



Do wood fibers from a pulp mill affect the distribution of total and methyl mercury in river sediments?

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ABSTRACT

The St. Lawrence River near Cornwall Ontario is affected by industrial mercury contamination of sediments and biota. It has been suggested that pulp and paper mill effluents may stimulate bacterial mercury methylation in these sediments, leading to contamination of aquatic biota. To test this hypothesis, we examined sediment–porewater dynamics of total mercury (THg) and methyl mercury (MeHg) at a site with high concentrations of wood fibers from a pulp and paper mill effluent and a nearby reference site with low wood fiber content. Dissolved phase THg (THg_{diss}) and MeHg (MeHg_{diss}) in porewater profiles showed that $38 \pm 30.9\%$ (SD) of THg in porewaters was in the methylated form regardless of wood fiber content. MeHg_{diss} and THg_{diss} concentrations were homogeneous between porewater and overlying water, indicating (a) that there is minimal net diffusion of MeHg_{diss} and THg_{diss} and (b) that redox-dependent processes such as sulfate reduction and Fe reduction were not associated with MeHg_{diss} distribution in these sediment profiles. MeHg and THg in solid phase showed coincident subsurface peaks at depths > 40 cm suggesting either that historical deposits of MeHg on particles (MeHg_(p)) are preserved in deep sediments, or that Hg methylation is active in deep sediments.

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Introduction

The St. Lawrence River at Cornwall, Ontario and Massena, NY was designated as an Area of Concern (AOC) by the International Joint Commission (IJC) in 1986 due to environmental contamination including high sediment concentrations of Hg along its northern coast and high PCBs (polychlorinated biphenyls) on its southern coast. Considerable attention has been given to an area downstream of a former pulp and paper mill (designated Zone 1) which contains wood fibers and high anaerobic microbial activity evidenced by rapid methane gas production and ebullition (Biberhofer and Rukavina, 2002; Delongchamp et al., 2010). This zone supports the most Hg contaminated fish and invertebrates within the AOC, despite having similar or lower Hg concentrations in sediment than in other embayments along the Cornwall waterfront (Fowlie et al., 2008; Yanch, 2007), suggesting Hg methylation may be an important mediating process in the Hg contamination of Zone 1 (Delongchamp et al., 2009; Yanch, 2007).

MeHg is a toxic form of Hg (Scheulhammer et al., 2007) that poses a potential risk to humans and aquatic animals. It is the only Hg form that biomagnifies in aquatic food webs leading up to fish and ultimately humans (Lindqvist et al., 1991). Sediments are the main Hg reservoir in the aquatic environment (Benoit et al., 1998) and play a major role in

Hg cycling of aquatic systems (Ramalhosa et al., 2001). Microbial methylation usually occurs under low oxygen or anoxic conditions near the sediment–water interface (Gilmour and Henry, 1991; Siciliano et al., 2002). Sulfate reducing bacteria (SRBs) are believed to be the primary Hg methylators (Avramescu et al., 2011; Compeau and Bartha, 1985) in freshwater and estuarine sediments. While sulfate reducing bacteria are the most important in this process (Avramescu et al., 2011), other microorganisms including methanogens and iron reducing bacteria may also contribute to Hg methylation (Pak and Bartha, 1998). Although abiotic methylation of Hg has been suggested (Celo and Scott, 2006), it is generally considered to be a small contribution to MeHg when compared to biotic pathways. Once deposited to sediments, Hg and MeHg may be subjected to postdepositional processes. For example, reduction of Fe and Mn oxides and their dissolution as a consequence of the microbial degradation of the organic matter, may remobilize Hg to the porewater (Froelich et al., 1977), though subsequent precipitation by sulfides may mediate this process (Ullrich et al., 2001). Fe and Mn oxides which are known as scavengers of trace metals in the environment (Lockwood and Chen, 1973) can scavenge Hg from surface waters to surface sediments and form stable complexes (Murray, 1975). Dissolved organic matter may also mediate Hg speciation, bioavailability, and facilitate its mobility in sediments and porewaters (Ramalhosa et al., 2006).

Here we examine how sediment mercury dynamics relate to the presence of wood fibers from a local pulp mill with a detailed seasonal analysis of total Hg and MeHg in sediments and porewaters.

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Previous studies on mercury in sediments at this site speculated on the role of wood fibers on mercury dynamics, but this study is the first to examine their impacts in a case-control design. Two sites were chosen for this comparison, one site containing high wood fibers in sediments (HWF site) and a nearby reference site with low wood fiber content in sediments. Based on underwater video and core sampling in the same area of the river, Biberhofer and Rukavina (2002) observed a correspondence between sites with high wood fiber and amounts of gas released when mechanically disturbed. Gas ebullition rates from the sediments of up to $2800 \text{ ml m}^{-2} \text{ day}^{-1}$ have been measured near these study sites, of which 29–84% was methane (Razavi et al., *in press*), indicating active populations of methanogens in these sediments. We hypothesized that increased methanogen activity in sediments containing wood fibers may elevate MeHg production in sediments, and enhanced respiration rates may lead to depletion of terminal electron acceptors, including oxygen and ferric iron, which may facilitate diffusion of MeHg from sediments to overlying water. Porewater analysis was used to study mercury dynamics in sediments because porewaters mediate the fluxes of metals between sediment and water column (Boudreau, 1996) and they also may reveal zones of active Hg methylation in sediments (e.g. Clarisse et al., 2011).

The specific objectives of this study were: (1) to compare the distributions of dissolved and particulate Hg and MeHg in sediments, porewaters, and overlying waters of two nearby sites in Zone 1 of the Cornwall AOC, one site containing high wood fibers in sediments (HWF), and a reference site with low wood fiber content; (2) to determine whether sediments containing high densities of wood fibers diffuse more THg and MeHg to overlying waters than sediments with low wood fiber content; and (3) to relate the distribution of THg and MeHg in sediments and pore waters to redox sensitive constituents (SO_4^{2-} , S^{2-} and Fe^{2+}) to identify areas of active MeHg production in sediments.

Materials and methods

Study site

The St. Lawrence River AOC includes an 80 km stretch of the St. Lawrence River, from the Moses-Saunders Power dam to the eastern outlet of Lac St. Francois in Quebec. This stretch of the river encompasses

many jurisdictions, including the provinces of Ontario and Quebec, the state of New York, the federal governments of Canada and U.S.A, the St. Regis Tribe and the Mohawks of Akwesasne.

The St. Lawrence River drains the Great Lakes to the Estuary and Gulf of the St. Lawrence. Water discharge, which averages about $8000 \text{ m}^3/\text{s}$ at Cornwall, has been regulated since the 1950s with the construction of the Moses-Saunders Dam. Below the dam the river splits around Cornwall Island, with about one third of the flow passing along the north shore by Cornwall. River flow is primarily from west to east, with back eddies creating depositional zones in bays along the waterfront. Our study sites were located along the Cornwall waterfront of the northern channel (Fig. 1), approximately 1 km downstream from the discharge of two local industries, the Domtar pulp and paper mill (closed in 2006), and ICI Forest Products, a chlor alkali plant (closed in 1995).

Despite regulations established in the 1970s by the federal government to limit the discharge of Hg to the river in liquid effluent by local industries, concentrations of Hg in surface sediments of Zone 1 have remained elevated and often exceed the sediment quality guideline (SQG) of 0.85 nmol g^{-1} , a limit set for the protection of biota by Environment Canada (Environment Canada, 1981). Also, MeHg concentration in large walleye in this area exceeded 2.32 nmol g^{-1} , the OMOE (Ontario Ministry of the Environment) guideline for fish consumption to protect the general population (Grapentine et al., 2003; OMOE, 2011) and this area is still listed as an AOC. A full history of industrial development at this site, as well as an account of total mercury and methyl mercury deposits in sediments of the Cornwall AOC is given in Delongchamp et al. (2009) and Ridal et al. (2009).

The high wood fiber (HWF) site is located immediately downstream of the pulp mill effluent discharge ($45^\circ 0'44.65''\text{N}$, $74^\circ 43'43.73''\text{W}$) and the reference site ($45^\circ 0'42.80''\text{N}$, $74^\circ 43'51.31''\text{W}$) is located nearby to the south west (Fig. 1). Samples were collected from June to August 2007. The physical setting of the two sites was similar low energy environments with depth integrated current velocities at the two sites $<0.1 \text{ m/s}$ (Nettleton 2004), total depths of approximately 8 m, and surface sediments consisting of brown-black clayed mud with a brownish surface. Benthic invertebrate species at nearby sites consist mainly of chironomids, tubificid worms, nauid worms, and gammarid amphipods (Milani and Grapentine, 2009).

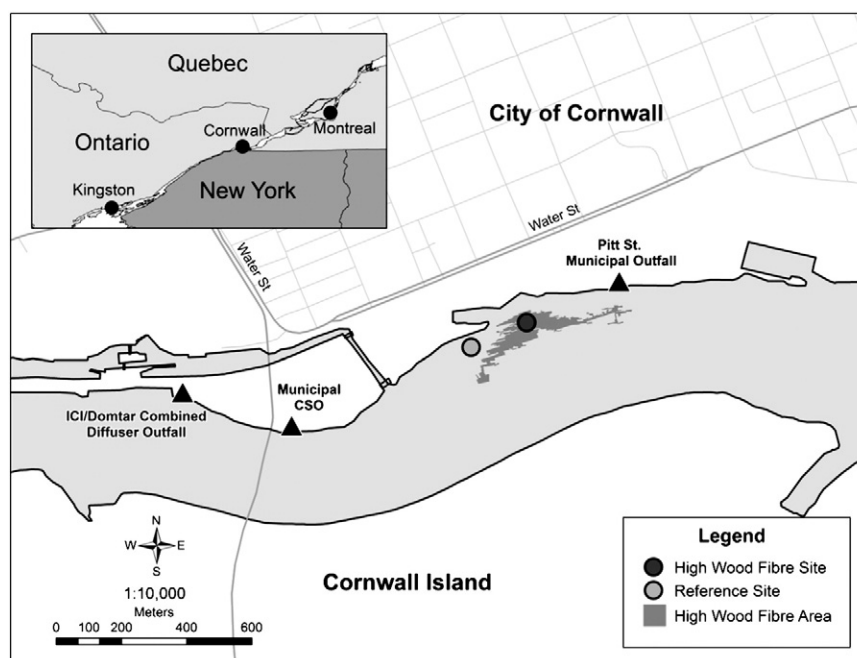


Fig. 1. Location of mercury sampling sites in the St. Lawrence River, showing the high wood fiber site and reference site.

Porewater sampling and analytical methods

Acrylic in situ dialysis membrane devices (peepers; 1-cm vertical resolution; two columns of 4-mL cells) of the type described by Carignan et al. (1985) and Carignan and Lean (1991) were used to sample porewater. Peeper cell and cover plates were cleaned by soaking in 5–10% nitric acid at room temperature for 1 week and then rinsed with de-ionized water (DIW). The peeper method relies on porewater equilibrium between porewater and de-ionized water trapped behind a membrane. Each peeper cell was filled with DIW and a sheet of 0.2 μm HT-200 membrane covering the cells held in place by a 0.5 cm plexiglass cover plate. Peepers were placed into plexiglass chambers and purged with O_2 free nitrogen ($\text{O}_2 < 0.5 \text{ mg/L}$) overnight and then for 15 min a day for 12 days thereafter, taking care to ensure there were no air bubbles in the cells or any leakage. Peepers were transferred to the field in nitrogen purged chambers. Once on site, the chambers containing peepers were immersed into water by divers and opened while immersed in the water to minimize exposure to O_2 . Three peepers were deployed by SCUBA divers at the HWF and reference sites in June, July, and August 2007 (total of 18 peepers). Approximately, two thirds of the peepers (approximately 22–26 cells out of 38 cells) were immersed into the sediments and approximately 12–16 peeper cells remained above the sediment–water interface so both the porewater and the overlying water were analyzed. The sediment–water interface was identified by counting the number of peeper cells exposed to the water column. Peepers were removed within 14 to 15 days after their initial deployment (Carignan et al., 1985).

Depth profiles for THg_{diss} , $\text{MeHg}_{\text{diss}}$, dissolved sulfate, sulfide, and ferrous iron in both sediment porewater and overlying water in the St. Lawrence River were measured using the peeper samples. Three peepers were deployed by SCUBA divers at each site (the HWF and the reference site) in June, July, and August 2007. Two peepers from each site were used for THg and MeHg analyses, and one peeper for THg , sulfate, sulfide and ferrous iron analyses. The sample collection was performed in the following order: THg_{diss} , $\text{MeHg}_{\text{diss}}$ in Hg peepers, sulfate, sulfide, and ferrous iron. This order was followed due to the sensitivity to contamination and/or environmental conditions of these sediment constituents. In order to retrieve an adequate volume, porewater samples were pooled from two consecutive peeper cells with 2 cm vertical resolution. Samples (5 mL) were collected using a calibrated Eppendorf pipette for THg analysis. Samples were transferred to 50 mL polypropylene centrifuge tubes, where sample volume was brought to 40 mL by adding 35 mL of DIW and then preserved with 300 μL of BrCl . Samples were kept at 4 °C in the dark.

THg_{diss} samples were analyzed using pre-oxidation with BrCl , reduction with SnCl_2 and pre-concentration on gold traps by two-stage amalgamation, followed with detection using cold vapor atomic fluorescence spectroscopy (CV-AFS). This analysis was conducted using a Tekran 2600 system, following the modified US EPA method 1631 guideline for mercury analysis (US EPA, 2001). The method detection limit was estimated at 4×10^{-2} pM. To ensure the accuracy of the analysis, blanks and spikes were run throughout the whole procedure. Analysis of field and laboratory blanks showed no mercury contamination during THg_{diss} analysis. The average recovery of the spikes was $102\% \pm 13$, ($n = 42$).

Samples (10 mL) were collected for $\text{MeHg}_{\text{diss}}$ analysis and transferred to 50 mL polypropylene tubes, acidified with 50 μL of concentrated HCl (38% Trace Metal Grade), and kept in the dark at 4 °C for future analysis.

$\text{MeHg}_{\text{diss}}$ concentrations were determined using capillary gas chromatography coupled with atomic fluorescence spectrometry (GC-AFS) (Analytical Mercury System Model PSA 10.723) as described by Cai et al. (1996). The detection limit was estimated at 3×10^{-2} pM. Analysis of procedural blanks consisting of DIW revealed no $\text{MeHg}_{\text{diss}}$ contamination during $\text{MeHg}_{\text{diss}}$ extraction and analysis. The average recovery of the spiked samples was $94\% \pm 8$, ($n = 12$).

Sulfate concentration in porewater was measured using the turbidity SO_4 assay and calibration method described by Rodier (1975). Sample

collections were performed from the bottom cells to the top and were completed in less than 5 min to minimize exposure time for anoxic porewaters. Vials were labeled and filled with 25 μL of concentrated HCl one day before sampling. Samples (1 mL) were collected from each peeper cell using a calibrated Eppendorf pipette by piercing the cell membrane. The collected samples were transferred to the 2 mL amber vials containing 25 μL of HCl and kept at 4 °C. Sulfate analysis was conducted within one day of sampling (less than 24 h). Each vial was vortexed for 30 s before analysis. The method detection limit (MDL) for sulfate was 1.0 μM . The sulfate concentration was determined by measuring the absorbance of the solution at 650 nm using a spectrophotometer (Hatch DR 2800 Loveland, Co, U.S.A.).

Sulfide concentration in porewater was measured using the assay and calibration method described by Cline (1969). Porewater sample collection for sulfide analysis was completed in less than 5 min. Amber vials (2 mL) were filled with Cline reagents in an anaerobic chamber one day prior to sampling. For sulfide determination, 2 mL of porewater was collected from each peeper cell using 3 mL N_2 purged polypropylene syringes (Norm-Ject Syringes). 1.5 mL of porewater was injected immediately into the amber vials containing Cline reagents by piercing the Teflon septum. Each vial was shaken to mix the sample and the reagent and kept at 4 °C. Field blanks were prepared by injecting 1.5 mL of DIW into vials filled with Cline reagent under an anaerobic chamber. The MDL for sulfide was 0.3 μM . Sulfide analysis was conducted at a maximum of 2 to 3 h after each sample collection. The sulfide concentration was determined by measuring the absorbance of the solution at 670 nm with a Hatch DR 2800 spectrophotometer (Loveland, Co, U.S.A.).

Ferrous iron concentration in porewater was measured using the assay and calibration method described by Viollier et al. (2000). A Ferrozin solution was prepared and added to the pre-labeled vials in an anaerobic chamber one day prior to sampling. 1 mL of porewater was collected from each peeper cell using 3 mL N_2 purged polypropylene syringes (Norm-Ject Syringes), and injected immediately into the amber vials containing Ferrozin solution by piercing the Teflon septum. Each vial was shaken and kept at 4 °C. The MDL for Fe^{2+} was estimated at 0.2 μM . Fe^{2+} analysis was conducted at a maximum of 2 to 3 h after sample collection. The ferrous iron (Fe^{2+}) concentration was determined by measuring the absorbance of the solution at 562 nm with a Hatch DR 2800 spectrophotometer (Loveland, Co, U.S.A.).

Sediment core sampling and analytical methods

One sediment core was collected from the HWF site and reference site in August 2007 using a 1.5 m long Lexan (polycarbonate) coring tube with 7.5 cm inside diameter. Sediments were uniform brown-black clayed mud with a brownish surface containing air bubbles through their lengths. The HWF site was covered with 3–4 cm of wood fibers, as well as 5–10% wood fiber content in deposits throughout the depth of the sediment cores, whereas only scant evidence of wood fiber deposits (<2%) was seen in sediment cores from the reference site. Few benthic invertebrates were seen in the cores.

Each sediment core was sectioned within 1 h of its collection under nitrogen atmosphere. Cores were extruded on site into 1 cm thick slices for the first top 10 cm of the core and the remainder of the core was sectioned into 2–4 cm slices. The sediment samples were placed into air-tight centrifuge tubes and plastic bags, placed on ice, and transported in a dark cooler to the laboratory the same day. Sediments were then stored in a freezer for future analysis. The sediments were sub-sampled and freeze-dried for 2 to 3 days, and the dried sediments were ground by mortar and pestle. Freeze-dried samples were used for $\text{THg}_{(\text{p})}$ and $\text{MeHg}_{(\text{p})}$ analysis.

$\text{THg}_{(\text{p})}$ analysis in sediment

Homogenized freeze-dried sediment samples were analyzed for $\text{THg}_{(\text{p})}$ using an automatic mercury analyzer based on thermal

decomposition, dual step gold amalgamation and detection via Cold-Vapor Atomic Absorption using a SP-3D mercury analyzer (Nippon Instrument Corp, Japan) with a detection limit of 0.046 pMol per sample size. The accuracy of this analysis was estimated by running blanks and spikes as well as two certified reference materials during the analytical procedure. Spikes from a stock of Mercury Reference Solution (certified $5 \mu\text{mol g}^{-1} \pm 1\%$; Fisher Scientific CSM114-100) were brought to a concentration of 0.025 nm and were tested every 5 samples. The average recovery of the spikes was $102\% \pm 5$ (SD), ($n = 12$). Procedural blanks showed no contamination during THg_(p) analysis. Reference materials were tested every 4–5 samples and average percentage recovery for MESS-3 (Marine Sediment Certified Reference Materials) from NRC with concentration of $0.455 \pm 0.0045 \text{ nmol g}^{-1}$ was $96\% \pm 4$ (SD), ($n = 7$). The average percentage recovery for CRM-580 (Commission of the European Communities Reference Material No 580, Total and Methyl Mercury for Estuarine Sediments with total mercury concentration of $660 \pm 15 \text{ nmol g}^{-1}$) was $101\% \pm 13$ (SD), ($n = 6$).

MeHg_(p) analysis in sediment

The concentration of MeHg_(p) was determined by capillary gas chromatography coupled with atomic fluorescence spectrometry (GC-AFS) as described by Cai et al. (1997), with a detection limit of 0.093 pMol per sample size. Sample mass ranged between 0.8 and 1.2 g.

The homogenized freeze-dried sediment samples were used for MeHg_(p) analysis. Procedural blanks, spiked samples, and certified reference materials were analyzed as part of the quality assurance and quality control measures. The average recovery of spiked samples was $98.5\% \pm 5$ (SD), ($n = 8$) and analysis of procedural blanks revealed no contamination during MeHg_(p) analysis. The average recovery of Reference Material IAEA-405 (Trace and Major Elements in Estuarine Sediments from IAEA, Monaco with concentration of 0.03 nmol g^{-1}) was $98\% \pm 4$ (SD), ($n = 4$).

Porewater diffusion

Molecular diffusive fluxes of Hg across the sediment–water interface were determined based on the concentration gradient between porewater and overlying water using Fick's First Law of molecular diffusion.

A generally accepted form of the Fick's First Law in the absence of bioturbation and bioirrigation is:

$$F = -(\varphi D_w / \theta^2) (\delta C / \delta x)$$

where F is the flux of solute with concentration C at depth x, θ is the tortuosity (dimensionless), φ is the sediment porosity, D_w is the diffusion coefficient of the solute of interest in water without the presence of the sediment matrix, and $(\delta C / \delta x)$ is the concentration gradient across the sediment–water interface.

Tortuosity is not readily measured but has been shown to be related to porosity and it was calculated using the following equation (Boudreau, 1996) for all the flux calculations:

$$\theta^2 = 1 - \ln(\varphi^2).$$

Porosity was calculated using the following equation:

$$\varphi = 1 - (\text{bulk density} / \text{particle density}).$$

A particle density of 2.65 g cm^{-3} was used (Brady and Weil, 2002).

In this study, we used the diffusion coefficient (D_w) for MeHgCl in water (25°C) of $1.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and a D_w value for inorganic Hg in water of $9.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (Gill et al., 1999). We adopted a D_w

value of $4.09 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for Fe^{2+} (Li and Gregory, 1974; Peine et al., 2000).

Results and discussion

Hg_{diss} in porewater and overlying water

The porewater profiles of THg_{diss}, MeHg_{diss}, sulfate (SO_4^{2-}), sulfide (S^{2-}) and ferrous iron (Fe^{2+}) were obtained at the HWF and reference sites (Fig. 2). Mean THg_{diss} of the HWF site was 90 ± 50 (SD) pM, ($n = 100$) in the porewater and 60 ± 40 (SD) pM, ($n = 57$) in the overlying water, whereas in the reference site, it was 90 ± 50 (SD) pM, ($n = 87$) in the porewater and 80 ± 40 (SD) pM, ($n = 50$) in the water column. The distribution of THg_{diss} (Fig. 2, panel A and F) in porewater and overlying water was relatively homogenous across depths above and below the sediment–water interface in these profiles, providing evidence that diffusion rates were low to negligible (Table 1). A three-factor ANOVA comparing site, month, and vertical depth also determined that there was no significant difference in THg_{diss} concentrations among these factors, nor were there any significant interaction terms ($p > 0.05$). In general, THg_{diss} concentration in porewater ranged between 10 and 40 pM ($n = 187$) in both HWF and reference sites, which were comparable to those reported along the Cornwall waterfront by Delongchamp et al. (2009) and Razavi (2008).

In some profiles, THg_{diss} concentrations decreased with depth (Fig. 2, panel A and F) which can be the consequence of insoluble mercury sulfide precipitation or iron sulfide co-precipitation (Gobeil and Cossa, 1993). Saturation index calculations using Phreeqc Version 2.17.5-4799 (U.S. Geological Survey, http://wwwbr.cr.usgs.gov/projects/GWC_coupled/phreeqc/) indicated that the sulfides formed from the activity of SRBs were sequestered in our profiles as metal sulfide phases such as FeS (saturation indices from 0.46 to 3.13 in porewaters) and mackinawite (saturation index from 0.40 to 3.87 in pore waters) as well as cinnabar (saturation index from 3.08 to 5.76 in porewaters). Generally, metal sulfides become oversaturated with depth due to a rise in dissolved Fe^{2+} and sulfide. Formation of iron sulfides may limit the availability of dissolved Hg and consequently inhibit MeHg production where Fe is abundant (Han et al., 2008). In addition, THg and MeHg may bind to thiol groups present in dissolved organic matter (Rydberg et al., 2008; Shchukarev et al., 2008; Zhang et al., 2004). Rydberg et al. (2008) showed that Hg is mainly bound to reduced sulfur groups attached to refractory organic matter in Lake Nylandssjön's sediments in northern Sweden. Between 30 and 60% of the sulfur in sediments of the Lake Nylandssjön is in the form of thiols, which are known as the most important form of sulfur for binding Hg to organic matter (Shchukarev et al., 2008). Similarly, Canário et al. (2008) concluded that THg(p) concentrations in upper St. Lawrence River surface sediments were strongly influenced by concentrations of organic sulfur compounds at the sediment–water interface.

Mean MeHg_{diss} concentrations in the HWF site were 30 ± 20 (SD) pM, ($n = 47$) in porewater and 20 ± 30 (SD) pM, ($n = 26$) in the water column, whereas in the reference site they were 30 ± 10 (SD) pM, ($n = 32$) in the porewater and 20 ± 10 (SD) pM, ($n = 22$) in the water column. MeHg_{diss} concentration in porewater ranged between 3 and 100 pM in both HWF and reference sites. In general MeHg_{diss} concentrations were relatively homogeneous between porewater and overlying water with no clear depth trend indicating (a) that there is very little net molecular diffusion of MeHg_{diss} and (b) that redox-dependent processes such as sulfate reduction and Fe reduction have little effect on the distribution of MeHg_{diss} on these sediment porewaters because a uniform concentration of MeHg_{diss} in porewaters extends well below the depths where sulfate and ferric iron are present. The percentage of MeHg_{diss} to THg_{diss} in porewater ranged between 4 and ~100%, with a mean of $38 \pm 31\%$ (SD), ($n = 106$). These results were within the same range as those reported in other areas of the Cornwall waterfront: $34 \pm 31\%$ (SD), (Delongchamp et al., 2010).

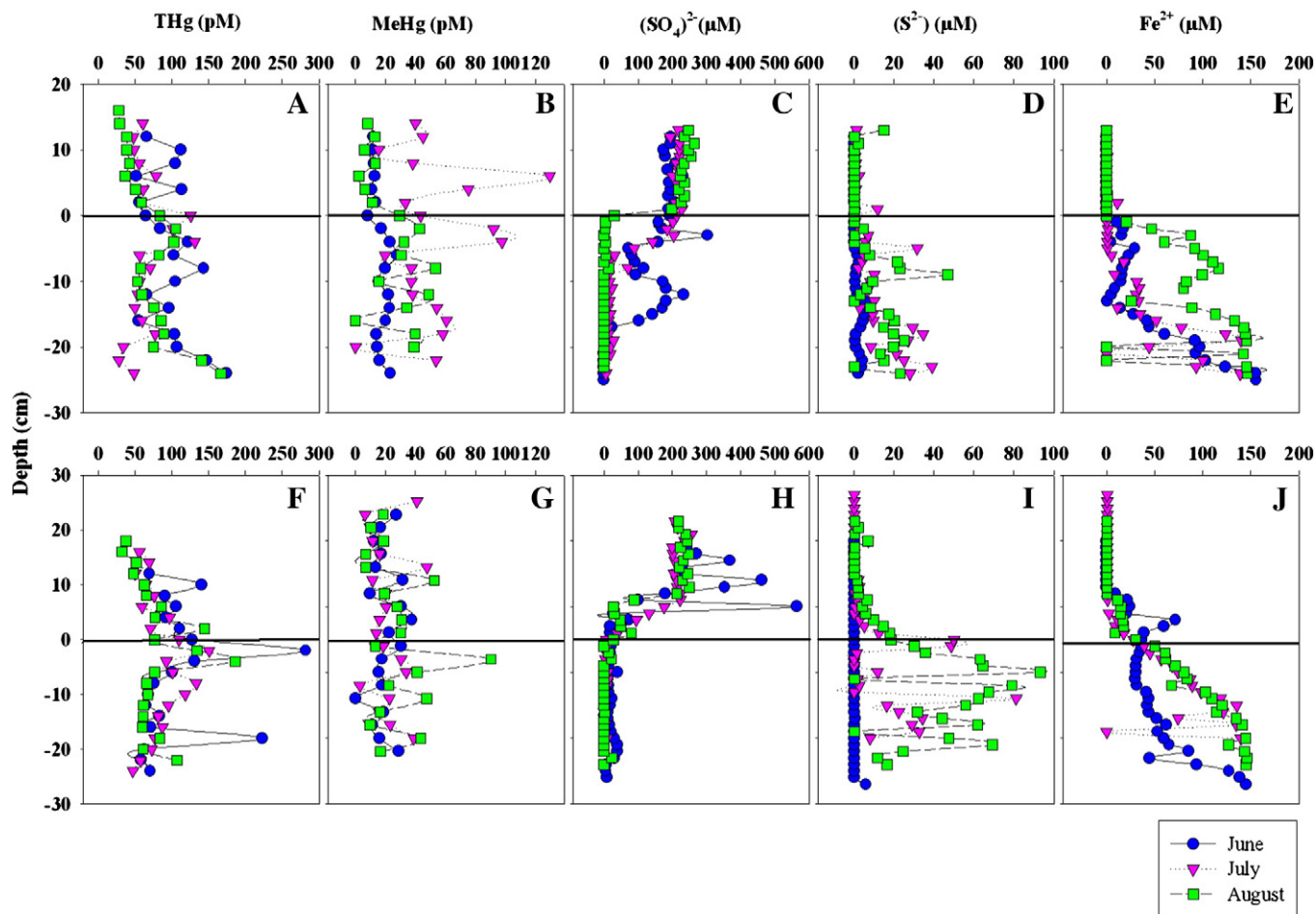


Fig. 2. Porewater profiles of (A and F) total mercury, (B and G) methyl mercury, (C and H) sulfate, (D and I) sulfide and (E and J) ferrous iron at HWF site (upper panels) and at the reference site (lower panels) of Zone 1 in the St. Lawrence River. The horizontal line indicates the sediment–water interface.

No correlation was observed between dissolved and particulate MeHg in both HWF and reference sites ($p > 0.05$) and percent dissolved to particulate MeHg ranged between 0.02 and 0.05% in the HWF and from 0.16 to 1.31% in the reference sites.

Table 1

Sediment–water diffusion flux of THg and MeHg in the HWF and reference sites. A negative value shows that diffusion is from water to sediment and a positive value shows that diffusion is from sediment to water. NA is not available. Fewer replicates were possible for MeHg analysis.

Site	Month	THg diffusion (pmol $\text{cm}^{-2} \text{yr}^{-1}$)	Standard error (pmol $\text{cm}^{-2} \text{yr}^{-1}$)	MeHg diffusion (pmol $\text{cm}^{-2} \text{yr}^{-1}$)	Standard error (pmol $\text{cm}^{-2} \text{yr}^{-1}$)
HWF	June	0.0	± 0.0	1.4×10^{-4}	$\pm 5.6 \times 10^{-1}$
HWF	June	0.0	± 0.0	0.0	± 0.0
HWF	June	0.0	± 0.0	NA	NA
HWF	July	0.0	± 0.0	NA	NA
HWF	July	0.0	± 0.0	NA	NA
HWF	July	0.0	± 0.0	0.0	± 0.0
HWF	August	$+3.9 \times 10^{-4}$	$\pm 1.4 \times 10^{-4}$	NA	NA
HWF	August	$+8.6 \times 10^{-4}$	$\pm 3.2 \times 10^{-4}$	NA	NA
HWF	August	$+1.5 \times 10^{-4}$	$\pm 4.3 \times 10^{-5}$	$+2.62 \times 10^{-4}$	$\pm 9.3 \times 10^{-4}$
Ref	June	-9.9×10^{-4}	$\pm 3.7 \times 10^{-4}$	0.0	± 0.0
Ref	June	$+5.0 \times 10^{-4}$	$\pm 1.8 \times 10^{-4}$	NA	NA
Ref	July	0.0	± 0.0	NA	NA
Ref	July	$+1.1 \times 10^{-3}$	$\pm 3.0 \times 10^{-4}$	0.0	± 0.0
Ref	July	0.0	± 0.0	NA	NA
Ref	August	0.0	± 0.0	NA	NA
Ref	August	0.0	± 0.0	NA	NA
Ref	August	0.0	± 0.0	0.0	± 0.0

A three-factor ANOVA determined that there was no significant difference in $\text{MeHg}_{\text{diss}}$ concentrations between sites, month, or depth, from June to August 2007 ($p > 0.05$).

Hg diffusion

Molecular diffusive fluxes of Hg across the sediment–water interface were determined based on the concentration gradient between porewater and overlying water (in most of the cases between 10 cm above and below the sediment–water interface). There was little evidence for molecular diffusion of THg_{diss} and $\text{MeHg}_{\text{diss}}$ from sediments to water. THg_{diss} diffusive flux ranged between 0 and $1 \times 10^{-6} \text{ nmol cm}^{-2} \text{ yr}^{-1}$ (Table 1). $\text{MeHg}_{\text{diss}}$ molecular diffusion rates ranged between 0 and $2.6 \times 10^{-7} \text{ nmol cm}^{-2} \text{ yr}^{-1}$ in the HWF site, whereas no molecular diffusion was observed in the reference site (Table 1). Observations of no or very little molecular diffusion of THg_{diss} and $\text{MeHg}_{\text{diss}}$ from sediment to water support the hypothesis that sediments in the St. Lawrence River act as a major sink for Hg. In addition, our data did not support the hypothesis that the presence of wood fibers in sediments from the pulp and paper mill influences the diffusion of THg or MeHg from sediments.

The mean THg_{diss} concentration ($70 \pm 4 \text{ pM}$) and mean $\text{MeHg}_{\text{diss}}$ concentration ($20 \pm 3 \text{ pM}$) in the water immediately above sediments were ten-fold higher than mean THg_{diss} and $\text{MeHg}_{\text{diss}}$ concentrations measured at 1 m below the water surface $6 \pm 0.5 \text{ pM}$, ($n = 12$) and $0.3 \pm 0.2 \text{ pM}$, ($n = 12$) respectively (Ridal et al., 2009). As there is little evidence of a molecular diffusion gradient at the sediment water interface, the data suggest alternative sediment transport pathways or other

Hg sources. Gas generation and ebullition from sediments have been shown to increase rates of porewater release (Klein, 2006; Martens and Klump, 1980; O'Hara et al., 1995). Ebullition rates up to $2800 \text{ mL m}^{-2} \text{ day}^{-1}$ have been measured near the study sites (Razavi et al., in press). Based on a 7% porewater release rate per gas volume (Klein, 2006), daily ebullition may account for as much as 200 mL of porewater release per m^2 of sediment. However, this represents only a 0.13% volumetric contribution to the immediate 15 cm of overlying water ($150 \text{ L of water/m}^2$) sampled by the peepers, which is too small to account for the high concentrations of THg_{diss} and $\text{MeHg}_{\text{diss}}$ in the overlying water. Another effect of ebullition is sediment resuspension (O'Hara et al., 1995) and contribution to the formation of a nepheloid layer, which has been widely reported in all of the Laurentian Great Lakes (Bell and Eadie, 1983). Nepheloid layers develop each summer (during thermal stratification), disappear in early fall (Hicks et al., 2004; Urban et al., 2004), and are characterized by high suspended solid particles (Hicks et al., 2004; Schneider et al., 2002; Urban et al., 2004) and low water transparency (Chambers and Eadie, 1981). These layers may maintain the elevated Hg concentration by stratification or particle resuspension, so benthic organisms may be exposed to elevated Hg as a result. Underwater video in areas near the sampling sites indicated that sediment–water interface was composed of a fine-silty layer and signs of disturbance from collapsing gas pockets from escape of gas from the sediments (Biberhofer and Rukavina, 2002); conditions which could contribute to nepheloid layer formation. The presence of a nepheloid layer may explain the observations of similar concentrations for THg_{diss} and $\text{MeHg}_{\text{diss}}$ in porewater and overlying water and consequently no or very low molecular diffusion rates across the sediment water interface.

The distribution coefficients (K_D), calculated as the mercury concentration on particles divided by the dissolved mercury concentration, were determined for both THg (39 to 750 L g^{-1}) and MeHg (K_D^{MeHg}) (0.2 to 5.95 L g^{-1}), and were generally higher than those reported in the nearby St. François Bay (6 to 34 L g^{-1}) and (0.004 to 2.6 L g^{-1}) respectively (Goulet et al., 2007). Large variations for sediment THg(p) and MeHg(p) K_D are commonly reported. According to Choe et al. (2004), sediment MeHg(p) distribution coefficient ranged between 0.3 and 100 L g^{-1} in San Francisco Bay. The elevated K_D for both THg and MeHg in this study revealed that a very low proportion of these metal forms ($<1.5\%$) was available for diffusion from sediments to water.

Complementary redox-dependent variables profiles

At both HWF and reference sites, sulfate concentrations in the water column decreased sharply near the sediment water interface (Fig. 2, Panel C and H), indicating that sulfate was reduced below the sediment–water interface by sulfate reducing bacteria (SRBs) which are believed to be the primary methylators of Hg in anoxic sediments (Celo and Scott, 2006; Compeau and Bartha, 1985). Increases

in sulfide concentration below the sediment–water interface (Fig. 2, panel D and I) were also consistent with this scenario.

In general, sulfide concentrations were near zero or very low in the overlying water but they increased in the sediment porewaters, except for the June HWF and reference profiles, where sulfide concentrations were very low in both the water column and the porewaters (Fig. 2, panel D and I). There was a sharp increase in the concentration of sulfide between 0 and 15 cm in sediment in July and August. In the July reference profile (Fig. 2, panel I), a larger sulfide peak was observed in the deeper porewaters suggesting sulfate reduction at these depths. Sulfide concentration in sediment porewaters increased at both sites as the summer progressed.

Production of Fe^{2+} in the anoxic sediments might be the result of iron reducing bacteria, which are also thought to contribute to Hg methylation (Chapelle and Lovley, 1992; Lonergan et al., 1996). The mean Fe^{2+} concentration in the present study was 0.89 ± 3.09 (SD) μM , ($n = 78$) in the overlying water which was 12 times higher than those reported in surface water in the St. Lawrence River 0.07 ± 0.19 (SD) μM , ($n = 39$); Quemerais et al. (1998). Fe^{2+} concentrations were zero or near zero in the water column and near the sediment–water interface, there was an increase in Fe^{2+} concentration with depth (Fig. 2, panel E and J). Upward Fe^{2+} molecular diffusion rates as calculated from these porewater profiles ranged between 2×10^{-4} and $5 \times 10^{-4} \mu\text{mol cm}^{-2} \text{ yr}^{-1}$ in the HWF and from 0.1×10^{-4} to $5 \times 10^{-4} \mu\text{mol cm}^{-2} \text{ yr}^{-1}$ in the reference site.

Solid phase Hg profiles

THg(p) concentrations in the HWF and reference cores ranged between 3.74 and $224 \text{ nmol g}^{-1} \text{ dw}$ (Fig. 3) which were comparable to values previously reported in surface sediments (top 5 cm) in this stretch of river (1.63 to 218 nmol g^{-1} , Delongchamp et al., 2009; 1.42 to 25.8 nmol g^{-1} , Canário et al., 2008; and 3.84 to 89.5 nmol g^{-1} , Razavi, 2008). THg(p) at the HWF and reference sites were much higher than the THg(p) in sites located upstream. For example, Hg(p) in sediment cores from sites upstream the Cornwall industries ranged between 0.38 and 0.70 nmol g^{-1} (Milani and Grapentine, 2009), and Hg(p) ranged between 0.99 and 1.7 nmol g^{-1} at another site located just 5 km upstream of our study site, and upstream of local industries (Hans Biberhofer, Environment Canada, personal communication). THg(p) concentrations measured here were also much higher than those reported by Goulet et al. (2007) in the St. François Bay wetlands along the St. Lawrence River (0.012 – $0.027 \text{ nmol g}^{-1}$) demonstrating the influence of Hg discharge from local industries near Cornwall to the river. Total mercury in surface sediments (0 – 5 top centimeter of the core) ranged between 6.2 and $8.7 \text{ nmol g}^{-1} \text{ dw}$ in the HWF core and from 3.83 to $6.1 \text{ nmol g}^{-1} \text{ dw}$ in the reference core.

Other studies in the same area of the St. Lawrence River (Zone 1) also showed that THg(p) concentrations of HWF and reference sediments exceeded the sediment quality guideline of $0.085 \text{ nmol g}^{-1}$,

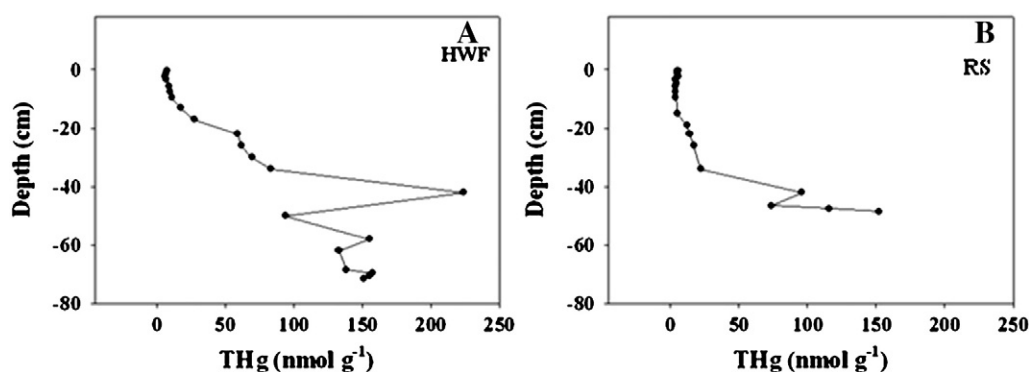


Fig. 3. Depth profile of total mercury in sediment cores from the HWF site (A) and reference site (B).

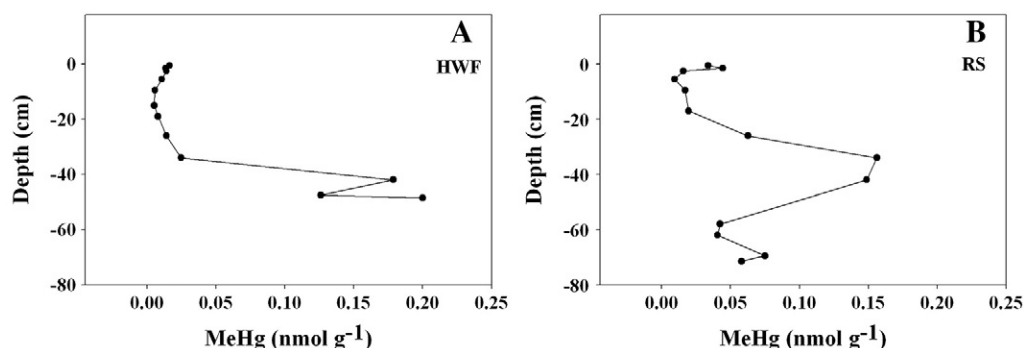


Fig. 4. Depth profile of methyl mercury in sediment cores from the HWF site (A) and reference site (B).

and the probable effect level of 2.43 nmol g^{-1} , which are the limits set by Canadian Council of Ministers of the Environment for the protection of aquatic life (Richman and Dreier, 2001; Grapentine et al., 2003; Razavi, 2008; Delongchamp et al., 2009). Consequently, high Hg concentrations in the sediments in this portion of the St. Lawrence River remain a concern.

MeHg(p) concentration in sediments ranged between 0.01 and 0.2 nmol g^{-1} dw in both cores, similar to concentrations reported previously in this area of the St. Lawrence River (Canário et al., 2008; Delongchamp et al., 2009), but higher than those reported in sediments from St. Lawrence River in the St. François Bay (0.001 to $0.008 \text{ nmol g}^{-1}$; Goulet et al., 2007). The higher MeHg(p) concentrations in the St. Lawrence AOC suggest high Hg methylation or low demethylation rates at this site and may explain the elevated mercury contamination in biota along the Cornwall waterfront in the St. Lawrence River (Choy et al., 2008; Fowlie et al., 2008).

The MeHg(p) profiles were similar to the THg(p) profiles (Figs. 3, 4), with peak concentrations at 34 cm in the HWF core, and 48 cm in the reference core. These results suggest either that high MeHg(p) deposits are preserved in these sediment archives, or that MeHg(p) production in these sediments is regulated by the amount of Hg present.

Marvin-Dipasquale and Oremland (1998) showed that demethylation rates decreased with increasing sediment depth, which may partly explain the presence of MeHg(p) in deeper sediment intervals. However, the presence of MeHg(p) in deep sediments well below the disappearance of sulfate (Fig. 2C and H) suggests that if Hg methylation occurs in deeper intervals, it is not by SRBs or iron reducing bacteria. Other potential Hg methylators include methanogens (Oremland et al., 1991; Pak and Bartha, 1998; Wood et al., 1968).

Large peaks of MeHg(p) in both HWF and reference sites (Fig. 4) occurred where THg(p) was elevated in deeper sediment horizons (Fig. 3). There is a strong correlation between THg(p) and MeHg(p) in sediment in both HWF and reference profiles (Pearson $r_s = 0.67$, $p = 0.012$, and $r_s = 0.81$, $p = 0.001$, respectively). Han et al. (2008) previously argued that Hg methylation rates are controlled by the availability of Hg (II), which is consistent with our findings. This effect of Hg (II) availability on Hg methylation rates was recently confirmed experimentally on sediments from the same part of the St. Lawrence River where our study was conducted (Avramescu et al., 2011).

Conclusions

MeHg_{diss} and THg_{diss} concentrations were similar among HWF and reference sites, and relatively homogenous in the sediment porewater and overlying water, indicating very little net molecular diffusion of MeHg_{diss} and THg_{diss}. Most of the Hg in the St. Lawrence River sediment near Cornwall is associated with particulate material (less than 0.16% dissolved to particulate THg and MeHg), largely preventing its diffusion to overlying waters. Coincident subsurface peaks in MeHg(p) and THg(p) in sediments suggest either preservation of historical MeHg(p) deposits or active Hg methylation in deep sediments well below the

oxidized microlayer. In general, porewater profiles of THg_{diss}, MeHg_{diss}, sulfate, sulfide and Fe^{2+} in summer 2007 revealed that redox processes in sediment such as sulfate reduction and Fe reduction appear to have little effect on the distribution of MeHg_{diss} and THg_{diss} on the sediment porewaters of the HWF and reference sites.

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