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Speciation and bioavailability of mercury in well-mixed estuarine sediments

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Abstract

Despite regulations controlling anthropogenic mercury sources in North America, high levels of mercury in coastal fish and shellfish are an ongoing problem in Maritime Canada and the Northeastern United States. This study presents sediment core data from a macrotidal estuary located at the mouth of the Bay of Fundy showing stratigraphic profiles of total and methylmercury concentrations and potential methylation rates measured using stable mercury isotopes. The results show that in contrast to the expected methylmercury profile typically observed in unmixed sediments, methylmercury production occurs throughout the estimated 15-cm-thick active surface layer of these well-mixed sediments. The resulting large reservoir of methylmercury in these sediments helps to explain why mercury concentrations in organisms in this system remain high despite emissions reductions. Current management policies should take into account the expected delay in the response time of well-mixed estuarine systems to declines in mercury loading, considering the greater reservoir of historic mercury available in these sediments that can potentially be converted to methylmercury and biomagnify in coastal food chains.

Keywords: Methylmercury; Estuaries; Enrichment factor; Sediment burial; Bay of Fundy

1. Introduction

Mercury emissions from anthropogenic sources in Maritime Canada and the Northeastern United States have declined by more than 50% from peak levels in the 1970s as a result of pollution control measures (Sunderland and Chmura, 2000). However, there is no

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evidence of similar declines in the concentrations of mercury in marine birds, fish and shellfish from the Bay of Fundy region of Canada, which is a catchment for atmospheric mercury contamination from industrialized regions of Central Canada and the United States (Chase et al., 2001; Evers et al., 1998; NESCAUM et al., 1998). Methylmercury (MeHg) levels in fish and invertebrates surpass Environment Canada's tissue residue guideline of 0.033 ppm (0.16 nmol g^{-1}) for the protection of all aquatic life (CCME, 2000; Chase et al., 2001), and at the highest trophic levels, total mercury concentrations exceed the Health Canada guideline of 0.5 ppm (2.5 nmol g^{-1}) for safe consumption by humans (Gaskin et al., 1973, 1979; NESCAUM et al., 1998). A better understanding of the relationship between concentrations in organisms and emissions reductions is needed to develop effective strategies for reducing potential human health impacts of mercury in the Bay of Fundy.

The conversion of inorganic mercury to methylmercury is a critical process affecting the relationship between mercury inputs and concentrations in biota. The majority of mercury released as a byproduct of human activities and present in the environment is inorganic mercury, but only the most toxic-organic form, MeHg, bioaccumulates in organisms (Bloom, 1992). There is considerable evidence that production of MeHg is principally a biologically mediated reaction carried out by sulfate-reducing bacteria in marine sediments (Benoit et al., 1999; King et al., 1999). Because these microbes are anaerobes, benthic sediments in coastal systems often provide the most suitable environment for MeHg production (Choi and Bartha, 1994). Coastal sediments also act as a reservoir for past and present mercury inputs due to the affinity of inorganic mercury species for particulates and organic matter (Gagnon et al., 1996; Mason and Lawrence, 1999). Two of the main factors determining the exposure of coastal organisms to mercury are therefore: (i) the amount of inorganic mercury in the sediments that is converted to MeHg; and (ii) the geochemical conditions that affect the activity of methylating bacteria and the availability of inorganic mercury for methylation. To gain insight into the temporal response of mercury concentrations to changes in mercury inputs, it is important to understand both of these factors.

The Bay of Fundy has the world's largest tides, reaching up to 16 m at the mouth of the bay (Gregory et al., 1993). Tseng et al. (2001) observed that mixing of sediments in the fluid mud profile of a turbid macrotidal estuary in France creates a distinct geochemical environment that facilitates the activity of microbial populations converting inorganic mercury to MeHg. Based on these data, we hypothesized that physical mixing in the Bay of Fundy will change the geochemical characteristics of the surface sediments and increase the depth of the active sediment layer where methylation takes place. The active sediment layer 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). The relatively thick active sediment layer in the Bay of Fundy may effectively increase the amount of total and methylmercury in the sediment compartment that is available to organisms, as compared to other more static estuarine systems.

In this paper, the effects of sediment mixing are explored by investigating ambient profiles of total mercury and MeHg and potential MeHg production rates measured in sediment cores from contrasting sites at the mouth of a freshwater tributary and in well-mixed regions of a coastal embayment located at the mouth of the Bay of Fundy. Evidence is presented that demonstrates the effects of mixing on the depth and geochemistry of the active sediment layer in this system. The implications for mercury uptake at the base of the food chain and the temporal response of this system to reductions in anthropogenic mercury emissions are discussed.

2. Methods

2.1. Study site

Sediment cores were collected in Passamaquoddy Bay and the St. Croix River Estuary between May and August 2001 (Fig. 1). Passamaquoddy Bay is a semi-enclosed macrotidal estuary located at the mouth of the Bay of Fundy. The mean tidal range in Passamaquoddy Bay is 6–8 m, making it a turbid, tidally

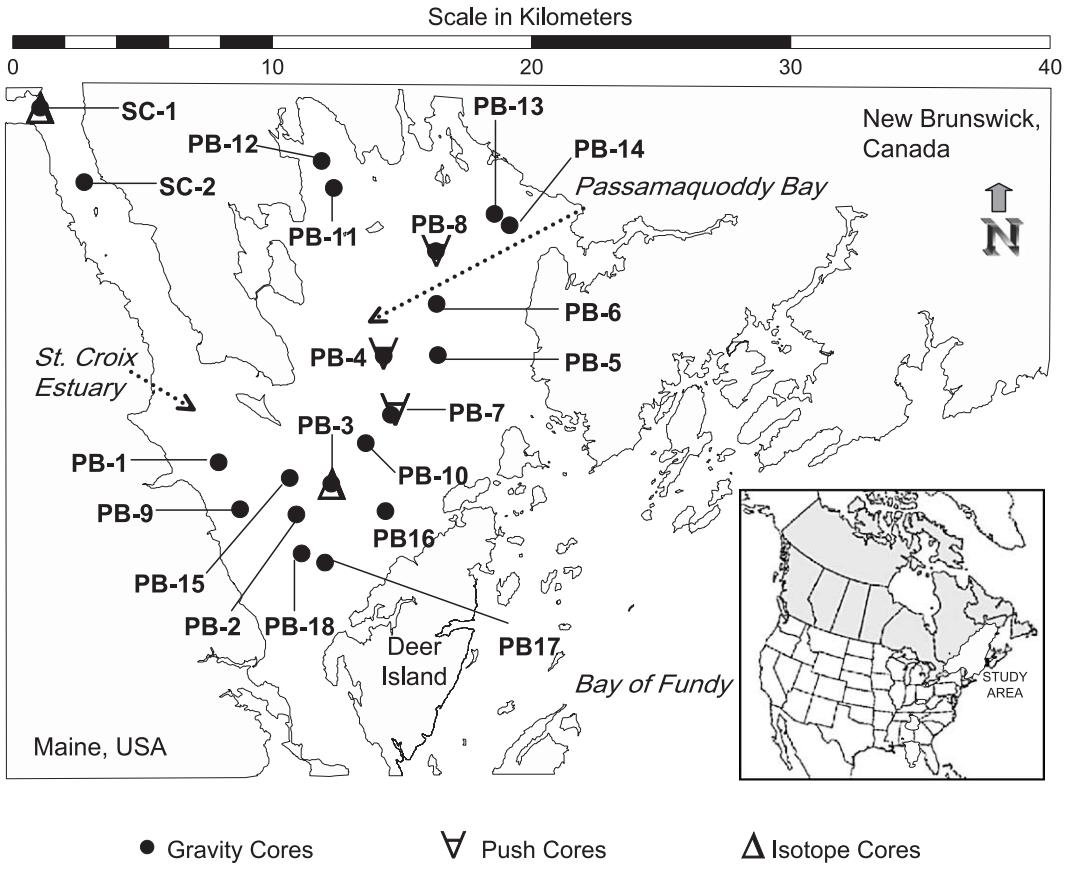

Fig. 1. Map of the study area showing sampling locations for gravity cores, push cores and isotope cores.

dominated system (Gregory et al., 1993). The St. Croix River is the main freshwater inflow to Passamaquoddy Bay and runs along the border between Canada and the United States. Related investigations (Sunderland, 2003) show that total mercury concentrations in surface sediments in Passamaquoddy Bay and the St. Croix River Estuary range between 50 and 750 pmol g^{-1} dry weight, with the highest concentrations found at the head of the St. Croix River Estuary.

2.2. Field sampling

2.2.1. Push cores

Eight 15-cm-long surface sediment push cores were obtained from a large volume, modified Van Veen grab sampler at selected locations in May and August 2001 using acid-washed PVC/Plexiglas core tubes (Fig. 1). Duplicate cores were collected at sites SC-1, PB-3 and PB-7 and analyzed for total mercury and MeHg. Push cores collected at sites PB-7 and PB-8 were only analyzed for total mercury. All cores were extruded at 2-cm intervals in the laboratory on shore, and all samples were frozen until analysis. Sulfide concentrations in the wet sediments of push core subsamples were analyzed using an ion-specific electrode after addition of sulfide antioxidant buffer according to the method outlined by Wildish et al. (1999). Redox potential (Eh) was measured at the sediment surface of gravity core and push core sampling locations using an Orion platinum redox electrode and a calomel reference electrode.

2.2.2. Gravity cores

Multiple gravity cores ($n=20$) were collected to characterize the geochemical profile of sediments in

Passamaquoddy Bay and the St. Croix River Estuary using a 1.5-m-long gravity corer (Fig. 1). Gravity cores were sectioned into 5-cm vertical intervals to a depth of 20 cm, after which they were divided into 10-cm increments. Sediments were placed in polyethylene sample containers and cooled at temperatures <4 °C to minimize chemical transformations following extrusion. Vertical gradients of dissolved ammonium and sulfate were measured in sediment porewaters within 24 h of sampling to estimate present-day sediment accumulation rates following the method developed by Cranston (1991, 1997). This method estimates sediment burial rates within a factor of 2 of radiometric dating (Cranston, 1991) and is particularly useful in erosion and transport regions of the estuarine basin where sediments cannot be dated using traditional methods. All cores were freeze-dried and archived for further analysis. In addition to total mercury, gravity cores were analyzed for a spectrum of metals including Fe, Li, Mn and Pb. Subsamples for metal analysis were prepared by digesting 1.0 g of freeze-dried sediment in 5.0 ml of concentrated nitric acid for approximately 24 h at 60 °C. Flame atomic absorption analyses were carried out using a Varian 220FS spectrometer for Fe, Li and Mn. Electrothermal atomic absorption analysis of Pb was carried out using a Varian 220FS spectrometer fitted with a Varian GTA110 graphite furnace. Relative precision and accuracy limits, estimated from replicate analyses of CANMET-certified reference materials (STSDs 1–4) and an internal GSC standard (EMG-017), were determined to be $\pm 3\%$ for Fe, Li and Mn and $\pm 5\%$ for Pb. Total and organic carbon was determined in 0.5 g of freeze-dried sediment using a Leco WR-112 carbon analyzer. Inorganic carbon was removed using 1 M hydrochloric acid prior to organic carbon measurements. Precision and accuracy were estimated to be ± 0.03 wt.% based on replicate analyses of calibration standards.

2.2.3. Sediment porewaters

Sediment porewater samples were separated from selected push cores ($n=2$) and surface sediment samples ($n=23$) collected at the push core and gravity core sampling locations. Porewaters were extracted under a nitrogen atmosphere by transferring the bulk sample into 50-ml acid-washed polycarbonate centrifuge tubes. Tubes were purged with N_2 prior to transfer, centrifuged at 3000 rpm for 30 min, followed by vacuum filtration with disposable 0.2-μm cellulose nitrate filter units. All filters were rinsed with 1% HCl and distilled deionized (18 Ω Millipore filtration system) water immediately prior to use. Porewater samples for total mercury analysis were preserved in 0.5% ultrapure HCl, while MeHg samples were immediately frozen until analysis.

2.2.4. Isotope cores

At two stations (SC-1 and PB-3), duplicate intact sediment cores were spiked at 1-cm intervals with inorganic mercury isotope [91.95% ^{199}Hg(II) from Oak Ridge Batch #168490] that was pre-equilibrated with seawater. Cores were incubated at ambient seawater temperature for 4 h, extruded and frozen until analysis for conversion of ^{199}Hg(II) into methylated mercury. The purpose of this work was to determine a methylation "potential" for these sediments rather than using the isotope as a tracer because the added ^{199}Hg(II) may be more available for methylation than the in situ Hg(II).

2.2.5. Polychaetes

Polychaete worms (*Nephtys* sp.) were collected from benthic sediments at the same sampling locations as push cores, gravity cores and isotope cores. Samples were obtained by immediately sieving the wet sediments collected using a modified Van Veen grab sampler on board the sampling vessel. Polychaetes were identified in the laboratory, flushed with deionized water for 24 h and frozen until analysis for mercury. Biological samples were analyzed for total mercury using the same methodology as sediment samples.

2.3. Mercury analyses

Samples for total and MeHg analyses were placed in 125-ml acid-washed polypropylene specimen jars and were immediately cooled to <4 °C. Upon returning to the laboratory, all samples were frozen until analysis. Wet sediment samples were analyzed for total mercury by digestion in 5:2 concentrated nitric–sulfuric acid solution and oxidation with bromine monochloride (BrCl) under Class 100 clean room conditions. Aqueous samples were digested with BrCl for at least 12 h before analyses.

Immediately prior to analysis, the excess bromine in all samples was neutralized with an equivalent volume of 10% hydroxylamine hydrochloride. 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). Methylmercury 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 same methods were used for samples spiked with ^{199}Hg(II) isotope except that detection was made using an HP4500 Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) (Gill and Fitzgerald, 1987; Hintelmann and Evans, 1997).

The method detection limit (MDL) for total mercury 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 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), were 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 rerun. 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 averaged $103\pm10\%$ ($n=12$) 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. For ICP-MS, the detection limit was 0.075 pmol g^{-1} and sample reproducibility was 10% for ambient MeHg and 23% for the $CH_3^{199}Hg$ isotope concentration. Isotope detection was further constrained to 0.5% of the ambient concentration. 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 $106\pm26\%$ ($n=12$). 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 determined for each sample analyzed by oven-drying subsamples of wet sediments for at least 24 h at 60 °C.

2.4. Statistical analysis

Nonparametric bivariate correlation matrices (Spearman rank correlation coefficients, r_s) were developed for gravity core and push core data to investigate covariation between total mercury (Hg-T), MeHg, %MeHg and potential methylation rates. For gravity core data, Hg-T profiles were analyzed as a function of other metals with known anthropogenic origins such as Pb and other geochemical data including porewater sulfate and ammonium concentrations.

3. Results

3.1. Speciation in the active sediment layer

Fig. 2 shows mercury speciation in sediment cores from contrasting physical regions. The St. Croix River station (SC-1) is located at the head of the St. Croix River Estuary where the sediment accumulation rate was estimated to be between 1 and 2 mm $year^{-1}$ based on the gradients in dissolved ammonium found in the gravity cores using the method developed by Cranston (1991, 1997). In contrast, stations PB-3 and PB-4 are located on opposite sides of the main basin of Passamaquoddy Bay (Fig. 1), near the center of two tidally dominated circulation gyres (Greenberg et al., 1997) that are expected to result in significant mixing of these sediments.

3.1.1. Total mercury (Hg-T)

At station SC-1 (Fig. 2a), there is a pronounced subsurface peak in total mercury (Hg-T) that may be the result of historic mercury discharges from a chlor-alkali facility that operated along the river in the 1970s. Concentrations of Hg-T in the sediments decrease from the head of the river estuary into the center of Passamaquoddy Bay. The uniform Hg-T

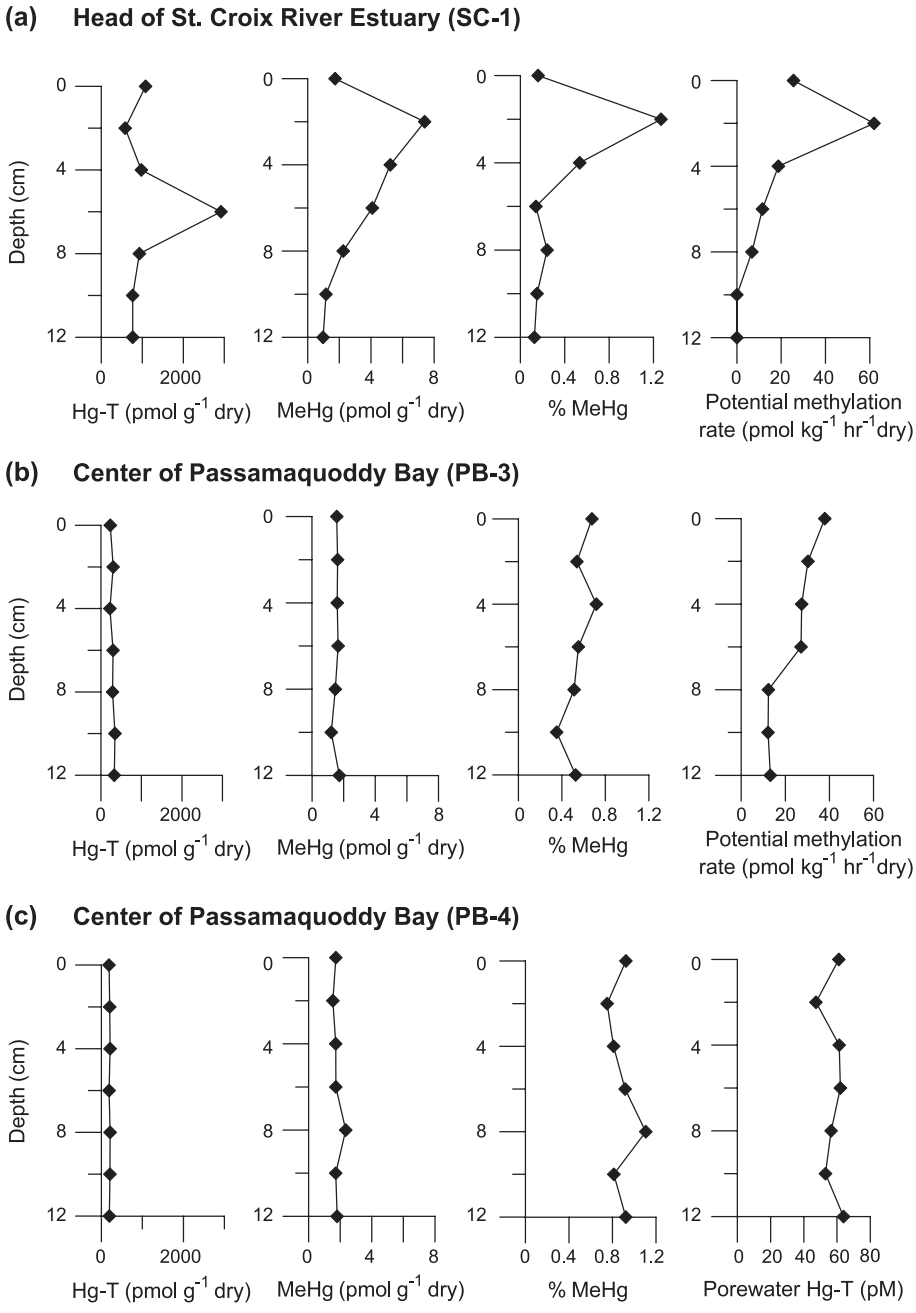

Fig. 2. Speciation of mercury measured in push cores from contrasting depositional (SC-1) and well-mixed sediments (PB-3 and PB-4). Data include ambient total mercury (Hg-T), methylmercury (MeHg) and the fraction of total mercury in the sediments present as MeHg (%MeHg). Mercury isotope experiments were used to estimate the potential methylation rates at the head of the St. Croix River Estuary (SC-1) and the center of Passamaquoddy Bay (PB-3).

profiles at stations PB-3 and PB-4 on both sides of Passamaquoddy Bay (Fig. 2b and c) provide further evidence that these sediments are also well mixed.

3.1.2. Methylmercury (MeHg)

The effects of differing physical dynamics on MeHg production are illustrated by the contrasting MeHg profiles (Fig. 2) at the head of the river estuary (SC-1) relative to the well-mixed areas in the center of Passamaquoddy Bay (PB-3 and PB-4). The fraction of total mercury present as methylmercury (%MeHg) in these sediments is strongly correlated with potential methylation rates measured in cores spiked with mercury isotopes ($r_s = 0.88$, $p < 0.01$), supporting the premise that %MeHg is a reasonable approximation of the relative rates of Hg methylation in these sediments. This relationship has also been seen in other estuarine sediments (Benoit et al., 2003).

At station SC-1, MeHg production is taking place in a narrowly constrained subsurface zone. There is a subsurface peak between 2 and 4 cm in ambient MeHg concentrations, %MeHg and potential methylation rates measured in isotope cores. Ambient MeHg concentrations decline rapidly in the oxic surface layer and beyond depths of several centimeters, while methylation rates indicated by both the %MeHg and the isotope core data are low to nondetectable, respectively, in these depth intervals. For example, the %MeHg ranges between 0.54% and 0.76% in the 2–4 cm subsurface peak in MeHg production at station SC-1, compared to 0.28% in the surface layer, and between 0.11% and 0.34% at depths greater than 6 cm. This profile is typical of those observed in other studies of relatively unmixed lake and estuarine sediments, which show that the %MeHg in estuarine sediments is generally less than 0.5%, particularly in the oxic surface sediments and at depth, and that MeHg production occurs in a relatively narrow subsurface zone within the sediments (e.g., Benoit et al., 1998a; Bloom et al., 1999; Gagnon et al., 1996).

In the mixed sediments at stations PB-3 and PB-4, the ambient MeHg profiles and %MeHg suggest that MeHg conversion is taking place at all depths in the surface sediment layer. Methylmercury concentrations and %MeHg are both relatively uniform at all depths (Fig. 2b and c) and potential methylation rates measured at station PB-3 are detectable throughout the entire profile studied. At station PB-4, the %MeHg ranges between 0.62% and 0.92%, which is in the same range as the 2–4 cm subsurface peak in %MeHg at site SC-1 that corresponds to maximum methylation rates. Additionally, the mean %MeHg in integrated surface samples (0–10 cm depth) from multiple locations throughout Passamaquoddy Bay ($n = 45$) was 0.88%, again, characteristic of sediments where MeHg is being actively produced in situ in the sediment column. These data support the premise that in the well-mixed sediments of Passamaquoddy Bay, MeHg production is taking place both at the sediment–water interface and throughout the 15-cm-thick active surface layer.

3.2. Porewater–solids partitioning

Porewater samples in this study represent "operationally defined" dissolved concentrations of total mercury and methylmercury since colloidal matter binds mercury in the < 0.2-μm size fraction (Guentzel et al., 1996). Porewater concentrations of Hg-T ranged between 50 and 150 pM (Table 1) and are significantly elevated above the levels expected on the basis of solid-phase concentrations, as they are in the same range as sites heavily impacted by historical pollution, such as Lavaca Bay, TX (Bloom et al., 1999). Accordingly, the range in partition coefficients (log K_d) for Hg-T between 3.12 and 3.76 (l kg^{-1}) in Passamaquoddy Bay is lower than those observed in other systems (Bloom et al., 1999; Leermakers et al., 1995; Turner et al., 2001). Elevated levels of Hg-T in porewaters of Passamaquoddy Bay sediments are consistent with the effects of mixing in this system, which is causing substantial recycling of Hg in the surface sediments and an increased fraction of colloidally bound Hg-T in the porewaters.

Table 1
Porewater Hg-T and MeHg data from surface sediment grab samples at stations SC-1 and PB-1 through PB-5

Station	Hg-T (pM)	MeHg (pM)
SC-1	135	2.3
PB-1	150[a]	4.7[a]
PB-2	55	N/A
PB-3	80[a]	2.7[a]
PB-4	50	3.4[b]
PB-5	80[b]	7.2[a]

[a] Means of triplicate samples.
[b] Means of duplicate samples.

Porewater MeHg concentrations are also elevated relative to systems with similar Hg-T concentrations in sediments such as the Patuxent River, MD (Benoit et al., 1998a), but partition coefficients (log K_d) ranging between 2.20 and 3.00 (l kg^{-1}) are in the same range as values found in other studies (Benoit et al., 1998a; Bloom et al., 1999). These results suggest that MeHg concentrations are enriched in both the solid and dissolved phases and support the hypothesized increase in MeHg production in well-mixed sediments.

3.3. Geochemical characteristics of the sediment column

Fig. 3 shows porewater ammonium (NH_4^+) and sulfate levels measured in gravity cores collected in Passamaquoddy Bay. Porewater NH_4^+ concentrations that are consistently >0.5 mM occur below a depth of 30 cm at station PB-3 (Fig. 3) and below 15 cm at station PB-4 (Table 2).

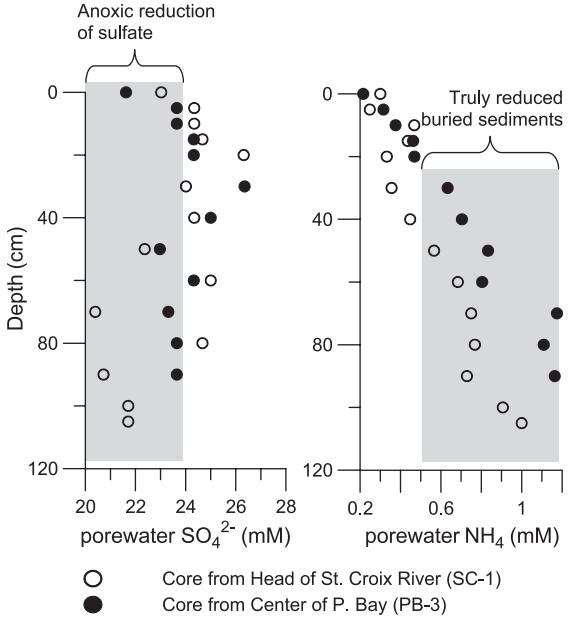

Fig. 3. Porewater sulfate and ammonium concentrations measured in gravity cores from Passamaquoddy Bay and the St. Croix River Estuary. Sulfate concentrations <24 mM indicate the anoxic reduction of sulfate and ammonium concentrations >0.5 mM indicate the presence of fully reduced buried sediments.

Porewater NH_4^+ concentrations >0.5 mM indicate anoxic sediments that are below the active sediment layer due to lack of oxidation of ammonium produced by decomposition of organic matter (Buckley, 1991; Buckley and Cranston, 1988) and allow an upper boundary to be placed on the depth of the active sediment layer. These sediments may be considered truly buried and effectively removed from further interaction with the sediment–water interface. Data from other cores collected throughout Passamaquoddy Bay further confirm that the depth of the active sediment layer based on porewater ammonium data is generally between 15 and 30 cm (Table 2). This relatively large volume of sediments in the active sediment layer results in a large pool of historic Hg-T that can potentially be converted to MeHg.

Data on porewater sulfate levels in gravity cores from Passamaquoddy Bay indicate that sulfate reduction is taking place at all depths within these sediments, including at the sediment surface (Fig. 3, Table 2). Anoxic reduction of sulfate based on a geochemical threshold established in the literature is indicated by porewater sulfate concentrations <24 mM (Buckley, 1991; Buckley and Cranston, 1988). In all Passamaquoddy Bay sediments, porewater sulfate levels are very close to this level, supporting the idea that these sediments are in the oxic-transitory range that is most conducive for the activity of SRB.

Although porewater sulfate data (Fig. 3) indicate anaerobic reduction of sulfate, which typically corresponds to a redox potential of approximately −200 mV (Wildish et al., 1999), redox potentials (Eh) measured in surface sediments varied between −213 and 512 mV (Sunderland, 2003). The large variability in redox measurements and length of time (>5 min) needed in the field for the redox probe to achieve equilibrium may both signify the presence of Eh microniches in the surface layer (Wildish et al., 1999); however, these data should be interpreted with caution as variability may also reflect measurement errors associated with these types of Eh measurements. Sulfide concentrations measured in the surface sediments using an ion-specific electrode were also highly variable, ranging between 10 and 4000 μM in replicate samples taken at a single sampling station (Table 3). The large variability in sulfide concentrations and the presence of Eh microniches show rapid transitions in the sediment geochemistry in the surface

Table 2
Geochemical characteristics of gravity cores from Passamaquoddy Bay

Station ID	Length (cm)	Organic carbon (%)	$NH_4^+ > 0.5$ mM depth interval(s) (cm)[a]	$SO_4^{2-} < 24$ mM depth interval(s) (cm)	Range in SO_4^{2-} mM[b]
SC-1	105	1.11–4.21	50–105	50–105	20–26
SC-2	55	0.41–1.05	NI	5–10	22–27
PB-1	50	0.24–1.37	NI	0–5; 10–15	22–24
PB-2	130	0.92–1.74	5–10; 15–130	50–60; 80–130	19–29
PB-3	100	1.01–1.77	30–100	0–5; 50–60; 70–80; 90–100	22–26
PB-4	130	1.05–1.65	15–130	0–5; 10–50	23–28
PB-5	130	0.76–1.48	NI	0–10; 50–60; 120–130	23–26
PB-6	130	1.11–2.17	5–130	0–5; 40–50; 120–130	23–26
PB-7	140	0.81–1.57	100–140	15–20; 60–80	23–26
PB-8	130	1.00–1.36	15–130	0–5; 40–50; 120–130	23–26
PB-9	127	0.28–1.15	60–127	0–5; 10–15; 90–100; 110–127	20–26
PB-10	105	0.94–1.39	40–105	60–70	23–28
PB-11	130	1.15–1.34	40–130	NI	24–27
PB-12	130	1.46–1.60	60–130	NI	24–27
PB-13	130	1.15–1.63	60–130	NI	24–27
PB-14	130	1.03–1.68	NI	NI	24–27
PB-15	130	0.79–1.69	70–100	NI	24–27
PB-16	130	0.87–1.04	50–130	NI	24–27
PB-17[c]	130	1.08–1.65	30–130	NI	24–27
PB–18	75	0.44–1.43	NI	NI	24–27

NI = no indication of reduction. There is an evidence of reduction in all cores except PB-14 and PB-18, and even in these cores, the sulfate levels are very close to the geochemical cutoff characterizing reducing conditions.

[a] Concentrations of $NH_4^+ > 0.5$ mM measured in porewaters indicates lack of oxidation of ammonium produced by decomposition of organic matter. In a number of cores, the presence of consistently >0.5 mM NH_4^+ at depth suggests anoxic buried sediments.

[b] Minimum to maximum SO_4^{2-} concentrations measured in porewaters throughout each core are reported. Note that the range in SO_4^{2-} concentrations are all very close to the geochemical cutoff (24 mM) indicating anoxic reduction of sulfate. This supports the supposition that most of these sediments are in the oxic transitory range where there is a large gradient in redox potential, ideal for the activity of sulfate-reducing bacteria.

[c] Top 30 cm of core PB-17 missing.

layer that provide conditions most favorable to methylating microbes and are indicative of the effects of organic-rich "mottles" or "pockets" in the surface sediments.

Table 3
Variability in sulfide concentrations measured in surface sediment grab samples from Passamaquoddy Bay

Sulfide concentrations (uM)				
Station	Mean	*N*	Min	Max
PB-1	213	9	23	1500
PB-2	659	7	190	1300
PB-3	554	12	32	1100
PB-4	667	6	480	800
PB-5	1471	9	10	4000
PB-6	363	6	33	1000
PB-8	167	3	42	370
PB-9	393	4	30	1200
PB-10	92	3	36	150

Visual inspection of sediment cores from Passamaquoddy Bay in the field revealed the presence of black, organic-rich mottles interspersed with the dominant light brown oxic clay muds. There was also detectible H_2S odour in the presence of these mottles, indicating anoxia. Based on these data, we hypothesize that the anoxic organic-rich "pockets" in Passamaquoddy Bay sediments effectively increase the volume of sediments suitable for formation of MeHg by SRB by increasing the transition zone between oxic and anoxic sediments. The resulting geochemical environment would be comparable to that observed by Tseng et al. (2001) in a turbid macrotidal estuary in France where methylation of mercury was measured in analogous "anoxic pockets" occurring within a fluid mud profile. These organic carbon "pockets" facilitate MeHg production throughout the relatively deep active sediment

Table 4
Concentrations of metals measured in gravity cores

Station	Sediment depth (cm)	Hg (pmol g^{-1})	Fe (nmol g^{-1})	Li (μmol g^{-1})	Mn (μmol g^{-1})	Pb (nmol g^{-1})
PB-7	0–2	204	48.0	5.48	6.46	67.6
	2–4	219	45.3	4.90	6.37	67.6
	4–6	219	44.8	5.48	6.70	72.4
	6–8	219	37.8	5.48	5.35	67.6
	8–10	214	39.2	5.33	5.44	72.4
	10+	219	41.0	5.48	5.72	72.4
PB–8	0–2	214	47.6	6.20	6.63	77.2
	2–4	219	49.2	6.34	7.15	67.6
	4–6	224	50.3	6.34	6.75	62.7
	6–8	209	50.9	6.20	7.41	67.6
	8–10	214	49.8	6.48	7.12	62.7
	10+	209	41.0	6.05	5.88	57.9
SC–1	0	284	44.2	4.76	5.37	38.6
	5	219	41.9	3.89	5.61	43.4
	10	244	46.9	5.62	6.13	48.3
	15	214	52.1	6.20	6.81	29.0
	20	125	54.1	4.47	6.55	38.6
	30	70	50.1	6.05	6.92	24.1
	40	55	53.7	6.20	7.15	24.1
	50	90	54.6	6.20	7.48	24.1
	60	184	54.4	6.48	6.83	24.1
	70	65	56.0	6.63	7.44	29.0
	80	65	63.6	6.92	8.17	24.1
PB-3	0	229	44.9	5.91	7.04	91.7
	5	249	41.9	5.91	6.84	91.7
	10	319	40.8	5.76	6.73	115.8
	15	379	44.4	6.05	7.19	91.7
	20	274	43.9	6.05	6.61	106.2
	30	189	41.5	6.48	7.06	62.7
	40	80	38.3	6.48	6.72	43.4
	50	80	39.2	5.76	6.12	33.8
	60	50	35.6	5.91	5.66	29.0
	70	40	35.8	7.06	5.39	33.8
	80	45	34.4	6.05	5.37	29.0
	90	40	36.2	5.76	5.97	33.8
	100	40	34.9	5.91	5.66	33.8
				−0.359		0.758
Correlation with Hg (r_s)		1	N/S	$p<0.05$	N/S	$p<0.001$

Pearson correlation coefficients (r) for metals as a function of Hg are shown below concentration data for each core. N/S = correlation is not significant.

layer in Passamaquoddy Bay, thereby accounting for the observed enrichment in MeHg in the sediment porewaters and the high %MeHg in the solid-phase sediments.

3.4. Anthropogenic mercury in Passamaquoddy Bay

Anthropogenic sediment enrichment factors (ASEFs) were calculated from Hg-T concentrations measured in sediment cores at stations SC-1 and PB-3. Mixing of these sediments means it is not possible to obtain detailed information on historical Hg-T loading from these cores and that traditional dating methods using ^{210}Pb and ^{137}Cs could not be applied (Smith, 2001). However, ASEFs calculated from the difference between mercury concentrations in the sediments that accumulated prior to human influence and those at the surface provide a simple method for

estimating the overall enrichment in this system resulting from anthropogenic pollution.

Present-day burial rates of approximately 1–2 mm year^{-1} measured in this study suggest that sediments below 40-cm depth in gravity cores should represent Hg-T concentrations in the sediments prior to significant human sources of mercury, while allowing a wide margin for integration of the sediment column due to mixing. Diagenetic remobilization of mercury in sediment cores can cause peaks in mercury concentrations in the surface sediments that are not indicative of anthropogenic pollution (Benoit et al., 1998b; Walton-Day et al., 1990). However, the lack of significant correlations between Hg-T concentrations and redox-sensitive metals such as Fe and Mn (Table 4) suggests that redistribution of mercury through diffusion and co-precipitation is not a significant factor in gravity cores from Passamaquoddy Bay. To isolate the natural and anthropogenic components of metal enrichment, iron (Fe) and lithium (Li) can both be used as normalizing factors to correct for the mineralogical and granulometric variability in the sediments (Loring, 1991). However, there were no significant correlations between Hg-T and Fe or Li in these sediments; thus, it can be assumed that the observed Hg-T profiles are not caused by changes in grain size and/or mineralogy. The range of "background" concentrations (i.e., those that are naturally occurring) of Hg-T in Passamaquoddy Bay cores was estimated from 95% confidence limits around Hg-T concentrations below 40 cm in the gravity cores. Anthropogenic sediment enrichment factors shown in Fig. 4 include the surface of gravity cores and push cores collected at stations SC-1 and PB-3. For surface sediments obtained from push cores at the same sampling stations (0–15 cm), Hg-T concentrations

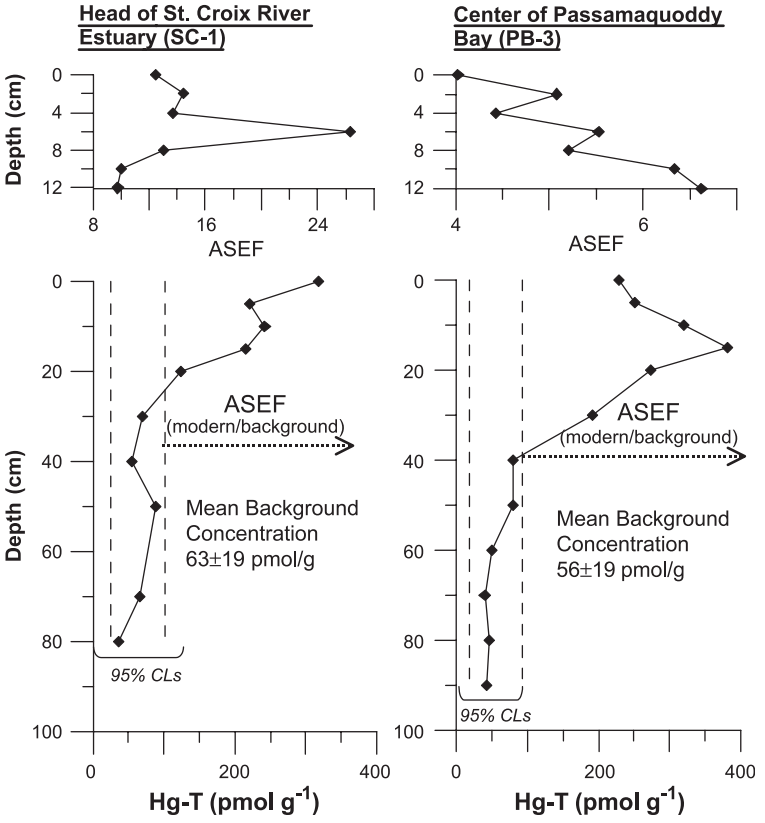

Fig. 4. Anthropogenic sediment enrichment factors (ASEFs) for Hg-T at the head of the St. Croix River and the center of Passamaquoddy Bay. ASEFs are used to estimate modern/background Hg-T levels in Passamaquoddy Bay sediments. The lower graphs in the figure depict gravity core Hg-T data, while ASEF profiles shown for the surface sediments are from push cores taken from the same sampling stations.

measured in the upper horizon of the sediments were divided by the upper 95% confidence limit value for background mercury levels to produce the plots of ASEFs shown in Fig. 4.

The results presented in Fig. 4 show that ASEFs in Passamaquoddy Bay range between 3 and 6 and up to 26.3 at the head of the St. Croix River where localized historical discharges are likely the most important source of contamination. The enrichment factors for Passamaquoddy Bay are in the same range as other studies that show a global scale increase in atmospheric mercury deposition of two to four times the pre-industrial levels (Swain et al., 1992; Engstrom et al., 1994), suggesting that the majority of Hg-T in these sediments is derived from atmospheric sources. The high degree of correlation between lead, which is known to exhibit a strong anthropogenic signal, and Hg-T concentrations ($r_s = 0.76$, $p < 0.001$; Table 4) provides further evidence of anthropogenic enrichment in these cores. The results of this analysis indicate that the majority of the mercury in the active sediment layer of Passamaquoddy Bay is from historic inputs of mercury from anthropogenic sources.

4. Discussion

This study presents evidence showing that mixing of the active sediment layer in Passamaquoddy Bay results in geochemical changes in the sediment column that enhance the activity of methylating microbes. In marine sediments, net methylation rates are highest in the transition zone between oxic and anoxic conditions because these conditions are most conducive to the activity of SRB (Hintelmann et al., 2000; King et al., 2001). In addition, these microbes require organic matter as a substrate for microbial activity (Mason and Lawrence, 1999). Physical mixing in the Bay of Fundy may enhance the transfer of sulfate and carbon and introduces more bioavailable inorganic mercury into the deeper sediment, potentially stimulating the methylating activity of SRB. Regular disturbances through mixing also appear to create a unique geochemical environment more likely to exhibit microzonal redox gradients, compared to the classic down profile gradients of sediments in which less physically dynamic conditions may limit the activity of microbial populations that methylate mercury. Fig. 5 is a conceptual diagram that contrasts the features of mercury speciation and sediment geochemistry observed in well-mixed sediments in this study with the characteristic profile of mercury speciation typical of depositional sediments.

As illustrated in Fig. 5, production of MeHg in sediments from unmixed depositional systems must be modeled as a two-compartment system, taking into account that MeHg production occurs in a narrow

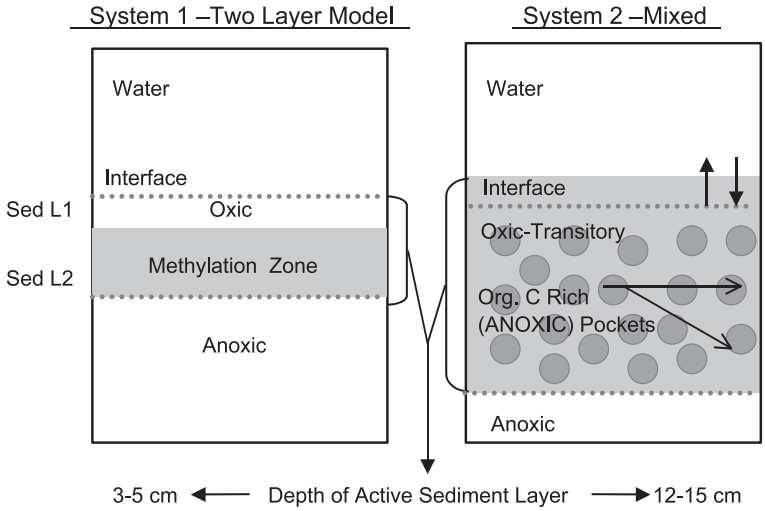

Fig. 5. Conceptual model of mercury speciation in contrasting depositional and well-mixed sediments.

zone in the redoxcline below the oxic surface layer of these sediments. In well-mixed systems, such as Passamaquoddy Bay, the sediment compartment is better described by System 2 (Fig. 5) where MeHg production occurs throughout a relatively deep active sediment layer and is facilitated by the presence of organic-rich anoxic "pockets" or mottles. Additionally, MeHg production occurs at the sediment–water interface in the well-mixed sediments, potentially providing a vector for MeHg entry into the water column and resulting in the exposure of organisms feeding at the sediment surface.

The dynamic physical mixing occurring in Passamaquoddy Bay results in the creation of an approximately 15-cm-thick active sediment layer. Burial provides the main removal mechanism for historic mercury that has accumulated over time. In Passamaquoddy Bay, the sediment burial rate estimated from this study is approximately 1–2 mm $year^{-1}$. This means that the active sediment layer is comprised of a relatively large reservoir of Hg-T consisting of mainly historical pollution (Fig. 4) that has accumulated in the sediments over many decades. In contrast, in a depositional system, the active layer is typically much shallower (e.g., 3–5 cm) resulting in a much smaller reservoir of Hg-T that can be potentially converted to MeHg by methylating microbes.

As an illustrative example, the reservoirs of MeHg in mixed and unmixed systems with comparable Hg-T concentrations were estimated using the Hg-T data from gravity cores SC-1 and PB-3 (Fig. 4) and push core data for %MeHg in the 14-cm surface horizon (Fig. 2). Using an average sediment density of 2.7 g cm^{-3} and an average concentration of solids in the sediments of 0.67 g cm^{-3} for both sites, the reservoir of MeHg on an areal (1 m^2) basis are approximately 3.5 and 2.4 μmol in the mixed and unmixed sediments, respectively. According to these calculations, the reservoir of MeHg is almost 50% higher in the well-mixed sediments when compared to depositional sediments with similar Hg-T concentrations.

The physical mechanism of mixing may also provide a vector for MeHg entry into the water column and food web through organisms feeding at the sediment–water interface. In the well-mixed sediments, MeHg production occurs throughout the active sediment layer, including at the sediment–water interface as illustrated in the push core profiles for Passamaquoddy Bay (Fig. 2b and c). In contrast, the oxic sediment layer in unmixed, depositional systems can act as a geochemical barrier to diffusing MeHg through the precipitation of MeHg with Fe and Mn hydroxides (Gagnon et al., 1996). In depositional areas, this oxic layer can inhibit the entry of MeHg to the water column and limit exposure of all but burrowing benthic organisms.

In the well-mixed sediments of Passamaquoddy Bay, the enhanced levels of Hg-T and MeHg in the porewaters of surface sediments are consistent with rapid cycling of mercury in this system at the sediment–water interface that is facilitated by the physical dynamics of the area. Preliminary evidence for increased availability of mercury to organisms in well-mixed sediments is provided by the observed differences in the mean concentrations of total mercury measured in polychaetes collected from sediment grabs at the head of the St. Croix River Estuary ($n=3$) compared to well-mixed sediments in Passamaquoddy Bay ($n=10$). These data show that concentrations of mercury in polychaetes are significantly higher ($p<0.01$) in the well-mixed sites (55 ± 14 pmol g^{-1} wet wt.) than at the head of the river estuary (38 ± 5 pmol g^{-1}), despite significantly lower spatially averaged concentrations of Hg-T in surface sediments from Passamaquoddy Bay (~ 150 pmol g^{-1}) relative to the head of the river estuary (~ 550 pmol g^{-1}) (Sunderland, 2003).

The results of this study help to elucidate why concentrations of mercury in organisms from this coastal system are still high despite large emissions reductions. In Passamaquoddy Bay, there is a linear relationship between Hg-T and MeHg in the sediments (Sunderland, 2003), which means that increases or decreases in Hg-T emissions should eventually translate into corresponding changes in MeHg concentrations in sediments and ultimately organisms. However, the results of this study suggest that there is a large lag time between reduced mercury inputs and changes in ambient concentrations because historic mercury inputs are slowly being converted to MeHg over the 15-cm-thick active sediment layer and removal of mercury through sediment burial is relatively slow. This hypothesis is currently being further tested through the application of a mercury cycling model for the region.

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