

Mercury Partitioning in Surface Sediments of the Upper St. Lawrence River (Canada): Evidence of the Importance of the Sulphur Chemistry

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Abstract An intensive survey of mercury speciation was performed at a site on the Upper St. Lawrence River near Cornwall, Ontario, Canada with a history mercury contamination in sediments. Surface sediments were collected every 1.50 h. Total mercury (Hg_{total}), methylmercury (MeHg), organic carbon, inorganic and organic sulphur were determined in the solid fraction.

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Dissolved Hg_{total} , MeHg and dissolved organic carbon (DOC) were measured in pore waters. Concentrations of Hg_{total} in the upper layers (first 5 cm) were high, ranging from 1.42 to 25.8 nmol g⁻¹ in solids and from 125 to 449 pM in pore waters. MeHg levels were also high, ranging from 4.34 to 34.1 pmol g⁻¹ in solids and from 40 to 96 pM in pore waters. This amounts to up to 1.4% of Hg_{total} present as MeHg in solids and 64% in pore waters. A daily pattern for Hg_{total} was observed in the solid fraction. The MeHg distribution in solids and pore waters was not correlated with Hg_{total} or DOC, suggesting that the concentrations of MeHg are probably more influenced by the relative rates of methylation/demethylation reactions in the sediment–water interface. Acid volatile sulphide levels and DOC were inversely correlated with organic sulphur (S_{org}) levels suggesting that both parameters are involved in the rapid production of S_{org} . A positive correlation was also observed between Hg_{total} and S_{org} in solids ($R=0.87$, $p<0.01$) illustrating the importance of organic sulphur in the retention and distribution of Hg in the solid fraction of the sediments. The results suggest that variations of Hg_{total} concentrations in Upper St. Lawrence River surface sediments were strongly influenced by the formation/deposition/retention of organic sulphur compounds in the sediment–water interface.

Keywords Mercury · Methylmercury ·
Organic sulphur · Cornwall · St. Lawrence River

1 Introduction

Mercury is a global pollutant that cycles between air, water, sediment, soil and organisms (Moreno et al. 2005). With the exception of eastern and central Europe and Asia, anthropogenic atmospheric mercury emissions have been approximately reduced by half in the last decade (Pacyna et al. 2006). However ongoing contamination is still a worldwide problem.

The influence of diagenetic reactions on remobilization of mercury in contaminated sediments is of great importance due to the well documented role of anoxic sediments as a primary site of toxic MeHg production (Covelli et al. 1999). A large number of studies have been published on mercury distribution in sediments, freshwater and organisms of contaminated areas (e.g., Coquery et al. 1995; Pereira et al. 1998; Bjerregaard et al. 1999). Many works show that mercury in freshwater is associated with the particulate matter, mainly due to complexation with organic matter (Mantoura et al. 1978; Quémerais et al. 1998). In several cases it was possible to relate the vertical profiles of total mercury in sediments with historical releases of mercury in the area (Gobeil and Cossa 1993; Pereira et al. 1998). By determining the distribution and speciation of mercury in both pore waters and solid phases these investigations have shown that mercury appears to be bound to particulate organic matter, a minor fraction is recycled with the Mn and/or Fe oxides near the redox boundary and some is adsorbed to or co-precipitates with acid volatile sulphides (Mantoura et al. 1978; Drobner et al. 1990; Morse and Luther 1999).

The St. Lawrence River (SLR) is a major world river (Milliman and Meade 1983) that has been subjected to several waves of anthropogenic disturbance over the past century, resulting in localized degradation of water and bottom sediment quality (Reavie et al. 1998). This has been the case near Cornwall, Ontario, where local industrial facilities (e.g. chlor-alkali, pulp and paper, textiles) historically discharged significant quantities of contaminants to the river (Sérodes et al. 1978; Lepage et al. 2000). As a result, the stretch of river along Cornwall waterfront was designated an Area of Concern by the International Joint Commission in 1985. Sediments from the Cornwall area have historically been contaminated by Hg (Sérodes et al. 1978). Mercury releases to the river have decreased since 1970s

(Kauss et al. 1988) when local industries began to alter their operating practices. However, concentrations are still above background levels, and exceed the Ministry of the Environment sediment criteria for the protection of aquatic life (Golder 2004). In fact, reported levels could vary between 1.9 and 28 nmol g⁻¹ and consequently are a potential source of contamination to the river system and its food chains (Grapentine et al. 2003).

This paper reports the results of an intensive scientific field campaign took place in 2005 in a contaminated area of the St. Lawrence River (Cornwall). The objective of the study was to quantify the importance of the sulphur cycle in mercury speciation, fate, and partitioning in surface sediments of a large river system.

2 Materials and Methods

2.1 Study Site

The Cornwall Area of Concern 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. Francois in Québec (Fig. 1). This stretch of the river impacts many jurisdictions, including the provinces of Ontario and Québec, the state of New York, as well as the land of the Akwasasme First Nations people. Within these boundaries, the river is divided into two branches by Cornwall Island: the South channel which contains high levels of PCBs, and the North Channel with Hg contaminated sediments (SLRRT 1992). This research was conducted in an area of mercury contaminated sediments in the Cornwall waterfront of the North Channel (Lat: 45° 01' 21.3" N; Log: 74° 41' 13.3" W).

2.2 Sampling

During 18 h (6:00 A.M.–12:00 P.M.), surface sediment samples (first 5-cm) were collected with a small Eckman dredge every 1.50 h at the same site (Fig. 1). This site was marked in order to ensure that the samples came as close as possible from the same place being five of the samples (45% of the total) were collected by hand using professional scuba divers. The sediments were sampled in duplicate, placed in air-tight centrifuge tubes and transported on ice to the laboratory for pore water separation. Immediately after the collection,

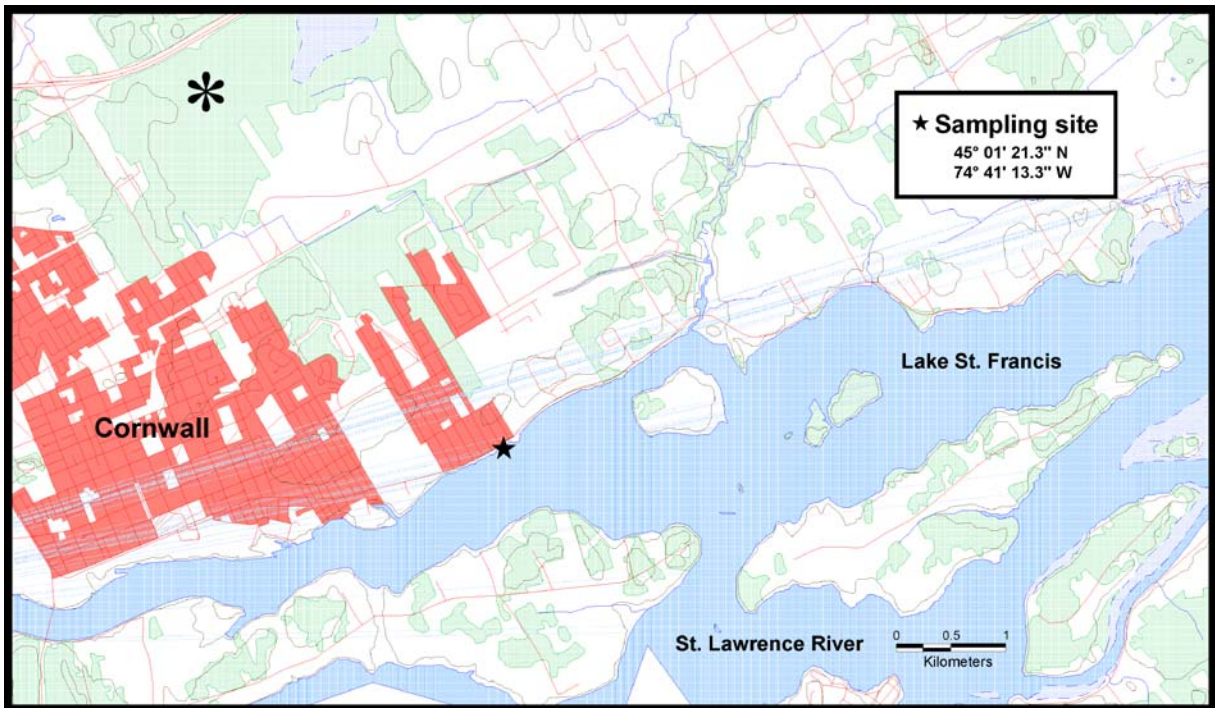


Fig. 1 Map of the St. Lawrence River near Cornwall with the indication of the sampling site

pH and redox potential (E_h) were measured using a glass combine electrode (Mettler) calibrated with 4.0, 7.0 and 10.0 buffers. Redox potential was measured using a platinum combined redox electrode (Ingold) calibrated with a solution of 220 mV (vs. Ag/AgCl, 25°C) and converted to hydrogen normal potential (E_H).

In the laboratory, pore waters were separated from duplicate sediment samples (taken on each sampling occasion) by centrifugation at 4,000-rpm for 30 min followed by filtration of the supernatant using 0.45- μ m syringe filters (HT Tuffryn membrane) under nitrogen atmosphere in a glove box. Pore water samples were preserved (1% BrCl for Hg_{total} ; 0.5% HCl for MeHg; no acidification for DOC) and refrigerated in the dark. Sediment solids were freeze-dried for subsequent analysis Hg, Al, Si, Fe, and Mn, total organic carbon (C_{org}), and total and organic sulphur concentrations as described below. Wet sediment samples were frozen for future MeHg analyses.

2.3 Analytical Methods

2.3.1 Total Determinations in Solids

Total determinations of Al, Si, Fe and Mn were performed by mineralization of the sediment samples

with a mixture of acids (HF, HNO_3 , HCl and H_3BO_4) according to the method described by Rantala and Loring (1975). Metal concentrations were obtained by flame-AAS (Perkin–Elmer AAnalyst 100) using direct aspiration into N_2O -acetylene flame (Al and Si) or air-acetylene flame (Fe and Mn). Total mercury (THg_p) was determined by atomic absorption spectrometry using a silicon UV diode detector LECO AMA-254 after pyrolysis of each sample in a combustion tube at 750°C under an oxygen atmosphere and collection on a gold amalgamator (Costley et al. 2000). $MeHg_p$ was determined in dried sediments by alkaline digestion (KOH/MeOH), preconcentration in dithizone/toluene solution and quantification by GC-ECD (Canário et al. 2004). Recoveries and the MeHg artifact formation during our process were evaluated by spiking several sediment samples with Hg(II) and MeHg standard solutions with different concentrations. Recoveries varied between 97 and 103% and no artifact MeHg formation was observed during our procedure. The concentrations of THg_p and $MeHg_p$ were also measured in the same samples at the University of Ottawa. For THg_p the analytical procedure was similar with the one described above and for $MeHg_p$ an alternative extraction and analysis methodology

(Cai et al. 1997) was used. No significant differences ($p < 0.01$) were found between the THg_p and MeHg_p results obtained with the different methodologies.

In all our metal analysis, precision, expressed as relative standard deviation of 4 replicate samples, was less than 4% ($p < 0.05$). International certified standards (MESS-2, PACS-1, IAEA-405 and BCR-580) were used to ensure the accuracy of our procedure. For all elements investigated, obtained and certified values were not statistically different ($p < 0.05$).

Total sulphur and carbon sediment content were measured in homogenized and dried sediments, using a CHNS Fissons NA 1500 Analyser. The calibration standard used was sulphanilamide. System blanks were obtained by running several empty ashed tin capsules. Organic carbon was estimated by difference between total carbon and inorganic carbon after heating samples at 450°C during 2 h in order to eliminate the organic carbon from the sediment.

2.3.2 Sulphur Speciation in Solid Sediments

Total inorganic sulphur was determined in a 100 mg sediment sample using the chromium reduced sulphur (CRS) method described by Canfield et al. (1986). This method is specific for inorganic sulphur ($\text{AVS} + \text{FeS}_2 + \text{S}^0$) with an accuracy that is not affected by the presence of organic sulphur. After determination of the total inorganic sulphur, inorganic sulphur species were determined individually. Before analysis, elemental sulphur (S^0) was extracted from 100 mg of sediment sample by 16-h of stirring with 20 ml of acetone followed by centrifugation at 3,000 rpm for 10 min and filtration through 0.45- μm Millipore[®] membranes. The residue was then placed in the reaction vessel with 10 ml HCl 1M and purged with N_2 for 20 min to release AVS. Finally the CRS method was used in the remaining residue to analyse the pyrite content. Elemental sulphur was determined using the same CRS method in the acetone extracts. The measurements of the released H_2S were made by Differential Pulse Polarography (DPP) using a Metrohm apparatus equipped with a 693 VA Processor and a 694 VA Stand. In another aliquot Acid Volatile Sulphides (AVS) (mainly amorphous iron sulphides and poorly crystallised Fe-oxides) were extracted with 1 M HCl (Henneke et al. 1991; Luther et al. 1985). Sulphide was trapped in a de-aerated NaOH solution and analysed by DPP. Recovery of standard sulphide

solutions in all analysed species was up to 97%. Detection limit for sulphide was $0.01 \mu\text{mol g}^{-1}$ and precision error were less than 5%. The sum of the individual sulphur species were not statistically different ($p < 0.05$) from the analysed total inorganic sulphur. Total organic sulphur was determined for each sample by subtracting the total inorganic sulphur concentrations from the total sulphur content (Likens et al. 2002).

2.3.3 Extraction with Hydroxylamine Chloride

100 mg of each sediment sample were stirred for 6 h with a $\text{NH}_2\text{OH}\cdot\text{HCl}$ (0.04 M) solution in CH_3COOH (25%) according to the method described by Chester and Hughes (1967). The extraction was performed in leak proof tubes sealed with Parafilm[®] to minimize possible losses of Hg^0 . The supernatant solution was obtained by centrifugation at 3,000 rpm for 10 min and filtered through 0.45 μm membranes. Iron and Mn in the overlying solution were determined by flame-AAS and Hg in the LECO analyser described above. Detection limits for Fe, Mn and Hg were 0.80, 0.60 $\mu\text{mol g}^{-1}$ and 0.02 nmol g^{-1} and precision errors were 7, 6 and 3%, respectively. Recoveries of 93 to 101% were obtained by spiking sediment samples with Fe, Mn and Hg standard solutions.

2.3.4 Pore Waters

Pore water samples were analysed for total dissolved mercury (THg_D) using a pre-oxidation by BrCl and SnCl_2 reduction with pre-concentration by two-stage gold-amalgamation followed with detection using cold-vapour atomic fluorescence spectroscopy (CV-AFS). The analysis was conducted using a Tekran 2600 system following the modified US-EPA Method 1631 (USEPA 2001) (detection limit of 1 pM). Dissolved methylmercury concentrations (MeHg_D) were determined by capillary gas chromatography coupled with atomic fluorescence spectrometry (GC-AFS) as described by Cai et al. (1996). The mean detection limit was estimated to be 0.08 pM. Analyses of procedural blanks consisting of Milli-Q water spiked with Hg and MeHg standard solution and submitted to the same analytical procedure were free of contamination and there was no evidence of MeHg artifact formation during either THg_D analysis or during MeHg_D extraction and analysis (Celo et al.

2004). The mean recovery of spiked samples was $105 \pm 11\%$ for TDHg ($n=10$) and $103 \pm 2\%$ for MeHg_{diss} ($n=4$).

Dissolved organic carbon (DOC) analysis were performed by high temperature catalytic oxidation (HTCO), using a commercial Shimadzu TOC-5000A analyzer. All glassware used for DOC was washed in 10% HCl, rinsed with Milli-Q water and dried at 450° C. The system was standardised/calibrated in the range of 0–850 μM with potassium hydrogen phthalate in Milli-Q water. The coefficient of variation (CV) for the slope of the seven 5-point calibration curves performed was 1.6%. System blanks was determined before and after analysis by injecting Milli-Q water, until the blank was low and stable (Benner and Storm 1993). The CV for the 3–5 replicate analyses of each sample was $<1.8\%$.

2.4 Statistical Analysis

Statistical tests were performed using the computer software Statistica 6.0®. The normality of all data was assessed by a Shapiro–Wilks test. Mean concentrations of the chemical parameters used to characterize the sediments samples were compared with ANOVA test (one-way). When no normal distribution was found, the non-parametric Mann–Whitney test was used (Zar 1996).

Correlations between chemical parameters were determined with Spearman correlation coefficient (R) (Zar 1996).

3 Results

3.1 Sediment Characteristics

The time course evolution of pH, E_{H} , Si/Al ratios, organic carbon and dissolved organic carbon in our sediments are presented in Fig. 2. The pH and redox potential values increased during day time reaching maximum values (pH=7.90; E_{H} =99.3 mV) around noon decreasing after. Si/Al ratios which indicate the mineralogical composition and the grain size of the sediment particles (Donazzolo et al. 1984) did not present any significant differences ($p < 0.05$) during our measurements. For Fe and Mn total concentrations, also no significant differences ($p < 0.05$) were found. Iron levels were $0.43 \pm 0.01 \text{ mmol g}^{-1}$ and Mn

was $9.1 \pm 0.4 \mu\text{mol g}^{-1}$. The particulate and dissolved organic carbon presented different pathways. Particulate organic carbon concentrations increased during the morning reaching 4.6% at 09:30 hours and then decreasing to 1.6% at 14:00 hours. In the afternoon, the same pattern is observed but with lower ranges. Dissolved organic carbon content varies irregularly but with a tendency to increase during the day. Its values varied between 5 and 16 mM, values unusually higher when compared to the DOC concentrations usually found in many aquatic systems (400–800 μM).

3.2 Mercury and Methylmercury

Figure 3 presents the time course evolution of total Hg and MeHg in solids and pore waters in the sediments from the St. Lawrence River. A clear pattern was observed for total mercury concentrations in solids (THg_p) and in pore waters (THg_D). These two parameters increased around noon reaching values of 25.8 nmol g^{-1} in solids and 449 pM in pore waters. Even if these maximum levels of particulate and dissolved Hg are considered outliers because of sample contamination or the sampling site was not exactly the same, the pattern is still observed with Hg maximum concentrations of 13.1 nmol g^{-1} in solids and 79 pM in pore waters. On other way, no tendency was observed for MeHg both in solids and pore waters. The MeHg levels varied between 4.34 and 34.1 pmol g^{-1} in solids and between 40 and 96 pM in pore waters.

3.3 Sulphur Speciation

Figure 4 presents the concentrations of total, inorganic and organic sulphur and AVS during our experiments. Clearly in the majority of our samples, inorganic sulphur species accounted to more than 70% of the total sulphur. Although, around noon, an increase of organic sulphur species was observed. In fact, the S_{org} levels increased from 5 $\mu\text{mol g}^{-1}$ at 11:00 hours to 31 $\mu\text{mol g}^{-1}$ at 14:00 hours. This enrichment in organic sulphur species corresponds to an increase of 42% relatively to the total sulphur present in our samples. Our results showed that AVS was the main inorganic sulphur species in sediments with concentrations varying between 0.9 $\mu\text{mol g}^{-1}$ (15:00 hours) and 218 $\mu\text{mol g}^{-1}$ (09:30 hours).

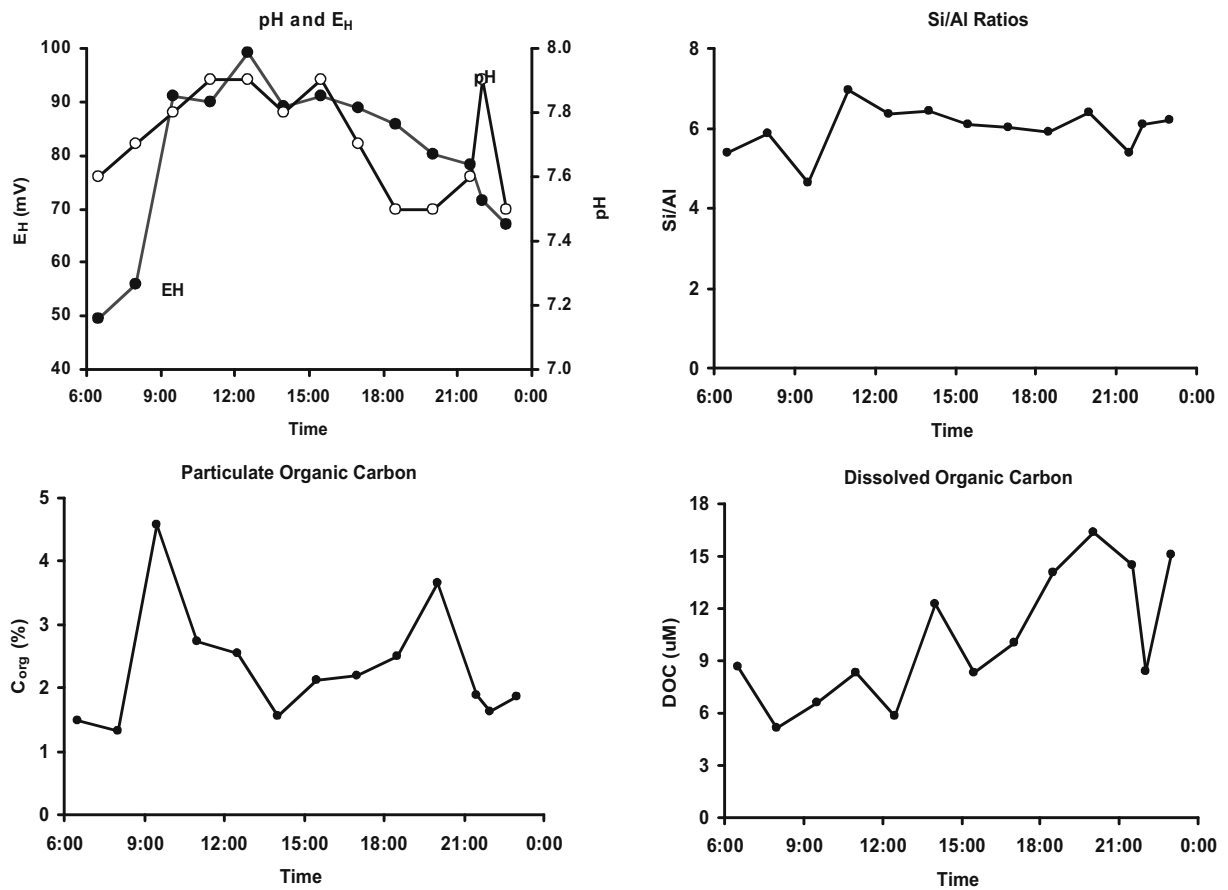


Fig. 2 Time course evolution of particulate (%) and dissolved (μM) organic carbon concentrations, Si/Al ratios and pH and redox potential values (mV) in sediments collected in SLR near Cornwall

Concentrations of pyrite and elemental sulphur were a minor fraction of the total inorganic sulphur in the majority of the samples with values generally not higher than 40% (max: pyrite 26%; S⁰ 40%).

3.4 Hydroxylamine Extraction

Figure 5 presents the proportion of Fe, Mn and Hg (%) extracted with the 0.04M NH₂OH·HCl solution.

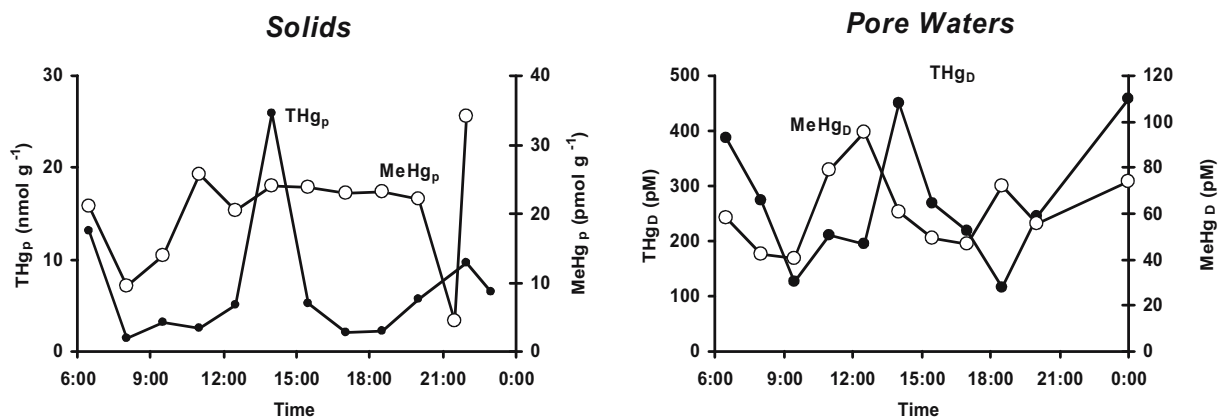


Fig. 3 Time course evolution of particulate—**a** (THg_p: nmol g⁻¹; MeHg_p: pmol g⁻¹), dissolved—**b** mercury and methylmercury concentrations (pM) in sediment solids and pore waters collected in SLR near Cornwall

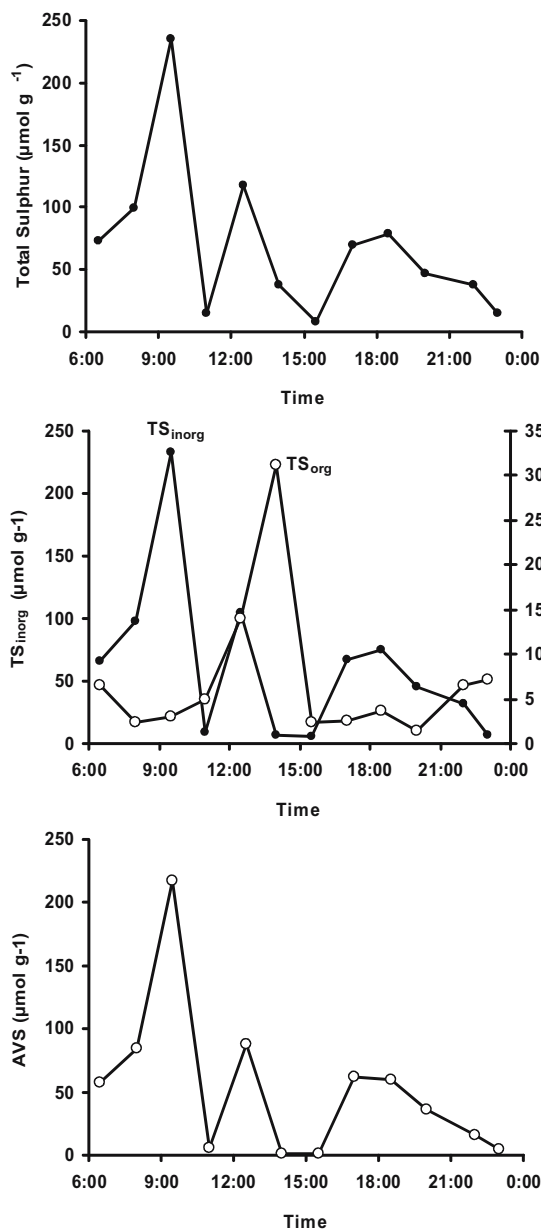


Fig. 4 Time course evolution of total, inorganic and organic sulphur and AVS concentrations ($\mu\text{mol g}^{-1}$) in solid sediments collected in SLR near Cornwall

A similar pattern was observed for all extracted metal with high values in the mid morning and afternoon (max: Fe 94%, Mn 2.3% and Hg 98%) and an abrupt decrease between these two periods reaching a minimum for Hg at 14:00 hours and for Fe and Mn at 21:00 hours. In terms of concentrations, iron levels varied between 99 and 328 $\mu\text{mol g}^{-1}$, Mn between 3.6 and 11 $\mu\text{mol g}^{-1}$ and Hg between 0.22 and 0.60 nmol g^{-1} .

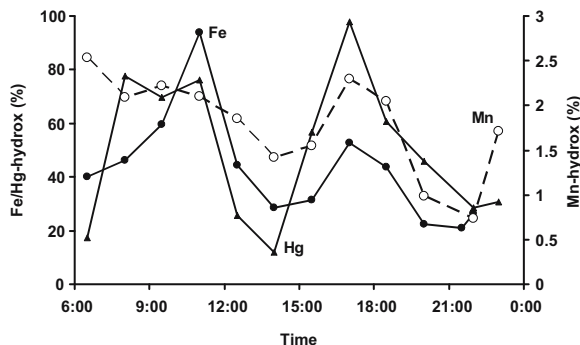


Fig. 5 Proportion of Fe, Mn and Hg (%) simultaneously extracted with a hydroxylamine solution from the solid sediments collected in SLR near Cornwall

4 Discussion

The range of THg_p concentrations found in our samples varying between 1.42 and 25.8 nmol g^{-1} indicate an Hg contamination of the system consistent with what is known about historical emissions of mercury in this area (Kauss et al. 1988). The levels obtained for all samples are above the Sediment Quality Guideline (SQG) of 0.85 nmol g^{-1} , and for the majority of the concentrations are above the probable effect level of 2.43 nmol g^{-1} established by the Canadian Council of Ministers of the Environment (CCME 2005). Previous sediments surveys performed by the Ontario Ministry of the Environment along the Cornwall waterfront reported Hg concentrations above 1 nmol g^{-1} (Persaud et al. 1993). Our results, measured 12 years later, are in good agreement with that study. As a comparison, concentrations of Hg up to 26 nmol g^{-1} are in a similar range to those reported in other contaminated aquatic systems like the Tagus Estuary in Portugal (Canário et al. 2005), in the Liverpool Bay in UK (Baldi 1997) and the Enores Estuary (Coquery and Cossa 1995). Methylmercury proportions in solids varied between 0.06 and 1.4% and are in line with other field studies which found levels ranging between 0.1 and 5.7% of the total mercury (Holmes and Lean 2006). Unlike other published works (e.g. Hintelmann and Wilken 1995) no correlations were found between MeHg concentrations in solids and total mercury or organic carbon. This lack of correlation suggests that relative rates of methylation/demethylation may be more important than absorption/desorption mechanisms in determining the concentrations of MeHg in the surface sediments

of the SLR. The lack of correlations also observed between dissolved MeHg (which accounts for as much as 61% of THg_D) and particulate MeHg_P, THg_D, or even DOC reinforce the above hypothesis. Similar conclusions for other aquatic systems have already been reported in literature (Mason and Lawrence 1999; Canário et al. 2005).

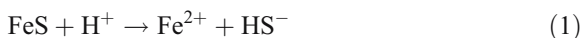
4.1 Sulphur speciation

The sulphur cycle in the SLR is mainly dominated by inorganic sulphur species (pyrite+S⁰+AVS) which in general accounts for more than 50% of the total sulphur. However, in our experiment, large variations were observed in organic sulphur concentrations (observed as much as 82% increases over a couple of hours).

The organic sulphur content in a sediment usually includes species like dimethylsulphide (DMS), methanethiol and other substances produced in the sediment/water interface during the early diagenetic reactions between inorganic sulphur species (H₂S, hydrogen polysulphides) with low molecular weight organic compounds, alkenes, aldehydes, ketones or lipids (Valisolalao et al. 1984; Kohen et al. 1990; Adam et al. 1993; Wakeham et al. 1995). The results obtained in the SLR experiment show an increase of S_{org} concentrations reaching 31 μmol g⁻¹ at 14:00 hours. This increase is observed after a decrease of C_{org} (Fig. 2) and S_{inorg} (mainly AVS) concentrations. Therefore, it is expected that the S_{org} formation should be related to the decrease in these two parameters.

It is well known that the mechanism of C_{org} degradation involves the degradation of organic molecules with a higher number of carbon atoms and the production of lower molecular weight organic molecules, prior to DOC and CO₂ production (Henrichs 1992; Deming and Baross 1993; Alperin et al. 1994; Burdige and Gardner 1998).

In other way, the decrease in solid inorganic sulphur compounds (AVS and Pyrite) should be followed for the formation of dissolved inorganic sulphur species like HS⁻ which could be further oxidized to sulphate in the oxic–suboxic layers (e.g. Rickard and Morse 2005). For AVS, the mechanism can be represented by the following equation



The dissolution of pyrite should not be also excluded, however in a lower scale since the equilib-

rium constant ($\log K_{\text{AVS}} \approx -3.88$; $\log K_{\text{pyr}} \approx -9.4$) for this dissolution is much lower (Rickard and Morse 2005). The mechanism involved may be represented by (Rickard and Morse 2005)



These two mechanisms involve also the consumption of H⁺ ions which may increase the sediment pH. In fact, Fig. 2 shows an increase of pH before 14:00 hours.

With the presence of dissolved inorganic sulphur compounds and low molecular weight organic molecules the formation of organic sulphur species should be favoured, thus explaining the sharp peak at 14:00 hours. This hypothesis is supported by the work of Wakeham et al. (1995) which observed that this process can occur during the very early stages of sedimentary diagenesis, even at the sediment water interface. Moreover, if the suggested mechanism does take place, negative correlations should be expected when S_{org} concentrations are plotted against DOC and AVS levels. Figure 6 presents the relationships between S_{org} concentrations (μmol g⁻¹) with DOC and S_{org} proportion (%) with AVS proportion (%). S_{org}/AVS was plotted in percentage to better illustrate the conversion between the two sulphur species. Figure 6 clearly shows negative correlations among S_{org} and DOC and AVS levels suggesting the S_{org} formation in SLR surface sediments. After 14:00 hours, there is a fast decrease in organic sulphur content in our sediments followed by an increasing of S_{inorg} (Fig. 4). Our results do not provide any explanation for this trend however, it is well described in the literature that S_{org} molecules can be quickly decomposed due to biotic processes (Stempvoort and Krouse 1994). For instance, the sulphatase enzymes synthesized by microorganisms are catalyzing the sulphate–ester bond hydrolysis of S_{org}, generating inorganic sulphate as a by-product (Ghosh 2005). Further investigation of this mechanism should be performed in the SLR sediment environment.

4.2 Mercury fractioning and partitioning in surface sediments

Total mercury in solids clearly shows a daily pattern (Fig. 3). The increase of concentrations in the solid fraction of sediment around noon suggests an

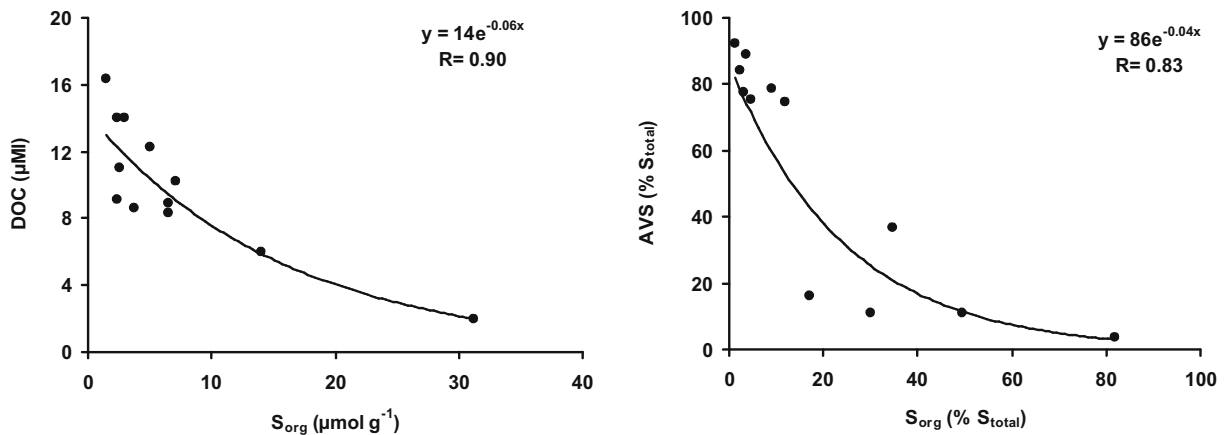


Fig. 6 Relationships between organic sulphur concentrations ($\mu\text{mol g}^{-1}$) and DOC levels (μM) and AVS proportion (%)

incorporation of Hg into the solid sediment. The particle size effect and organic carbon effect were also investigated since Hg has a high affinity for fine particles and/or rich organic carbon sediments (Duinker 1983; Donazzolo et al. 1984; Bloom and Creclius 1987; Muhaia et al. 1997). These effects are usually accessed by normalizing the Hg concentrations to the Al and C_{org} content. However, after Hg normalization for Al and C_{org} no changes were observed indicating no particle size or organic carbon effect.

By plotting THg_p and S_{org} together (Fig. 7) we can see a clear correlation between the two species (correlation $R=0.87$, $p<0.01$) and even if the levels at 14:00 hours are considered outliers (see Section 3.2) a good correlation is still observed ($R=0.73$, $p<0.05$). These results suggest that Hg_p will quickly bind to organic sulphur compounds recently formed in the solid fraction of the sediments. The high affinity of Hg to organic sulphur compounds is well described in literature (e.g. Mantoura et al. 1978; Jackson 1998; Ravichandran 2004) and the processes involving these pathways are greatly responsible for Hg distribution, partitioning and speciation in the sediment environment. Although, it is expected, that this retention/incorporation is preceded by the existence of Hg “chemically” available, probably in dissolved form. Assuming that pore water Hg (THg_D) is responsible for Hg incorporation into S_{org} form, we would expect to find a sharp decrease in THg_D during the increase in Hg/S_{org} levels. However, a good positive correlation between particulate and dissolved Hg ($R=0.82$; $p<0.05$) was observed in our results. This positive correlation suggests the existence of equilibrium between $\text{THg}_p/\text{THg}_D$ and not an incorporation or

remobilization of Hg_D . As a consequence, Hg must be continuously remobilized from solids, quickly incorporated in S_{org} compounds recently formed and a new equilibrium between Hg_p/THg_D is rapidly achieved. Two pathways could be responsible for this remobilization: First, the Hg release during oxidation of particulate organic matter (e.g. Canário et al. 2003), and indeed C_{org} abruptly decreases before 14:00 hours (Fig. 2); Second, the remobilization of Hg by the dissolution of Fe and Mn oxy-hydroxides. In fact, it is well known that Fe and Mn oxides may act as a sink of mobile Hg forms (Gobeil and Cossa 1993; Matty and Long 1995; Canário et al. 2003). The $\text{NH}_2\text{OH}\cdot\text{HCl}$ extraction is usually used as an indicative measure of the amount of Mn and Fe oxy-hydroxides present. Since this method also extracts some amorphous iron sulphides (Anschutz et al. 1998), determination of Hg simultaneously extracted with this procedure, could also measure the contribution of these sediment

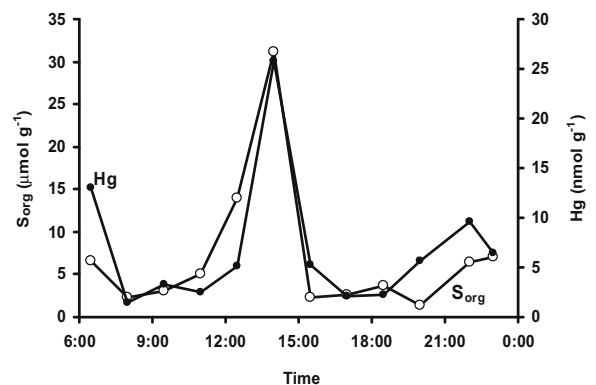


Fig. 7 Relationship between total mercury (nmol g^{-1}) and organic sulphur ($\mu\text{mol g}^{-1}$) concentrations during the experiment at SLR

compounds. Moreover, these oxy-hydroxides/sulphides are redox, pH and dissolved oxygen sensitive (Gobeil and Cossa 1993; Gagnon et al. 1997) and consequently changes in these parameters may contribute to the Fe and Mn oxy-hydroxides/sulphides dissolution remobilizing the associated trace elements (Jenne 1968; Gobeil and Cossa 1993; Matty and Long 1995; Canário et al. 2003). These redox and pH changes are clearly illustrated in Fig. 2. Figure 5 clearly shows that at 14:00 hours (when Hg/S_{org} presents a sharp peak) the sediment fraction extracted with $NH_2OH \cdot HCl$ solution in impoverished not also in Hg but also in Fe and Mn. These sediments present the higher concentration of particulate Hg and a lower proportion of Hg extracted with $NH_2OH \cdot HCl$ (<25%) which suggests that a considerable amount of Hg is associated with the S_{org} fraction. Moreover, before 14:00 hours Hg associated with the $NH_2OH \cdot HCl$ fraction presents a sharp decrease suggesting that Hg could have been remobilized during Fe/Mn oxy-hydroxides/sulphides dissolution becoming then available for being incorporated in S_{org} recently formed. This hypothesis is supported by the decrease of Fe and Mn associated with this sediment fraction (total Fe and Mn levels did not vary, Section 3.1). Additionally, the remobilization of Hg from the oxidation of iron sulphides (AVS) and pyrite in the oxic/suboxic layers should not be excluded since these compounds usually incorporate Hg (Cooper and Morse 1998a,b). However, we do not have any support for this hypothesis since Hg simultaneously extracted with sulphides was not measured.

The main reason why we do not see THg_D enrichment in pore waters could be the fast kinetics of the reaction between of Hg and S_{org} . This may be due to the large period of time between sampling. In fact, 1:50 h could be an extremely large time interval to see measurable effects of this remobilization. On the other hand, the hypothesis that Hg is coming from the overlaying water should also not be excluded. Although we have no data to support this assumption (dissolved mercury concentrations were not measured in the overlaying water), the unbalanced situation between the mass of Hg remobilized and Hg incorporated in S_{org} suggest that part of the mercury should come from the overlaying water. Molecular diffusion of dissolved Hg from deeper sediments should also be taken into account but in lower proportion since Hg diffusion coefficient is very low (e.g. Boudreau 1997)

therefore not explaining the fast and large Hg enrichment in the solid fraction of the SLR surface sediments. The assumption of Hg coming from the overlaying water should also be extrapolated for particulate and dissolved organic carbon. The higher carbon content of these sediments and the huge variations during the experiment is likely a result of frequent inputs of both carbon species into the system. Inputs of effluent from sewage treatment plants in the Cornwall area may explain the higher variability and concentrations of both carbon species in the St. Lawrence River (LaRiviere 2005). These inputs may not also change early diagenetic reactions occurring involving POC/DOC but also other associated/related compounds like AVS or other sulphur compounds. Rapid changes in carbon and sulphur speciation in organic rich carbon sediments from wetlands (e.g., Madureira et al. 1997) are well documented, Future research should be performed in order to better clarify this biogeochemical process.

5 Conclusions

The results obtained in our survey in the Saint Lawrence River at Cornwall point to the following conclusions:

1. The SLR sedimentary environment is a very dynamic system with diurnal variations in some chemical parameters. Post-deposition reactions occur in surface sediments that change mercury concentrations, partitioning and distribution. The driving force for these daily changes could be the frequent inputs of both dissolved and particulate organic carbon to the system from the sewage treatment plants.
2. Up to 90% of the Hg in the SLR surface sediments can be quickly remobilized into pore waters. In future studies it would be important to quantify the proportion of this Hg that could be available for the biota.
3. Good negative correlations were found between S_{org}/DOC and S_{org}/AVS . These results suggest the rapid formation of S_{org} species possibly resulting from a reaction between inorganic sulphur species and low molecular weight organic compounds.
4. Although 98% of Hg_{total} is found associated with Fe/Mn oxy-hydroxides, the distribution/partitioning

of Hg in SLR sediments may be largely controlled by very quick and dynamic changes in the S_{org} concentrations.

Sulphur chemistry in the sediments from the upper St. Lawrence River is essential in determining Hg speciation/partitioning/distribution in surface sediments. The conclusions assume particular importance when it is well known that Mn chemistry is quite important in the SLR surface sediments. In fact several publications have shown that the SLR is an important source of very fine manganese-rich particles in suspension which by settling in the top sediments could have an important role in the early diagenetic reactions (e.g. Sundby et al. 1981; Quémerais et al. 1998) and thereby affect Hg biogeochemistry. However, further research examining sulphur and Mn speciation in the Upper St. Lawrence River is required to test these hypotheses.

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