Water Qual. Res. J. Can. 2010 · Volume 45, No. 1, 69–80
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Contaminant Trends in Suspended Sediments in the Detroit River-Lake St. Clair-St. Clair River Corridor, 2000 to 2004

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Suspended sediments from the Detroit River-Lake St. Clair-St. Clair River corridor over the period of 2000 to 2004 were analyzed to examine the spatial distributions of contaminants including polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and mercury. Contaminant spatial distributions were similar over the five-year study period, but concentrations varied considerably among sampling locations. Concentrations of PCBs ranged from 22 to 1,200 ng/g (dry weight) in 2004, and from 10 to 2,700 ng/g (dry weight) in 2000; concentrations of PAHs ranged from 640 to 52,000 ng/g (dry weight) in 2004, and from 240 to 82,000 ng/g (dry weight) in 2000; and concentrations of mercury ranged from 0.063 to 0.478 mg/kg (dry weight) in 2004, and from 0.060 to 0.514 mg/kg (dry weight) in 2002. The highest PCB and PAH concentrations were associated with suspended sediments in the lower and middle reaches of the Detroit River in the area of the Trenton Channel, and the outflow of the Rouge River. The spatial distributions of mercury were more consistent throughout the entire corridor, indicating the presence of sources in both the lower reaches of the Detroit River and the upper reaches of the St. Clair River. Both the Trenton Channel area of the Detroit River and the upper reaches of the St. Clair River are characterized by heavy historical industrial activity, including steel manufacturing and chlor-alkali production.

Key words: **Detroit River-Lake St. Clair-St. Clair River corridor, spatial distribution, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, mercury**

Introduction

The Detroit River-Lake St. Clair-St. Clair River corridor is a major connecting channel system in the Great Lakes-St. Lawrence Seaway. This waterway is a vitally important binational resource shared by the United States and Canada. Water resources in this binational corridor are heavily used by millions of residents in Michigan and Ontario for recreational boating and angling, navigation, and drinking water. The corridor supports multimillion dollar shipping, manufacturing, mining, and fishing industries.

The corridor has been subjected to loadings of persistent toxics from a variety of sources, including over ten thousand commercial and industrial discharges, sewage treatment plants and combined sewer overflows, and urban runoff (Michigan Department of Environmental Quality 1996). High concentrations of contaminants including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/PCDFs) have been detected both in sediments and biota (Furlong et al. 1988; Kannan et al. 2001; Marvin et al. 2002). Chlorobenzenes, chlorophenols, organochlorines, and a host of heavy metals have also been determined in surface water and fish in the corridor (Kaiser et al. 1985; Gewurtz et al. 2003; Marvin et al. 2004). The Trenton Channel area of the lower Detroit River contains areas of sediment contaminated by PAHs, PCBs, and heavy metals due to historic industrial activities. Kannan et al. (2001), Metcalfe et al. (2000), and Furlong et al. (1988) reported Trenton Channel sediment concentrations of 44,000, 129,700, and 130,000 ng/g, respectively, for PAHs, and concentrations of 25,000, 8,018, and 14,000 ng/g, respectively, for PCBs. Drouillard et al. (2006) published the results of a comprehensive survey of contaminants in Detroit River sediments conducted in 1999; the study found wide-spread contamination of PCBs and PAHs in the Trenton Channel, and the authors concluded that contaminated sediments from the area have the potential to impact environmental quality in western Lake Erie.

The Detroit and St. Clair rivers have been designated as Areas of Concern (AOCs) by the International Joint Commission (Great Lakes Information Network 2009). Currently there are impairments of nine beneficial uses in the corridor (Michigan Department of Environmental Quality 1996), including contamination of fish tissues due to elevated levels of five pollutants (mercury, mirex, chlordane, PCDDs/PCDFs, and PCBs). Most of the advisories (48%) have been issued for PCBs. Between 1993 and 2001, a total of 10 sediment remediation projects were undertaken in the Great Lakes; two were conducted in the Detroit River-western Lake Erie basin. Consequently, the total estimated mass of PCBs removed in the 10 projects was 198 tons (Hartig et al. 2004). However, historically-contaminated sediments continue to be sources of contaminants. The Detroit River watershed is reportedly a dominant source of

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contaminants to the western basin of Lake Erie (Oliver and Bourbonniere 1985; Kelly et al. 1991; Carter and Hites 1992). Environment Canada routinely measures the occurrence and spatial distribution of toxic substances in AOCs to further understand the role human activities play in releasing these compounds to the environment, and to provide information on the transport and fate of contaminants in aquatic systems. A program was initiated in 1997 to investigate contaminants associated with suspended sediments in the western Lake Erie-Detroit River-Lake St. Clair-St. Clair River corridor. The goals of this program were to assess the relative importance of sources of contaminants both to the corridor and downstream in western Lake Erie, and to assess the effectiveness of remedial measures to address areas of historically-contaminated sediment. In this paper, we present an overview of the spatial distributions of contaminants including PCBs, PAHs, and mercury in suspended sediments in the corridor over the period of 2000 to 2004.

Materials and Methods

Sample Collection

Suspended sediment samples accumulated over one-month periods from May to October using single-point sediment trap moorings (Fig. 1) at stations ranging from the outflow of the Detroit River at Lake Erie to southern Lake Huron (Fig. 2 to 4). These sediment trap assemblies were modified from a design previously used for the study of the downflux and composition of particulate matter in the Great Lakes (Charlton et al. 1981; Charlton 1983). The key parameter in the design of the traps is the aspect ratio, defined as the ratio of the internal diameter of the trap tube to the length. The features of this apparatus were described in detail previously (Marvin et al. 2002). The moorings were refurbished monthly, and accumulated material deposited in the traps was removed, transferred to Nalgene containers, and refrigerated. Samples were returned to the laboratory and frozen. Samples collected over the period of 2000 to 2003 were characterized according to particle size and percent total organic carbon (TOC) (Table 1).

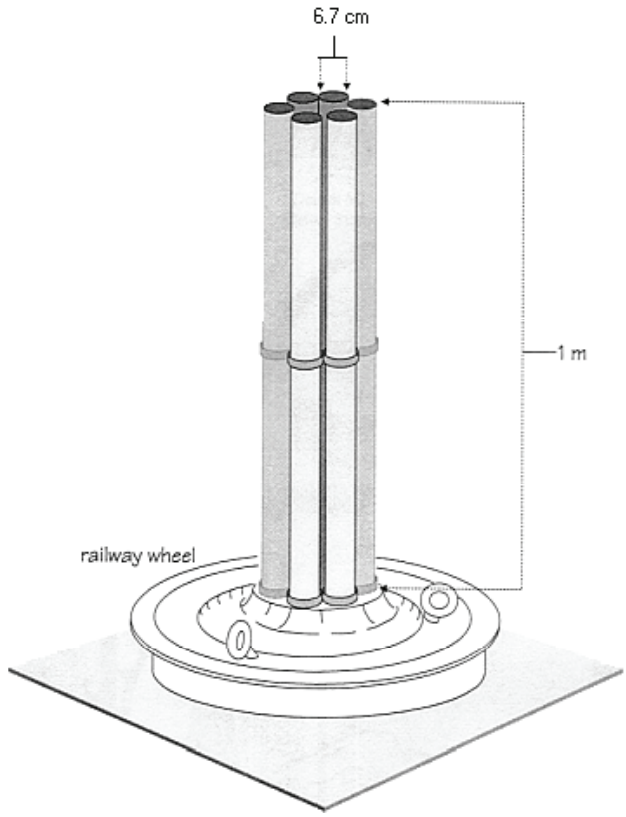

Fig. 1. Schematic of a single-point sediment trap mooring of the type deployed at stations in the Detroit River in 2000 to 2004.

Extraction and Fractionation

Samples (~5 g) were air-dried and ground with a mortar-pestle, and homogenized. Samples were then spiked with a laboratory surrogate standard containing naphthalene-d_8, fluorene-d_{10}, pyrene-d_{10}, benzo[a]pyrene-d_{12}, PCB 30, and PCB 204. Method blanks were carried through the complete sample preparation and analysis procedures.

Samples were extracted using an ASE (accelerated solvent extraction) with dichloromethane followed by an open-column silica gel cleanup procedure. These procedures have been described elsewhere in detail (National Laboratory for Environmental Testing 1997).

TABLE 1. Percent TOC and particle size characterization of suspended sediments collected in the Detroit River in July 2000 to 2003

Station	*TOC (%)*	*Sand (%)*	*Silt (%)*	*Clay (%)*
1167	2.07 ± 0.60	4 ± 2.9	67 ± 1.1	29 ± 4.0
1175	0.61 ± 0.10	52 ± 5.6	31 ± 6.7	18 ± 3.9
1172	0.63 ± 0.0	57 ± 1.5	26 ± 2.0	17 ± 0.40
1165	0.62 ± 0.30	57 ± 3.9	36 ± 9.1	13 ± 1.2
510	1.13	0	70	30
1168	1.78 ± 0.70	8 ± 4.2	57 ± 6.2	35 ± 2.5
1161	1.27 ± 0.80	6 ± 3.9	61 ± 1.6	33 ± 2.9
1159	1.55 ± 1.1	8 ± 3.1	61 ± 5.7	30 ± 3.0
1156	0.79 ± 0.50	1 ± 1.0	61 ± 8.3	38 ± 8.2
1157	1.03 ± 0.60	3 ± 3.9	65 ± 8.1	32 ± 6.8

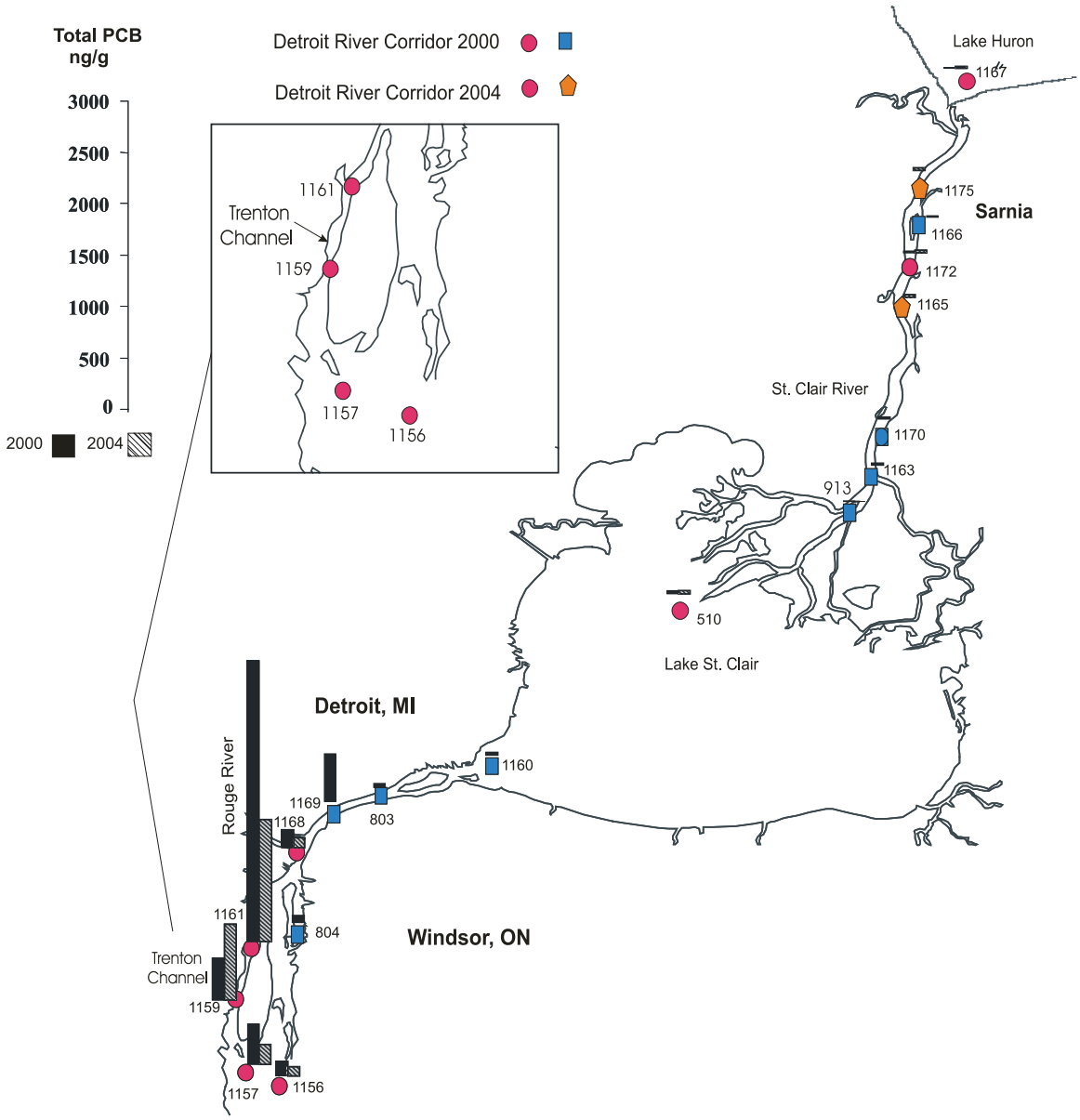

Fig. 2. Spatial distribution of PCBs in suspended sediments collected in July 2000 and July 2004 in the Detroit River-Lake St. Clair-St. Clair River corridor.

The column contained anhydrous sodium sulphate and activated silica gel. The column was prewashed with pentane, and then eluted with pentane to collect the PCBs and some low-molecular weight PAHs (Fraction A), followed by elution with of 1:1 (vol/vol) pentane in dichloromethane to collect organochlorines and the remaining PAHs (Fraction B). Fraction volumes were then reduced by rotary evaporation, treated with mercury to remove sulphur, solvent exchanged to isooctane, and transferred to amber vials and refrigerated.

Analyses

The total PAH concentration was determined as the sum of the following 20 individual compounds: naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[1,2,3-c,d]pyrene, dibenzo[a,h]anthracene, and benzo[g,h,i] perylene. The estimated detection limit for PAHs was 0.06 pg/µL (signal to noise ratio = 3). Spike recoveries, exclusive of naphthalene-d_8, were typically greater than 80%.

PAHs were quantified using a Hewlett-Packard Series II 5890 Gas Chromatograph (GC) (Agilent) with a 30-m HP-5MS column (0.25-mm internal diameter, 0.25-µm film thickness, J&W Scientific), and a Hewlett-Packard 5971A Mass Selective Detector operated in selected ion

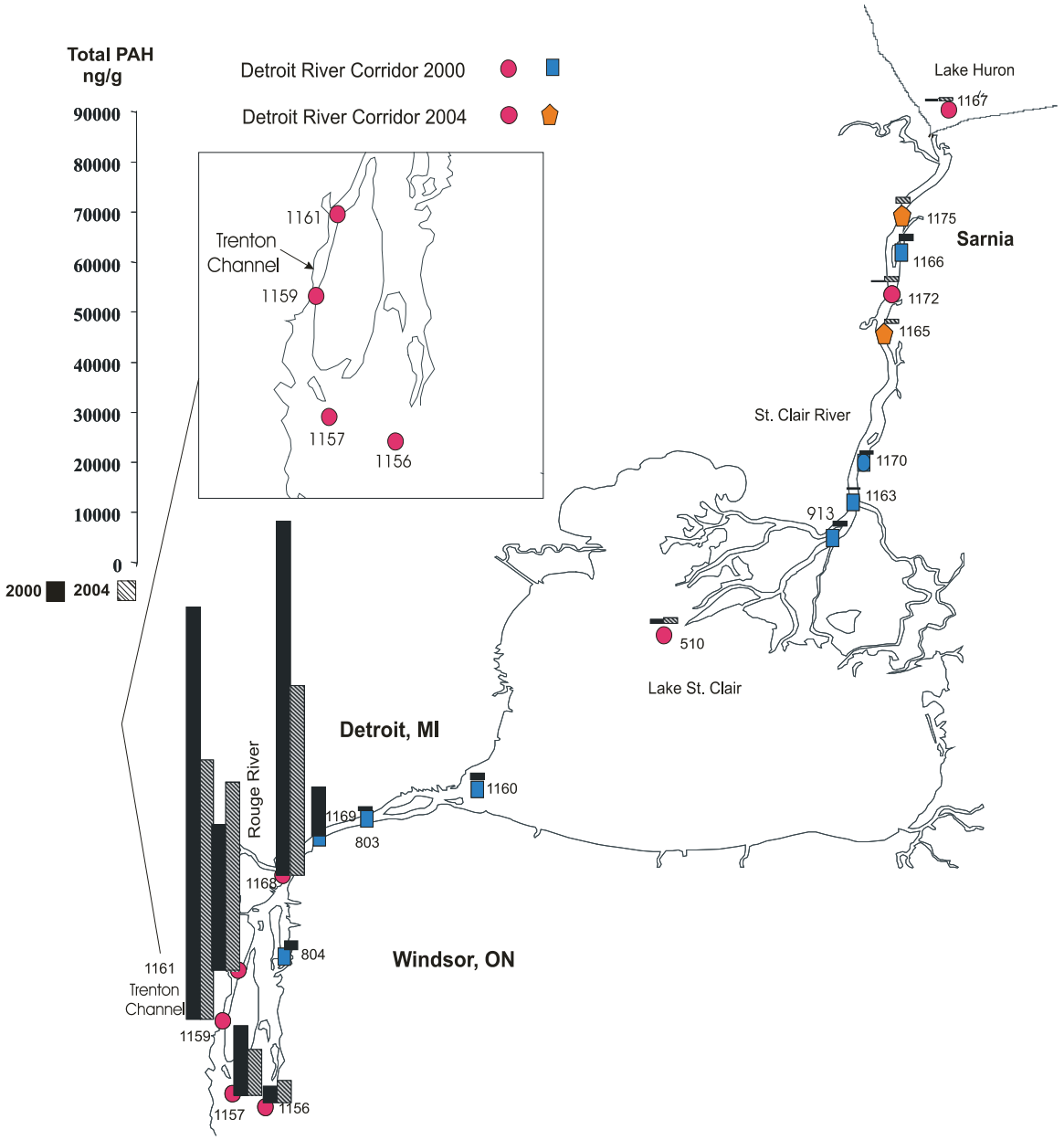

Fig. 3. Spatial distribution of total PAH concentrations (ng/g dry weight) in Detroit River-Lake St. Clair-St. Clair River corridor suspended sediments in July 2000 and July 2004.

monitoring (SIM) mode. GC/MS analyses were performed in the positive ion electron impact mode (EI^+) with helium as the carrier gas at a flow rate of 1.0 mL/min. Samples were injected using an on-column injector. The temperature program was as follows: initial temperature 70°C; 70 to 160°C at 10°C/min; 160 to 300°C at 5°C/min; hold for 15 min. The instrument equilibration time was 3 min. The GC column performance was monitored every 4 to 5 samples using a calibration solution containing PAHs at concentrations of roughly 1 ng/µL.

PCBs were analyzed using a Hewlett-Packard Series II 5890 GC equipped with dual electron capture detectors, hydrogen as the carrier gas at a flow rate of 1.0 mL/min, splitless injection, and dual columns (30 m, 0.25-mm internal diameter, 0.25-µm stationary phase DB-5MS; and 30 m, 0.25-mm internal diameter, 0.25-µm stationary phase DB-1, J&W Scientific). The temperature program was as follows: initial temperature 70°C; 70 to 150°C at 15°C/min; 150 to 270°C at 2°C/min; 270 to 300°C at 20°C/min; hold for 5 min. Instrument equilibration time was 3 min. Instrument calibration was performed using five levels of a mixed 132-congener PCB standard (4 to 6 pg/µL, 40 to 60 pg/µL, 80 to 120 pg/µL, 200 to 300 pg/µL, and 400 to 600 pg/µL). Method blanks and standard reference materials were processed with each set of 10 field samples.

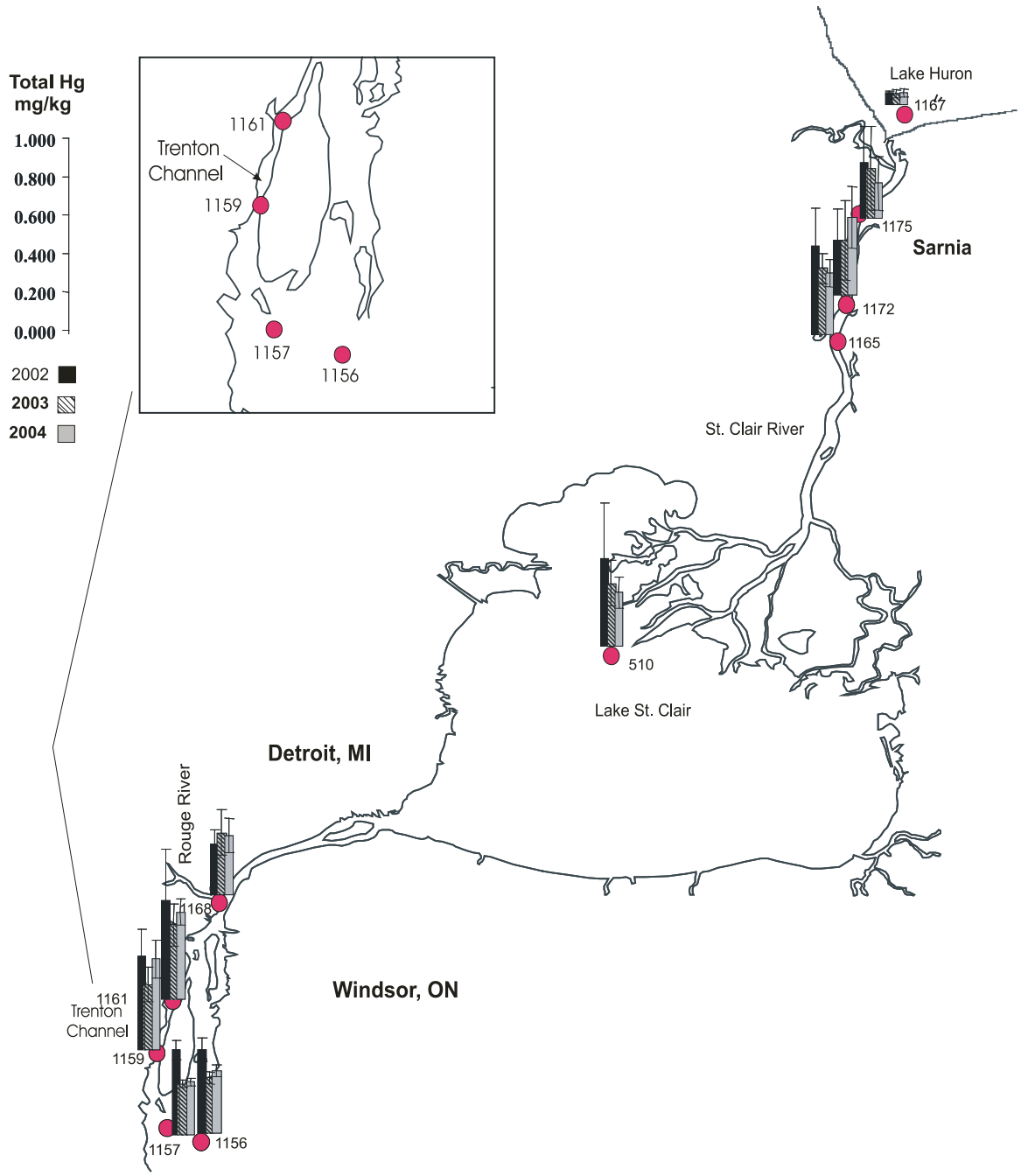

Fig. 4. Spatial distributions of mercury (mg/kg dry weight) represented by annual mean concentrations in Detroit River-Lake St. Clair-St. Clair River corridor suspended sediments over the period of 2002 to 2004. Error bars represent ±4 standard deviations of the annual means.

Total mercury was determined by digestion with hot nitric acid and hydrochloric acid followed by cold vapour atomic absorption spectrometry according to standard United States Environmental Protection Agency methods (United States Environmental Protection Agency 1981).

Samples for particle size analysis were weighed (5 to 8 g) and mixed with sodium metaphosphate for 15 minutes. Sand/gravel content was calculated by passing sediments through a nest of sieves from 3.5-mm down to 0.063-mm openings. Silt/clay ranging from 0.063 mm down to 0.00024 mm was analyzed by a sedigraph analyzer. TOC was calculated by summing percentages of organic carbon and inorganic carbon. Analyses were performed using a two-temperature dry combustion method. Sediments were dried in the oven for a minimum of 2 hours and then weighed to 0.5000 g for both organic and inorganic carbon content analyses. Organic carbon was analyzed by burning samples at 500°C for 250 seconds and then recording the percentage of carbon. Inorganic carbon was analyzed using the same sample

by burning at 1,370°C for 60 seconds and recording the percentage of carbon.

Results and Discussion

Suspended Sediment Characterization

Particle size distributions and percent TOC of suspended sediments in the corridor generally remained consistent over the period of the study (Table 1). Data presented for different contaminant classes represent different sampling intervals; for PCBs and PAHs, data for 2000 and 2004 represent a single monthly sampling interval (July). July samples were selected due to the propensity for severe summer storms to result in considerable runoff from the watershed and significant resuspension and transport downstream of contaminated sediments. Data presented for mercury correspond to annual means resulting from analysis of all samples collected over the period of 2002 to 2004. Therefore, mercury is the only contaminant class presented in this study for which any statistical analysis of interseasonal or interannual trends can be presented.

Spatial Distribution of PCBs

Previous studies of Detroit River sediments reported PCB concentrations ranging from 35 to 14,000 ng/g (Kaiser et al. 1985; Furlong et al. 1988; Marvin et al. 2002). PCBs were found in all suspended sediment samples with concentrations in 2004 ranging from 21 to 1,200 ng/g (dry weight), and from 10 to 2,800 ng/g in 2000. Tables 2 and 3 show homologue (sum of Cl_2 to Cl_{10} homologues) and total PCB concentrations in the Detroit River-Lake St. Clair-St. Clair River corridor in July 2004 and July 2000, respectively. Spatial distributions of PCBs in corridor suspended sediments were similar among the two years (Fig. 2). Sum PCB concentrations increased (8- to 20-fold) from upstream to downstream locations along the U.S. side of the Detroit River in both 2000 and 2004. A similar, but less substantial (3-fold), trend was observed along the Canadian side of the river. These results were similar to the findings of Drouillard et al. (2006) and indicated the presence of multiple inputs of PCBs on the U.S. side of the river.

The highest concentrations of PCBs throughout the entire corridor in both 2000 and 2004 were associated with stations in the Trenton Channel in the lower reaches of the Detroit River; this area is characterized by large areas of sediment severely contaminated as a result of historical industrial activities. It has been reported that the Trenton Channel contains the greatest volume of contaminated sediment within the Detroit River-Lake St. Clair-St. Clair River corridor (Michigan Department of Environmental Quality 1996). The highest concentrations of PCBs were observed at station 1161 in both 2000 and 2004; this station is located in the upper Trenton Channel near the mouth of Monguagon Creek, an area of intensive historical industrial activity (Fig. 2). Another station further downstream in the lower Trenton Channel (station 1159) also exhibited relatively high PCB concentrations.

Station 1169 was sampled in 2000 and exhibited a total annual mean PCB concentration of 675 ng/g dry weight (range of 180 to 1,125 ng/g over a seven-month period). This station was located downstream of Connors Creek, which was identified as a potential source of PCBs to the upper Detroit River (Kannan et al. 2001). During 2003 to 2004, contaminated sediments in Connors Creek were removed during remediation activities; it was estimated that 302 kg of PCBs were removed from Connors Creek (Hartig et al. 2004). Follow-up sampling of this area is ongoing.

The PCB concentrations at station 1168 near the mouth of the Rouge River were roughly 10- to 15-fold lower than at station 1161 (Tables 2 and 3). The Rouge River is one of the major tributaries draining from the U.S. shoreline into the Detroit River, and more than 50% of the land use in the basin is residential, commercial, and industrial (Michigan Department of Environmental Quality 1996). It has been reported that PCBs, PAHs, PCDDs/PCDFs, PCNs, and other organic compounds are prevalent in sediments of the Rouge River basin (Hamdy and Post 1985; Kannan et al. 2001). The typically lower PCB concentrations at upstream sites, compared with sites in the Trenton Channel, indicate that a substantial portion of the total PCB loading to the western basin of Lake Erie

TABLE 2. Individual homologue and total PCB concentrations (ng/g dry weight) in Detroit River-Lake St. Clair-St. Clair River corridor suspended sediments collected in July 2004

Number of chlorines	*Homologue*	*Stations (2004)*									
		510	*1156*	*1157*	*1159*	*1161*	*1165*	*1167*	*1168*	*1172*	*1175*
3	Trichlorobiphenyl	3.0	9.2	14	26	46	1.3	2.5	6.4	1.1	1.3
4	Tetrachlorobiphenyl	8.0	36	59	130	190	4.9	4.7	9.6	2.2	5.8
5	Pentachlorobiphenyl	7.8	19	36	140	320	3.6	6.7	9.4	2.6	5.8
6	Hexachlorobiphenyl	9.8	15	41	98	230	12	2.9	44	4.3	9.5
7	Heptachlorobiphenyl	0.40	6.7	27	235	300	0.16	2.6	22	10	1.8
8	Octachlorobiphenyl	2.0	1.9	6.4	110	86	1.3	1.6	4.9	0.66	0.27
9	Nonachlorobiphenyl	0.32	0.86	4.5	0	0	0.23	0.28	2.4	0.21	0.11
	TOTAL PCBs	33	89	190	735	1,185	23	22	99	22	25

TABLE 3. Individual homologue and total PCB concentrations (ng/g dry weight) in Detroit River-Lake St. Clair-St. Clair River corridor suspended sediments collected in July 2000

Number of chlorines	*Homologue*	*Stations (2000)*															
		510	*1156*	*1157*	*1159*	*1161*	*1167*	*1168*	*1172*	*803*	*804*	*913*	*1160*	*1163*	*1166*	*1169*	*1170*
3	Trichlorobiphenyl	3.7	8.7	41	11	120	2.3	7.9	0.72	5.3	6.5	2.3	2.4	2.2	2.6	69	1.5
4	Tetrachlorobiphenyl	18	34	130	130	700	3.6	20	7.1	13	26	5.2	12	9.5	5.9	160	9.5
5	Pentachlorobiphenyl	12	31	140	110	690	6.0	34	1.8	8.1	21	4.8	8.3	6.2	5.3	160	5.2
6	Hexachlorobiphenyl	2.9	23	84	110	320	2.2	34	5.4	5.8	8.1	2.0	2.0	1.8	3.4	120	1.3
7	Heptachlorobiphenyl	1.4	23	34	85	180	0.56	60	0.15	6.1	7.6	2.4	1.1	1.9	1.1	63	1.7
8	Octachlorobiphenyl	0.36	32	16	30	64	0.14	10	0.23	1.9	3.0	0.20	0.38	0.18	0.60	103	0.14
9	Nonachlorobiphenyl	0.02	11	3.1	2.9	3.1	0.01	1.4	ND[a]	0.38	0.56	0.03	0.07	0.01	0.14	0.84	0.02
	TOTAL PCBs	37	163	450	480	2100	15	170	15	40	72	17	27	22	19	675	19

[a] ND denotes not detected.

is the result of legacy sources associated primarily with historical industrial activities in the lower reaches of the Detroit River. These results are corroborated by those of Drouillard et al. (2006); although multiple sources of PAHs and PCBs were detected in the upper and middle reaches of the River along the U.S. shoreline, the greatest degree of sediment contamination was found within the Trenton Channel.

The influence of contaminated sediments in the Trenton Channel as a source of PCBs to western Lake Erie was also evidenced through the comparison of stations 1157 and 1156, which are located at the same latitude, but on opposite sides at the mouth of the Detroit River (Fig. 2). Station 1157 is influenced primarily by flow emanating from the Trenton Channel, while station 1156 is influenced primarily by the water flowing east of Grosse Ile. Drouillard et al. (2006) reported that high flow rates within the shipping channels segregate material originating from either side of the river. The PCB concentrations in both 2000 and 2004 were roughly two-fold higher at station 1157 compared with station 1156.

The PCB levels at sites in the upper reaches of the St. Clair River (stations 1165, 1172, and 1175) and in Lake St. Clair (station 510) were relatively low in comparison with the PCB levels measured in the Trenton Channel (Tables 2 and 3). The southern Lake Huron station exhibited the lowest concentrations of PCBs (15 to 20 ng/g). These relatively low PCB levels are typical of PCB concentrations in bottom sediments of southern Lake Huron, and provide an upstream reference value against which the downstream connecting channels can be assessed. These data indicate that industrial areas in the upper reaches of the St. Clair River do not represent substantial sources of PCBs to the corridor.

Spatial Distribution of PAHs

PAHs were detected in all suspended sediment samples analyzed; total PAH concentrations in the Detroit River-Lake St. Clair-St. Clair River corridor ranged from 640 to 52,000 ng/g dry weight in 2004, and from 240 to 82,000 ng/g dry weight in 2000 (Tables 4 and 5, Fig. 3). Sources of PAHs are primarily related to the combustion of fossil fuels and are predominant in areas of intense industrial activities. The spatial distributions shown in Fig. 3 reflect the urban and industrial land use patterns in the corridor (Michigan Department of Environmental Quality 1996). The total PAH concentrations measured in this study were within the range of those reported for bottom sediments collected in 1988 from the Trenton Channel (350 to 130,000 ng/g dry weight) (Furlong et al. 1988), and from the Detroit River (394 to 43,800 ng/g dry weight) (Kannan et al. 2001).

The comparison of PAH concentrations in 2004 at all ten study sites yielded a spatial pattern similar to that observed In 2000 (Fig. 3). The highest PAH concentrations were found in the Trenton Channel area

TABLE 4. PAH concentrations (ng/g dry weight) in Detroit River-Lake St. Clair-St. Clair River corridor suspended sediments collected in July 2004

	Stations (2004)									
	510	*1156*	*1157*	*1159*	*1161*	*1165*	*1167*	*1168*	*1172*	*1175*
Phenanthrene	220	120	300	2,318	1,838	91	153	3,200	140	110
Anthracene	6	32	87	729	529	10	3	840	24	13
Fluoranthene	94	370	700	4,327	3,591	87	59	4,400	98	100
Pyrene	96	330	660	3,962	3,201	80	46	3,800	98	97
Benz[a]anthracene	21	170	280	2,172	1,618	19	10	1,800	27	30
Chrysene	59	250	420	2,594	1,863	54	31	1,900	72	70
Benzo[b]fl + benzo[k]fl. [a]	193	1,200	2,700	12,816	8,977	150	122	8,200	200	180
Benzo[e]pyrene	93	480	1,000	4,980	3,488	101	55	3,100	150	150
Benzo[a]pyrene	65	470	1,000	6,833	4,522	59	37	4,500	92	100
Perylene	64	200	320	1,797	1,257	57	18	1,100	62	57
Indeno[1,2,3-cd]pyrene	60	300	680	4,025	2,507	40	40	2,300	59	47
Dibenz[a,h]anthracene	18	57	100	695	433	11	5	440	16	34
Benzo[ghi]perylene	106	400	850	4,618	3,868	89	64	2,600	120	150
phenanthrene/anthracene	37	4	3	3	3	9	45	4	6	8
Benzo[e]pyr./benzo[a]pyr. [b]	1	1	1	1	1	2	1	1	2	1
Total PAH (ng/g)	1,100	4,300	9,100	52,000	38,000	850	640	38,000	1,200	1,100

[a] Benzo[b]fluoranthene + benzo[k]fluoranthene.
[b] Benzo[e]pyrene/Benzo[a]pyrene.

of the lower Detroit River (stations 1159, 1161) and near the mouth of the Rouge River (station 1168, Fig. 3); PAH concentrations at these sites ranged from 38,000 to 82,000 ng/g. Comparison of PAH concentrations at the two stations at the outflow of the Detroit River to western Lake Erie (1156 and 1157) yielded results similar to those of PCBs in that concentrations were substantially higher on the west side of the river; PAH concentrations at station 1157 were roughly two- to four-fold higher than concentrations at station 1156 (Tables 4 and 5). The spatial distributions of PAHs and PCBs in the corridor were generally similar, except for station 1168. While PCB concentrations at this station were substantially lower than the downstream locations, PAH concentrations were typically similar to or higher than those of the Trenton Channel stations. Kannan et al. (2001) previously identified the Rouge River as a major source of PAHs to the Detroit River. More than 50% of land use in the Rouge River watershed is residential, commercial, or industrial. We attributed our observations to the fact that PAHs continue to be produced by a myriad of combustion sources, and are typically prevalent in sediments in proximity to highly industrialized areas. The magnitude of contamination at stations 1168, 1161, and 1159 indicate an additional contribution from resuspended PAH-contaminated bottom sediments in these areas; there are no apparent land-based activities or sources in this area that could account for the observed increased PAH contamination. However, this possibility cannot be entirely discounted.

The PAH concentrations in the upper reaches of the St. Clair River (stations 1165, 1172, and 1175) and in Lake St. Clair (station 510) were typically elevated, compared with the southern Lake Huron station (station 1167, Tables 4 and 5); total PAH concentrations in 2004 in the St. Clair River and Lake St. Clair were roughly two-fold higher compared with the southern Lake Huron station (Table 4). However, in 2000 total PAH concentrations were more similar among all of the Lake St. Clair, St. Clair River, and southern Lake Huron stations (Table 5). The upper reaches of the St. Clair River on the Canadian side are characterized by intensive urbanization and industrialization, including the presence of coal-fired power generating plants.

Comparison of PAH profiles among these sites was conducted to provide further information on local and/or regional sources. The ratios of phenanthrene/anthracene and benzo[e]pyrene/benzo[a]pyrene were roughly 45 and 1.5, respectively, in Lake Huron suspended sediments, and reflected the relative short half-life for the photolysis of anthracene and benzo[a]pyrene (Behymer and Hites 1985). We hypothesize that suspended sediments collected at the southern Lake Huron site would contain absorbed PAHs subjected to greater exposure to sunlight, compared with urbanized areas of the corridor such as the Detroit River, where the ratios of phenanthrene/anthracene and benzo[e]pyrene/benzo[a]pyrene were roughly 3.0 and 0.7. These results were similar to those reported by Furlong et al. (1988) for Trenton Channel sediment samples. Water quality data, including Secchi depth, conductivity, and turbidity (unpublished data), all indicate substantially greater water clarity, and presumably greater exposure to ultraviolet light in the water column, at the southern Lake Huron station compared with the stations in the rivers.

TABLE 5. PAH concentrations (ng/g dry weight) in Detroit River -Lake St. Clair-St. Clair River corridor suspended sediments collected in July 2000

	Stations (2000)															
	510	*1156*	*1157*	*1159*	*1161*	*1167*	*1168*	*1172*	*803*	*804*	*913*	*1160*	*1163*	*1166*	*1169*	*1170*
Phenanthrene + Anthracene	80	280	770	2,270	1,650	20	10,000	30	90	170	100	150	40	230	550	70
Fluoranthene	120	440	2,680	7,180	4,650	50	16,000	40	120	250	170	210	50	220	1,540	120
Pyrene	130	420	2,250	7,190	4,390	40	12,000	30	100	210	170	200	60	170	1,390	100
Benz[a]anthracene	40	270	1,120	5,020	3,060	10	6,100	10	30	120	50	80	20	80	760	40
Chrysene	90	360	1,250	4,110	3,160	30	5,100	30	80	190	100	140	40	140	960	70
Benzo[b]fl. + benzo[k]fl. [a]	60	320	1,400	4,330	3,080	30	4,700	20	60	160	70	110	20	70	1,040	60
Benzo[e]pyrene	60	250	1,140	39,240	N/A	20	3,400	20	60	130	70	100	30	100	800	50
Benzo[a]pyrene	50	310	750	4,220	2,690	20	4,500	10	40	130	60	100	20	80	840	50
Perylene	30	110	290	1,160	790	20	1,400	10	70	100	40	70	20	20	280	30
Indeno[1,2,3-cd]pyrene	50	240	1,060	3,500	2,580	40	3,600	20	50	110	60	80	20	40	850	60
Dibenz[a,h]anthracene	20	50	270	980	730	10	1,100	4	10	20	10	20	10	30	220	10
Benzo[ghi]perylene	60	230	950	3,160	2,440	30	2,800	20	60	140	70	90	20	90	750	60
Total PAH (ng/g)	780	3,300	13,900	82,000	29,000	310	71,000	240	770	1,700	970	1,400	350	1,300	10,000	720

[a] Benzo[b]fluoranthene + benzo[k]fluoranthene.
[b] N/A = not analyzed.

Spatial Distribution of Mercury

Mercury data presented are the annual mean concentrations corresponding to a total of 60 samples collected in the Detroit River-Lake St. Clair-St. Clair River corridor over the period of 2002 to 2004 (Table 6, Fig. 4). Mercury concentrations were elevated throughout the corridor, with annual means at stations 1159 and 1161 exceeding the Canadian probable effect level (PEL, 0.486 mg/kg; CCME 1999) for bottom sediments in 2002, and at station 1175 in 2003. In contrast to the results for PCBs and PAHs, the spatial distributions of mercury were more consistent throughout the corridor over the period of 2002 to 2004 (Fig. 4).

The prevalence of mercury in suspended sediments throughout the corridor is reportedly due to historical contamination arising primarily from chlor-alkali production both in the lower reaches of the Detroit River and upper reaches of the St. Clair River (Walters et al. 1972, 1974; Kovacik and Walters 1973; Thomas and Jaquet 1976; Marvin et al. 2004). Historic mercury cell plants located in Sarnia, Ontario and operated since 1949 in the upper reaches of the St. Clair River reportedly discharged up to 90 kg per day of mercury to the river during their periods of operation (Toms 1999), resulting in areas of severely-contaminated sediments adjacent to the shoreline (OWRC 1970; Wolery and Walters 1974; Johnson and Kauss 1989). In 1970, treatment facilities were installed to eliminate mercury discharges to the river; these plants were voluntarily decommissioned shortly thereafter. However, three highly-impacted sediment zones remained and continued to act as in-place sources of contamination (St. Clair River Remedial Action Plan 2001). Dow Canada completed a clean up of approximately 200 m^3 of sediment in this area in 1996, and initiated further sediment remediation activities in 2002 that ultimately resulted in the removal of approximately 13,370 m^3 of bottom sediment (Lake St. Clair Canadian Watershed Coordination Council 2005). Since target reductions in discharges of mercury continue to be met (90% reduction in releases in the Great Lakes basin between 1988 and 2006, GLBTS 2009), we presume that in-place contaminated sediments in the St. Clair River are responsible for the observed mercury distribution rather than shoreline-based inputs.

The presence of upstream sources of mercury is evidenced through comparison of stations 1156 and 1157 at the mouth of the Detroit River; while PCB and PAH data exhibited an apparent gradient toward increasing concentrations across the river from east to west, mercury concentrations were indistinguishable between these two stations (Fig. 4, Table 6). Drouillard et al. (2006) presented a similar argument for octachlorostyrene in that the lack of cross-river gradients in concentrations in the Detroit River was indicative of the prevalence of sources upstream. We would expect a cross-river gradient at stations 1156 and 1157 approximating those for PAHs and PCBs if more local sources associated with urbanization/industrialization were the major contributors to mercury loadings.

TABLE 6. Annual mean concentrations of mercury in Detroit River-Lake St. Clair-St. Clair River corridor suspended sediments collected over 2002 to 2004 [a]

	Hg (mg/kg dry sediment)			*Hg (mg/kg of TOC)*		
Stations	*2002*	*2003*	*2004*	*2002*	*2003*	*2004*
1167	0.060 ± 0.01	0.058 ± 0.02	0.063 ± 0.02	2.90	2.80	3.04
1175	0.289 ± 0.19	0.259 ± 0.22	0.182 ± 0.14	47.4	42.5	29.8
1172	0.287 ± 0.16	0.287 ± 0.21	0.405 ± 0.16	45.6	45.6	64.3
1165	0.465 ± 0.20	0.345 ± 0.08	0.322 ± 0.07	75.0	55.6	51.9
510	0.460 ± 0.29	0.327 ± 0.12	0.281 ± 0.08	40.7	28.9	24.9
1168	0.265 ± 0.07	0.322 ± 0.12	0.307 ± 0.09	14.9	18.1	17.2
1161	0.514 ± 0.27 *	0.391 ± 0.11	0.456 ± 0.07	40.5	30.8	35.9
1159	0.491 ± 0.14 *	0.343 ± 0.09	0.478 ± 0.10	31.7	22.1	30.8
1156	0.438 ± 0.06	0.290 ± 0.03	0.325 ± 0.03	55.4	36.7	41.1
1157	0.444 ± 0.05	0.264 ± 0.02	0.274 ± 0.02	43.1	25.6	26.6

[a] Asterisk (*) denotes an exceedance of the Canadian sediment quality probable effect level (PEL) guideline value of 0.486 mg/kg (CCME 1999).

Mercury concentrations in the corridor were also calculated normalized to TOC (Table 6). In considering the physical characteristics of the suspended sediments (Table1), it was evident that trapped material accumulated at stations in the upper reaches of the St. Clair River (stations 1175, 1172, and 1165) was of a coarser nature; suspended sediments from these stations were greater than 50% sand, with correspondingly low TOC concentrations. When normalized to TOC, mercury concentrations at the upper St. Clair River stations were generally higher than stations in the lower reaches of the Detroit River. The highest TOC-normalized mercury concentrations throughout the entire corridor were observed at stations 1165 (75 mg/kg TOC) and 1172 (64.3 mg/kg TOC) (Table 6). In addition, TOC-normalized mercury concentrations in the upper St. Clair River were roughly 15- to 25-fold higher than the upstream station in southern Lake Huron.

Mercury contamination in bottom sediments at Station 510 in the central area of Lake St. Clair (0.434 mg/kg) (Gewurtz et al. 2007), as measured during a lake-wide survey conducted in 2000, was within the range of the annual mean concentrations (0.281 to 0.460 mg/kg) for suspended sediments reported in this study. Similarly, the mean mercury concentration of bottom sediments in the western basin of Lake Erie (0.402 mg/kg) was within the range of annual means for suspended sediments in the Detroit River (0.264 to 0.514 mg/kg, Table 6). In both cases, mercury in sediments of open-lake areas of lakes Erie and St. Clair represents significant enrichment due to anthropogenic activities; accumulation of these sediments in our sediment traps provide evidence that contaminated sediments in the Detroit and St. Clair rivers are mobile and continue to migrate and potentially impact downstream areas. However, it should also be noted that the most recent bottom sediment data for both lakes St. Clair and Erie show dramatic declines in mercury contamination of the past 30 years; the estimated reduction in mercury sediment contamination in western Lake Erie has been estimated to be 60% (Marvin et al. 2004).

Concentrations of mercury throughout the corridor were consistently above the Canadian threshold effect level (TEL) guideline (0.170mg/kg; CCME 1999), except in southern Lake Huron where concentrations were consistently relatively low. Exceedances of the Canadian PEL (0.486 mg/kg) are shown in bold typeface in Table 6; this guideline was exceeded at stations 1159 and 1161 in the lower reaches of the Detroit River in the Trenton Channel in 2002. The TEL represents the concentration below which adverse biological effects are expected to occur rarely, while the PEL defines a level above which adverse effects are expected to occur frequently (CCME 1999). Although these guidelines should only be used as a screening tool as opposed to a risk assessment tool, the guideline exceedances in the Trenton Channel area suggest these suspended sediments have the potential to illicit adverse biological effects. The range of annual mean average mercury concentrations in suspended sediments at the Lake Huron station (0.058 to 0.063 mg/kg, Table 6) were only slightly higher than the lake-wide average bottom sediment concentration (0.043 mg/kg) (Marvin et al. 2004). Mudroch et al. (1988) estimated the background concentrations in bottom sediments of the depositional basins of Lake Huron to be in the range of 0.040 to 0.080 mg/kg. Therefore, Lake Huron does not appear to represent a significant source of mercury to the corridor.

Conclusions

Spatial distributions of all contaminants in suspended sediments showed little variation over the course of the study. The highest concentrations of PCBs in the Detroit River-Lake St. Clair-St. Clair River corridor in both 2000 and 2004 were associated with stations in the Trenton Channel in the lower reaches of the Detroit River. Assessment of the spatial pattern in PCB contamination indicated that a large portion of PCB loadings to the western basin of Lake Erie are associated with historical industrial activity in the Trenton Channel. The spatial distributions of PAHs and PCBs in the corridor were generally similar; however, data from a station at the mouth of the Rouge River in the middle reaches of the Detroit River suggested contributions from both

contemporary industrial emissions and contaminated sediments associated with historical industrial activities.

In contrast to the results for PCBs and PAHs, the spatial distributions of mercury were more consistent throughout the entire length of the corridor. This consistency was attributed to the presence of sources to both the Detroit and St. Clair rivers, and more specifically historical bottom sediment contamination associated with chlor-alkali production. This same rationale, i.e., a lack of upstream/downstream gradients, was used by Drouillard et al. (2006) in concluding that octachlorostyrene in Detroit River bottom sediments is derived primarily from upstream sources in the St. Clair River. In the case of all contaminants, the comparison of concentrations at two stations (1156 and 1157) located at the mouth of the Detroit River assisted in the identification of primary source areas. While PCB and PAH data exhibited a definitive gradient toward increasing concentrations from east to west, and thereby implicating the lower and middle reaches of the Detroit River as source areas, mercury concentrations were indistinguishable between these two stations. In the case of mercury, sediments of open-lake areas of lakes Erie and St. Clair exhibited significant enrichment due to anthropogenic activities, which indicated that contaminated sediments originating in the Detroit and St. Clair rivers are mobile and able to impact downstream areas. Other groups have reported that contaminated sediments in the lower reaches of the Detroit River can influence contaminant loadings to Lake Erie, particularly during periods of certain meteorological conditions (Drouillard et al. 2006).

The results of the aforementioned studies show that the focus of the binational agencies on the St. Clair and Detroit rivers through the respective Remedial Action Plans (RAPs), and the associated expenditures on sediment remediation activities ($130 million USD over the past decade [Heidtke et al. 2006]), have been well justified. The assessment of temporal trends in environmental compartments of the Detroit River over the period of the 1970s to the mid-1990s revealed dramatic reductions in levels of PCBs (Heidtke et al. 2006). However, our current study, and those collectively reported by Heidtke et al. (2006) for PCBs, show less definitive improvement since the mid-1990s. It should be acknowledged that considerable additional sediment remediation activities were undertaken in both the lower reaches of the Detroit River and upper reaches of the St. Clair River over the period during which our study was being conducted; future suspended sediment data from our sediment trap studies may reflect additional reductions in sediment contamination.

Acknowledgments

We thank the Captain and crew of the CCGS Limnos and Environment Canada Technical Operations Burlington for technical support.

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Received: 9 March 2009; accepted: 12 January 2010.