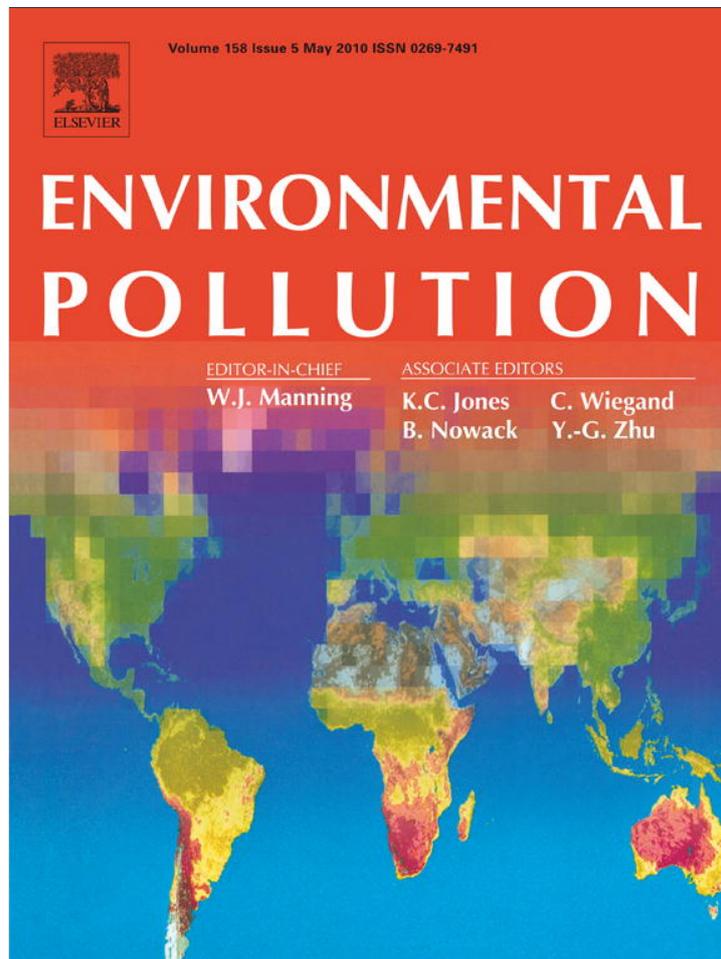


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Mercury transport between sediments and the overlying water of the St. Lawrence River area of concern near Cornwall, Ontario

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Sediments in the St. Lawrence area of concern near Cornwall are a net sink for mercury.

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ABSTRACT

Contaminated sediments in the St. Lawrence River remain a difficult problem despite decreases in emissions. Here, sediment and pore water phases were analyzed for total mercury (THg) and methyl mercury (MeHg) and diffusion from the sediment to the overlying water was 17.5 ± 10.6 SE $\text{ng cm}^{-2} \text{yr}^{-1}$ for THg and 3.8 ± 1.7 SE $\text{ng cm}^{-2} \text{yr}^{-1}$ for MeHg. These fluxes were very small when compared to the particle-bound mercury flux accumulating in the sediment (183 ± 30 SE $\text{ng cm}^{-2} \text{yr}^{-1}$). Studies have reported that fish from the westernmost site have higher Hg concentrations than fish collected from the other two sites of the Cornwall Area of Concern, which could not be explained by differences in the Hg flux or THg concentrations in sediments, but the highest concentrations of sediment MeHg, and the greatest proportions of MeHg to THg in both sediment and pore water were observed where fish had highest MeHg concentrations.

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1. Introduction

The St. Lawrence River (Canada, U.S.A.) drains the most industrialized region of North America (Carignan and Lorrain, 2000). The rapid industrialization of populated areas over the past century has resulted in localized degradation of water quality and bottom sediments (Reavie et al., 1998). This has been the case near Cornwall, Ontario, where local industrial activity (e.g., chlor-alkali, pulp and paper, and textiles) has resulted in PCB and mercury (Hg) contamination. The International Joint Commission (IJC) identified the St. Lawrence River near Cornwall as one of 42 'problem areas' for the aquatic environment, and it was designated an Area of Concern (AOC) in 1985. Hg contaminated sediments are one of the major environmental issues in the area. Hg concentrations in these sediments exceed background levels, and exceed Ministry of the Environment (MOE) sediment criteria for the protection of aquatic life (Richman and Dreier, 2001). Previous studies in the area indicate that Hg concentrations in surface sediment layers have decreased since the 1970s, and that cleaner sediments are covering the more contaminated historical discharges

(St. Lawrence River RAP, 1997). Nevertheless, contaminated sediments remain a potential source of Hg to the system, posing a risk to fish, wildlife, and humans.

Most mature fish caught near the Cornwall waterfront have Hg concentrations that exceed the MOEs consumption guidelines (Grapentine et al., 2003). Research in other locations suggests that methyl mercury (MeHg) in fish originates primarily from sediments (Benoit et al., 1998; Krabbenhoft et al., 1998; Gill et al., 1999; Covelli et al., 1999), suggesting that elevated Hg in sediments from the Cornwall AOC contribute to the elevated Hg in top predators.

In the Cornwall AOC, where sediment Hg concentrations are elevated (Richman and Dreier, 2001), there is potential for Hg to diffuse from sediments to the water column, where it becomes more accessible to aquatic organisms. The sites selected for this study along the Cornwall AOC (Fig. 1) were described previously by Richman and Dreier (2001) and Ridal et al. (2009) and are characterized by a high spatial heterogeneity in sediment type and composition likely from sediment redistribution from water turbulence (Biberhofer and Rukavina, 2002). However, these sites are removed from the main river channel and a restricted flow rate results in fairly rapid sediment deposition rates in these locations (Delongchamp et al., 2009).

The objectives of this study were: (1) to compare concentrations of dissolved and particulate Hg in surface sediments and overlying water at three different sites within the AOC that were affected by

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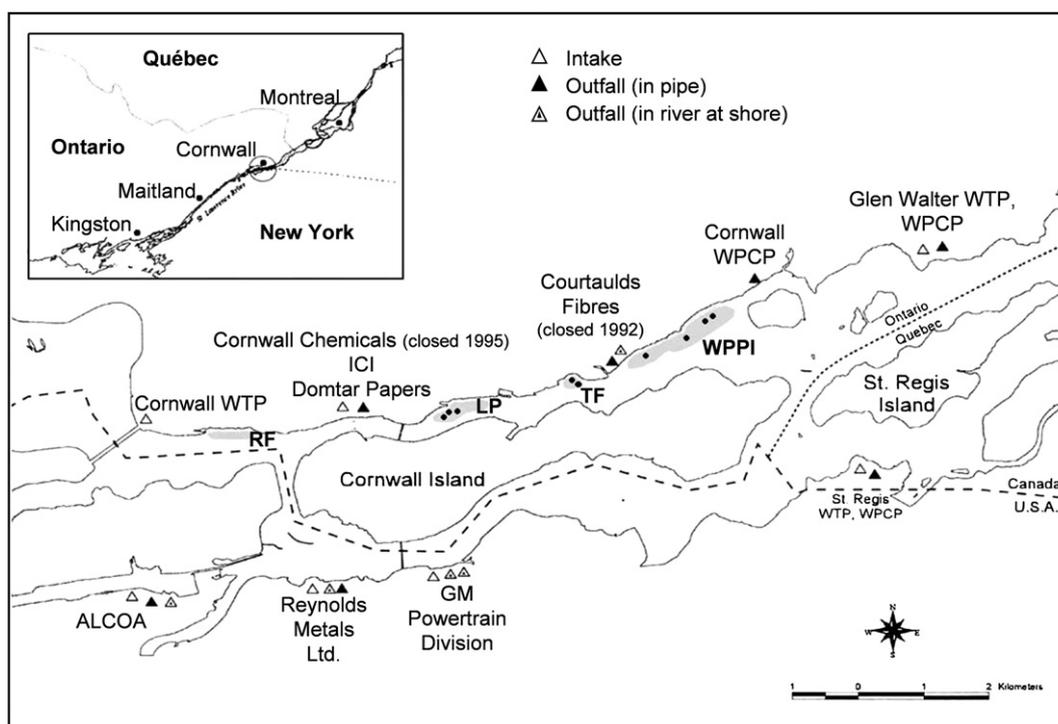


Fig. 1. Location of sampling sites in the St. Lawrence River near Cornwall. Sampling was conducted in three sites designated as LP, Lamoureux Park (left); TF, Tank Farm (centre); and WPPI, Windmill Point to Pilon Island (right). An upstream site was used as a reference (RF). The coring sites are indicated by numbers (modified from *St. Lawrence River RAP*, 1997).

industrial activities; (2) to quantify deposition rates of THg and MeHg to the sediments; and (3) to determine whether sediments contribute significant THg and MeHg to the overlying water via diffusion.

2. Materials and methods

2.1. Study site

The Cornwall AOC includes a stretch of the St. Lawrence River approximately 80 km long, from the Moses-Saunders power dam to the eastern outlet of Lake St. Francis in Québec. This stretch of the river impacts many jurisdictions, including the provinces of Ontario and Québec, the state of New York, as well as the Mohawk Territory of Akwesasne. Within these boundaries, the River is divided into two branches by Cornwall Island; the South Channel, which contains high PCBs in the sediments, and the North Channel, with Hg contaminated sediments (*St. Lawrence River RAP*, 1992). Sampling was conducted in three sites located along the Cornwall waterfront of the North Channel (Fig. 1). Lamoureux Park (LP) was the westernmost sampling location, and is closest to an industrial complex formerly comprised of a pulp and paper mill (Domtar) and a chlor-alkali plant (ICI). Windmill Point to Pilon Island (WPPI) was the largest and easternmost site, stretching from the former site of a textile mill (Courtaulds) to the eastern edge of Pilon Island. The Tank Farm (TF) was the smallest sampling site and is situated between the LP and WPPI sites. A reference site (RF, Fig. 1) was selected upstream and outside of areas exposed to past industrial effluents.

2.2. Sample collection

Sediment cores were collected from all sites along the Cornwall waterfront of the St. Lawrence River (Fig. 1) from May to August 2004 and 2005 (LP-1, 45°00'40.2" N, 74°43'55.4" W; LP-2, 45°00'40.2" N, 74°43'54.5" W; LP-3, 45°00'40.2" N, 74°43'54.1" W; TF-1, 45°00'57.6" N, 74°42'23.0" W; TF-2, 45°00'57.6" N, 74°42'23.9" W; WPPI-1, 45°01'13.2" N, 74°41'25.4" W; WPPI-2, 45°01'33.5" N, 74°40'50.4" W; WPPI-3, 45°01'33.7" N, 74°40'50.8" W). Sediments were collected using a Glew corer (Glew, 1989). Using acoustic data and maps of the river bed, cores were collected from depositional areas at depths ranging from 7 to 12 m. Redox potential was measured throughout the cores within 1 h of collection. Cores were extruded on-site at 1 cm intervals, under a nitrogen atmosphere to minimize changes in redox potential. The sediment slices were placed in air-tight centrifuge tubes, and were transported on ice to the laboratory for pore water separation. Grab samples were collected from a reference site using an Eckman dredge, and frozen until further analysis.

Mercury is released to the sediment pore waters by processes such as organic matter degradation, Fe–Mn oxide dissolution, as well as the oxidation of Hg-laden iron sulfides. Once in solution, dissolved mercury in anoxic sediments may diffuse to the sediment–water interface along a concentration gradient. Several methods have been used to measure sediment pore water profiles of mercury, including centrifugation, sediment filtration (by gravity or vacuum), whole-core squeezing, and *in situ* dialysis. A critical review of these techniques was conducted by Mason et al. (1998), who showed that centrifugation under an inert atmosphere was the most reliable method for quantifying mercury. Pore water profiles were obtained from duplicate sediment cores that were extracted in a glove box under a nitrogen atmosphere. In the lab, pore water was separated from sediment samples by centrifugation at 4000-rpm for 30 min followed by filtration using 0.45 µm syringe filters (with HT Tuffryn membrane), also performed under a nitrogen atmosphere. Pore water samples were acidified and refrigerated in the dark for THg (1% BrCl), MeHg (0.5% HCl), and metals (0.5% HNO₃) analysis. Sediment subsamples were freeze-dried for dating and THg analysis and wet sediments were frozen for future MeHg analysis. Gas bubbles released at the sediment surface were collected on-site using a stainless steel cone covering an area of 2685 cm². The gases were collected by water displacement, into a 0.5 L Teflon sample bottle fitted to the top of the steel cone. The sample bottle was removed by a diver, and was stored in the dark at 4 °C until analysis (Poissant et al., 2007; Chau et al., 1977).

2.3. Analytical methods

Methyl mercury in sediments was extracted and analyzed by capillary gas chromatography coupled with atomic fluorescence spectrometry (GC-AFS) as described by Cai et al. (1997). Sediment THg analysis was conducted on homogenized freeze-dried sediment using an automatic Mercury Analyzer based on thermal decomposition, dual-step gold amalgamation, and detection via Cold-Vapor Atomic Absorption using an SP-3D mercury analyzer (Nippon Instruments Corp). Sample mass ranged from 0.9 to 34.2 mg of sediment, with a mean weight in milligrams of 5.5 ± 4.8 SD. The method detection limit (MDL) was 0.01 ng per sample, or 2 ng/g for a typical sample mass of 5 mg. Precision, as indicated by the relative percent difference (RPD) of duplicate samples, was found to average 5.5% for THg in sediments ($n = 62$ pairs), and 8.2% for MeHg in sediments ($n = 79$ pairs). The accuracy of our THg and MeHg determinations in sediments was estimated by analyses of analytical procedural blanks, and spiked samples. The mean recovery of spiked samples was 102 ± 0% for THg ($n = 5$), and 107 ± 8% for MeHg ($n = 7$). Reference materials were tested every 6 samples and average recovery for THg in MESS-3 (Marine Sediment Certified Reference Materials) from the National Research Council (NRC Canada) was 97 ± 4% ($n = 10$). The average recovery for methyl mercury in Reference Material IAEA-405 (Trace and Major Elements in Estuarine Sediments from IAEA, Monaco) was 98 ± 4% ($n = 8$).

In order to retrieve an adequate volume of pore water for analysis, 1 cm interval samples from duplicate cores were pooled. A 10 mL volume of pore water was collected using a calibrated Eppendorf pipette with a Acrodisc 25 mm diameter, 0.2 µm HT tuffryn membrane filter (Gelman Laboratories), and transferred to 50 mL Teflon tubes, where they were acidified with 50 µL of quartz distilled HCl (J.T. Baker). Methyl mercury concentrations were determined in pore water by capillary gas chromatography coupled with atomic fluorescence spectrometry (GC-AFS) as described by Cai et al. (1996). The MDL was calculated to be 0.02 ng L⁻¹. Water samples were analyzed for THg using pre-oxidation by BrCl, and SnCl₂ reduction with pre-concentration by two-stage gold amalgamation, followed with detection using cold-vapor atomic fluorescence spectrometry (CVAFS). The analysis was conducted using a Tekran 2600 system following the modified US EPA Method 1631 guideline for mercury analysis (USEPA, 2001). Procedural blanks consisting of deionized water revealed no mercury contamination during THg analysis, or during MeHg extraction and analysis. The mean recovery of spiked samples was 105 ± 11% for THg (*n* = 10), and 103 ± 2% for MeHg (*n* = 4).

CH₄ and CO₂ concentrations in gas were measured by flame ionization detection (FID) using a chromatographic RGA5 system (Trace Analytical, Maryland). Sediment subsamples were dried to determine water content and analyzed for loss on ignition (550 °C, 950 °C) to measure organic content.

2.4. ²¹⁰Pb dating

Analysis of ²¹⁰Pb was performed on each core at selected depths to determine age and sediment accumulation rates. ²¹⁰Pb, ²²⁶Ra, and ¹³⁷Cs activity were measured by gamma spectrometry, using a digital high purity germanium well detector (DSPec, Ortec), following methods described by Appleby (2001). Supported ²¹⁰Pb, as determined by ²²⁶Ra activity, was subtracted from total ²¹⁰Pb activity to determine the unsupported ²¹⁰Pb fraction, which is used for the calculation of sediment dates, and sedimentation rates. The mean sedimentation rate for each core is calculated from the slope of unsupported ²¹⁰Pb activity versus cumulative dry mass. The ²¹⁰Pb dating for these cores are already presented in a separately published paper (Delongchamp et al., 2009), based on the Constant Flux/Constant Sedimentation model, which assumes a constant sedimentation rate. Using Spearman's correlation, these sedimentation rates were compared to sedimentation rates calculated using the Constant Rate of Supply (CRS) model, which accounts for variable sediment accumulation rates. Both models (Appleby and Oldfield, 1978) estimated similar sedimentation rates (*R*² = 0.76, SE_{est} = 0.08 g cm⁻² yr⁻¹).

2.5. Hg flux calculations

Mercury diffusion from sediments was determined based on the Hg concentration gradient in the top 1 cm of interstitial fluid obtained from 2 different cores at each site and the overlying water column Hg concentration. For diffusion of Hg across the sediment–water interface, in the absence of bioturbation and bio-irrigation, a generally accepted form of Fick's first law is

$$\text{diffusive flux}(F) = -(\phi D_W / \theta^2) (\partial C / \partial x) \quad (1)$$

where *F* is the flux of a solute with concentration *C* at depth *x*, *θ* is the tortuosity (dimensionless), *φ* is the sediment porosity, and *D_W* is the diffusion coefficient of the solute of interest in water without the presence of the sediment matrix. We used a *D_W* value for inorganic Hg in water of 9.5 × 10⁻⁶ cm² s⁻¹, and *D_W* for MeHg in water was 1.3 × 10⁻⁵ cm² s⁻¹ based on Gill et al. (1999).

Tortuosity has been shown to be related to porosity. For all flux calculations, tortuosity was calculated using the empirical relationship of Boudreau (1996)

$$\theta = 1 - \ln(\phi^2) \quad (2)$$

Porosity (*φ*) was calculated by measuring the weight loss of sediments freeze-dried over 48 h to constant weight and calculating

$$\phi = 1 - (\text{bulk density} / \text{particle density}) \quad (3)$$

where a particle density of 2.65 g cm⁻³ was applied (Brady and Weil, 2002).

3. Results and discussion

3.1. Description of cores

The cores consisted of a uniform, brown-black clayey mud with a brownish surface coloration in the top 1–2 cm. Small pores, pieces of wood or shell were noted during sampling. Although small pieces of shell were rarely seen, small pores and pockets of gas were present throughout the length of many cores, especially those from the LP site. Layers of wood chips were observed at various depths in cores WPPI-1 (12–18 cm and 24–28 cm), and LP-2 (2–10 cm and

12–18 cm). Traces of oil were present in all cores, and were especially prevalent in sediments from the TF site. Benthic organisms were rarely seen in the cores that were collected from the Cornwall waterfront.

3.2. ²¹⁰Pb Inventories and sedimentation rates

Activity of unsupported ²¹⁰Pb decreased with depth in all cores, with the exception of cores TF-1 and TF-2. In other cores, irregularities were observed only in surface layers. Despite these irregularities, the natural log of unsupported ²¹⁰Pb activity plotted decreased almost linearly with cumulative dry mass in most instances (Delongchamp et al., 2009). Decay curves could be fitted with *R*² values > 0.59, indicating a uniform accumulation of sediments for all cores, and sedimentation rates were calculated below the mixing depth, if any. Carignan and Lorrain (2000) measured sedimentation rates of 0.11–1.78 g cm⁻² yr⁻¹ in the St. Lawrence River. Sedimentation rates for the Cornwall AOC were within this range, with values from 0.18 g cm⁻² yr⁻¹ for site LP-3 to 0.58 g cm⁻² yr⁻¹ for site WPPI-4 (Table 2). We could not determine a sedimentation rate for the TF site because there was no decline in ²¹⁰Pb activity with sediment depth, probably due to sediment mixing during recent waterfront development at this site.

3.3. Hg in surface sediments

On average, concentrations of THg (640 ± 248 SE ng g⁻¹ d.w.) and MeHg (22.2 ± 13.8 SE ng g⁻¹ d.w.) in surface sediments from the three contaminated sites (LP, TF, and WPPI) are substantially greater than THg (15.9 ± SE 2.88 ng g⁻¹ d.w.) and MeHg (0.24 ± SE 0.09 ng g⁻¹ d.w.) concentrations in sediments from the reference site (RF), located upstream of the area exposed to past industrial effluents. A comparison of mercury concentrations across all sites, including the reference site, revealed that the difference in THg and MeHg concentrations among sites is statistically significant (ANOVA, *P* < 0.001). The higher mercury concentrations observed at the study sites compared to the upstream reference site are evidence that Hg accumulation in the AOC is from local sources, rather than regional sources, which corroborates other assessments (Filion and Morin, 2000; Richman and Dreier, 2001; Grapentine et al., 2003).

THg concentrations in surface sediments (0–1 cm) across the three contaminated sites ranged from 406 to 1220 ng g⁻¹ dry weight (Table 1). In addition to the comparison of the reference and study sites, a comparison of the mean THg concentrations in surface sediments between the three contaminated sites was also conducted, revealing no significant difference in THg concentrations, thus we were unable to identify a specific contamination source based on the spatial distribution of Hg among the contaminated sites. In order to assess the potential risk to aquatic life from exposure to contaminated sediments, THg concentrations in surface sediments were compared to the Canadian Council of Ministers of the Environment's (CCME) Sediment Quality Guidelines (CCME, 2005) for mercury. Even the lowest THg levels exceeded the lowest effect level of 170 ng g⁻¹, and most exceeded the probable effect level (PEL) of 486 ng g⁻¹. Other studies of the St. Lawrence River reported THg concentrations similar to those found in this study. For example, surveys performed by the MOE along the Cornwall waterfront reported THg concentrations above 200 ng g⁻¹ (Persaud et al., 1993) at all three contaminated sites, and above 2000 ng g⁻¹ at the WPPI site (Richman, 1994, 1996, 1999, 2000) and the TF site (Grapentine et al., 2003).

Surface sediment MeHg levels ranged from 9.41 to 45.5 ng g⁻¹ dry weight (Table 1), and differed among sites (one-factor ANOVA, *P* < 0.001). According to a Tukey post hoc test, the reference site (RF) had the lowest MeHg concentrations among all sites

Table 1
Concentrations of THg and MeHg in sediment^a and pore water.^b

site	Sample Date	Sediment THg (ng g ⁻¹)	Sediment MeHg (ng g ⁻¹)	% MeHg/THg in sediment	Pore water THg ^c (ng L ⁻¹)	Pore water MeHg (ng L ⁻¹)	% MeHg/THg in pore water
LP-1	7-7-04	557	45.5	8	–	11.1	–
LP-2	7-19-04	592	34.5	6	7.03	4.20	60
LP-3	6-21-05	727	39.3	5	34.6	6.57	19
TF-1	8-11-05	1217	9.60	1	–	25.4	–
TF-2	8-24-04	405	15.1	4	91.8	11.1	12
WPPI-1	7-28-04	780	18.6	2	–	8.40	–
WPPI-2	7-15-05	442	15.0	3	–	4.15	–
WPPI-3	8-17-04	508	12.6	2	198	7.50	4
WPPI-4	5-25-05	532	9.41	2	70.6	52.1	74
Reference	6-22-05	16.0	0.24	1	–	–	–
Mean (excluding reference site)		568	22.2	3.7	80.5	14.5	33.8
SD		130	13.8	2.3	73.6	15.5	31.2
SE		43.2	4.58	0.76	32.9	5.2	13.9

^a Sediment concentrations are for the top 1 cm sediment layer of one core.

^b Pore water concentrations are for the top 1 cm sediment layer obtained from 2 separate cores. Concentrations for site WPPI-4a refer to the top 2 cm sediment layer.

^c THg analysis was only done on samples collected in 2005, not on samples collected in 2004 due to inadequate sample volume.

(0.24 ± 0.08 (SD) ng g⁻¹ $P < 0.001$), whereas the TF and WPPI sites had similar MeHg concentrations (12.3 ± 3.9 ng g⁻¹ and 13.9 ± 3.9 ng g⁻¹, respectively), and the LP site had the highest MeHg concentrations (39.7 ± 5.5 ng g⁻¹, $P < 0.01$) (Fig. 2). The LP site also had the highest fraction of MeHg relative to THg, ranging from 5 to 8% (Table 1). Other field surveys found the proportion of MeHg in sediments to range between 0.3 and 5.7% of the total mercury (Holmes and Lean, 2006). Regression analysis of our sediment cores showed no relationship between MeHg and THg in the surface sediment layer, suggesting that methylation is not controlled solely by total concentrations of inorganic mercury in the sediment.

3.4. Hg deposition and diffusion

The fine scale assessment of mercury in pore water allowed us to calculate the THg, and MeHg diffusive fluxes at the sediment–water interface (Table 2). Sediment–water diffusional fluxes were determined based on the concentration gradient between the Hg concentration in the top 1 cm of interstitial fluid and the overlying water column Hg concentration. Redox potentials in surface sediments ranged between -116 and -213 mV, indicating near-surface reducing conditions, and were similar among sites (one-factor ANOVA, $p > 0.05$). Pore water concentrations in surface sediments ranged from 7.03 to 198 ng L⁻¹ for THg, and from 4.15 to 254 ng L⁻¹ for MeHg (Table 1), and was unrelated to temperature. Interstitial concentrations at the sediment surface were from 7 to 340 times

higher than the concentrations in overlying water for THg (0.58 – 1.02 ng L⁻¹), and from 220 to 8200 times higher than the concentrations in overlying water (0.02 – 0.04 ng L⁻¹) for MeHg. Gobeil and Cossa (1993) did not observe such high enrichments (up to 14 times) of THg in sediments of the Laurentian Trough, however, Gagnon et al. (1997) measured THg enrichments ranging from 12 to over 100 times in the Laurentian Trough.

The calculated diffusive flux of THg from pore water gradients for the 3 study sites along the Cornwall waterfront varied from 1.2 to 48.2 ng cm⁻² yr⁻¹, while MeHg flux had a smaller range from 1.2 to 14.6 ng cm⁻² yr⁻¹, and were not different among the three contaminated sites (one-factor ANOVA, $p > 0.05$). These diffusive fluxes were calculated with Eq. (1) based on THg concentrations in surface waters measured to range between 0.58 and 1 ng L⁻¹. We found that the calculated THg diffusive fluxes from sediments were not sensitive to variation in THg concentrations in surface waters. For example, varying THg concentration in surface water at site LP-2 from 1 to 0.5 ng/L only resulted in a shift of the calculated THg diffusion rate from 1.2 to 1.3 ng cm⁻² yr⁻¹, demonstrating that molecular diffusion is relatively insensitive to variation in THg concentration in overlying water. THg diffusive fluxes in this study were within the range of fluxes measured in heavily contaminated sediments of the Gulf of Trieste in the northern Adriatic Sea, which ranged from 0.99 to 236 ng cm⁻² yr⁻¹ (Covelli et al., 1999), and of those measured in the Saguenay Fjord in Canada, which ranged from 3.8 to 36.0 ng cm⁻² yr⁻¹ (Gagnon et al., 1997). MeHg fluxes measured in the Cornwall AOC were higher than MeHg fluxes (0.006 ng cm⁻² yr⁻¹) measured in Spring Lake in northern Minnesota (Hines et al., 2004), but within the range of fluxes measured in Lavaca Bay, Texas (0.01 – 54.7 ng cm⁻² yr⁻¹) (Gill et al., 1999), the Gulf of Trieste (-3.83 – 86.5 ng cm⁻² yr⁻¹) (Covelli et al., 1999), and from Barn Island Salt Marsh (1.14 – 16.1 ng cm⁻² yr⁻¹) (Langer et al., 2001).

The lowest sediment to water flux of THg and MeHg was observed at site LP-2. Site WPPI-3 had the highest THg flux, reflecting the abundance of THg in the pore water at this site. The highest MeHg flux was seen at site TF-1, but no differences in MeHg fluxes were observed among the three contaminated sites (one-factor ANOVA, $p > 0.05$). Note that the above fluxes are diffusive fluxes only. Additional fluxes caused by bioturbation, bioirrigation, and resuspension of sediments can also affect the extent of exchange across the sediment–water interface (Aller and Aller, 1998; López, 2004). Van der Loeff et al. (1984) found that bioturbation increased fluxes of organic and inorganic complexes at the sediment–water interface up to 2–10 times more than those calculated on the basis of molecular diffusion alone. Also, there is evidence that sediments of the Cornwall AOC are conducive to the

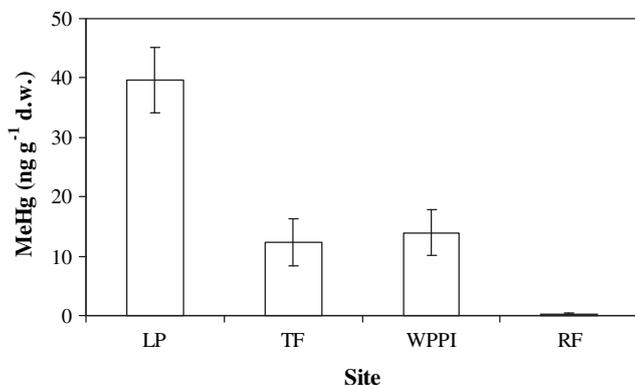


Fig. 2. Mean concentration of methyl mercury (MeHg) in surface sediments (0–1 cm) of three study sites and a reference site from the St. Lawrence River (Cornwall) Area of Concern. Error bars represent the standard deviation.

Table 2
Sedimentation rates, accumulation rates, and sediment–water diffusive fluxes^a of THg and MeHg.

site	Sedimentation rate (g cm ⁻² yr ⁻¹)	THg accumulation (ng cm ⁻² yr ⁻¹)	Diffusion from sediment to water (ng cm ⁻² yr ⁻¹)		% Remobilization	
			THg	MeHg	THg	MeHg
LP-1	0.27	148		4.0		2.7
LP-2	0.32	186	1.2	1.2	0.6	0.6
LP-3	0.18	128	6.8	1.8	5.4	1.4
TF-1				14.6		
TF-2			9.1	1.5		
WPPI-1	0.32	249		1.8		0.7
WPPI-2	0.16	70		1.5		2.1
WPPI-3	0.38	192	48.2	2.5	25.1	1.3
WPPI-4	0.58	309	13.7	14.0	4.4	4.4
Mean	0.32	183.1	17.5	3.83	8.88	1.89
SD	0.14	78.9	21.1	4.58	11.01	1.33
SE	0.05	29.8	10.6	1.73	5.51	0.50

^a Flux determinations based on average pore water Hg concentration in the top 1 cm sediment layer obtained from 2 separate cores. A positive value indicates the flux is from the sediment to the overlying water.

production and release of methane gas (Poissant et al., 2007), and calculations do not account for losses of mercury with bubbles of gas (Bothner et al., 1980).

The mercury accumulation rate for the surface stratum of a sediment core (Table 2) is calculated as the products of particle deposition rates calculated from ²¹⁰Pb (in g cm⁻² yr⁻¹) and contaminant concentrations on those particles (in ng g⁻¹) (Hermanson, 1998; Heyvaert, et al., 2000). The potential importance of the diffusive flux on the cycling of mercury is calculated by comparing the upward diffusion of mercury with net particle fluxes (i.e. burial rate) of mercury to the sediment. The ratio between diffusive flux and burial rate indicates the fraction of deposited heavy metals that is remobilized from the sediment. In general, flux estimates show that the rate of remobilization at the sediment–water interface by diffusion is approximately 5% of the sediment burial rate (Table 2). Site WPPI-3 was an exception, with 25% of THg remobilized at the sediment surface. Also, less than 5% of THg deposited to the sediments was returned to bottom waters through MeHg diffusion. It is interesting that at site WPPI-4, 100% of the THg released at the sediment–water interface, corresponding to 4.5% of deposited THg, occurs in methylated form. This is an indication that site-specific conditions are conducive to mercury methylation. In these calculations it was assumed that the whole amount of MeHg associated with sediments, pore waters and related fluxes is produced *in situ*.

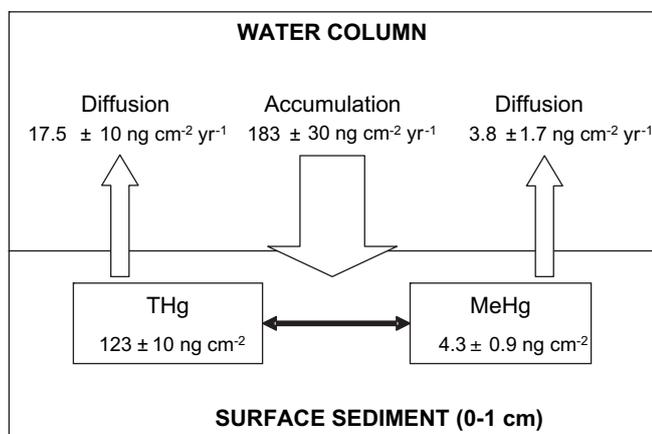


Fig. 3. Reservoirs and fluxes of mercury (average ± standard error) in surface sediments (0–1 cm) and at the sediment–water interface from the Lamoureux Park (LP) and Windmill Point to Pilon Island (WPPI) sites of the St. Lawrence River near Cornwall. The LP and WPPI sites have a combined surface area of 0.86 km².

This data set allowed us to estimate the annual sediment Hg budget at these deposition sites. The steady-state Hg sediment budget was constructed for the LP and the WPPI sampling points (Fig. 3). For the TF site, the sedimentation rate was not calculated because ²¹⁰Pb activity showed no decline with depth, thus we could not calculate a sediment burial rate, and it was not included in the Hg budget. At these sites, the top surface sediment (0–1 cm) contains an average of 123 ± 10 ng cm⁻² THg and 4.3 ± 0.9 ng cm⁻² MeHg. On an annual basis, 183 ± 30 ng cm⁻² yr⁻¹ of THg is accumulating at the sediment surface in these depositional sites in the St. Lawrence River. Losses from the sediments via diffusion are 17.5 ± 10 ng cm⁻² yr⁻¹ THg and 3.8 ± 1.7 ng cm⁻² yr⁻¹ MeHg, representing less than 12% of the net accumulation. This budget indicates that despite decreases in mercury inputs to the system over the years, accumulation rates of mercury in sediments remain elevated at these sites. Potential mercury sources include contaminated upstream sediments, discharges from shoreline industries and municipalities, atmospheric deposition, and resuspension of contaminated sediments.

3.5. Gas production

Methanogenesis is a terminal sink for electrons generated during the anaerobic degradation of organic matter and is important in the diagenesis of recently deposited sediments. Methanogenic bacteria proliferate below the surface layer in organic-rich sediments in which oxygen penetration is limited. Both elevated CH₄ and CO₂ concentrations, and high sediment–water fluxes characterize the most anaerobic sites. As indicated in Table 3, the LP site was the richer in terms of CH₄ concentration whereas the WPPI site was richer in terms of CO₂ concentration. CH₄ and CO₂ concentrations in the gas collector were typical and similar to those of other hypereutrophic lakes (e.g. Huttunen et al., 2001). Furthermore, CH₄ flux in the LP site was 1.36 times that of the WPPI site, whereas CO₂ flux in the WPPI site was 2.5 times that of the LP site (Table 3). CH₄/CO₂ ratios indicated that the LP site was the most active area of anaerobic organic matter decomposition, a factor which likely contributes to higher MeHg concentrations and

Table 3
Concentration of CH₄ and CO₂ evolved from St. Lawrence River sediment.

site	[CH ₄] ppmv	CH ₄ flux ppmv cm ⁻² h ⁻¹	[CO ₂] ppmv	CO ₂ flux ppmv cm ⁻² h ⁻¹	Ratio CH ₄ /CO ₂
LP (August 5, 2005)	308 000	0.68	5710	0.013	53.9
WPPI (July 29, 2005)	227 000	0.50	14 860	0.033	15.2

percent MeHg. CH₄/CO₂ ratios also show that the LP site is the most important in the diagenesis of recently deposited sediments.

Recent evidence indicates that fish from the LP site have higher Hg concentrations than fish collected from other sites along the Cornwall waterfront (Fowlie et al., 2008). The high Hg in fish from the LP site could not be explained by differences in THg concentrations in sediments among sites, or Hg diffusive fluxes among sites. However, our observations suggest that the LP site has unique characteristics, including (1) the highest solid-phase MeHg concentrations; (2) the highest proportions of MeHg to THg in both surface sediments, and pore waters; and (3) the presence of sub-surface layers of wood chips and high releases of methane bubbles from the sediments. It is possible that lower levels of the food chain, such as benthic invertebrates, are exposed to higher levels of MeHg at the LP site from contaminated sediments, translating to higher levels of MeHg in top predators.

4. Conclusions

Results of this study show that the diffusive flux of mercury to the overlying water is small compared to the flux of particulate bound mercury depositing to the sediments of the St. Lawrence River near Cornwall. Despite this, the anoxic sediments appear to provide an environment conducive to Hg methylation, and this study suggests that the flux of dissolved methyl mercury from sediments is a source to the river. Exposure of benthic organisms to this bioavailable form of Hg may result in uptake of, and adverse biological effects associated with, this trace metal. The sediments in the Cornwall AOC have historically been contaminated with mercury (Kauss et al., 1988) and although concentrations have decreased since the 1970s they still remain high (Anderson, 1990). These elevated Hg deposition rates near the Cornwall waterfront suggest other Hg sources to sediments may be active, such as erosion, and focusing of contaminated sediment deposits in the river. At present, the contaminated sediments are a probable source of methyl mercury to the biota and the river system.

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