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Horizontal and vertical variability of mercury species in pore water and sediments in small lakes in Ontario

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Abstract

Mary Lake, St. George Lake, and Philips Lake are located in the Greater Toronto Area, Ontario, Canada. These lakes are relatively small and have no direct inflow and outflow channels. Mercury (Hg) input to the lakes comes mainly from atmospheric deposition. Sediment cores from the points of the maximum lake depth and surface sediment samples from the points of maximum lake depth to the bank of each lake were collected in October 2005. Total and methyl mercury concentrations in the pore water and sediments of these samples were determined. In these small lakes with high organic content, there was no correlation between organic content and total mercury (THg) in the samples throughout the entire sediment cores while strong positive correlation between these two parameters was observed in all the surface sediments. Compared with typical methylmercury (MeHg) depth-profiles of sediment cores in other studies, where MeHg concentrations and methylation rates decreased sharply with increasing depth, MeHg distributions in the sediment cores in this study showed that MeHg might have been produced not only in the upper sediment but also in the deeper sediments, which resulted in a larger MeHg reservoir in the sediment. Organic matter, to some extent, affected MeHg distributions in the samples throughout the entire sediment cores. Concentrations of MeHg in all the surface sediments, however, were not controlled by organic matter, whereas they were largely a function of water column depths. Total mercury concentrations in pore water were relatively homogenous in both the sediment cores and surface sediment while MeHg in pore water generally deceased with increasing depth in the sediment cores and increasing distance from the centre of the lakes in surface sediments. Methylmercury contributed 1% to 76% of THg in the pore water samples. Concentrations and distributions of MeHg in overlying water and sediment-surface water in Mary Lake and St. George Lake suggested that both in situ production of MeHg in lake water and the release of MeHg from sediment contributed to high MeHg in deep anoxic water.

Keywords: Total mercury; Methylmercury; Sediment core; Surface sediment; Pore water; Lake

1. Introduction

Some studies have found elevated MeHg concentrations in fish even in lakes located far from point sources in Northern America and Northern Europe (e.g. Verta, 1990; Lindqvist et al., 1991). Although numerous studies have been conducted on the mechanisms of elevated MeHg in biota, many accumulation, transformation, and distribution mechanisms operating in the biota and lakes are still poorly understood because of the complexity in the geochemical cycling of Hg in the

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environment. Sediment has long been recognized as a key location of microbial methylation (Hammerschmidt and Fitzgerald, 2004), thus understanding geochemical cycling of Hg in sediment and pore water is essential to understanding the modes of transfer of Hg to overlying water and biota.

A number of studies have been published on Hg distributions and methylation in sediments and pore water of coastal marine systems (e.g. Sunderland et al., 2004; Hammerschmidt and Fitzgerald, 2004). There is considerable evidence that methylation is carried out by sulfate-reducing bacteria (e.g. Gilmour and Henry, 1991; Benoit et al., 1999), and MeHg production occurs in a relatively narrow subsurface zone within the sediments (e.g. Bloom et al., 1999; Hammerschmidt and Fitzgerald, 2006). Sunderland et al. (2004), however, found that MeHg production occurred throughout the estimated 15 cm-thick active surface layer in estuarine well-mixed sediments, which resulted in a larger MeHg reservoir in sediment. Covelli et al. (1999) reported that the highest benthic efflux and pore water concentrations of Hg and MeHg appeared during autumn and winter in the gulf of Trieste while maximal fluxes were observed in late winter to early spring in Lavaca Bay (Gill et al., 1999). Hammerschmidt and Fitzgerald (2006) observed that the efflux and production of MeHg from coastal marine sediments were limited by Hg(II) from atmospheric deposition, and organic matter controlled the distribution of Hg species and sediment–water partitioning of Hg species.

In lake environments, however, most studies have focused on factors controlling Hg accumulation in biota, biogeochemistry of Hg species in lake water, and THg history in sediment profile (e.g. Kainz and Lucotte, 2002; Lockhart et al., 2000). Less attention has been paid to total and methyl mercury distribution and controlling factors in pore water and sediment. Hines et al. (2004) observed that distinct peaks of MeHg roughly correlated with maxima in sulfate-reducing activity at 5 and 15-cm depths in a bog lake. In recent research, however, an iron-reducing bacterium has been showed to methylate Hg at environmentally significant rates in Clear Lake for the first time (Fleming et al., 2006). This shows that many of the transformation and distribution mechanisms operating in sediment are still unclear because the synthesis of MeHg in aquatic systems is influenced by a wide variety of environmental factors and the complexity of processes in the natural environment.

In this paper, we investigated distributions of Hg species in pore water and sediment in three lakes located near Toronto, Ontario, Canada.

2. Methodology

2.1. Sampling site description

Mary Lake, St. George Lake, and Philips Lake, (Fig. 1), are located north of the Greater Toronto Area (GTA), the largest metropolitan area in Canada, with a population of more than 5.6 million. The areas of the lakes are 0.16, 0.10, and 0.08 km^2 and the maximal water depths are 16, 16, and 26 m, respectively. The lakes are located in rural areas and their surrounding areas are well covered with trees and vegetation. To our knowledge, there is no document showing the history of managed timber cutting and dredging of the lakes. The lakes have no direct inflow and outflow channels. There are no commercial activities on the lakes and the levels of human activities are low despite their proximity to the GTA. Mercury input to the lakes mainly comes from atmospheric deposition, runoff, and falling tree leaves and debris. The lakes were well stratified even in October. The data from the National Atmospheric Deposition Program/Mercury Deposition Network (NADP/MDN) showed that the average wet deposition of Hg was 5.0 $\mu g\ m^{-2}\ yr^{-1}$ (2001–2005) in Egbert, a town that is about 40 km away from Philips Lake. Considering the effect of differences in surface sediment composition and depth of water column on the distribution of Hg speciation, we collected not only sediment cores but also surface sediment and pore water samples from the point of maximum lake depth to the bank of each lake.

2.2. Lake water sampling

Water samples for THg and MeHg were collected in Mary Lake and St. George Lake. All water samples were collected in borosilicate glass bottles (125-mL) that were cleaned by acid leaching, rinsing with ultrapure deionized water and heating for several hours in a muffle furnace at 500 °C. The filtered samples were collected by filtering with a 0.45-μm filter (Millipore) on site. All water samples were acidified using a 0.5% HCl solution, stored in clean double zipped-type bags, transported to the lab within 24 h, and then stored at 3–4 °C in the absence of light until analysis. Water quality parameters such as pH, temperature (T), and dissolved oxygen (DO) were measured on site using a YSI model 57 (Yellow Springs Instrument Co. Inc).

2.3. Sediment and pore water sampling

Sediment cores approximately 30-cm long were collected from the point of maximum lake depth in St.

George Lake and Philips Lake in October 2005, while no core was collected in Mary Lake because of the high water content in the sediment. The cores were sectioned at 1 and 2-cm intervals (1-cm intervals for sediment core dating and 2-cm intervals for chemical analysis). Each core section was sliced into 45-mL centrifuge tubes in nitrogen gas (N_2). At the same time, 17 surface sediment samples (about upper 4 cm) from the point of maximum lake depth to the bank of the lake, which corresponded to a series of water depths, were collected by a grab sampler. All the samples were transported in an ice-cooled container to the lab and stored in a refrigerator at 3–4 °C. Pore water was extracted from wet sediment within 48 h by centrifugation at 3000 r min^{-1} for 30 min at *in situ* bottom-water temperature (5 °C), and then filtered through a 0.45 μm polyvinylidene fluoride (PVDF) membrane (Millipore). The resulting pore water was collected in borosilicate glass bottles and acidified using a 0.5% HCl solution. All bottles were capped and then sealed with parafilm. The whole process was done in an N_2 bag with gloves and acid-cleaned filters were rinsed with de-oxygenated reagent-grade water immediately prior to sample filtration (Mason et al., 1998). All the resulting pore water samples were stored in a refrigerator at 3–4 °C until analysis. Solid phase samples were freeze-dried and homogenized with a mortar.

2.4. Mercury analysis

Mercury species in the samples of lake water, pore water, and sediment were measured using the methods that are based on purging, trapping and cold vapor atomic fluorescence detection.

United States Environmental Protection Agency's (USEPA) method 1631 was followed for the analysis of THg in water (USEPA, 2002). Mercury in water samples was oxidized with 0.5% BrCl. After oxidation, NH_2·OH·HCl was added to destroy the free halogens before adding stannous chloride ($SnCl_2$) to convert Hg(II) to volatile Hg(0). The resulting sample was then purged with Hg-free N_2 and Hg(0) was absorbed onto a gold trap.

Total mercury in sediment was measured following the procedure of Fleck et al. (1999). Sediment samples of ~0.2 g were placed in acid-cleaned 30-mL Teflon digestion bombs. Volumes of 10 mL concentrated sulfuric acid and 10 mL of concentrated nitric acid were added. The bombs were sealed tightly and placed in an oven at 45 °C overnight. The acids were neutralized using hydroxylamine solution before an appropriate volume (generally 0.4 mL) of the digested sample was transferred to a borosilicate bubbler for Hg analysis following the procedure described previously.

Methylmercury in water was measured following USEPA Method 1630 (USEPA, 2001). An aliquot of 45 mL sample was placed in a fluoropolymer distillation vessel and the distillation was carried out at 125 °C under Hg-free N_2 flow until approximate 35 mL of water was collected in the receiving vessel. The sample collected was adjusted to pH 4.9 with an acetate buffer and the Hg in the sample was ethylated in a closed 200-mL bubbler by the addition of sodium tetraethyl borate. The ethyl

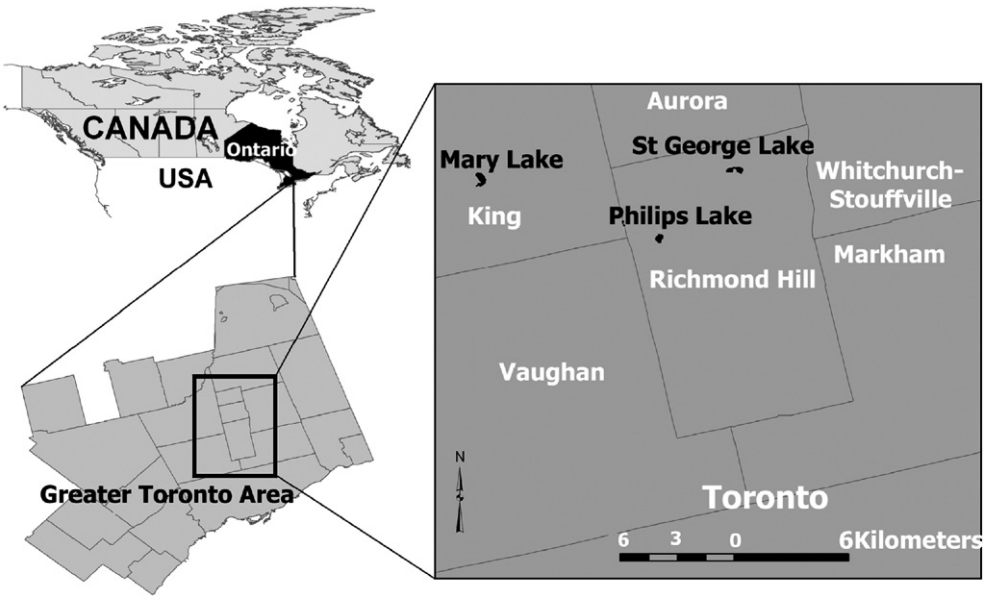

Fig. 1. Locations of the study area and the lakes.

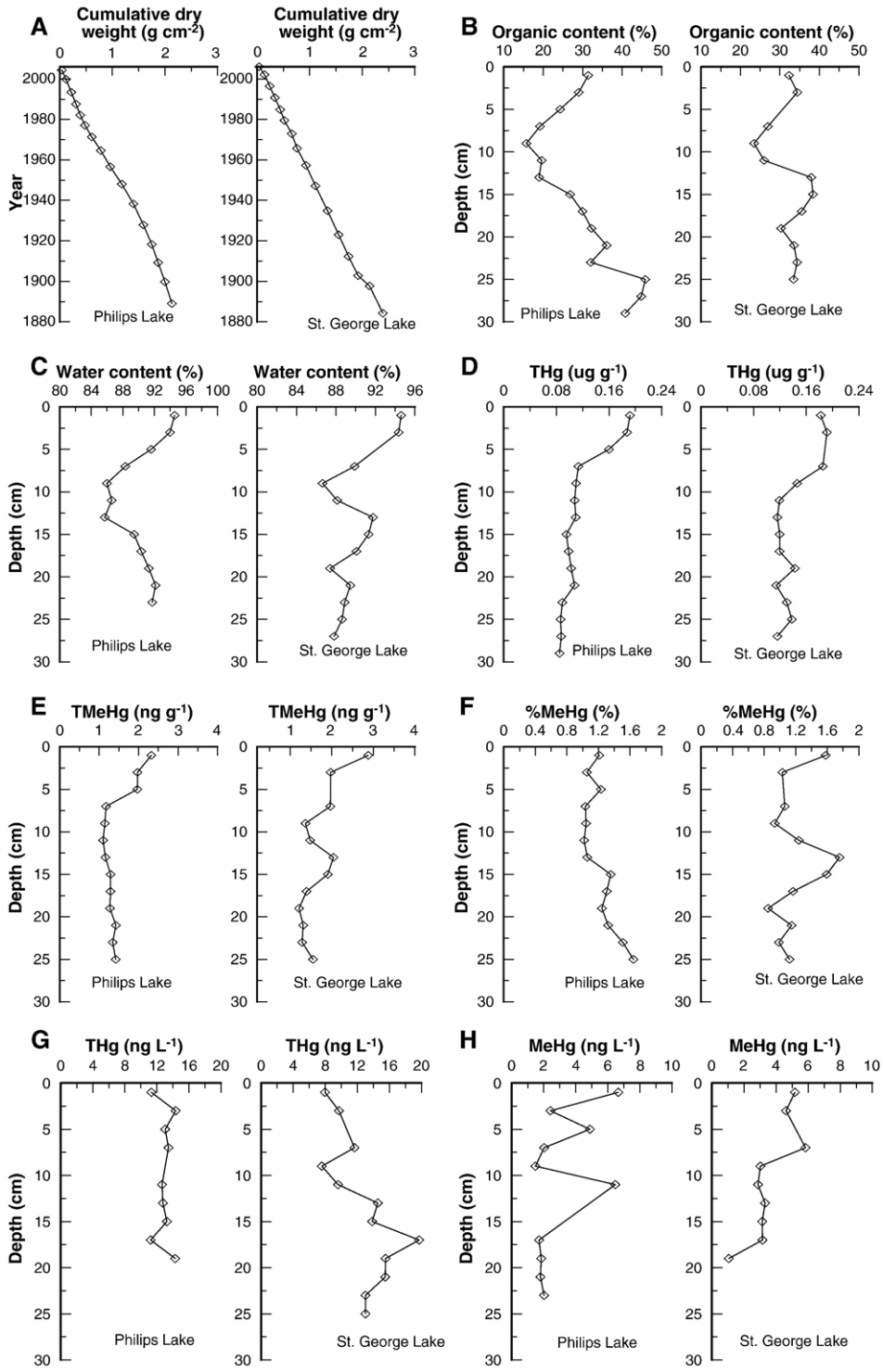

Fig. 2. Depth profiles of accumulative dry weight (A), organic content (B), water content (C), THg (D), TMeHg (E). %MeHg (F), THg (G) and MeHg (H) in solid phase and pore water of the sediment cores in Philips Lake and St. George Lake.

analog of CH_3Hg, $CH_3CH_3CH_2Hg$, was separated from solution by purging with N_2 onto a Tenax trap. The trapped $CH_3CH_3CH_2Hg$ was then thermally desorbed, separated from other Hg species by an isothermal gas chromatography (GC) column, decomposed to Hg(0) in a pyrolytic decomposition column (700 °C) and then carried into the cell of a cold-vapor atomic fluorescence spectrometer (CVAFS) for detection.

Analysis of MeHg in sediment was performed following the procedure developed by Liang et al. (2004). Approximately 0.3 g of sediment was placed into a 50-mL centrifuge tube. 1.5 mL of 1 M $CuSO_4$, 7.5 mL of 3 M HNO_3 and 10 mL of CH_2Cl_2 were added. The tube was closed and shaken for 30 min. 5 mL of the CH_2Cl_2 layer was pipetted into another 50-mL centrifuge tube after the tube was centrifuged at 3000 rpm for 30 min. About 40 mL of double-deionized water was added to the tube. The tube was heated at 45 °C in a water bath until no visible solvent was left in the tube and the remaining liquid was then purged with N_2 for 8 min in a water bath at 80 °C to remove solvent residue. The sample was brought to 50 mL with double-deionized water before an appropriate volume (generally 15 mL) of the sample was transferred to a borosilicate bubbler for MeHg analysis following the procedure described previously.

Quality assurance and quality control of the process of analysis were carried out by using duplicates, method blanks, matrix spikes, and certified reference material (IAEA 405, marine sediment). A mean MeHg concentration of 5.48±0.52 (n=7) was obtained from IAEA 405 with a certified value of 5.49±0.53 ng g^{-1}. The average THg concentration of IAEA 405 was 0.81±0.03 μg g^{-1} (n=6), which was comparable with the certified value of 0.81±0.04 μg g^{-1}.

3. Results

3.1. Sediment cores

3.1.1. ^{210}Pb dating

^{210}Pb activity profiles of the sediment cores were used to determine the chronological age of the sediment as well as the sedimentation rate. The results of the ^{210}Pb analysis are presented in Fig. 2A. The average dry mass sedimentation rates in sediment cores in St. George Lake and Philips Lake were determined to be 0.018 and 0.017 g cm^{-2} yr^{-1} respectively using the CIC2 model (the Constant Initial Concentration). These rates are relatively low due to the fact there is no direct inflow to the lakes and that the surrounding areas of the lakes are well covered with trees and vegetation. Most of the sediment came from falling tree leaves and debris in the areas and settling of aquatic organisms and plants in the water column. Sediment core data are characterized by a high degree of temporal variation. Analyses indicated that porosity decreased with increasing depth in about the top 10 cm and then increased with increasing depth.

3.1.2. Geochemical characteristics of the sediment cores

Fig. 2B and C show the depth-profiles of organic content and water content in Philips Lake and St. George Lake. The average water content in sediment cores in St. George Lake and Philips Lake was 90.2% and 90.1%, while the average organic content was 32.2% and 29.8%, respectively. In both lakes, water and organic content in sediments was much higher than in most of the aquatic systems reported (e.g. Mann and Wetzel, 2000; Rasmussen et al., 1998). The organic and water content decreased with increasing depth in the top 10 cm of sediment and then increased with increasing depth, whereas organic content in sediment cores has been found to decrease with increasing depth in other studies (e.g. Mann and Wetzel, 2000; Rasmussen et al., 1998). The sediments in these lakes contained small amounts of coarse debris, mostly of woody stems. The pH values ranged from 6.98 to 6.63, and decreased with depth in sediment cores.

3.1.3. THg in solid phase

The depth-profiles of THg in sediment cores from St. George Lake and Philips Lake are presented in Fig. 2D. Total mercury ranged from 0.09 to 0.19 μg g^{-1} in Philips Lake and from 0.12 to 0.18 μg g^{-1} in St. George Lake. The profiles of THg for the two sediment cores show that Hg concentrations generally increased towards the sediment–water interface. Enrichment of Hg in surface sediments has often been reported, even in some remote lakes (e.g. Rasmussen et al., 1998; Lockhart et al., 1998). The correlations between organic matter and Hg species in the sediment cores are listed in Table 1. We did not observe any correlation (r=−0.18, P>0.05, Table 1) or similar distribution trends (see Fig. 2B and D) between organic matter and THg in the sediment cores.

3.1.4. MeHg in solid phase

Fig. 2E shows MeHg profiles of the two sediment cores. Methylmercury concentrations ranged from 1.09 to 2.32 ng g^{-1} in Philips Lake and from 1.21 to 2.88 ng g^{-1} in St. George Lake. The concentrations of MeHg decreased with increasing depth in the top 6 cm of sediment in both lakes. The values then remained

Table 1
Correlation (r) between measured parameters in solid phase and water phase (pore water) in the sediment cores and the surface sediments, *$P<0.05$, **$P<0.01$, ***$P<0.001$

r		OM	Water content	MeHg (solid)	THg (solid)	MeHg (water)	THg (water)	%MeHg (solid)	log Kd (MeHg)	log Kd (THg)	%MeHg (water)
Sediment cores	OM	1	0.63**	0.31	−0.18	−0.09	0.09	0.58**	0.24	−0.05	−0.18
	Water content		1	0.78**	0.53**	0.06	−0.11	0.5*	0.11	0.42	0.09
	MeHg (solid)			1	0.74**	0.80	−0.36	0.4	0.03	0.67**	0.19
	THg (solid)				1	0.04	−0.2	−0.3	0.04	0.79**	0.08
	MeHg (water)					1	−0.09	0.13	−0.92***	−0.03	0.96***
	THg (water)						1	−0.02	0.1	−0.75**	−0.34
Surface sediments	OM	1	0.83***	0.68**	0.88***	0.73**	0.16	0.02	−0.68**	0.85***	0.75**
	Water content		1	0.57*	0.72**	0.52	0.36	0.11	−0.76**	0.87**	0.49
	MeHg (solid)			1	0.78**	0.69**	0.46	0.54*	−0.29	0.55*	0.64**
	THg (solid)				1	0.81***	0.34	−0.02	−0.65**	0.91***	0.79**
	MeHg (water)					1	0.23	−0.01	−0.72**	0.67**	1.00***
	THg (water)						1	0.23	−0.19	0.10	0.15

relatively unchanged in Philips Lake while the concentration started to increase at the depth of 8-cm and reached a peak value of 2.03 ng g^{-1} at the depth of 14-cm in St. George Lake. The ratios of MeHg and THg concentrations (%MeHg) as a function of depth are presented in Fig. 2F. In Philips Lake, the %MeHg values were relatively consistent (~1%) at all depths, while there was a peak (~1.7%) at the depth of 14-cm in St. George Lake. A number of studies found %MeHg was a reasonable approximation of the relative rates of Hg methylation in uncontaminated sediments (e.g. Benoit et al., 2003; Sunderland et al., 2004). In typical profiles observed in other studies (e.g. Bloom et al., 1999; Benoit et al., 1998), MeHg production was observed to take place in a narrowly constrained surface or subsurface zone, and MeHg concentration and methylation rate (%MeHg) in solid phase declined sharply with increasing depth. The %MeHg in the deep part of these sediment cores was also generally less than 0.5%. In our investigation, however, MeHg did not decrease with increasing depth sharply but remained relatively uniform below some depth and higher %MeHg values were observed in the deeper sediments. These MeHg and %MeHg profiles suggested that MeHg production occurred not only in the upper sediments but also in the deeper sediments. On the other hand, Marvin-Dipasquale and Oremland (1998) reported that demethylation rates decreased with increasing sediment depth. Lack of demethylation, therefore, might also contribute to the observed preservation of MeHg in the deeper sediments in this study.

Table 1 shows a modest ($r=0.58$, $P<0.01$) correlation between %MeHg and organic content in sediment cores. Although there was also no correlation between MeHg concentration and organic matter (Table 1), the depth-profiles for MeHg and for organic matter, especially in St. George Lake, were similar (see Fig. 2B and E). These data show organic matter can, to a certain degree, affect MeHg distribution in these sediment cores.

3.1.5. THg and MeHg in pore water

Fig. 2G shows the profiles of THg in the pore water of the two lakes. The distribution of THg in the pore water was relatively homogenous within depths in Philips Lake and the concentrations ranged from 11.20 to 14.30 ng L^{-1}. In St. George Lake, the concentrations of THg in pore water ranged from 7.58 to 19.70 ng L^{-1} and were lower in the upper 12 cm of the profile, whereas the THg concentrations were higher in solid phase. The range (3.78 to 4.35) in partition coefficients (log Kd) for THg was relatively small and was similar to that reported in literature (e.g. Hammerschmidt and Fitzgerald, 2004; Bloom et al., 1999). In a coastal marine deposit, a strong correlation between organic matter and log Kd of THg was observed (Hammerschmidt and Fitzgerald, 2006), but we did not observe any relationship between these two parameters in these lakes.

Methylmercury profiles in pore water, Fig. 2H, show higher values in the top several centimeters in the two cores. The values ranged from 1.04 to 6.64 ng L^{-1} and they were positively correlated with concentrations of MeHg in solid phase ($r=0.80$, $P<0.001$, Table 1). Methylmercury contributed 13% to 65% of THg in pore water in the sediment cores. They were much higher than those in the solid phase of the sediments (0.80% to 1.7%). High proportions of MeHg in pore water were

also observed in other aquatic systems (e.g. Hines et al., 2000; Ullrich et al., 2001).

3.2. Surface sediment

3.2.1. THg in solid phase

Concentrations of Hg species in solid and pore water of the surface sediments in the three lakes are shown in Fig. 3. The THg concentrations varied from 0.03 to 0.20 μg g^{-1} and MeHg ranged from 0.17 to 2.86 ng g^{-1} at all the surface sediment locations. All the horizontal profiles of THg, MeHg and organic matter in surface solid phase show that these values decreased generally with increasing distance (decreasing in overlaying water depths) from the centre to the shore of the lakes. In contrast with vertical profiles of THg and organic matter, the horizontal profiles show that THg was well correlated with organic matter in all the surface sediment samples (Fig. 4A, $r=0.88$, $P<0.001$). This shows that organic matter was a major control in the distribution of THg in the surface sediments. The affinity of Hg to organic matter is well known both in water and sediment. Hammerschmidt and Fitzgerald (2006) observed a strong correlation between Hg species and organic matter in surface sediments of coastal oceans, and the authors thought this correlation was a result of scavenging of Hg in the water column by organic particles. The average THg and organic contents in the surface sediments in St. George, Philips and Mary Lake are presented in Fig. 5, which shows that THg increased with increasing organic matter. In addition, concentrations of THg and organic matter in the sediment core from St. George Lake were generally higher than those in Philips Lake at the same depths (see Fig. 2B and D). These relationships of THg and organic matter in the lakes show that organic matter affected the concentrations of THg in the sediments, especially in the surface sediments.

3.2.2. MeHg in solid phase

Fig. 4B shows that MeHg was related to organic matter ($r=0.68$, $P<0.01$, Table 1) in the surface sediments of the lakes, but this correlation was not highly significant ($P<0.01$). For example, in Philips Lake, the organic content was almost the same at 26-m, 17-m, and 8-m locations, but the concentration of MeHg

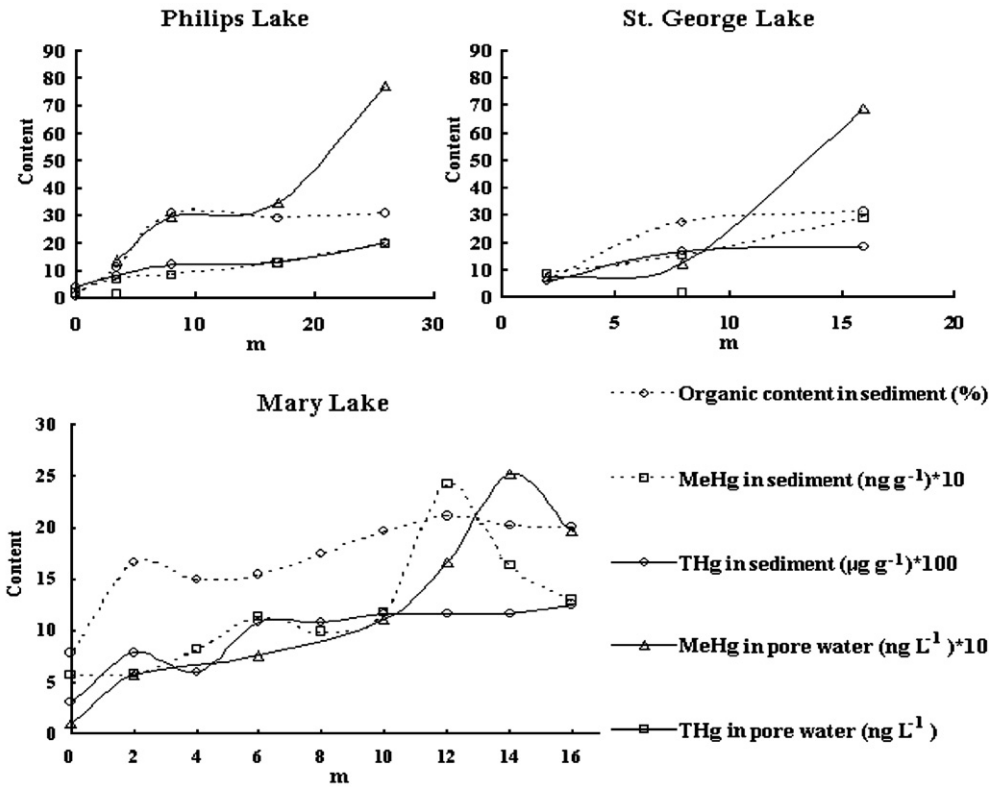

Fig. 3. Geochemical characteristics and mercury species distributions of surface sediment in the lakes. *X*-axis shows the depth of water column under where the surface sediment samples were collected.

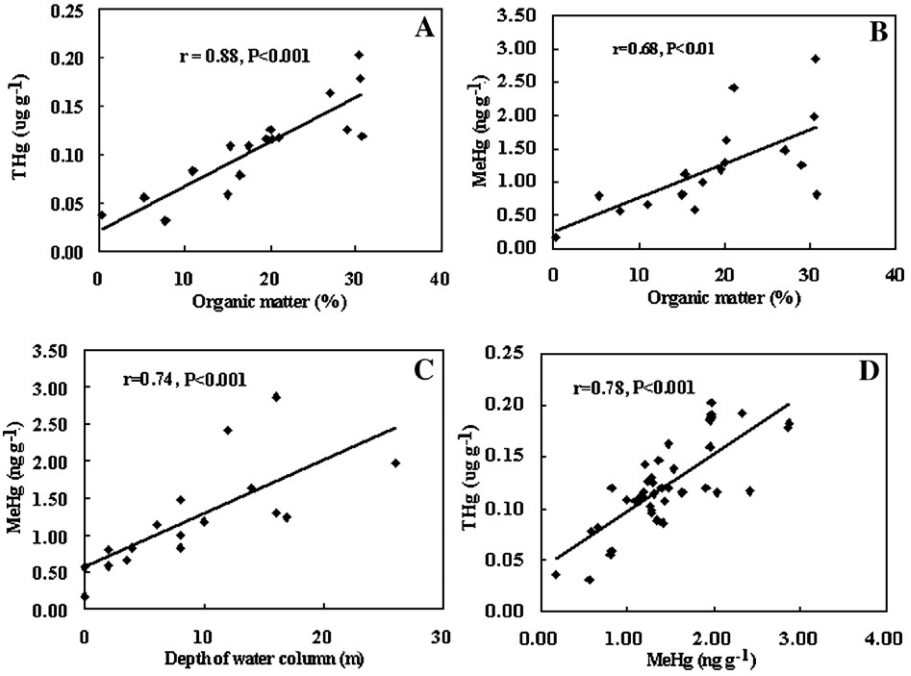

Fig. 4. Relationships between mercury species and organic matter in all surface sediments in the three lakes (A, B); MeHg in the surface sediments and the depths of overlying water columns (C); THg and MeHg in all the sediment samples in the three lakes (D).

varied significantly. In addition, the %MeHg values varied from 0.50% to 2.1% and they were not correlated with organic matter ($r=0.02$, Table 1). These poor relationships indicate that organic matter was not a major factor influencing MeHg levels in surface sediments in these lakes. This shows that concentrations of MeHg in the surface sediment were a function of other factors, such as redox potential, which is a factor that significantly influences methylation (Ullrich et al., 2001) and is related to water depth in stratified lakes. We did indeed observe a strong correlation (Fig. 4C, $r=0.74$, $P<0.001$) between MeHg in surface sediment and the depths of overlying water columns, which suggests that MeHg concentrations may be largely a function of water depth in these lakes. Furthermore, as focusing frequently happens in some lakes with a steep slope (Hákanson and Jansson, 1983), it might also play a role in the distribution of Hg species in the surface sediment in these lakes. The analysis shows that MeHg was positively correlated with THg in both surface and core sediment samples (Fig. 4D, $r=0.78$, $P<0.001$). Although THg is a poor predictor of MeHg, a strong relationship was observed in some uncontaminated sediment (Hammerschmidt and Fitzgerald, 2006). This suggests that a similar mechanism may influence the solid phase ratio of MeHg to THg in the sediments of these lakes.

3.2.3. THg and MeHg in pore water

The THg concentrations in pore water in the surface sediment varied from 6.98 to 12.60 ng L^{-1} from the centre to the bank in the three lakes (Fig. 3). The lowest concentration of THg in pore water corresponded to the lowest THg in solid phase. MeHg in pore water in surface sediment lay in a range of 0.10 to 7.69 ng L^{-1} and decreased with increasing distance from the centre of the lakes (i.e., decreasing depth of overlaying water column). In contrast with the poor relationship between organic content and log Kd of THg in the samples throughout the

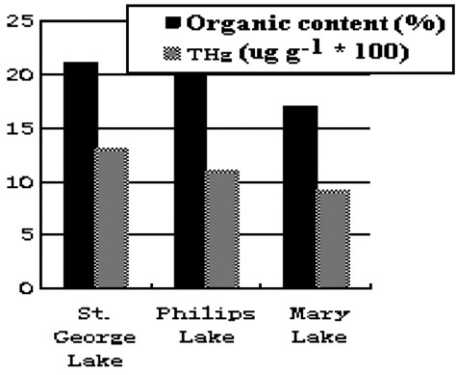

Fig. 5. Average THg and organic contents in the surface sediments in the lakes.

entire sediment cores, a positive correlation ($r=0.85$, $P<0.001$, Table 1) between these two parameters was observed in all the surface sediments.

3.3. MeHg in the water column and its sediment–water flux

The water quality parameters and MeHg concentrations in water samples from St. George Lake for October are listed in Table 2. The DO profile of the water column showed that the lake water was still well stratified even in October. The lake water was significantly anoxic from 8-m to 15-m of depth. The levels of total methylmercury (TMeHg) were higher in water below the seasonal thermocline compared to those in the surface water. Studies have shown that the increased MeHg in the hypolimnion mainly comes from increased methylation rates or from the settling of particulate matter, not from the sediment (e.g. Regnell et al., 1997; Ullrich et al., 2001). Gilmour and Henry (1991) thought that both low pH and negative redox potential, which are common in anoxic hypolimnia, not only increased methylation rates but also decreased demethylation rates, leading to an increase in MeHg. Some studies have also shown that the accumulation of settling particulate matter from the epilimnion and dissolution of hydrous ferric and manganese oxides in the hypolimnion have contributed to high concentrations of MeHg in deep water (e.g. Meili, 1997; Regnell et al., 2001). The study of Furutani and Rudd (1980), however, indicated that the increased MeHg mostly came from the release of MeHg in sediment with high Hg pollution. At the depth of 8-m, TMeHg and dissolved methylmercury (DMeHg) concentrations (1.20 and 0.65 ng L^{-1}) were higher than those at 15-m (0.60 and 0.45 ng L^{-1}), suggesting MeHg production at the depth of 8-m. It, however, can't be excluded that MeHg-associated particles sedimented from the epilimnion and dissolved in the hypolimnion. Methylmercury in the sediment–water interface and in pore water showed that the release of MeHg from sediment was also an important source to the lake water. A diffusive flux of 38 ng m^{-2} day^{-1} of MeHg from sediment to water column was estimated using Fick's law. The sediment–water flux was calculated from the concentration gradient between surface pore water and bottom water, with a value of 1.3×10^{-5} cm^2 s^{-1} for D_w (the diffusion coefficient of the solute in water in the absence of the sediment matrix). A number of studies (e.g. Bloom et al., 1991; Watras et al., 1995) showed that methylation of Hg in water columns mainly occurred in the anoxic layer. Eckley et al. (2005) reported that an average methylation rate in the hypolimnion was 0.016 ng $L^{-1}day^{-1}$ in Pallette Lake, which has similar geochemical characteristics with St. George Lake. St. Louis et al. (2004) found that the atmospheric deposition rate of MeHg in northwest of Ontario was 0.62 mg ha^{-1} yr^{-1} (0.17 ng m^{-2} day^{-1}) and MeHg from direct upland runoff was much lower than this value. If these methylation and atmospheric deposition rates were applied to this study and MeHg from direct runoff was ignored, the total MeHg input to the lake water was estimated to be about 150 ng m^{-2} day^{-1} and the MeHg flux from sediment would be up to 25% of total MeHg input. Further research is needed to verify these estimated values.

Table 2
Mercury species in lake water and pore water samples

	Depth	TMeHg (ng L^{-1})	DMeHg (ng L^{-1})	DO (mg L^{-1})	pH	T (°C)
Water column	0 m	0.14		9.98	8.30	19.0
	6 m	0.18		4.56	7.94	12.2
	8 m	1.20	0.65	0.12	7.76	10.9
	15 m	0.60	0.49	0.13	7.78	5.3
Sediment–water	Interface		0.92			
Pore water	0–2 cm		5.17			
	2–4 cm		4.61			

4. Discussion

4.1. Distribution of THg in solid phase in the sediment cores

Enrichments of Hg in surface sediments have often been reported in the past, even in some remote lakes (e.g. Rasmussen et al., 1998; Lockhart et al., 1998). There are two types of explanations about Hg distribution in sediment cores: some studies thought that the enrichment of Hg in sediment usually was attributed to modern contamination, and distribution of Hg in sediment core reflects the history of atmospheric Hg trends and fluxes (e.g. Lockhart et al., 1998; Engstrom and Swain, 1997). Other studies, however, have considered the role of chemical speciation of Hg and their affinity to organic and inorganic fractions when interpreting vertical Hg concentration profiles in lake sediments (e.g. Bilali et al., 2002; Rasmussen et al., 1998). It was thought that Hg profiles had been produced by Hg redistribution during diagenesis.

The lakes we studied have no direct inflow and outflow channels, and Hg to the lakes mainly comes from deposition of the atmospheric Hg, runoff, and falling tree leaves and debris. Sunderland and Chmura

(2000) reported that Hg emissions from anthropogenic sources in Maritime Canada and the Northeastern United States have been reduced by more than 50% from peak levels in the 1970s as a result of pollution control measures. The sediment profiles from the lakes, however, do not show a decline in modern THg accumulation in our study. This observation may be a result of redistribution of Hg in the sediment cores. Based on THg concentrations in the upper 4 cm sediment in Philips Lake, the average accumulation rate for THg in the last decade was 22.1 $\mu g\ m^{-2}\ yr^{-1}$ (The sedimentation rate in the lake was assumed to be constant.). According to the model for modern rates of atmospheric Hg deposition in Midcontinental North America (Swain et al., 1992), the direct net atmospheric deposition rate on a lake surface is 12.5 $\mu g\ m^{-2}\ yr^{-1}$. The difference between the observed accumulation rate and the model atmospheric deposition rate might be attributed to Hg input from watershed areas and redistribution of Hg in the sediment cores.

Strong correlations between organic matter and Hg were observed in surface sediment and sediment cores in aquatic systems (e.g. Rasmussen et al., 1998; Gobeil et al., 1999). Rasmussen et al. (1998) thought that the gradual decrease in Hg content down the core might be related to compositional changes in organic matter during decay. Gobeil et al. (1999) concluded that the remobilization mechanisms for Hg were apparently related to organic carbon both by initial direct or indirect association. However, some studies have shown that a portion of the THg deposited was recycled along with Fe during redox changes (e.g. Gobeil and Cossa, 1993; Gobeil et al., 1999). Wolfenden et al. (2005) found that Hg occurs in a sulfide phase with a local structural environment akin to that in cinnabar, despite the substantial amounts of organic matter in the sediments of Botany Pond.

In our research, both the correlation and similar profile trends of THg and organic matter were not observed in sediment cores while there was a positive correlation in surface sediments in three lakes. This shows that organic matter was not a controlling factor of the vertical distribution of THg in these lakes. Other factors, such as reduced sulfur and iron cycling, might play a role in controlling the distribution of THg in the sediment cores. All of these factors suggest that the role of organic matter in redistribution of Hg in sediment cores still remains unclear.

4.2. MeHg in solid phase in the sediment cores

The relatively high %MeHg was observed in deep sediments and the depth-profiles for MeHg and %MeHg and for organic matter were similar (see Fig. 2B, E, and F). These distributions of MeHg and %MeHg in the sediment cores indicate the occurrence of methylation through relatively deep sediments in these lakes, although it cannot exclude the possibility that MeHg was preserved in the sediment due to a decrease in demethylation rate. There have also been some studies that observed Hg production occurring in relatively deep sediments (Hines et al., 2004; Sunderland et al., 2004).

Sunderland et al. (2004) reported that MeHg production occurred throughout the estimated 15-cm thick active surface layer of well-mixed estuarine sediments, and it was thought that mixing of the active sediment layer in Passamaquoddy Bay resulted in geochemical changes in the sediment column, and enhanced the methylating activity of SRB (sulfate-reducing bacteria). Hines et al. (2004) observed a peak in pore water MeHg at 31-cm in September and thought that increased temperature in deep sediment contributed to the higher SRB activity.

Mercury can be converted to MeHg in anoxic sediments via sulfate-reducing bacteria (e.g. Gilmour and Henry, 1991; Benoit et al., 1999). Sulfate reduction is usually confined to the upper 5 to 10 cm in sediment and this is why MeHg production takes place in a constrained surface or subsurface zone in the typical profile of estuarine and lake sediment. Fleming et al. (2006), however, found for the first time that an iron-reducing bacterium can methylate Hg at environmentally significant rates, and solid phase ferric iron can also be an electron acceptor. This discovery has changed the way we view the vertical distribution of Hg methylation in freshwater sediments, as methylation can occur in the sediment zones with not only strong sulfate reduction but also iron reduction processes.

By comparison, Schallenberg and Kalff (1993) found that the amount of organic matter present and the water content in the sediment are important to sediment bacterial abundance. In our study, whole sediment cores contained high water content and high organic content. All of these might have enhanced the activity of a methylating microbe, SRB or iron-reducing bacteria in deeper sediments, leading to MeHg production there, although it was much weaker than in upper sediment layers. A modest ($r=0.58$, $P<0.01$) correlation between %MeHg and organic content in sediment cores and similar distribution trends between organic content and MeHg content (see Fig. 2B and E) in the sediment cores also suggested that high organic content favoured methylation in our study.

The role of organic matter in methylation of Hg has not been well understood. Observed increases in MeHg concentrations in water, sediment, or fish tissue with

increasing levels of organic carbon generally have been attributed to a stimulating effect of organic nutrients on microbial methylation activity (e.g. Furutani and Rudd, 1980; Lee and Hultberg, 1990). However, some researchers have also reported decreased methylation at high concentrations of organic matter because complex reactions reduced the availability of Hg^{2+} in natural waters (e.g. Barkay et al., 1997; Driscoll et al., 1995). The observed differences might partly reflect different methylation mechanisms. High concentrations of organic content were found to enhance anaerobic methylation, whereas aerobic methylation has frequently been observed to be suppressed by high organic matter (Ullrich et al., 2001).

5. Summary

Compared to other aquatic systems, the lakes we studied have some different characteristics. They have no direct inflow and outflow channels, and the sediment of the lakes mainly comes from the settlement of aquatic organisms and falling leaves. The whole sediment cores contain high water and organic content. In addition, although these lakes are small, they were well stratified, even in October, due to a relatively deep water column.

Compared to those typical MeHg profiles of sediment cores in other studies, where concentration of MeHg and methylation rate decreased sharply with increased depth, MeHg and %MeHg in the sediment cores in this study showed that MeHg production probably occurred not only in the upper sediments but also in the deeper sediments. This process was closely related to high organic and water content in the sediment cores. Concentrations of MeHg in surface sediments, however, were not controlled by organic matter. They were largely a function of water depth.

There was no relationship between organic content and THg in the samples throughout the sediment cores while positive correlation was observed in all of the surface sediments. The other factors, such as reduced sulfur and iron cycling might have an effect on the distribution of THg in the sediment cores.

Concentrations and distributions of MeHg in overlying water and sediment-surface water in Mary Lake and St. George Lake showed that both in situ production of MeHg in water and the release of MeHg from sediment contributed to high MeHg concentration in deep anoxic water.

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