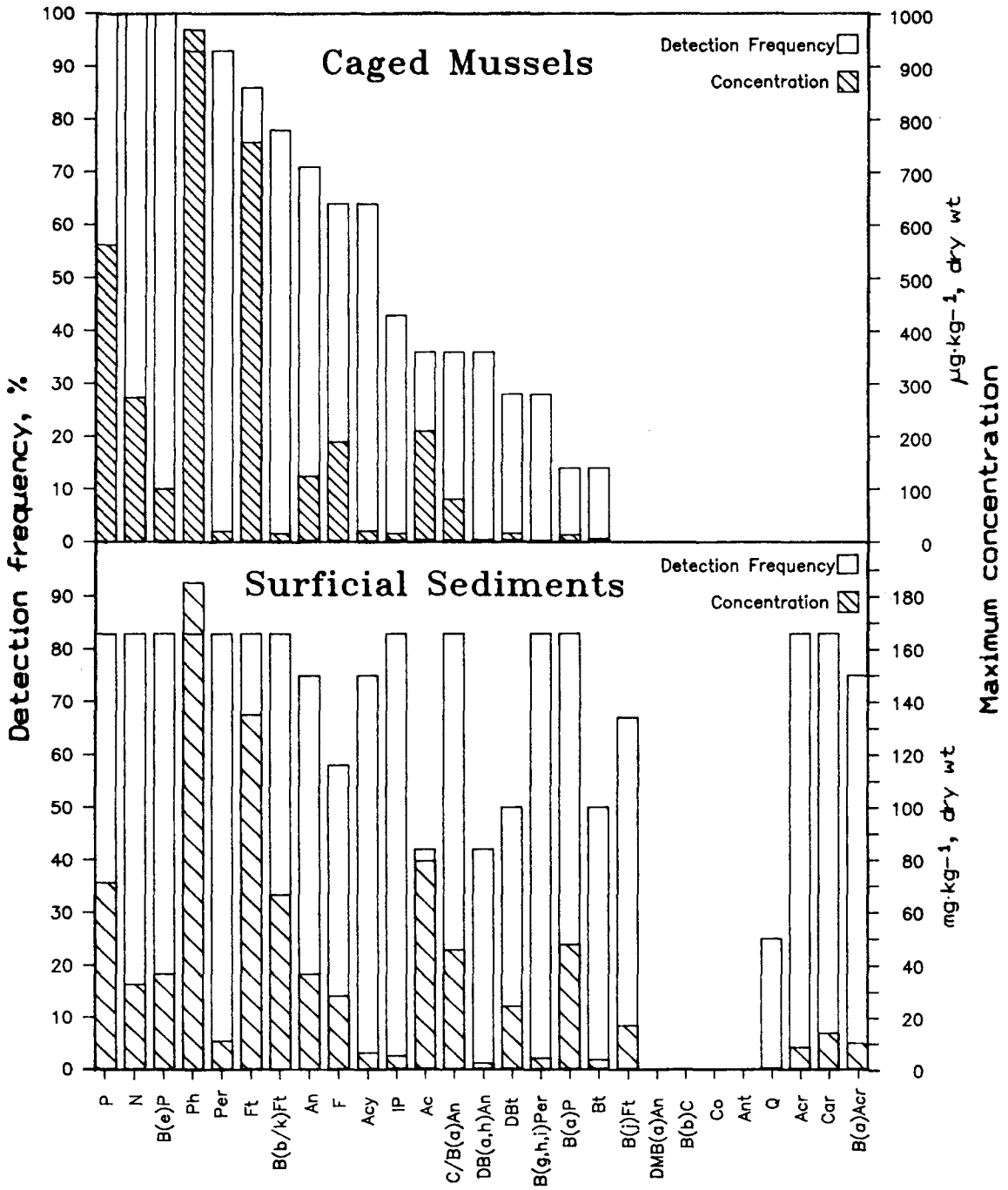

Fig. 2. Polycyclic aromatic hydrocarbons detected in caged mussels and surficial sediments of the St. Marys River in 1985. Abbreviations as per Table 1.

the low levels of particulates (0.5–1.0 mg l^{-1}) in the river's major source, Lake Superior (Eadie, 1984). The above-noted spatial and temporal variability is unlikely to have had adverse effects on the biomonitor, however, since both the actual concentrations as well as their ranges were similar to those experienced by the mussels in Balsam Lake, their native environment (Table 2).

3.2. PAHs detected in sediments and mussels

For the sake of convenience, individual PAH compounds in this and following sections are referred to by their abbreviations (see Table 1).

Of the 29 PAHs analyzed for, more compounds were detected in St. Marys River surficial sediments than in mussel tissues (Fig. 2). The largest number, 24 to 25 [B(b)Ft and B(k)Ft isomers could not be resolved in sediment samples], was found at Station 115 in the Algoma Slip, and 17 to 18 of these PAHs were also identified at > 50 percent of the sediment sampling locations. These included, in decreasing order of frequency: [P = N = B(e)P = Ph = Per = Ft = B(b/k)Ft = IP = C = B(a)An = B(g,h,i)Per = B(a)P = Acr = Car] > [An = Acy] > B(j)Ft > F. In contrast, a maximum of 16 to 18 compounds [B(b)Ft and B(k)Ft isomers as well as C and B(a)An could not be resolved in mussel tissues] were found in *E. complanata* after three weeks' exposure at Station 115. Of these, 10 to 11 were also detected at > 50 percent of the biomonitoring stations. In decreasing order of detection frequency, these were: [P = N = B(e)P] > [Ph = Per] > Ft > B(b/k)Ft > An > [F = Acy].

DMB(a)An, B(b)C, Co, and Ant were not detected in either matrix at the method detection levels employed in this study (Tables 3 and 5), indicating that there were no recent inputs of these compounds to the river.

In contrast, the nitrogen heterocycles Q, Acr, Car, and B(a)Acr were not accumulated by mussels, although the latter three were present in most of the sediment samples.

For those PAHs common to both sediments and mussels, there was generally a similar pattern of relative maximum concentrations (Fig. 2). At the majority of sampling stations, both sediments and mussel tissues were dominated by the 3- and 4-ring compounds Ph, Ft and P (Tables 3 and 5), suggesting that high temperature combustion of fossil fuels (e.g., burning of coal or wood, coke manufacturing) was the major contributor of PAH's to the local aquatic environment (Gschwend & Hites, 1981; Helfrich & Armstrong, 1986). This same predominance was observed in urban runoff (Marsalek & Ng, 1987) and snowpack samples (Boom & Marsalek, 1988) collected in Sault St. Marie, Ontario during 1986 and 1987, respectively. The relatively high concentrations of the lower molecular weight 2- and 3-ring compounds N, Acy, Ac, and F relative to the high molecular weight C, B(a)An, B(e)P, B(a)P, and IP suggest that fossil fuel spills (e.g., coal, petroleum) are also important sources of anthropogenic PAHs in this area (Helfrich & Armstrong, 1986). This is particularly evident for the sediments at Stations 115 and 117 in the Algoma Slip and at Station 9A at Sault Ste. Marie, Michigan. Sediments of all three stations generally contained elevated levels of nitrogen heterocycles [Q,Car,Acr, B(a)Acr] and sulfur heterocycles (Bt, DBt) (Table 3). Both Bt and DBt are components of petroleum (Lake & Hershner, 1977) and DBt and Acr (in addition to unsubstituted and substituted PAHs) have been identified in certain coals (Barrick *et al.*, 1984; Bender *et al.*, 1987; Tripp *et al.*, 1981). Q and Acr are also found in wastewaters from high temperature industrial processes such as coal coking and conversion (Cassidy *et al.*, 1988). It is worth noting that coal pellets or dust were observed in the sediments of these three stations during their collection (Burt *et al.*, 1988). Spills are also possible sources of the heterocyclic PAHs detected in the Algoma Slip. DBt and Car were detected in coal tar, and these compounds as well as Bt, Q and Acr were identified in creosote manufactured by a nearby plant (Domtar) from Algoma Steel coal tar (OME, 1988, unpublished data).

Table 3. Concentration of polycyclic aromatic hydrocarbons, oil and grease and organic carbon and percent fines in St. Marys River surficial sediments, 1985.

Compound	MDL	Station											
		124	123	121	115	117	9C	9A	107	27C	27A	88	92
Naphthalene	0.02	*	*	0.06	29.0	3.3	5.90	0.69	6.60	1.70	0.03	0.13	0.13
Acenaphthylene	0.02	*	*	0.08	4.80	0.42	0.55	4.60	0.52	0.55	*	0.18	0.07
Acenaphthene	0.02	*	*	*	19.5	0.93	0.18	0.62	0.17	*	*	*	*
Fluorene	0.02	*	*	*	28.5	1.90	0.47	3.40	0.36	0.17	*	*	0.03
Phenanthrene	0.02	*	*	0.86	185	14.0	3.90	25.0	2.20	1.10	0.09	0.40	0.25
Anthracene	0.02	*	*	*	37.0	3.50	1.40	10.0	1.00	0.52	0.03	0.18	0.07
Fluoranthene	0.02	*	*	4.00	135	13.0	6.40	30.0	3.70	1.70	0.12	0.59	0.43
Pyrene	0.02	*	*	3.00	71.5	7.40	3.60	17.0	2.20	1.10	0.07	0.36	0.27
Chrysene	0.02	*	*	3.40	9.30	1.50	1.00	9.90	1.00	0.45	0.02	0.14	0.06
Benzo(a)anthracene	0.02	*	*	18.0	32.0	5.50	4.60	36.0	4.20	2.10	0.09	0.55	0.28
Benzo(b/k)fluoranthene	0.04	*	*	16.0	32.5	4.30	6.20	67.0	11.0	2.80	0.13	0.97	0.33
Benzo(j)fluoranthene	0.02	*	*	1.10	5.50	0.64	1.10	17.0	3.00	*	*	0.16	0.05
Benzo(e)pyrene	0.02	*	*	7.40	16.0	2.10	3.00	37.0	7.00	2.00	0.08	0.56	0.18
Perylene	0.02	*	*	2.20	7.30	0.79	1.20	11.0	2.30	0.55	0.03	0.33	0.11
Dimethylbenz(a)anthracene	0.02	*	*	*	*	*	*	*	*	*	*	*	*
Benzo(a)pyrene	0.02	*	*	9.20	24.5	2.80	4.40	48.0	8.40	1.90	0.11	0.71	0.21
Indeno(1,2,3-c,d)pyrene	0.02	*	*	3.60	5.30	0.82	1.10	4.90	0.69	*	0.04	0.34	0.07
Dibenzo(a,h)anthracene	0.02	*	*	1.50	2.30	0.35	0.46	2.50	*	*	*	0.11	0.03
Benzo(g,h,i)perylene	0.02	*	*	3.50	4.50	0.82	0.88	1.70	0.21	*	0.04	0.31	0.07
Anthanthrene	0.02	*	*	*	*	*	*	*	*	*	*	*	*
Benzo(b)chrysene	0.02	*	*	*	*	*	*	*	*	*	*	*	*
Coronene	0.04	*	*	*	*	*	*	*	*	*	*	*	*
Quinoline	0.02	*	*	*	0.46	0.12	*	*	*	*	*	*	0.03
Carbazole	0.02	*	*	0.28	14.0	1.70	0.81	2.20	0.30	0.10	0.04	0.26	0.19
Acridine	0.02	*	*	0.58	8.70	1.30	0.61	1.20	0.22	0.16	0.08	0.25	0.20
Benz(a)acridine	0.02	*	*	2.70	10.2	1.50	0.84	5.70	0.49	0.31	*	0.13	0.19
Benzothiophene	0.02	*	*	*	3.80	0.39	0.31	0.06	0.26	*	*	*	0.06
Dibenzothiophene	0.02	*	*	*	24.5	1.70	0.59	2.30	*	0.14	*	*	0.15
Oil & Grease	–	117	123	237	4722	2276	9612	1216	4651	4053	505	2258	2178
Total Organic Carbon ($g \cdot kg^{-1}$)	–	5.0	5.0	10.0	335	140	100	22.0	57.0	36.0	22.6	22.0	18.0
$<62\ \mu m$ diameter (%)	–	3.3	47.6	36.0	37.7	35.1	74.4	12.0	26.0	27.8	8.5	75.8	81.1

Notes: 1) Station numbers correspond to locations on Fig. 1.
2) Concentration units are mg kg^{-1} (dry weight) except as noted.
3) '*' indicates not detected at method detection limit (MDL) shown.

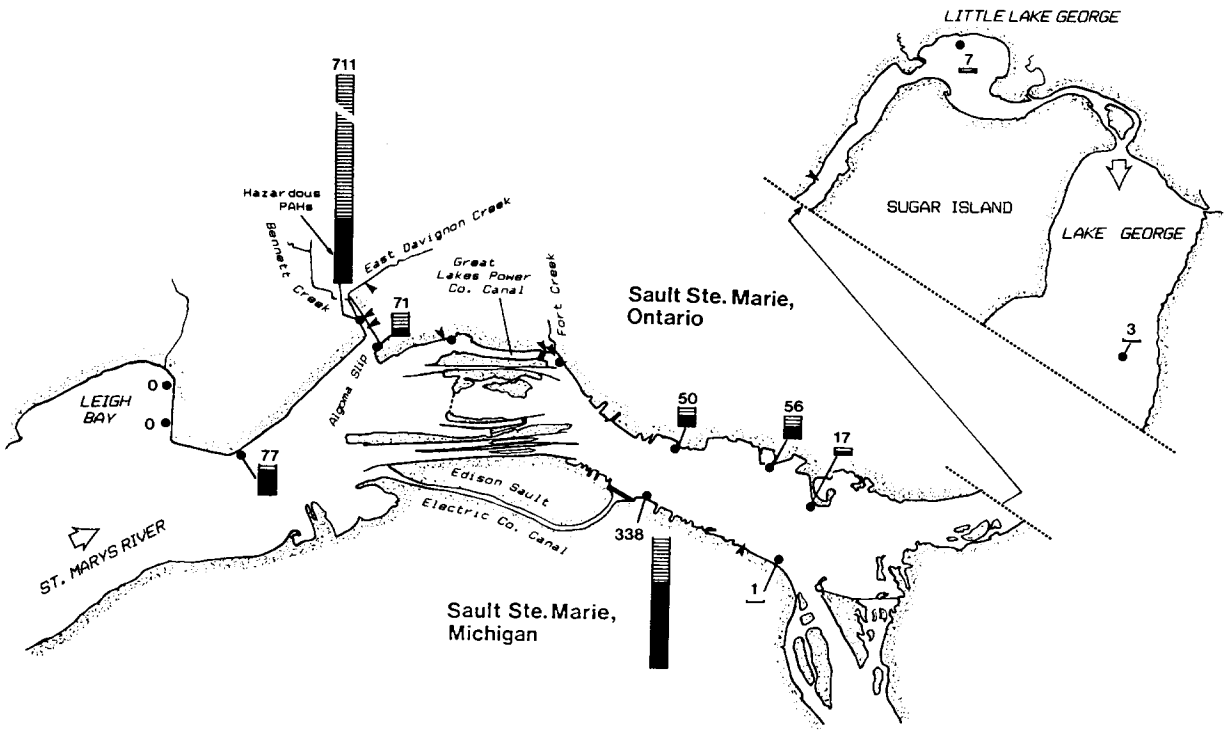

Fig. 3. Total polycyclic aromatic hydrocarbons (mg kg^{-1}, dry wt) in surficial sediments of the St. Marys River in 1985. Bar height is proportional to concentration; shaded portion of bars indicates the proportion of the total comprised of mutagenic and/or carcinogenic compounds.

3.3. PAH concentrations in sediments

The sum of individual PAHs at each station ('total PAHs' in Fig. 3) was highest in surficial sediments collected at Station 115 in the Algoma Slip (711 mg kg^{-1} dry wt). This station also had the highest concentrations of the following individual PAHs: N, Acy, Ac, F, Ph, An, Ft, P, IP, B(g,h,i)Per, Q, Car, Acr, B(a)Acr, Bt, and DBt. Concentrations of both total and individual PAHs generally decreased with increasing distance downstream (Table 3 and Fig. 3). The second highest concentration of total PAHs (338 mg kg^{-1}) was found along the U.S. shore immediately downstream of the Edison Sault Electric Co. Canal discharge at Station 9A. Maximum survey concentrations of C, B(a)An, B(b/k)Ft, B(a)P, DMB(a)An, B(e)P, B(j)Ft, and Per were also recorded at this location (Table 3).

Figure 3 also shows the relative contribution of 'hazardous PAHs' to the total PAH levels at each station. This sub-group was comprised of 13 compounds considered to be mutagenic and/or carcinogenic (see Table 1): Ac, C, B(a)An, B(b)Ft, B(j)Ft, B(e)P, DMB(a)An, B(a)P, IP, DB(a,h)An, Q, Acr, and B(a)Acr. The percentages of these hazardous PAHs varied greatly between stations, from a low of 23 to 30 percent in the Algoma Slip to a maximum of 80 percent upstream of Algoma Steel discharges (Stn. 121). At the remaining downstream stations, percentages ranged between 45 and 63 percent. The major contributors to these percentages were: B(a)An, B(b/k)Ft, B(e)P, and B(a)P (Table 3).

Table 4 compares the ranges of concentrations (minimum to maximum) of individual PAHs in St. Marys River sediments with those from five other areas in the Great Lakes basin that also receive inputs from steel and/or coke manufacturing facilities, in addition to urban inputs.

Table 4. Comparison of polycyclic aromatic hydrocarbon concentrations (mg kg^{-1}, dry wt) in Great Lakes and tributary sediments.

Compound	Lake Superior 1978 (a)	Colin Scott Lake, Ont. (b)	St. Marys River 1985 (c)	Detroit River 1982 (d)	Detroit River 1985 (e)	Black River 1980 (f)	Black River 1984 (g)	Lackawanna & Union Canals 1981 (h)	Buffalo River 1981 (h)	Buffalo River 1983 (i)	Hamilton Harbour 1982 (j)
*Naphthalene			ND–29.0	0.12–16.8	ND–4.40	31.0	14.0	ND–23.0	ND–239.1		
*Acenaphthylene			ND–4.80	ND–1.34	ND–1.00	40.0	17.0	ND–2.5	ND		
*Acenaphthene			ND–19.5	ND–42.3	ND–2.60	36.0	2.50	ND–49.0	ND–80.0		
*Fluorene			ND–28.5	ND–5.10	ND–12.6		16.0	ND–2.20	ND–5.10	ND–0.64	
*Phenanthrene	0.027		ND–185	0.10–55.2	ND–85.6	390	52.0	4.2–16.7	ND–16.3	0.67–9.60	
*Anthracene	0.003		ND–37.0	ND–18.7	ND–55.0		15.0			0.20–3.40	
*Fluoranthene	0.091	0.038	ND–135	ND–31.4	ND–119	220	33.0	5.5–63.9	ND–35.6	2.45–10.1	1.9–4.3
*Pyrene	0.055	0.023	ND–71.5	ND–31.5	ND–86.1	140	24.0	5.5–49.6	1.0–26.7	1.40–21.9	
*Chrysene	0.091	0.023	ND–9.90			51.0	10.0			0.24–1.77	
*Benzo(a)anthracene	0.027	0.007	ND–36.0	ND–35.6	ND–81.9	51.0		3.5–66.4	ND–60.2	0.46–2.60	
*Benzo(b)fluroanthene		0.025						ND–63.0	ND–96.9	ND–5.50	
*Benzo(k)fluoranthene		0.025	ND–67.0	ND–57.9	ND–63.5	75.0	15.0			0.32–1.15	1.1–9.0
*Benzo(j)fluoranthene		0.008	ND–17.0								
Benzo(e)pyrene	0.082	0.028	ND–37.0			28.0	6.00			ND–4.51	
Perylene		0.020	ND–11.0			12.0	3.60		ND	2.10–13.7	1.2–9.7
Dimethylbenz(a) anthracene			ND								
*Benzo(a)pyrene	0.036	0.013	ND–48.0	ND–23.7	ND–67.5	43.0	8.80	ND–106.5	ND–72.5	0.21–2.54	1.2–11.1
*Indeno(1,2,3-c,d)pyrene			ND–5.30	ND–8.15	ND–13.8	26.0	6.40	ND ~ 10.0	ND	0.62–2.80	1.1–9.7
*Dibenzo(a,h)anthracene			ND–2.50			9.40	1.60			0.12–6.31	
*Benzo(g,h,i)perylene		0.028	ND–4.50	ND–12.6	ND–14.3	24.0	5.40	ND–14.0	ND	0.21–2.61	1.6–8.6
Coronene		0.006	ND								
Quinoline			ND–0.46								
Carbazole			ND–14.0								
Acridine			ND–8.70				ND				
Benz(a)acridine			ND–10.2				0.67				
Benzothiophene			ND–3.80								
Dibenzothiophene			ND–24.5			22.0	3.70				
Total PAHs (sum of *)			ND–621	0.58–254	0.60–600	1144	221	9.70–392	0.6–285	8.74–60.2	
Number of Samples	1	1	12	36	20	1	1	8	17	10	6

Data sources: (a) Gschwend & Hites (1981); 1955–78 section of core. (b) Brown & Starnes (1978); surficial, using pipe dredge. (c) This study; surficial (top 3 cm.) section of dredge sample. (d) Pranckevicius (1987); surficial section of dredge or core. (e) Pranckevicius & Kitsuse (1989); unspecified depth of sample. (f) Baumann *et al.* (1982); unspecified depth of sample. (g) Fabacher *et al.* (1988); complete dredge sample. (h) Rockwell *et al.* (1984); unspecified depth of dredge sample. (i) Niagara River Toxics Committee (1984); unspecified depth of sample. (j) Poulton (1987); surficial (top 3 cm.) section of dredge sample.

Notes: 1) The highest concentrations are underlined when more than one data set is available.

2) ND = not detected.

3) 'Total PAHs' range is the minimum and maximum of summed concentrations at individual stations.

Where comparisons are possible, it is evident that the range of concentrations of individual compounds in these other areas was similar to those in the St. Marys River. It is noteworthy that the highest B(a)P concentrations in all six areas (and 58, 56 and 31%, respectively, of stations in the St. Marys River, Detroit River and Detroit River tributaries) exceeded the recommended IJC objective of 1 mg kg^{-1} (IJC, 1983). Unfortunately, there are no available objectives or guidelines for other PAHs in sediments. Nevertheless, the maximum concentrations found in these six urban/industrial areas were from an order of magnitude [B(g,h,i)Per in the Buffalo River] to four orders of magnitude (Ph in the Black River, a tributary of Lake Erie) higher than in 'background' sediment samples from Lake Superior and a wilderness lake (Colin Scott) in Ontario (Table 4), indicating significant localized contamination.

Differences in the number of PAH compounds analyzed for makes a comparison of 'total PAH' concentrations from different studies difficult. Consequently, concentrations of only the 16 asterisked compounds in Table 4 (representing 94% of the PAHs on the USEPA Priority Pollutants List) were summed for individual stations in the St. Marys River, Detroit River and tributaries, Black River, Lackawanna and Union Canals, and the Buffalo River. The ranges of 'total PAHs' are presented in Table 4. Of the six data sets, sediment collected from the Black River in 1980 contained the highest concentration of total PAHs (1 144 mg kg^{-1}), whereas samples from the Buffalo River in 1983 had the lowest (8.74–60.2 mg kg^{-1}). The maximum concentration of total PAHs in the St. Marys River (621 mg kg^{-1}) was intermediate between these extremes and similar to the maximum total PAH concentration found in sediments of tributaries to the Detroit River in 1985 (600 mg kg^{-1}). This similarity is partially a reflection of the low energy

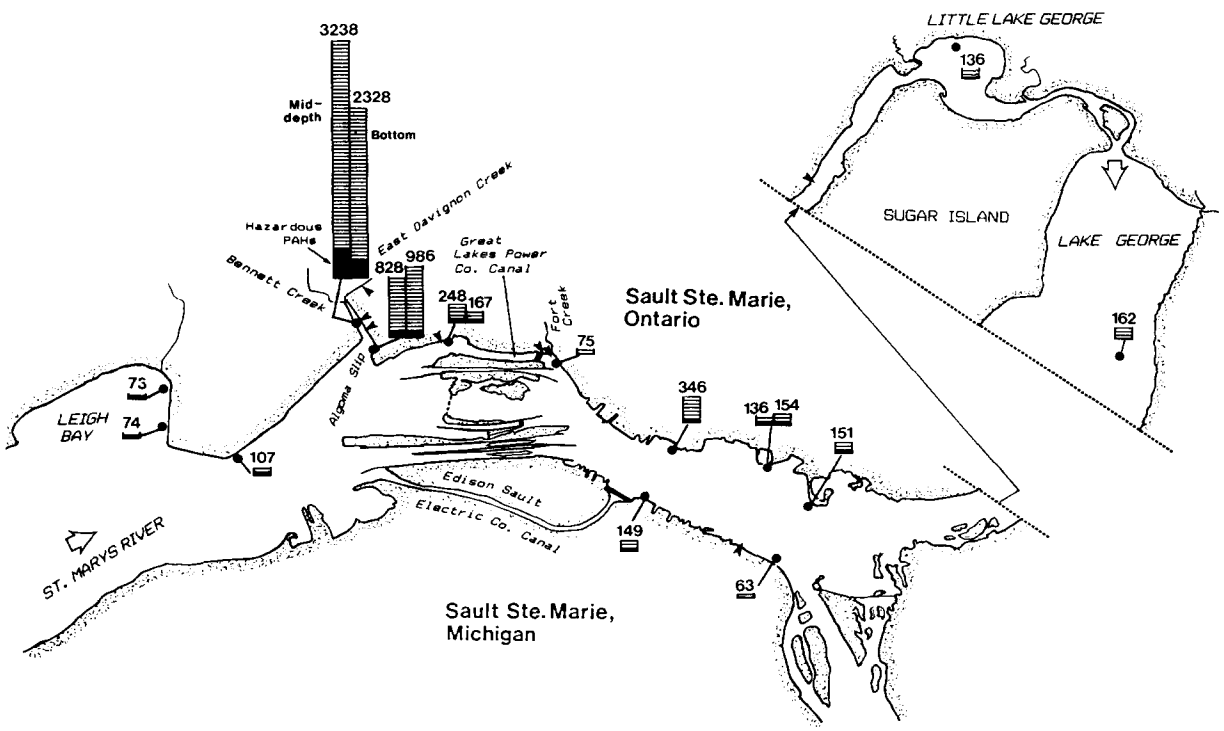

Fig. 4. Total polycyclic aromatic hydrocarbons ($\mu g\ kg^{-1}$, wet wt) in caged mussels (*Elliptio complanata*) after 3 weeks' exposure in the St. Marys River in 1985. Bar height is proportional to concentration; shaded portion of bars indicates the proportion of the total comprised of mutagenic and/or carcinogenic compounds.

Table 5. Concentrations of polycyclic aromatic hydrocarbons in mussels (*Elliptio complanata*) after three weeks' exposure in the St. Marys River, 1985.

Compound	MDL	Station																		
		124	123	121	115		117		167		29	9C	9A	107		27C	27A	88	92	Balsam Lake
					M	B	M	B	M	B				M	B					
Naphthalene	1	45	17	86	184	116	43	40	37	27	21	275	89	44	41	73	25	30	103	11
Acenaphthylene	1	0.4	*	*	20	8	*	5	8	0.9	*	*	*	10	5	4	3	5	1	*
Acenaphthene	1	*	0.9	*	208	145	7	40	12	2	*	*	*	1	1	*	*	*	*	0.3
Fluorene	1	0.4	12	*	189	146	19	44	5	2	*	*	*	*	*	4	1	1	1	1
Phenanthrene	1	2	8	0.8	969	751	163	331	72	45	14	22	*	11	11	14	6	12	3	1
Anthracene	1	0.8	1	2	123	83	29	39	14	1	5	*	*	*	0.6	0.6	2	*	*	2
Fluoranthene	1	13	21	5	756	570	304	356	23	*	*	13	3	23	36	17	2	36	13	1
Pyrene	1	9	12	3	563	392	180	30	64	49	6	11	2	15	15	10	1	17	3	2
Chrysene/ Benzo(a)anthracene	2	*	*	*	79	57	48	39	2	*	*	2	*	1	4	*	*	2	*	*
Benzo(b/k)fluoranthene	2	0.8	0.6	0.6	16	8	*	*	*	*	0.8	0.7	49	2	3	2	13	*	12	0.8
Benzo(j)fluoranthene	1	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Benzo(e)pyrene	1	0.7	1	3	100	42	36	40	9	31	7	9	4	20	30	20	4	18	7	*
Perylene	1	0.4	*	0.9	13	6	8	8	2	8	21	4	2	7	5	3	6	8	5	1
Dimethylbenz(a)anthracene	1	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Benzo(a)pyrene	1	*	*	*	13	1	1	*	*	*	*	0.2	*	1	1	1	*	*	*	*
Indeno(1,2,3-c,d)pyrene	1	*	*	*	1	*	*	*	*	1	*	4	*	1	1	1	*	2	14	*
Dibenzo(a,h)anthracene	1	*	*	*	1	*	*	*	*	*	*	4	*	1	1	1	*	1	0.2	*
Benzo(g,h,i)perylene	1	*	*	*	1	0.7	*	*	*	*	*	1	*	0.2	0.2	1	*	2	*	*
Anthanthrene	1	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Benzo(b)chrysene	1	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Coronene	1	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Quinoline	1	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Carbazole	1	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Acridine	1	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Benz(a)acridine	1	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Benzothiophene	1	*	*	5	2	0.2	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Dibenzothiophene	1	*	*	*	*	2	*	14	*	*	*	0.4	*	0.2	*	*	*	2	*	0.3
Tissue wet weight(g)	–	8.1	8.2	8.2	9.1	10.1	8.2	8.7	8.6	8.3	8.7	8.6	10.9	9.4	8.9	8.5	8.6	9.3	8.8	8.8
Age (yr)	–	8	8	9	11	8	9	9	9	9	10	9	8	14	9	9	10	10	8	9

M = mid-depth; B = bottom.

Notes: 1) Station numbers correspond to locations on Fig. 1.

2) Concentrations are $\mu g\, kg^{-1}$ wet weight and are the geometric means of 3 replicates; other parameters are arithmetic means.

3) '*' indicates not detected at method detection limit (MDL) shown.

nature of these highly contaminated areas (i.e., Algoma Slip and slow-flowing tributaries) and the resultant deposition of contaminated materials. However, since other factors such as field methodology (depth of sample collected, proximity to source-see Table 4), sediment physical and chemical characteristics [%fine (<62 μm diam.) particles, total organic carbon content] and even analytical methodology can be important determinants in the final 'bulk' concentrations of PAHs reported, the magnitude of differences (or similarities) between areas may not be as significant as they at first appear.

3.4. PAH concentrations in mussels

The presence of detectable PAH concentrations in *E. complanata* from some stations after three weeks' exposure indicates a rapid accumulation of these compounds. Pittinger *et al.* (1985) observed that this occurred within as short a period as three days in the oyster *Crassostrea virginica*. As with surficial sediments, total PAHs in mussel tissues were highest at Station 115 in the Algoma Slip (2328–3238 $\mu g\,kg^{-1}$ wet wt). The mean concentrations of the following compounds were also highest at this and at nearby Station 117: Acy, Ac, F, Ph, An, Ft, P, C/B(a)An, B(e)P, and B(a)P (Fig. 4 and Table 5). Downstream, total PAH concentrations decreased rapidly to 151 $\mu g\,kg^{-1}$ at Station 27C. However, similar concentrations were still observed in Little Lake George (136 $\mu g\,kg^{-1}$) and Lake George (162 $\mu g\,kg^{-1}$), some 13 km and 20 km distant, respectively, and along the Michigan shoreline at Station 9A (149 $\mu g\,kg^{-1}$). This suggests inputs or biological availability of PAHs in the Sault Ste. Marie, Ontario and Michigan areas, with additional input along the Lake George Channel.

The proportion of total PAHs represented by 'hazardous PAHs' varied considerably in mussels (Fig. 4), but generally was less than that observed in sediments and did not correspond with the areas of maximum and minimum values noted for the latter. Percentages of this sub-group more than doubled in the Algoma Slip (11–13%) from the low levels present in mussels prior to their exposure (5%) and at upstream stations (2–3%). At the remaining stations, percentages ranged from 6 percent (Stn. 9C) to a maximum of 36 percent (Stn. 9A), with the remainder being around 20 percent. Compounds contributing most to these percentages differed between Ontario and Michigan stations in the Sault Ste. Marie area. The former were dominated by B(e)P and additionally by Ac and C/B(a)An in the Algoma Slip, whereas at the latter, B(b/k)Ft was the major contributor (Table 5). It is noteworthy that even the maximum concentration of B(a)P in mussels (13 $\mu g\,kg^{-1}$) was about two orders of magnitude lower than the recommended objective of 1000 $\mu g\,kg^{-1}$ for organisms serving as a food source for fish (IJC, 1983).

Statistical analysis on $\log_e$-transformed replicate data (one-way ANOVA; Tukeys Multiple Range Test) was used to determine those stations or station groups with significantly different ($\alpha = 0.05$) concentrations of individual PAHs in *E. complanata* exposed to the sediments. Although mean concentrations of many PAHs were highest in the Algoma Slip, the high variability between replicates for some compounds resulted in no significant station-to-station differences for seven of the compounds: N, Acy, B(b/k)Ft, B(a)P, DB(a,h)An, B(g,h,i)Per, and DBt. [Similar large variability among individual replicates has been observed for this organism (Kauss & Hamdy, 1985) and for the marine bivalve *Rangia cuneata* (Neff & Anderson, 1975). The latter felt that this was typical of molluscs that can close their valves and remain isolated from the external environment for variable time periods.] The remaining 11 compounds exhibited varying degrees of difference or overlap between stations and the areas with significantly higher concentrations were compound-specific (Fig. 5). For example, mussels exposed at one or both stations in the Algoma Slip contained significantly higher mean concentrations of the following: Ft(356–570 $\mu g\,kg^{-1}$), Ph(331–751 $\mu g\,kg^{-1}$), Ac(40–145 $\mu g\,kg^{-1}$), F(146 $\mu g\,kg^{-1}$), An(39–93 $\mu g\,kg^{-1}$), B(e)P(40–42 $\mu g\,kg^{-1}$), P(392 $\mu g\,kg^{-1}$), and C/B(a)An (39–57 $\mu g\,kg^{-1}$).

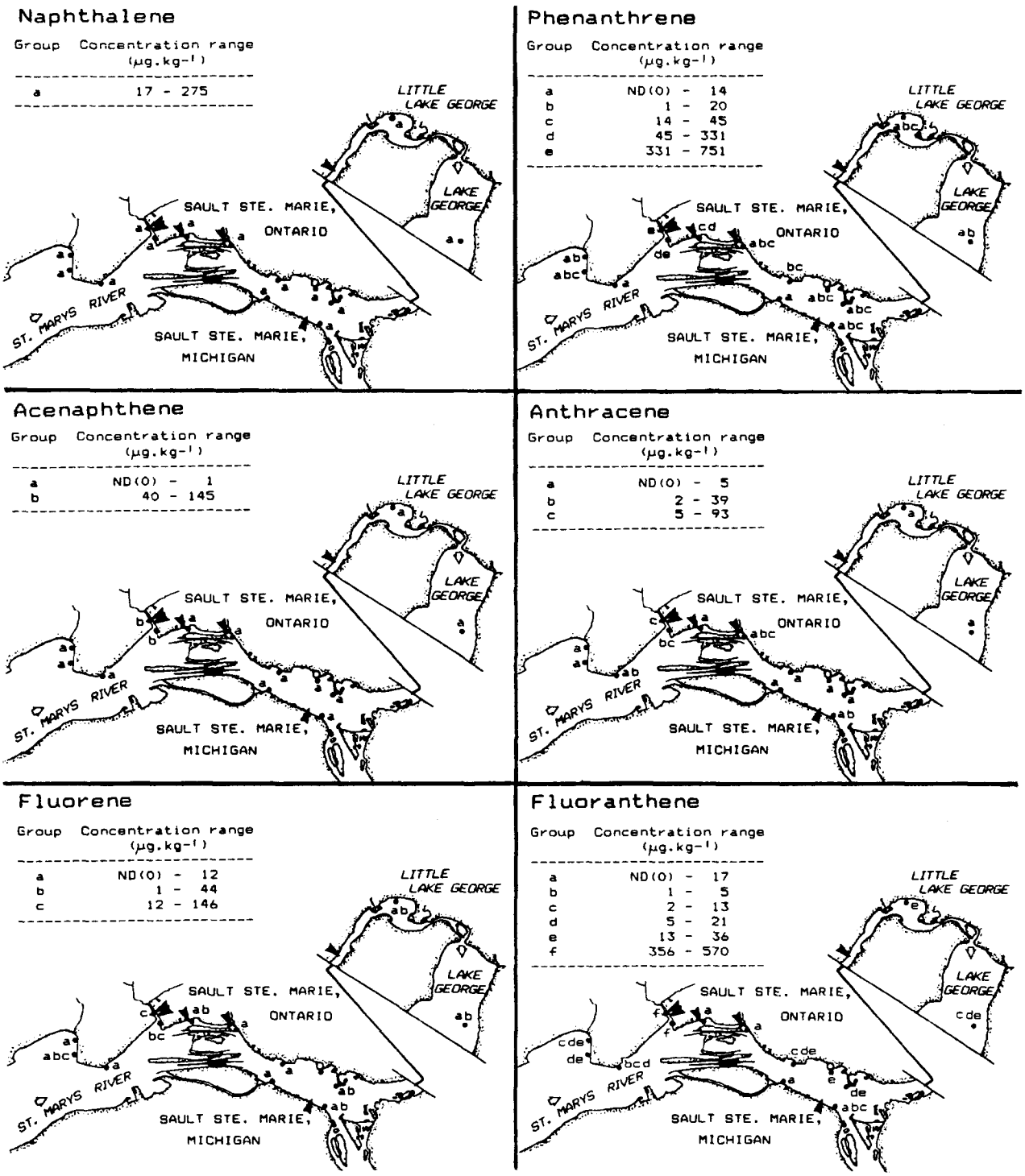

Fig. 5. Distribution of naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene/benzo(a)anthracene, benzo(e)pyrene, perylene, indeno(1,2,3-cd)pyrene and benzothiophene concentrations in caged mussels (*Eliptio complanata*) after 3 weeks' exposure in the St. Marys River in 1985. Letters delineate groups of significantly different ($\alpha = 0.05$) stations.

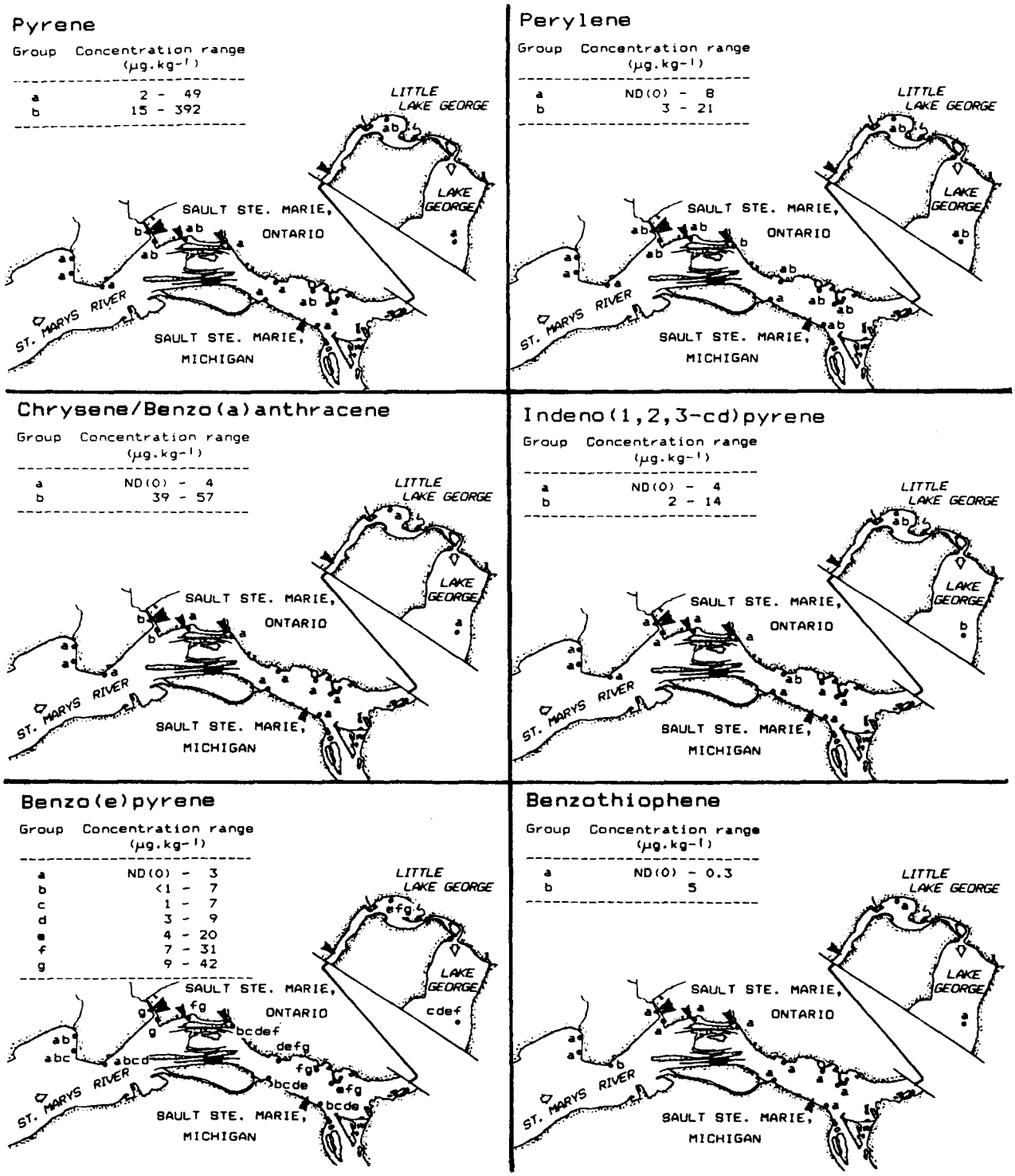

Fig. 5. (Continued).

Table 6. Comparison of polycyclic aromatic hydrocarbon concentrations ($\mu g\ kg^{-1}$, wet wt) in clams and mussels from various studies.

Compound	Freshwater		Marine										
	Elliptio complanata	*Elliptio complanata & Lampsilis radiata*	*Crassostrea gallo provincialis*	*Crassostrea virginica*			*Macoma inquinata*	*Mytilus californianus*	*Mytilus edulis*			*Rangea cuneata*	
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(h)	(i)	(j)	(d)	(e)
Naphthalene	ND–275			14700	35	12000						3800	51–120
Acenaphthylene	ND–20				36								34–130
Acenaphthene	ND–208		7–8		46								24–46
Fluorene	ND–189	<0.2–59	2	1000	21							300	ND
Phenanthrene	ND–969	<0.2–9.6	8–9	1900	220		38–96					500	72
Anthracene	ND–123		8–9		44	2500							36–43
Fluoranthene	ND–756		7		80	4000							ND
Pyrene	1–563	<0.2–72	4		200								ND
Chrysene	ND–79	<1.6	≤8–≤18		58		297–308						ND
Benzo(a)anthracene			2–4		9.9	1800							ND
Benzo(b)fluoranthene	ND–49												
Benzo(k)fluoranthene					12								ND
Perylene	ND–21	<1.6–48	1–14				297–856						
Benzo(a)pyrene	ND–13	<1.6	2			300	37–59	<0.1–2.3	0.4–8.2	17–215		7200	
Dimethylbenz(a)-anthracene	ND–4		≤1–≤2										
Benzo(g,h,i) perylene	ND–2		4–5										
Coronene	ND		3–4										
Dibenzothiophene	ND–14	<0.2–0.6		300							34–809	100	

Data sources: (a) This study, caged mussels exposed for 3 weeks; range of means for stations. (b) Heit *et al.* (1980); native species homogenate, range of samples; dry weight data converted to wet weight basis by dividing by 6.25. (c) Iosifidou *et al.* (1982); Chrysene includes Triphenylene; Dimethylbenz(a,h)anthracene includes (a,c) isomer; range of means for native species from two locations. (d) Neff *et al.* (1976); after 24 h exposure to No. 2 fuel oil (1%) or to 0.0305 g m^{-3} B(a)P. (e) McFall *et al.* (1985); native species. (f) Lee *et al.* (1978); after 8 days' exposure to Prudhoe Bay crude oil dispersion enriched with PAHs. (g) Roesijadi *et al.* (1978); after 7 days' exposure to detritus containing 2000 mg kg^{-1} Prudhoe Bay crude oil and spiked with ^{14}C-labelled PAH compounds; range of means. (h) Dunn & Young (1976); homogenates of native species from various locations. (i) Dunn & Stich (1976); homogenates of native species from various locations. (j) Kira *et al.* (1983); homogenates of native species from various locations.

Note: ND = not detected.

A decreasing downstream gradient was most evident for Ac, F, An, B(e)P, Ph, and P, while elevated levels of C/B(a)An and Ac were restricted to the Slip. In contrast, the highest concentrations of Bt(5 $\mu g\ kg^{-1}$), Per(21 $\mu g\ kg^{-1}$), and IP(14 $\mu g\ kg^{-1}$) were found at the eastern end of the Algoma Slag Dump, immediately downstream of the Algoma Steel Terminal Basins discharge and in Lake George, respectively.

Table 6 compares the range of PAH concentrations detected in *E. complanta* after exposure in the St. Marys River with levels found in various freshwater and marine bivalves. Differences between studies with respect to duration and type of exposure (short-term vs. life-long; field vs. laboratory), route of major exposure (water vs. sediment), analytical methodology, and species (filter-feeder vs. detritovore; lipid content, etc.) make such comparisons difficult at best. However, it is evident that the ranges of concentrations of individual PAHs detected in our study are similar to those reported by other researchers, particularly for native species.

With respect to *E. complanata*, the presence of high concentrations of certain PAHs in tissues after only three weeks' exposure indicates an ability to accumulate these compounds quite rapidly from its environment. It also suggests that this species lacks the necessary mixed function oxidase (MFO) enzymes to metabolize such contaminants. While this would seem to be the case for most bivalves, the issue is not yet completely resolved. For example, Vandermeulen & Penrose (1978) could detect no induction of aryl hydrocarbon hydroxylase (AHH) or N-dimethylase activity in the marine species *Mya arenaria, Mytilus edulis* or *Ostrea edulis* exposed to oils for both short (4 day) or long (6 years) periods in the field. Similarly, Livingstone *et al.* (1985) found no increase in the activity of B(a)P hydroxylase (an AHH) in *M. edulis* exposed to diesel oil for eight days, but detected elevated activity of the cytochrome P-450 monooxygenase system. In contrast, B(a)P hydroxylase activity was found in *Mercenaria mercenaria* exposed to B(a)P, the greatest activity being in the digestive gland (Giam *et al.*, 1987). Preliminary tests have not detected the presence of AHH in *Elliptio complanata* (D. Rokosh, OME, pers. comm., Dec., 1988). Although lack of such enzymes in an organism may protect it from exposure to carcinogenic PAH metabolites, it may have adverse effects on higher trophic levels possessing such toxicogenic/detoxification systems, since they would be exposed to higher concentrations of the procarcinogenic parent compounds if they are not metabolized by their prey.

3.5. Sources of PAHs to mussels

PAHs such as N, F, Ph, An, Ft, P, B(e)P, and Per were present at low levels in mussels exposed at stations upstream of dischargers as well as in mussels from Balsam Lake prior to their exposure (Table 5). This is suggestive of a general background source of a more diffuse nature. In fact, PAHs have been detected in both air (vapour and particulate phases) and precipitation samples from the Great Lakes basin (Eisenreich *et al.*, 1981) and atmospheric input appears to be a major source of PAHs to the Great Lakes (Eadie, 1984). Eisenreich *et al.* (1981) estimated the atmospheric fluxes of Ph, An, P, B(a)An, B(a)P, and Per to Lake Superior at 4.8, 4.8, 8.3, 4.1, 7.9, and 4.8 tonnes y^{-1}, respectively.

Nevertheless, the higher total PAH concentrations in both sediments and mussels along the Canadian shoreline and the significantly higher concentrations of certain PAH compounds near Algoma Steel discharges suggest the presence of additional ongoing sources, or of greater biological availability in these areas of the St. Marys River.

Sediments can be an important source of contaminants to benthic organisms. However, the magnitude of this contribution not only varies with the species and its life habits (Eadie *et al.*, 1983), but also depends on the degree of sediment contamination, sediment particle size distribution, and organic content (Eadie *et al.*, 1982b) as well as the particular compound in question (Eadie *et al.*, 1983; Roesijadi *et al.*, 1978).

Statistical analysis (one-way ANOVA; Tukeys

Table 7. Correlation matrix of interrelationships between polycyclic aromatic hydrocarbon concentrations in sediments and mussels.

Sediment	Mussel																	
	N	Acy	Ac	F	Ph	An	Ft	P	C/B(a)An	B(b/k)Ft	B(a)P	IP	DB(a,h)An	B(g,h,i)P	B(e)P	Per	Bt	DBt
N	.260	.552	.553	.157	.635	.156	.579	.575	.786	.012	.464	.211	.333	.274	.903	.667	.092	.637
Acy	.374	.293	.273	−.041	.377	−.052	.356	.363	.519	.200	.567	.138	.326	.327	.657	.377	.222	.422
Ac	.187	.282	.626	.123	.452	.219	.437	.476	.713	.110	.593	−.174	−.096	−.088	.602	.460	.168	.622
F	.326	.281	.488	.111	.421	.074	.355	.348	.566	.287	.552	.016	.105	−.004	.654	.428	.084	.466
Ph	.350	.301	.415	.000	.406	.120	.354	.382	.625	.158	.533	−.016	.117	.121	.691	.487	.291	.542
An	.176	.423	.436	.133	.514	.018	.422	.416	.668	.223	.536	.094	.188	.184	.755	.588	.011	.591
Ft	.420	.202	.367	−.046	.329	.159	.284	.333	.578	.116	.533	−.086	.016	.038	.600	.431	.431	.542
P	.420	.202	.367	−.046	.329	.159	.284	.333	.578	.116	.533	−.086	.016	.038	.600	.431	.431	.542
C/B(a)An	.434	.087	.252	−.175	.133	.123	.137	.193	.430	.158	.404	−.141	.047	.017	.460	.305	.512	.388
B(b/k)Ft	.420	.116	.236	−.297	.063	.045	.109	.165	.414	.250	.404	−.062	.047	.058	.446	.263	.512	.263
B(a)P	.420	.116	.236	−.297	.063	.045	.109	.165	.414	.250	.404	−.062	−.047	−.058	.446	.263	.512	.263
IP	.416	.072	.281	−.223	.113	.086	.127	.211	.510	.152	.536	−.102	−.134	−.084	.381	.354	.574	.465
DB(ah)An	.471	−.140	.073	−.159	.007	−.030	.036	.109	.307	.066	.479	−.121	−.202	−.129	.196	.188	.530	.470
B(ghi)Per	.437	.065	.235	−.194	.127	.111	.141	.232	.503	.053	.053	.536	−.094	−.059	.360	.352	.644	.511
B(e)P	.420	.116	.236	−.297	.063	.045	.109	.165	.414	.250	.404	−.062	.047	.058	.446	.263	.512	.263
Per	.371	.177	.281	−.297	.091	.020	.151	.200	.461	.274	.404	−.023	.094	.096	.495	.298	.442	.263
Bt	.329	.352	.630	.126	.512	.130	.471	.490	.746	.113	.632	.125	.092	−.044	.682	.531	.124	.612
DBt	.440	.106	.302	.249	.384	.059	.224	.205	.379	.273	.568	−.012	−.029	−.151	.497	.370	.123	.504

Underlined values are significantly different at the 95% confidence level ($\alpha = 0.05$; $r = 0.671$, 10 d.f.) Abbreviations as per Table 1.

Multiple Range Test) showed that overall, there was no significant difference ($\alpha = 0.05$) between the concentrations of individual PAHs in mussels exposed to sediments or only to water at stations near or downstream of point sources (Stns. 115, 117, 167 and 107). There was significant interaction ($\alpha = 0.05$) for F and B(e)P and this seemed related to Station 167. This may be due to incomplete vertical mixing at this station which is located below an Algoma Steel discharge to the power plant headrace.

Correlation analysis performed on $\log_e$-transformed data for the PAH compounds common to both sediments and mussels (bottom exposure) at the 12 coincident stations showed that there were no significant correlations ($\alpha = 0.05$) between concentrations of the same compound in the two media. However, there were significant correlations between: C/B(a)An in mussels and N and Bt in sediments; and between B(e)P in mussels and N, Ph, An and Bt in sediments (Table 7).

Mussel-sediment concentration factors (dry weight basis) were usually < 1 for all compounds at all stations (range: < 0.0001–0.62, Table 8). A similarly low range of values was obtained for Ph, C, B(a)P, and DMB(a)An in *Macoma inquinata* exposed to detritus (Roesijadi *et al.*, 1978), for N, Ph, Ft, P, C, and B(a)An in caged *Crassostrea virginica* relative to creosote-contaminated sediments (Elder & Dresler, 1988) and generally also for Ph, F, P, B(a)An, B(e)P in *E. complanata/L. radiata* relative to sediment from northern Lake George in New York State (Heit

Table 8. Comparison of bivalve-sediment concentration factors and partition coefficients.

Compound	Concentration factor (dry wt)			Partition coefficient	
	(a)	(b)	(c)	$\log_{10}K_{OC}$	$\log_{10}K_{OW}$
Naphthalene	0.02 –8.96			2.81–2.82[h]	3.35[f], 3.36[e], 3.59[d]
Acenaphthylene	< 0.007 – ≥ 1.88			3.31[h]	3.96[g]
Acenaphthene	< 0.005 –0.27			3.32[h]	3.92[f]
Fluorene	< 0.0009–0.21			3.48–3.49[h]	4.18[f]
Phenanthrene	< 0.0001–0.42	< 0.007–0.4	0.20	3.62[h]	4.46[d], 4.57[f]
Anthracene	< 0.003 –0.42			4.38–4.45[h]	4.34[i], 4.45[e], 4.54[f]
Fluoranthene	0.008 –0.38	< 0.006–2.3		4.02[h]	4.30[g], 5.22[f]
Pyrene	0.0007–0.30	< 0.007–3.0		4.15[h]	4.88[i], 4.90[d], 5.18[f]
Chrysene			0.04	5.25–5.28[h]	5.48[g], 5.79[f]
Benzo(a)anthracene	< 0.0001–0.03	< 0.33		4.75[h]	5.61[g]
Benzo(b/k)fluoranthene	< 0.0002–0.62			5.19–5.34[h]	5.35[g]
Benzo(j)fluoranthene	0(ND)			5.07[h]	5.35[g]
Benzo(e)pyrene	0.0007–0.31	< 0.62 –19		4.96[h]	5.90[g]
Perylene	0.001 –1.25			5.51[h]	5.27[e]
Dimethylbenz(a) anthracene	0(ND)		0.06	4.33[h]	6.49[g], 6.50[f]
Benzo(a)pyrene	< 0.0006–1.25	< 0.33	0.09	5.18[h]	5.98[g], 6.06[f]
Indeno(1,2,3-c,d)-pyrene	< 0.0006–1.25			5.69[h]	5.70[g]
Dibenzo(a,h)-anthracene	< 0.001 –0.05			5.10[h]	6.50[e], 7.19[f]
Benzo(g,h,i)perylene	< 0.001 – ≥ 0.62			5.61[h]	6.25[g]
Quinoline	0(ND) – < 0.10			1.01[h]	2.03–2.06[l]
Carbazole	< 0.0002 – < 0.08				3.29[l]
Acridine	< 0.0003 – < 0.04			2.19–3.41[j], 4.22[j]	3.30[f], 3.40[m]
Benzo(a)acridine	0(ND) – < 0.02				4.45[l]
Benzothiophene	0.0003 – ≥ 3.12			2.51[h]	3.10[k]
Dibenzothiophene	0(ND) – ≥ 1.25			2.92–4.17[j], 4.05[j]	4.40[k]

Data sources: (a) This study: caged *Elliptio complanata*; mussel wet weight concentration data multiplied by 6.25 (Kauss & Hamdy, 1985) to convert to dry weight basis. (b) Heit *et al.* (1980); homogenate of native *E. complanata* & *L. radiata*. (c) Roesijadi *et al.* (1978); *Macoma inquinata* exposed for 7 days. (d) Abernethy & Mackay (1987). (e) Freitag *et al.* (1985). (f) Gobas *et al.* (1987). (g) Kamlet *et al.* (1988). (h) Kenaga & Goring (1980); using formula $\log_{10}K_{OC} = 3.64 - 0.55 \log_{10}S$ and solubility (S) data in Billington *et al.* (1988); Das (1983); Eadie *et al.* (1982a); Mackay & Shiu (1975); Vasillaros *et al.* (1982); Verschueren (1983); and Zachara *et al.* (1987). (i) Mackay (1982). (j) Sabljic (1987). (k) Vasillaros *et al.* (1982). (l) Verschueren (1983). (m) Zachara *et al.* (1987).

Notes: 1) Concentration factors prefixed by '≥' or '<' indicate that there were no detectable concentrations in sediments or mussels, respectively and half the detection limits (see Tables 3 and 4) were used.

2) ND = not detected.

et al., 1980). In our study, concentration factors for N ranged up to almost 9 and for Bt ≥ 3 at Station 121. This may be due to the greater water solubility of these compounds, a decreased tendency to associate with organic matter in sediment (see '$\log K_{oc}$' in Table 8) and hence, greater biological availability. PAH concentrations in sediment pore water and on the fine fraction of sediments ($< 62\ \mu m$ dia.) can be much higher than in overlying water and in bulk sediments (Eadie *et al.*, 1982b) and may therefore be important sources of PAHs to some benthic organisms. However, for *E. complanata*, such exposure routes would tend to further decrease the concentration factors. Consequently, our data indicate that sediment-associated PAHs had only limited bioavailability to *E. complanata* and that the major exposure route was via the water filtered by these organisms and hence, from discharges to the river.

Due to the low water solubility of higher molecular weight PAHs and their correspondingly high organic carbon partition coefficients (K_{oc}), they will tend to partition out onto fine particulate matter (solids) suspended in the water column. It might therefore be argued that particulate-associated PAHs are the major source of the elevated concentrations in mussels at certain stations. However, concentrations of suspended solids during this study were mostly below 10 mg l^{-1} (Table 2), even near point sources. At these concentrations, most (70–100%) of the PAHs in the water column would be in the dissolved phase (Eadie, 1984) and would therefore accumulate in the lipids of aquatic organisms through equilibrium partitioning as a result of their high octanol-water partition coefficients (see $\log K_{ow}$ in Table 8).

Similarly, leaching of PAHs from the coal particles or dust detected at Stations 115, 117 and 9A is not likely to have contributed to mussel body burdens. Bender *et al.* (1987) were unable to detect any elevation of PAHs above background in estuarine water after contact with fine coal dust. However, since the mussels in our study were not allowed to clear their guts prior to analysis, coal dust in the water filtered by these organisms may have contributed to elevated tissue levels, but only if present at high concentrations, i.e., > 1 mg l^{-1} (Bender *et al.*, 1987).

The higher concentrations of many PAHs in mussels exposed in the Algoma Slip are not necessarily reflective of higher loadings relative to other areas, but are probably a function of limited initial dilution and hence, higher water concentrations of these contaminants. Flow rates of the two creeks and two Algoma Steel blast furnace sewers discharging to the slip average a total of ~ 3.1 m^3 s^{-1} (OME, 1986 unpubl. data). In contrast, lower concentrations of many PAHs were found in mussels at Station 29, just downstream of the major discharge of Algoma Steel, the Terminal Basins (see Fig. 1). This unexpected result may be due to two phenomena: (i) a high initial nearshore dilution of this discharge (averaging 3.9 m^3 s^{-1} in 1985) by cleaner water from the Great Lakes Power Corp. tailrace (~ 1000 m^3 s^{-1}) and incomplete lateral mixing (McCorquodale & Yuen, 1987; McCorquodale, pers. comm., Dec., 1988); and (ii) incomplete vertical mixing of the thermally buoyant plume until it moves further downstream (Abdel-Gawad, 1985). The higher concentrations observed at downstream Stations 9C, 107 and 27C suggests that these mussels were exposed to a more homogeneous plume, or that additional PAH inputs to the waterfront, such as urban runoff (Marsalek & Ng, 1987), resulting from local atmospheric inputs (Boom & Marsalek, 1988) are also important. However, there were insufficient monitoring stations in our study to permit an evaluation of the contribution of individual storm sewers to the Sault Ste. Marie, Ontario nearshore.

4. Summary

Sampling in the St. Marys River during 1985 identified the presence of up to 25 PAH compounds in surficial sediments. As many as 18 of these PAHs were also accumulated by caged mussels during a three-week exposure period at the same locations. The highest concentrations of many of these compounds were detected in both

media in the Sault Ste. Marie area along the Canadian shore in the Algoma Slip, which receives effluent from Algoma Steel Corp., and in sediments along the U.S. shore, immediately downstream of the Edison Sault Electric Co. Canal discharge. At and downstream of major discharges, from 23 to 63 percent of the total PAHs concentrations in sediments and from 6 to 27 percent in mussels were comprised of compounds with mutagenic and/or carcinogenic properties. Sediments from 58 percent of the stations sampled contained concentrations of B(a)P above the proposed IJC objective of 1 mg kg^{-1}. However, levels of this compound in mussels were well below the proposed IJC objective of 1 000 $\mu g\ kg^{-1}$ for the protection of higher trophic levels.

The predominance of high molecular weight compounds such as Ph, Ft, and P in both sediments and mussel tissues at most stations indicates that the major source of PAHs in the St. Marys River is the high temperature combustion of fossil fuels, such as from coal coking. However, the presence of lower molecular weight PAHs (as well as N- and S-containing PAHs in sediments) in the Algoma Slip and at the outlet of the Edison Sault Canal also indicates spills of fossil fuels such as coal and additionally, coke oven by-products in the slip. Therefore, in the Algoma Slip, elevated PAH concentrations likely result from a combination of: (i) contamination of cooling water sewers discharging to the slip with process water from blast furnace operations; (ii) previous spills to the two creeks discharging to the Slip; and iii) input from coal piles in the vicinity of the Slip, either via wind or run-off.

The ability of the mussel, *Elliptio complanta*, to accumulate significantly elevated concentrations of compounds in three weeks indicates that it is a useful biomonitor for detecting spatial differences in the biological availability of PAHs in freshwater aquatic ecosystems. Present evidence suggests that this is due to the absence of inducible metabolic enzymes in this organism.

Although mussel tissues indicated the presence of some PAHs even upstream of point sources (i.e., at background levels), the significantly higher concentrations in the Sault Ste. Marie, Ontario area suggest ongoing inputs from Algoma Steel, or greater biological availability in these areas as a result of past losses. However, statistical analysis showed that PAH concentrations in sediments had no significant effect, or correlation with, levels in mussels, indicating that exposure is primarily via water for this filter-feeding organism and therefore due to ongoing inputs.

Although *E. complanata* was used as an introduced (caged) organism in this study, the fact that it indicated the presence of PAH compounds in the river that can potentially be accumulated by native benthic species poses some concern and merits further work to determine the present distribution, concentration and effect of these compounds in indigenous biota. It also indicates the necessity to reduce inputs of PAHs to the St. Marys River ecosystem.

In this regard, as part of MISA, an Effluent Monitoring Regulation for the Ontario iron and steel sector was served in draft form by OME for a 21-day public review on February 6, 1989. This draft regulation is a step towards the virtual elimination of persistent toxic chemicals such as PAHs from discharges. The detailed monitoring results from this regulation will be used to set stringent discharge limits for the iron and steel mills.

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