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Environmental controls on the speciation and distribution of mercury in coastal sediments [☆]

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Abstract

Methylmercury production by sulfate reducing bacteria in coastal sediments leads to bioaccumulation of mercury in fish, shellfish, and ultimately humans. Sulfur, organic carbon, and sediment structure and composition can all affect methylmercury production by changing the amount of bioavailable inorganic mercury and by stimulating the activity of methylating microbes. This study investigates total and methylmercury in solids and porewaters relative to total sulfide concentration, redox potential, sediment grain size, and total organic carbon in a range of sediment types from the Bay of Fundy region of Canada. Using these data, we construct a conceptual model of the biogeochemical environment surrounding methylating microbes in high sulfide, organically enriched sediments. Whereas other studies of methylmercury dynamics measured porewater sulfide concentrations in relatively low-sulfide systems (~20–300 μM), we measured total sulfide levels using a method developed to indicate organic enrichment across a much wider range of sulfidic sediments (10–4000 μM). We observed that higher sulfide concentrations correspond to an elevated fraction of mercury in methylated form suggesting higher net methylation rates in these sediments. This relationship is strongest in sediments that are moderately impacted by organic enrichment, but weak in less impacted, aerobic sediments. Higher sulfide concentrations in porewaters containing dissolved organic matter appear to yield a geochemical environment that is conducive to uptake of Hg(II) by methylating bacteria. Data collected in this study imply that moderate levels of organic enrichment through fish farming may enhance methylmercury production in the Bay of Fundy.

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1. Introduction

Despite the fact that the majority of human exposure to mercury in the United States is the result of consumption of estuarine and marine fish and shellfish (Carrington and Bolger, 2002; Tran et al., 2004), information on mercury fate and transport in coastal ecosystems is limited. Only the organic form of mercury, methylmercury (MeHg), biomagnifies to signifi-

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icant concentrations inside living cells and tissues of aquatic organisms (Lawrence and Mason, 2001; Lawson and Mason, 1998). Methylmercury produced in near-shore sediments accounts for the majority of mercury in primary producers that is bioaccumulated at higher trophic levels (Hammerschmidt et al., 2004; Sager, 2002). Coastal ecosystems that produce large amounts of MeHg may therefore lead to localized “hot spots” in human exposure. Since direct measurements of MeHg in coastal systems are often limited, environmental managers would benefit from screening level models that identify geographic regions likely to produce significant amounts of MeHg. This study analyses several factors that may assist in developing such models for MeHg production in coastal sediments.

Many coastal systems contain large reservoirs of “legacy” mercury in the sediment compartment (Hammerschmidt and Fitzgerald, 2004; Sager, 2002; Sunderland et al., 2004). Microbes convert a small fraction of this pool of inorganic mercury (Hg(II)) to MeHg over time. The rate of Hg(II) conversion to MeHg in coastal sediments is therefore crucial for anticipating accumulation of mercury in coastal organisms.

Sulfate reducing bacteria are thought to be the principal agents responsible for MeHg production in coastal sediments (Compeau and Bartha, 1984; Gilmour et al., 1992; King et al., 1999). These microbes thrive at the geochemical interface between oxic and anoxic conditions (Hintelmann et al., 2000). A number of environmental factors may affect the rate of MeHg formation by influencing the supply of bioavailable Hg(II) and/or activity of methylating microbes. In addition to Hg(II) concentrations, effective proxy indicators for MeHg production and accumulation identified by previous research include sulfide concentrations, total organic carbon (TOC), and redox potential (Eh) (Baeyens et al., 1998; Benoit et al., 1999a, 2001; Compeau and Bartha, 1984; Mason and Lawrence, 1999; Stoichev et al., 2004).

Past studies show organic matter can influence MeHg production by reducing the amount of bioavailable Hg(II) in the dissolved phase and stimulating the activity methylating bacteria by providing a substrate for mineralization (Hammerschmidt et al., 2004; Hammerschmidt and Fitzgerald, 2004; Mason and Lawrence, 1999; Stoichev et al., 2004). In addition, a number of studies show that in certain systems elevated sulfide concentrations inhibit mercury methylation by reducing the bioavailable pool of Hg(II) (Benoit et al., 1999a,b, 2001). Overall, the ultimate influence of changes in environmental factors on methylation

appears to depend largely on the initial characteristics of a specific ecosystem that limit the production of MeHg by methylating microbes, whether this is the pool of bioavailable Hg(II) or other factors that affect microbial activity.

This study investigates some of the main geochemical factors known to affect the speciation and distribution of mercury in coastal sediments from the Bay of Fundy, Canada. Although there are no large point sources of mercury in this region, high levels of mercury in fish and wildlife continue to be a problem (NESCAUM, 1998). Organic enrichment of sediments from salmon mariculture is another ongoing management concern in this region. To help identify impacted regions, Wildish et al. (1990, 1993, 1999, 2001) developed an empirically derived organic enrichment gradient based on benthic macrofaunal characteristics. Geochemical indicators like Eh and S^{2-} have been widely applied in the region to monitor the level of organic enrichment in the sediments. A recent interlaboratory calibration exercise found that total sulfide measurements in interfacial marine sediments are the most reliable indicator of enrichment in the Bay of Fundy; i.e. sulfides increase after organic materials are added to an ecosystem (Wildish et al., 2004).

We hypothesized that the Bay’s predominantly clay mineral sediments (Loring, 1979; Loring et al., 1998) support higher levels of mercury methylation when the amount of organic matter is enhanced by activities such as fish farming. To test this hypothesis, we measured concentrations of total mercury (THg) and MeHg in the solid and dissolved phases as a function of TOC, Eh, sediment grain size and total sulfides in surface sediments from multiple sites across the mouth of the Bay of Fundy. In this paper, we calculate the covariance between sulfide, Eh and TOC throughout the Bay, and assess the utility of these measurements as indicators of an ecosystem’s ability to methylate mercury. We use the empirical data on mercury distributions as a function of different environmental characteristics to make inferences about mechanistic processes controlling MeHg production in coastal sediments. By isolating these relationships in the context of empirical data collected in this study, we gain useful insights into the mechanism of MeHg formation in coastal sediments that can be tested with future research.

Other studies that have investigated MeHg dynamics have focused on coastal systems that are moderately to highly contaminated by urbanization and industry (Bloom and Fitzgerald, 1988; Hammerschmidt and Fitzgerald, 2004; Mason and Lawrence, 1999; Sager,

2002; Stoichev et al., 2004). The majority of data presented in this study were collected in a region where the enrichment of mercury in surface sediments can be attributed mainly to enhanced atmospheric deposition from a combination of regional and global mercury sources (Sunderland et al., 2004). Therefore, results from this study present new information on the biogeochemical cycling of atmospherically derived mercury in a macrotidal estuary that has not been significantly impacted by local mercury sources. Finally, we use the empirical data to develop simple statistical models of MeHg distribution across the Bay of Fundy. Combined with our previous work (Sunderland et al., 2004), this information contributes to the development of a mercury cycling model for this region (Sunderland, 2003).

2. Theory

When interpreting empirical measurements of total mercury (THg) and MeHg concentrations in terms of methylation rates and MeHg production, it is useful to consider the conceptual and theoretical framework that is applicable to MeHg generation. The inherent assumption in the design of this study is that, in Bay of Fundy sediments, ambient concentrations of MeHg reflect the competing rates of in situ MeHg formation and demethylation. We model the rate of MeHg formation as a product of three factors: (a) a rate constant (k_m) that describes and quantifies the activity of sulfate reducing bacteria, which methylate mercury; (b) the sediment volume where methylation is taking place (V_{sed}); and (c) the fraction of inorganic mercury that is actually “bioavailable” to the sulfate reducing bacteria. We denote this bioavailable fraction as $Hg(II)^*$ and its concentration is denoted $C(Hg(II)^*)$. Thus, the rate of MeHg formation is:

$$MeHg_{formation} = k_m * V_{sed} * C(Hg(II)^*). \quad (1)$$

Numerous physical and biological factors affect bioavailability of inorganic mercury. In general, the bioavailability of inorganic mercury is difficult to measure directly because the analytical procedures for isolating and identifying such mercury species in the field do not exist at this time.

Similarly, the rate of demethylation is modeled as a product of three corresponding quantities: (a) a rate constant (k_e) describing MeHg degradation by demethylating microbes and abiotic processes, (b) the sediment volume over which this breakdown occurs (V_{sed}), and (c) the ambient concentration of MeHg.

Some sediment may sequester a fraction of MeHg making it unavailable to demethylating microbes. To account for this, a more detailed model might represent a rapidly cycling pool of MeHg that combines abiotic methylation and microbially mediated demethylation with a more stable, slowly reacting pool by different rate constants. These rate constants could be multiplied by the MeHg concentrations in each respective compartment. The model used here represents these two processes by one rate constant. This implicitly assumes that these two compartments are either in fast equilibrium with each other or that one dominates in size. Thus:

$$MeHg_{degradation} = k_e * V_{sed} * C(MeHg). \quad (2)$$

The amount of MeHg formed or net MeHg production (in units of moles per day) is therefore:

$$\frac{d[MeHg]}{dt} = k_m * V_{sed} * C(Hg(II)^*) - k_e * V_{sed} * C(MeHg). \quad (3)$$

We assume steady state (i.e., $d[MeHg]/dt=0$), so Eq. (3) becomes:

$$C(MeHg) = \frac{k_m}{k_e} * C(Hg(II)^*). \quad (4)$$

If gain or loss through advective transport of MeHg are relatively constant among stations, then ambient MeHg concentrations should reflect net in situ production. This condition has been verified in a number of other systems (e.g., Benoit et al., 2003; Gilmour et al., 1998), so we assume it to be the case in the Bay of Fundy. We will revisit this assumption in the Results section.

Eq. (4) illustrates that net MeHg production in Bay of Fundy sediments is a function of the methylation rate (k_m), the demethylation rate (k_e) and the amount of inorganic mercury ($Hg(II)^*$) that can potentially be converted to MeHg.

MeHg generally comprises <1% of THg in coastal sediments (Morel et al., 1998), so $Hg(II)$ (e.g., the concentration of inorganic mercury in the sediments) is approximately equal to THg. However, $Hg(II)$ and THg are not equivalent to the fraction of inorganic mercury that is available to methylating microbes ($Hg(II)^*$) in Eq. (4). A widely accepted definition of $Hg(II)^*$ that has been modeled in low sulfide environments is the concentration of dissolved mercury species in sediment porewater that readily crosses the membranes of methylating bacteria (SRB) (Benoit et al., 1999a,b). Regardless of the bioavailable $Hg(II)$ species, it follows that at station “*i*” some fraction of THg

(denoted as ϕ_i) is bioavailable and can potentially be converted to MeHg, i.e.:

$$C(\text{Hg(II)}^*)_i = \phi_i C(\text{THg})_i \quad (5)$$

Eq. (5) can be substituted into Eq. (4) to give MeHg as a function of THg:

$$C(\text{MeHg})_i = \frac{k_m}{k_e} * \phi_i C(\text{THg})_i \quad (6)$$

Eq. (6) can be rearranged to express MeHg as a fraction of the total mercury pool (%MeHg):

$$\% \text{MeHg}_i = \frac{C(\text{MeHg})_i}{C(\text{THg})_i} = \frac{k_m}{k_e} \phi_i \quad (7)$$

Thus, %MeHg represents the product of the rate constant quotient (k_m/k_e) and the fraction of THg potentially available for conversion to MeHg (ϕ_i), or:

$$\% \text{MeHg}_i = K_i * \phi_i \quad (8)$$

Where K_i is the net methylation rate at site i , and ϕ_i is the fraction of inorganic mercury that is bioavailable at site i .

When the bioavailable fraction of total mercury available to methylating microbes (ϕ_i) remains relatively constant among stations (i.e., $\phi_i = \phi_j = \dots \phi_n$), %MeHg provides a reasonable first approximation of the *net* methylation rate in the sediment compartment (k_m/k_e). Similarly, when the net methylation rate is relatively constant among stations (i.e., $K_i = K_j = \dots K_n$), %MeHg will vary reflecting differences in the pool of bioavailable mercury (ϕ) among stations.

Environmental factors such as TOC, Eh, sulfides (S^{2-}), and THg influence K or ϕ or both. Thus, relationships between these factors and %MeHg or $C(\text{MeHg})$ indicate changes in methylation rate, bioavailable Hg(II) or production of MeHg, respectively. Based on the results of other research reviewed above, we anticipate that not all of the factors measured in this study will influence both K and ϕ . These equations will be revisited in the discussion to help explain the mechanistic implications of correlations observed in this study.

3. Methods

3.1. Study site

Integrated 15–20 cm surface sediment samples ($n=95$) were collected from Passamaquoddy Bay, the St. Croix River estuary and the outer Bay of Fundy on five cruises between July 2000 and November 2001

using a modified Van Veen grab sampler. This depth is consistent with the measured active zone of the sediments (Sunderland et al., 2004), which is operationally defined in this study as sediments that can potentially exchange mercury with the water column and buried sediments through resuspension, diffusion and burial. Thus, the thickness of the active layer is a function of the depth of biological mixing and the depth of physical mixing/continual reworking (Boudreau, 2000).

Passamaquoddy Bay is a semi-enclosed coastal embayment that is located at the mouth of the Bay of Fundy on the southwestern coast of New Brunswick, Canada. It has a surface area of 172.3 km² and a maximum water depth of 67 m (Gregory et al., 1993; Loring et al., 1998). The St. Croix River is the major freshwater inflow to Passamaquoddy Bay and runs along the border between Canada and the United States.

Sampling locations (Fig. 1) included a number of monitoring sites previously studied by Fisheries and Oceans Canada (Loring et al., 1998) and Gulfwatch Monitoring Program (Chase et al., 2001) that were analyzed for total mercury ($n=28$). The entire region is subject to the extreme tidal range of the Bay of Fundy, averaging between 6 and 8 m in Passamaquoddy Bay and up to 16 m at the mouth of the Bay of Fundy (Gregory et al., 1993). Water temperatures during the sampling periods ranged from a low of 7 °C in November 2001 to a high of 19 °C during August 2000. The median water depth across all sampling stations in Passamaquoddy Bay was 28 m, with a minimum of 8 m and a maximum depth of 78 m. Water depths at stations from the outer Bay of Fundy were in excess of 120 m. Salinities at sampling stations varied within a relatively narrow range (26.9–33.0), with a median value of 29.6.

3.2. Sediment sample collection

All sampling equipment and storage containers were prepared following standard trace metal ultra-clean techniques (Gill and Fitzgerald, 1987; Mason et al., 1998). Triplicate grabs were obtained at 17 sampling stations to provide an estimate of both inter- and intra-site variability. In addition, between August 2000 and November 2001 selected sites highlighted in Fig. 1 ($n=7$) were monitored in the spring (May 2001), summer (August 2000, 2001) and fall (November 2001) to investigate temporal variability in total mercury and MeHg concentrations over several seasons. Samples collected in November 2001 were limited ($n=9$) by the occurrence of a hurricane during the collection period.

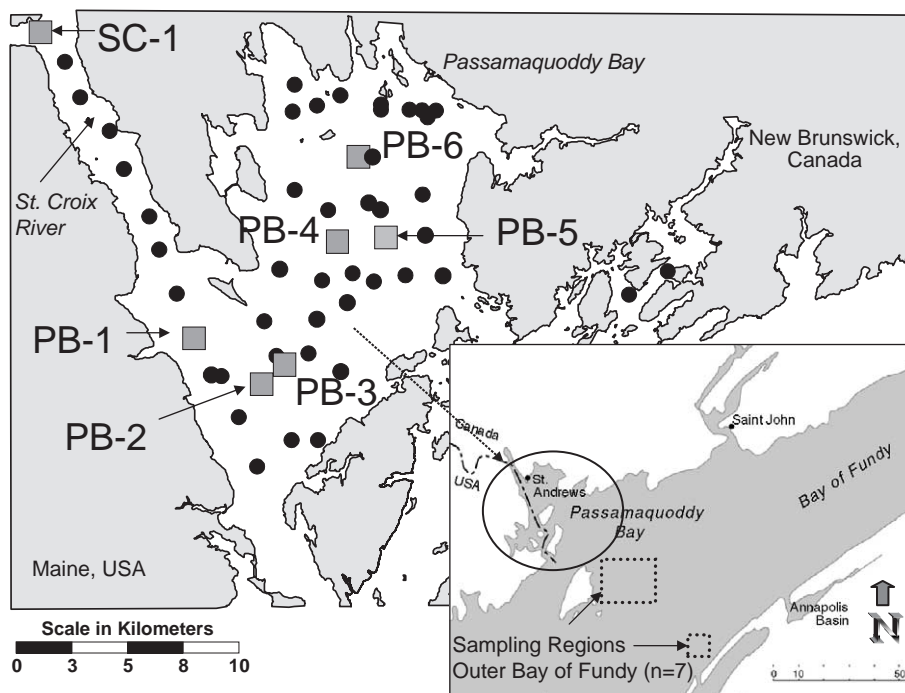


Fig. 1. Map of study area showing sampling locations in Passamaquoddy Bay, the St. Croix River Estuary and the outer Bay of Fundy. Squares depict stations that were sampled repeatedly in May, August and November between 2000 and 2001. Stations in the outer Bay of Fundy (dashed squares) were sampled in June 2001.

3.3. Sediment geochemistry

Redox potential (Eh) of the surface sediments was measured using an Orion platinum redox electrode and a calomel reference electrode. Efforts were made to minimize disturbances of the sediment–water interface during measurement of redox status and sulfide concentrations. Sub-samples for grain size (August 2000 only) and sulfide (all grab samples) analyses were obtained from the top layer of the sediments using a cutoff 5 cm³ syringe. The particle dynamics laboratory at Bedford Institute of Oceanography conducted disaggregated inorganic grain size spectral analyses using a Coulter Multisizer IIE on samples collected in August 2000, as well as sediments from stations sampled by Loring et al. (1998). Organic carbon content of the samples was estimated through loss on ignition (LOI), by heating each sample at 550 °C overnight. Selected samples ($n=27$) were analyzed for total organic carbon (TOC) by combustion/nondispersive infrared gas analysis using a Shimadzu 5050A TOC analyzer. TOC is calculated as the difference between measured total carbon and total inorganic carbon. For all grab samples, LOI was converted to organic carbon content by fitting the relationship between independently measured LOI and TOC ($r^2=0.87$, $p<0.001$).

3.4. Sulfide measurements

Sediment samples collected for total sulfide analysis were put on ice until they were returned to the laboratory. Sulfide antioxidant buffer (SAOB) was added to the wet sediments in the lab on shore immediately after sampling and sulfide concentrations were determined using an ion-specific electrode using the method developed by Wildish et al. (1999). The SAOB was prepared from 20 g NaOH and 17.9 g EDTA diluted with deionized water to 250 ml volume. Just before addition to the sediment sample, 8.75 g of L-ascorbic acid was added to the SAOB solution. The maximum time between sampling and sulfide measurement was four hours. Intensive labor and handling procedures made it infeasible to complete pore–water extractions within the window of time known to be most reliable for sulfide analyses (Mason et al., 1998; Wildish et al., 1999).

3.5. Sediment pore waters

Sediment pore waters were separated from a sub-set of samples by transferring the bulk sediment into 50 ml acid washed polycarbonate centrifuge tubes under a nitrogen atmosphere. Tubes were purged with N₂

prior to transfer, centrifuged at 3000 RPM for 30 minutes, followed by vacuum filtration with disposable 0.2 μm cellulose nitrate filter units. All filters were rinsed with 1% HCl and deionized distilled (18 M Ω .cm) water immediately prior to use. Pore water samples for total mercury analysis were preserved in 0.5% ultrapure HCl, while MeHg samples were immediately frozen until analysis.

3.6. Mercury analyses

Solid samples for THg and MeHg analyses were placed in 125 ml acid washed polypropylene specimen jars, and were immediately cooled to <4 °C and frozen upon return to the laboratory until analysis. Bulk phase wet sediment samples were analyzed for THg by digestion in concentrated 5:2 nitric-sulfuric acid solution and oxidation with bromine monochloride (BrCl) under Class 100 conditions. Immediately prior to analysis, the excess bromine was neutralized with 10% hydroxylamine hydrochloride. Aqueous samples were digested with BrCl for at least 12 hours prior to analyses and then neutralized with an equivalent volume of hydroxylamine hydrochloride immediately before analysis. All samples were then reduced with stannous chloride, purged with nitrogen gas, and trapped on gold packed columns. Quantification was by dual-stage gold amalgamation and cold-vapor atomic fluorescence spectroscopy (CVAFS). This procedure was based on EPA Method 1631, Gill and Fitzgerald (1987) and Bloom (1989). MeHg was determined by steam distillation, aqueous phase ethylation using sodium tetraethylborate, purging onto Tenax packed columns, gas chromatography separation and CVAFS detection following a technique by Bloom and Fitzgerald (1988) and Horvat et al. (1993), modified by Branfireun et al. (1999).

The method detection limit (MDL) for THg in sediment solids was 0.95 pmol g^{-1} ($n=19$), determined as three times the standard deviation of the mean of the sample blanks. For aqueous samples, the MDL for THg based on a 150 ml sample volume was 0.20 pM ($n=18$). Precision, measured as the relative percent difference (RPD) between digest duplicates (sediment solids), and analytical duplicates (aqueous phase) was 9.6% ($n=24$ pairs) and 5.7% ($n=2$ pairs) respectively. Calibration curves of at least $r^2=0.99$ were achieved daily or samples were re-run. Accuracy was measured both by spike recoveries and using the MESS-3 marine sediment certified reference material (454 ± 45 pmol g^{-1}) from the National Research Council of Canada. Recoveries aver-

aged $103\% \pm 10\%$ ($n=12$) and 459 ± 80 pmol g^{-1} for all MESS-3 samples ($n=9$). Samples from runs with poor recoveries ($<80\%$) were reanalyzed. For MeHg, the MDL was 0.032 pM ($n=6$) in the aqueous phase and 0.035 pmol g^{-1} ($n=16$) for sediment solids. The RPD for distillation duplicates was 18.1% ($n=21$), while the average recovery of spikes between 0.5 and 2.5 pmol g^{-1} of wet sediment was $106 \pm 26\%$ ($n=12$). Some of this variability can be attributed to uncertainty as to the true concentration of the sediment sample being spiked, as reflected in the RPD of distillation duplicates. A wet to dry weight conversion was calculated for each sample analyzed by oven drying sub-samples of wet sediments for at least 24 hours at 60 °C.

3.7. Statistical analysis

Bivariate correlation matrices for each sampling period (Hg, MeHg, Eh, sulfide, TOC and grain size) were used to identify the predominant variables controlling production and accumulation of MeHg in Fundy sediments. Linear and stepwise regression analysis was used to investigate the amount of variability in MeHg concentrations and MeHg normalized to THg (%MeHg) that could be explained by the geochemical indicators Eh, sulfide, TOC and to develop statistical models for MeHg and THg distribution in Bay of Fundy sediments. All correlations presented are significant at the 95% confidence level.

4. Results

4.1. Total mercury distribution

Overall, sediments in the sampling region contain relatively low levels of THg (50–700 pmol g^{-1}) compared to other estuarine systems discussed in the literature such as Lavaca Bay, the St. Lawrence River, and the Scheldt estuary (700–10,000 pmol g^{-1}) (Baeyens et al., 1998; Bloom et al., 2004; Cossa and Gobeil, 2000). Total mercury concentrations in this study were highest at the mouth of the St. Croix River, where average THg concentrations exceeded 500 pmol g^{-1} (Fig. 2). Elevated THg concentrations in this area are the result of historical mercury releases by a chlor-alkali plant that operated upstream along the river in the 1970s (Fink et al., 1976).

Strong empirical relationships between THg and TOC ($r^2=0.66$, $p<0.001$) and sediment grain size ($r^2=0.67$, $p<0.01$) show that THg concentrations are highest in depositional areas with elevated TOC and

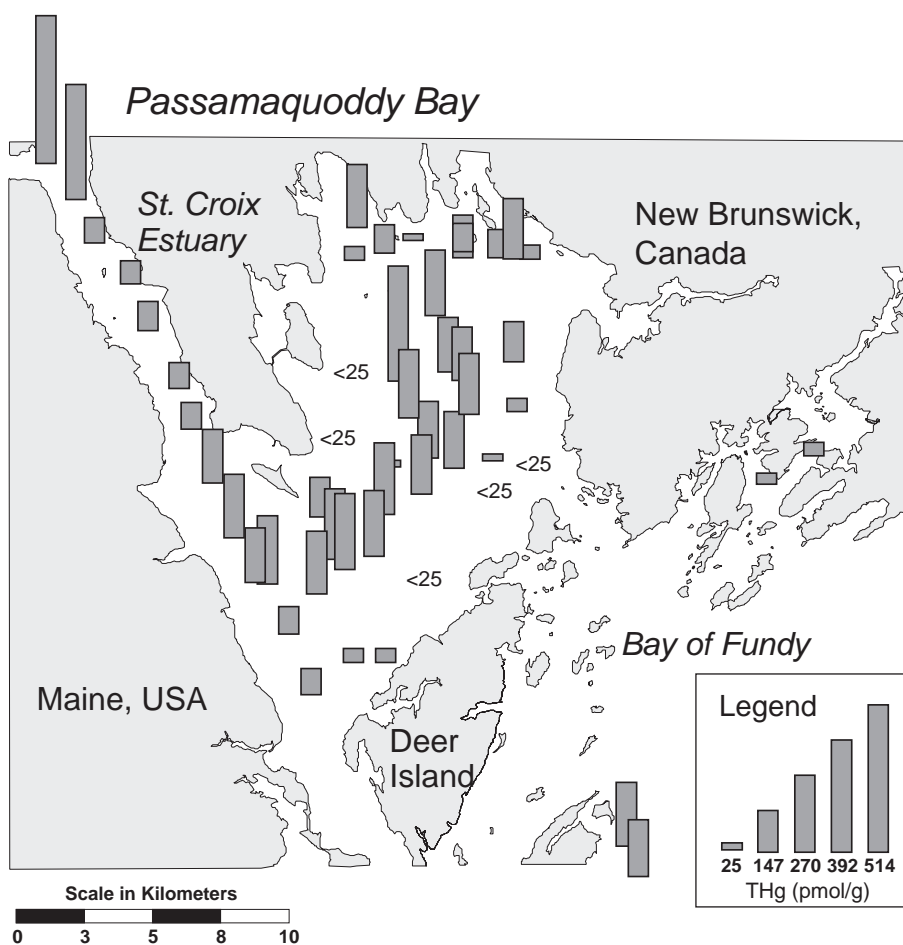


Fig. 2. Spatial distribution of total mercury (THg) in Passamaquoddy Bay and the St. Croix River Estuary. THg concentrations are station means over all sampling periods.

relatively fine-grained sediments (Figs. 2 and 3a, Table 1). Sediment grain size and TOC are also interrelated ($r^2=0.84$, $p<0.01$), suggesting a common

mode of THg delivery from the water column in depositional areas. “Sticky” fine-grained sediments that are high in organic carbon effectively scavenge

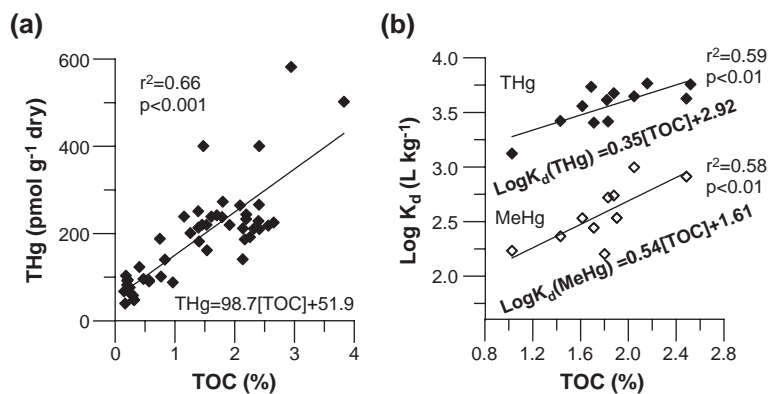


Fig. 3. Relation between total organic carbon (TOC) and (a) THg concentrations (means of all stations sampled over all stations shown), and (b) partitioning of mercury between the dissolved and solid phases ($\log K_d$) in Passamaquoddy Bay. Samples shown in panel (b) were collected in August 2001.

Table 1
Total mercury (THg), TOC and sediment grain size

Station ^a	THg (pmol g ⁻¹)	TOC (% dry weight)	Grain size (% <63 μm)
1	140	3.30	n/a
2	180	2.92	n/a
3	42	0.85	n/a
4	43	1.25	n/a
5	516	4.92	87.5
6	369	4.35	75.5
7	81	1.80	30.0
8	74	0.95	7.0
9	100	1.89	24.0
10	83	0.95	6.0
11	86	0.97	6.0
12	168	2.13	35.0
13	212	2.77	69.0
14	212	3.40	n/a
15	83	2.47	22.5
16	83	1.80	n/a
17	186	4.02	87.5
18	253	4.06	96.0
19	391	3.22	94.0

^a Stations are those sampled by Loring et al. (1998).

metals like THg as they settle out of the water column (Milligan and Loring, 1997). Thus, it follows that TOC content and the grain size of surficial sediments dominate the areal distribution of THg concentrations across all stations sampled resulting in the distribution shown in Fig. 2. Excluding the St. Croix River estuary, when THg concentrations are normalized to TOC there are no significant differences using a *t*-test for paired mean concentrations at all other sampling locations. Thus, normalizing sediment THg levels to TOC contents can account for much of the variability in THg among sites in Passamaquoddy Bay and the outer Bay of Fundy.

4.2. Dissolved solid phase partitioning

In contrast to the solid phase THg concentrations described above, porewater THg levels measured in this study are in the same range as concentrations in estuarine environments more heavily impacted by historical pollution (Sunderland et al., 2004). These relatively high concentrations of THg may indicate the presence of significant quantities of inorganic mercury in the colloidal phase (Guentzel et al., 1996).

Accordingly, partition coefficients (in L kg⁻¹) that describe the ratio of mercury in the solid phase relative to the dissolved phase are relatively low for THg (log K_d : THg=3.12–3.76; MeHg=2.20–3.00) (Fig. 3b). As discussed in the theory section, past research shows that bioavailable Hg(II) consists of some fraction

of the total mercury pool (ϕ) in the dissolved phase. Depending on the speciation of Hg(II) in the porewaters, high concentrations of THg in the dissolved phase may therefore lead to a greater pool of available Hg(II).

In addition to its influence on the spatial distribution of THg, TOC can also be used to describe variability in the partition coefficients (K_d) for THg and MeHg (Fig. 3b). The linear relationship showing higher K_d for MeHg and THg in sediments with more TOC demonstrates the importance of organic matter as a control on partitioning between the solid and dissolved phases. Studies in Lavaca Bay and Long Island Sound found similar relationships to those observed in this study; i.e. that increased TOC levels resulted in higher fractions of THg and MeHg in the solid phase of the sediments (Bloom et al., 1999; Hammerschmidt and Fitzgerald, 2004). As mentioned above, partitioning between the dissolved and solid phases is an important control on the amount of Hg(II) that is potentially available to methylating microbes. Thus, a declining fraction of dissolved Hg(II) with increasing levels of TOC may have a negative effect on MeHg production if the fraction of bioavailable Hg(II) remains constant with the addition of organic matter.

4.3. Methylmercury distribution

Concentrations of MeHg are used in this study as a proxy for production in the sediments, assuming advective inputs and losses are relatively small. As we discussed in the theory section, normalizing the solid phase MeHg concentrations to THg levels allows us to develop another indicator for methylation rate (%MeHg) and explore the effects of sulfides, Eh and TOC on the bioavailable pool of Hg(II) and microbial activity reflected by the methylation rate. Variability in the spatial distribution of both MeHg and %MeHg is discussed below.

Methylmercury concentrations in Bay of Fundy sediments ranged between 0.25 and 7.38 pmol g⁻¹ dry weight. Both MeHg concentrations and %MeHg were significantly elevated in May and November relative to August (*t*-test, paired two-sample for means, $p < 0.05$). This pattern of seasonal variation is consistent with other studies (Benoit et al., 1998; Gill et al., 1999; Hammerschmidt et al., 2004). In this study, elevated levels of MeHg in May may be due to increased inputs of MeHg from the watershed and rivers. For example, in Passamaquoddy Bay, over 40% of the river discharges occur in the spring (Gregory et al., 1993). If advective inputs of MeHg from river discharges are

significant in May, MeHg concentrations measured during this sampling period will be less reliable indicators of in situ production.

4.3.1. Multivariate analysis summary

As a starting point for our analysis, we used stepwise regression analysis to select the best variables among THg, TOC, S^{2-} , and Eh for predicting variability in MeHg concentrations. In May, only TOC was selected using the stepwise linear regression model (see Fig. 3b), while THg, Eh, and total sulfide were all excluded from the model. For the August data set, both THg and total sulfide were significant variables in the model ($\text{MeHg} = 0.0041 [\text{TOC}] + 0.0032 [S^{2-}] + 0.14$). This model explains over 75% of the variability in the MeHg concentrations in August. These relationships help to summarize these data and develop simple statistical indicators of MeHg production in Bay of Fundy sediments. In the following sections, we discuss the mechanisms driving relationships among MeHg concentrations, %MeHg and geochemical characteristics of the sediments.

4.3.2. Total mercury (THg) and total organic carbon (TOC)

Methylmercury concentrations are significantly related to both THg concentrations and TOC in May and August (Fig. 4a,b,d,e). MeHg concentrations are highest in sediments with elevated THg

Table 2

Correlation matrix for sediment redox potential (Eh), sulfide concentrations, and total organic carbon content (TOC) in sediments from Passamaquoddy Bay

	May 2001		August 2000/2001	
	Sulfide	TOC	Sulfide	TOC
Eh	-0.363	-0.671	NC	-0.508
Sulfide	1	0.715	1	0.566

NC=no significant correlation.

and TOC. Because there is no relationship between %MeHg (methylation rate) and TOC, co-deposition of THg and TOC may be driving the relationship between TOC and MeHg. These results suggest that MeHg production in these sediments may be limited by the supply of total mercury as expressed in Eq. (6). If this is the case, reductions in inorganic mercury inputs from national and international emission control strategies would result in a proportional decrease in MeHg production in these sediments if all other factors remained constant. However, the relatively large scatter around the relationships between MeHg and THg/TOC suggests that additional factors are needed to explain variability in MeHg production in this region.

4.3.3. Redox potential (Eh)

Redox potential appears to have limited utility as a predictor of MeHg production in these sediments (Fig. 4c,f). A weakly significant relationship showing

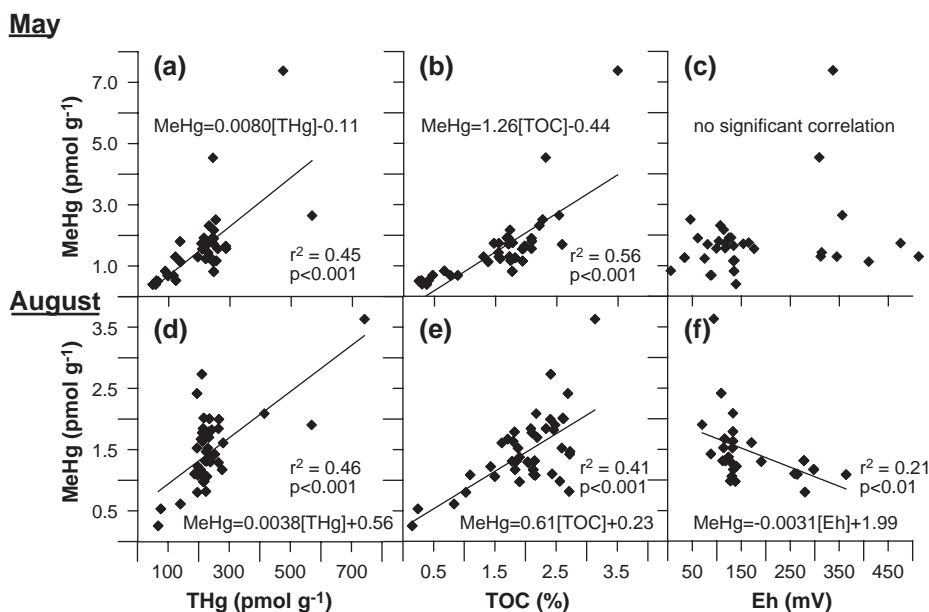


Fig. 4. Methylmercury (MeHg) concentrations in Bay of Fundy sediments as a function of THg, TOC, and redox potential (Eh) in May (2001) and August (2000/2001) sampling periods.

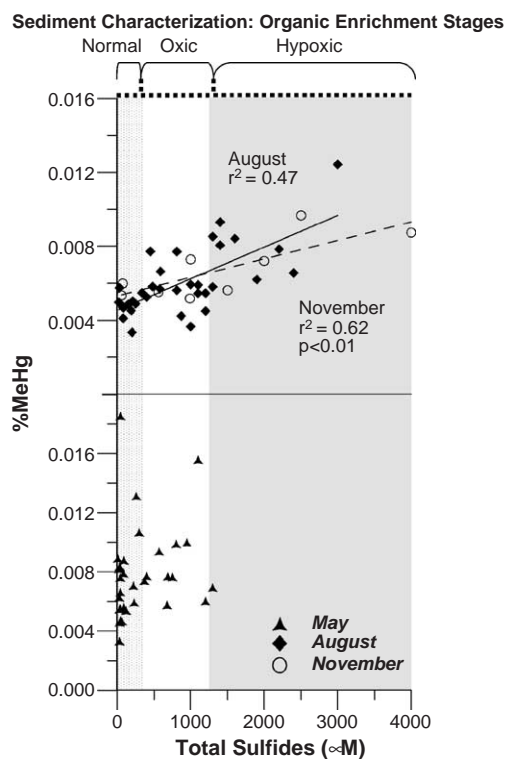


Fig. 5. Relation between %MeHg and organic enrichment status of the sediments reflected by total sulfide concentrations using the classification scheme of Wildish et al. (1999, 2004).

a decline in MeHg concentrations with increasing Eh was observed in August (Fig. 4f). However, this relationship may be an artifact of the interrelationships among TOC, Eh and sulfide levels in these sediments (Table 2). Declining surface Eh is also an indicator of organic enrichment because the chemical oxygen demand in sediments is proportional to the concentration of organic carbon undergoing mineralization (Hargrave et al., 1997). However, a recent review demonstrated numerous problems with probe calibration and the reliability of Eh measurements, restricting their usefulness as geochemical indicators of either organic enrichment or MeHg production potential (Wildish et al., 2004).

Table 3

Summary of variability in %MeHg in Bay of Fundy sediments with organic enrichment classes defined by total sulfide concentration (S^{2-}) (Wildish et al., 1999, 2004)

Organic enrichment classification	S^{2-} (μM) range	Mean %MeHg	95% Confidence intervals %MeHg	<i>n</i>
Normal	<300	0.63	0.53–0.73	35
Oxic	300–1300	0.68	0.60–0.77	32
Hypoxic	1300–6000	0.80	0.69–0.90	14
Anoxic	>6000	No data	No data	No data

4.3.4. Total sulfides (S^{2-})

Although no statistically significant relationships were observed between %MeHg and TOC or Eh, higher total sulfide concentrations in organically enriched sediments corresponded to elevated %MeHg (Fig. 5). These results suggest higher net methylation rates in high sulfide sediments and/or a higher fraction of bioavailable Hg(II). Using the sediment classification scheme for organic enrichment developed by Wildish et al. (2004, 1999), the fraction of THg as MeHg is greatest in high sulfide sediments that are moderately impacted by organic enrichment and fall into the “hypoxic” category ($S^{2-} = 1300\text{--}6000 \mu M$). Table 3 reinforces these findings by comparing the %MeHg of samples in the normal, oxic, and hypoxic sediment classification classes (Wildish et al., 1999). An independent samples t-test for equality of means showed that %MeHg was significantly higher in hypoxic sediments relative to normal sediments (mean difference = -0.16 , $p < 0.05$). Differences between sample means for hypoxic and oxic sediments were less pronounced but also significant at a higher p -value (mean difference = -0.11 , $p < 0.10$). There was no statistically significant difference between %MeHg in normal and oxic sediments (mean difference = -0.05). This difference is consistent with the lack of correlation between %MeHg and total sulfide in May where all sediments sampled fell in the normal-oxic range. In contrast, sites sampled in August and November exhibited a much wider range of total sulfide concentrations (Fig. 5).

5. Discussion

We hypothesized that sediments in the Bay of Fundy region will support higher levels of mercury methylation when the amount of organic matter is enhanced by activities such as aquaculture. Although TOC is a direct measure of the organic matter content of the sediment, the lack of correlation between %MeHg and TOC in this study did not support this hypothesis. Instead, our results suggested the main role of TOC was as a control on the distribution of Hg(II) (reflected by sediment THg

levels), and partitioning of THg and MeHg between the dissolved and solid phases.

However, using sulfides as an alternate indicator of organic enrichment in Bay of Fundy sediments, we found a significant increase in %MeHg in hypoxic sediments relative to normal and oxic sediment classes (Fig. 5, Table 3). Although TOC, Eh, and sulfides were all interrelated in this study (Table 2), sulfides appear to be the most sensitive indicator of the effects of organic enrichment on variability in %MeHg in these sediments. This is consistent with the findings of Wildish et al. (2004) on the utility of sulfides as a highly sensitive geochemical indicator of organic enrichment from the salmon mariculture industry in Bay of Fundy sediments. We therefore conclude that the relationship between %MeHg and sulfides observed in Bay of Fundy sediments supports our original hypothesis.

Differences between the utility of TOC and sulfides as indicators in this study may be the result of more pronounced increases in dissolved organic matter (DOM) rather than TOC as a byproduct of the salmon mariculture industry. TOC will vary with different sources of carbon and the rates associated with different types of organic matter degradation by microbes. The source and composition of the organic matter therefore influences TOC. Similarly, the total sulfur content of refractory organic substances or humic acids is dependent on the origin of the organic material. For example, Abbt-Braun and Jahnel (2001) showed that carbon-to-sulfur atomic ratios (C/S) varied with the stage of humication in a number of naturally occurring samples. We therefore posit that increased levels of DOM in sulfidic porewaters were a side effect of the organic enrichment observed in this study.

Consistent with observations in other estuarine environments, high levels of THg in porewaters measured in this study may in turn suggest the high affinity of organic colloidal material for Hg(II) in this system (Guentzel et al., 1996). It is therefore plausible that the increase in %MeHg in high sulfide sediments containing high levels of DOC is the result of the formation of bioavailable Hg(II) complexes that contains both sulfur and dissolved organic carbon. In this study, higher sulfide concentrations in porewaters containing organic matter appear to yield a geochemical environment that is conducive to uptake of Hg(II) by methylating bacteria. We speculate that this may be the result of enhanced bioavailability of inorganic mercury in mixed complexes that contain both dissolved organic matter and reduced sulfur groups (DOM-Hg-SH) in high sulfide, organically enriched marine sediments.

In contrast, past research has shown that at lower sulfide levels than those observed in this study (~20–300 μM), increasing levels of sulfides inhibit MeHg production (Benoit et al., 2001; Gilmour et al., 1998; Hammerschmidt and Fitzgerald, 2004). Mechanistically, this is thought to be the result of a shift in the speciation of inorganic mercury away from neutral complexes that readily cross the cell membranes of methylating bacteria (e.g., $\text{HgS}^0(\text{aq})$), toward charged polysulfide complexes that do not readily diffuse (Benoit et al., 1999a, Benoit et al., 2001). Effectively, these studies show that increasing concentrations of sulfides lower the amount of Hg(II) available to methylating microbes or as represented in Eq. (6), the effective fraction of the total mercury pool (ϕ) that crosses the cell membranes of methylating microbes.

Our results suggest that across a range of sulfide concentrations that exceed 300 μM , increasing sulfide levels in organically enriched marine sediments enhances the fraction of bioavailable Hg(II). Haitzer et al. (2003) compared the speciation of Hg(II) between DOM and S^{2-} in porewaters across the range of concentrations found under natural conditions. Although their results showed that concentrations of Hg(II)-sulfide species are expected to be higher than Hg(II)-DOM species, the authors acknowledged the possibility of mixed (DOM-Hg-SH) complex formation that may increase overall binding constants for DOM. We concur with these authors that an experiment evaluating the significance of Hg(II)-DOM complexes in sulfidic porewaters is needed. Such a study could explore the possibility of a potentially important mixed complex containing sulfur that comprises part of the bioavailable pool of Hg(II). In summary, data collected in this study imply that moderate levels of organic enrichment through fish farming may enhance MeHg production in the Bay of Fundy.

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