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The effect of sediment mixing on mercury dynamics in two intertidal mudflats at Great Bay Estuary, New Hampshire, USA

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Abstract

Estuarine sediments store particulate contaminants including mercury (Hg). We studied Hg sediment dynamics in two intertidal mudflats at Great Bay estuary, NH, over multiple years. Sediments at both mudflats were physically mixed down to ~10 cm, as determined by ⁷Be measurements, albeit via different mechanisms. Portsmouth mudflat (PT) sediments were subject to bioturbation by infaunal organisms and Squamscott mudflat (SQ) sediments were subject to erosion and redeposition. The presence of higher concentrations of fresh Fe(III) hydroxide at PT suggested bioirrigation by the polychaetes (*Nereis virens*). At depths where infaunal bioirrigation was observed, pore-water inorganic Hg (Hg_i) and methylmercury (MeHg) were lower potentially due to their interaction with Fe(III) hydroxide. Methylmercury concentrations increased immediately below this zone in some samples, suggesting that the observed increase in material flux in bioirrigated sediments may initiate from lower depths. Pore water in sediment at PT also had higher fractions of more protein-like and labile DOC than those at SQ that can lead to increased MeHg production in PT, especially at depths where Hg_i is not removed from solution by Fe(III) hydroxide. Where sediment erosion and redeposition were observed at SQ, Hg species distribution was extended deeper into the sediment column. Moreover, methyl coenzyme M reductase (MCR) and mercury reductase (*mer-A*) genes were higher at SQ than PT suggesting differences in conditions for Hg cycling. Results showed that the near-surface region of high MeHg concentrations commonly observed in unmixed sediments does not exist in physically mixed sediments that are common in many estuarine environments.

Keywords

Mercury; Methylmercury; Sediment; Estuary

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Appendix A. Supplementary information

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.marchem.2015.10.011>.

1. Introduction

Mercury (Hg) is a global pollutant that in its methylated form has effects on human health including neurological, cardiovascular, and immunological (Grandjean et al., 1997; Mergler et al., 2007; Karagas et al., 2012). Most people are exposed to Hg through consumption of fish particularly from open ocean and coastal fisheries. As of 2010, all 50 states in the USA have had fish consumption advisories pertaining to Hg including coastal advisories along the Atlantic coast and Gulf of Mexico (USEPA, 2011). Mercury is also considered a priority pollutant in the Gulf of Maine (Gulf of Maine Council on the Marine Environment, 2007).

Estuaries act as a repository for Hg due to the sedimentation of river-borne particulates associated with Hg (Coquery et al., 1997). Near-shore sediments may be an important source of MeHg to marine organisms, including fish consumed by humans (Chen et al., 2008). Estuaries are highly variable with respect to geochemical characteristics and have a high potential for sequestration and methylation of Hg (e.g., Hines et al., 2006; Lambertsson and Nilsson, 2006; Merritt and Amirbahman, 2008; Schartup et al., 2013; Liu et al., 2015) due to high pore-water sulfate (SO_4^{2-}) concentrations, great amounts of labile sediment organic carbon, and a relatively shallow redox transition in the sediment. The fate of Hg in the sediment is dependent on sediment disturbances (e.g. bioturbation and advection at the sediment-water interface), chemistry of the sediment, and the movement of Hg from sediment to organisms. Sulfate reducing bacteria (SRB) have been shown to be the dominant methylators of Hg in the environment (Compeau and Bartha, 1985), while methanogens and iron reducing, fermentative, acetogenic, and cellulolytic bacteria have also been found to methylate Hg (Gilmour et al. 2013, Kerin et al., 2006). In undisturbed estuarine sediments, a near-surface maximum of MeHg production is consistently observed (Merritt and Amirbahman, 2009). However, MeHg profiles for sediments in physically dynamic systems are less widely considered.

Sediment in estuarine and coastal zones can also be subject to physical mixing via different mechanisms, for example, sediment transport (erosion and deposition), dredging, and bioturbation. These processes lead to sediment reworking by introducing oxygen and dissolved organic carbon (DOC) into otherwise anoxic sediment and enhancing the sediment benthic efflux of chemical species to the water column. Benthic macroinvertebrates transfer reduced sediments to the sediment-water interface, resulting in their oxidation and also transfer freshly-precipitated and more labile organic matter from the sediment surface to depth, resulting in their decomposition (Aller and Yingst, 1980; Aller et al., 2001). The burrowing and bioirrigation activities of some species of polychaetes in the Great Bay sediment result in solute exchange between the pore water and the overlying water. This zone near the sediment-water interface is where accumulated solutes and metabolites in the pore water are removed via flushing, and the subsurface sediment is subsequently oxidized by the introduction of the overlying water (Aller, 1984; Hines and Jones, 1985). Sediment mixing by bioturbation involving polychaetes results in a high frequency of solute exchange between pore water and surface water (Kristensen, 2001; Shull et al., 2009). This frequent solute exchange has been shown to enhance material decomposition rate and efflux (Aller, 1984; Kristensen, 2001). Moreover, coastal benthic polychaetes are known to enhance

sediment MeHg production (Sizmur et al., 2013) and efflux to the overlying water (Benoit et al., 2009).

This study focuses on sediment Hg dynamics at two intertidal mudflats in Great Bay, New Hampshire (Fig. S1). Several potential sources of Hg are located on the estuary, including Portsmouth Naval Shipyard, and the former Pease Air Force base, a Superfund Site that is a known source of Hg and lead (Jones et al., 2001), and the Schiller power plant, a coal and wood fired plant. We chose these two sites because of their known Hg concentrations as well as their contrasting sediment characteristics. Areas of industrial land use are found at the mouth of Great Bay; however, due to tidal flux and dynamic mixing, contaminants have also moved to more forested regions (McLaughlin et al., 2003). Sediments at the Portsmouth (PT) and the Squamscott (SQ) mudflats (Fig. S1) are subject to physical mixing, albeit with two different mechanisms; the dominant forms of sediment mixing at PT and SQ were bioturbation and sediment transport, respectively. We analyzed solid-phase and pore-water inorganic Hg (Hg_i) and MeHg as well as microbial DNA and ancillary parameters to investigate the effects of mixing mechanisms on sediment mercury dynamics at the two mudflats.

2. Methods

2.1. Study area

The Great Bay estuarine system in New Hampshire and Maine (Fig. S1) has freshwater input from seven rivers, a ~3 m tidal range (Hines and Jones, 1985), and a surface area that ranges from 23 km² at high tide to 11 km² at low tide (Short, 1992). The channel portions of the lower estuary consist of poorly sorted coarse sands and gravel, and the mudflats consist of fine-grained, well-sorted silt (Winston and Anderson, 1971). In general, surface water salinities decrease and salinity variability increases from the ocean to the inner estuary, and salinity ranges of $S = 29\text{--}33$ near the outlet (Portsmouth Harbor) and $S = 4\text{--}28$ at a mudflat near the head of the estuary (South Newington) have been observed (Short, 1992). Bioturbation varies from the head to the mouth of Great Bay with greater activity in more saline environments (Winston and Anderson, 1971). Benthic invertebrates in Great Bay consist of polychaetes (45%), crustaceans (26%), bivalves (15%), and gastropods (11%) (Short, 1992). In general, higher concentrations of heavy metals have been measured in tributary sediments than in Great Bay potentially due to watershed inputs, and higher concentrations of total Hg have been measured in Piscataqua River sediment than in tributary sediments potentially due to the use of Hg steam at the Schiller power plant between 1950 and 1968 (Short, 1992). Potential sources of metal contamination include municipal and industrial discharges, transportation from the upper estuary, and activity from Portsmouth Naval Shipyard prior to 1976 (Short, 1992).

The sampling locations (Fig. S1) were Portsmouth mudflat (PT) and Squamscott mudflat (SQ). PT is located in a cove in Kittery, Maine, near the Portsmouth Naval Shipyard (43° 5'10.87"N; 70°44'24.61"W). SQ is a mudflat at Chapman's Marsh in Stratham, New Hampshire, at the mouth of the Squamscott River (43° 2'24.07"N; 70°55'38.73"W). PT has higher salinity, similar to that of Portsmouth Harbor ($S = 29\text{--}33$; Winston and Anderson, 1971). SQ has lower salinity and a greater range in salinity, comparable to the South

Newington site ($S = 4\text{--}28$; Winston and Anderson, 1971) due to the freshwater input from the Squamscott River. Both mudflats are tidal with low tide at PT 2–2.5 h earlier than at SQ. Sampling took place in August 2008, May 2009, June 2010 and September 2010.

2.2. Sediment pore-water collection and analyses

Pore-water samples from PT and SQ were collected with multichambered equilibrium dialysis frames (“peepers”) following a field deployment of three weeks (Merritt and Amirbahman, 2007). The frames contained 20 2.5 cm^3 cells on 1.5 cm centers spaced by 0.5 cm. Peeper assembly, deployment, and retrieval, core collection and processing, peeper and core sub-sampling, and sample preservation methods are described in the Supplemental Information (SI) section. Samples were collected with peepers for Hg_i , MeHg, iron [Fe(II)], sulfide [S(–II)], dissolved organic carbon (DOC), pH, and alkalinity analyses.

Mercury speciation was determined by isotope dilution purge and trap GC-ICP-MS at the Trace Element Analysis Core at Dartmouth College (Hanover, New Hampshire), using methods adapted from EPA 1630. Species-specific isotope spikes were prepared from ^{199}Hg and ^{201}Hg were in the form of HgO . Inorganic ^{199}Hg (91.09% purity) was prepared by dissolution of ^{199}HgO in 0.4% HCl, and $^{201}\text{MeHg}$ was prepared by reacting the ^{201}HgO with methylcobalamin according to Bancon-Montigny et al. (2004). Ethylating reagent was prepared from >98% sodium tetraethylborate in 100 mL of 2% KOH under Ar gas, placed in vials and frozen until use.

Pore-water samples were analyzed for Hg_i and MeHg using a method adapted from Jackson et al. (2009). Aliquots of 0.5 g pore water were weighed and spiked with an appropriate amount of $^{201}\text{MeHg}$ and ^{199}Hg and allowed to equilibrate overnight. Samples were then diluted to 70 mL with deionized H_2O (Ultrapure (18 M Ω), ethylated, and analyzed by purge and trap GC-ICP-MS. Method detection limits were 2 and 0.75 pg L^{-1} for Hg_i and MeHg, respectively. Due to a lack of certified reference materials for Hg speciation in water, spike recoveries were used to determine precision and accuracy, and were determined to be $101 \pm 8\%$ ($n = 7$) for MeHg and $111 \pm 10\%$ ($n = 5$) for Hg_i .

Excitation-emission matrix spectroscopy (EEMS) was performed on DOC samples using a fluorescence spectrophotometer (Hitachi F-4500). DOC concentrations were measured using a Model 1010 Wet Oxidation Total Organic Carbon Analyzer (OI Analytical) in syringe injection mode (50 μL ; detection limit 0.5 mg L^{-1}). Fe(II) (1 mL; detection limit $5\text{ }\mu\text{M}$; Viollier et al., 2000), S(–II) (1 mL; detection limit $1\text{ }\mu\text{M}$; Cline, 1969) and alkalinity (1 mL; detection limit 2 mM; Sarazin et al., 1998) were determined colorimetrically.

2.3. Sediment solid-phase collection and analyses

Three sediment cores were collected: the first for Hg_i and MeHg, the second for porosity, percent loss on ignition (%LOI), ^7Be isotope, and acid volatile sulfide (AVS), and the third for Fe(III) and microbial DNA analyses in the vicinity of the pore-water sampling locations. The sediment was extruded from the cores and immediately sectioned into slices ranging from 0.25 cm to 1.25 cm, transferred to Whirl-pack bags, and frozen with dry ice. Sediment was also collected and sieved to determine the species and relative abundances of benthic polychaetes present at each site. Polychaetes were stained with rose Bengal, picked from

sediments samples, and sent to Jeremy Miller of Wells National Estuarine Research Reserve for identification.

For sediment MeHg analysis, 0.5 g sediment was extracted with KBr/H₂SO₄/CuSO₄, followed by CH₂Cl₂ and back-extracted into H₂O according to Bloom et al. (1997). Samples were then analyzed by isotope dilution GC-ICP-MS as described above. For sediment total Hg (THg) analysis, 0.25 g of freeze-dried sediment was digested using microwave at 105 °C for 30 min in 10 mL 9:1 HNO₃:HCl. Digested samples were diluted 100 times and analyzed by solution mode ICP-MS (Thermo Electron Element 2 sector field instrument). Quality assurance for MeHg was determined by analysis of BRC 580 (Institute for Reference Materials and Measurements, Belgium), with a certified value 75 ng g⁻¹ MeHg, and recoveries of 111 ± 7% (n = 4). The method detection limit (MDL) for MeHg was 4 pg g⁻¹. The certified reference material IAEA-433, with a certified value of 168 ng g⁻¹ was used for THg, with recoveries of 97 ± 8% (n = 4). The MDL for THg was 13 ng g⁻¹.

Methods to measure porosity, %LOI, AVS, and amorphous, microbially-available Fe(III) are described in the SI section. The ⁷Be analysis was conducted by gamma spectroscopy at 477.6 keV photoemission using a germanium detector (Canberra Industries, Meriden, CT) within two days of sample collection.

Microbial DNA was analyzed on ~1 g of sediment by quantitative polymerase chain reaction (qPCR) using the Ultraclean soil DNA Kit (MoBio Laboratories, Inc., Carlsbad, CA) to determine concentrations of total DNA, dissimilatory sulfate reductase gene (DSR), methyl coenzyme M reductase gene (MCR), mercury reductase gene (*mer-A*), and *Geobacter* (GEO) in a Stratagene MX3000P using the Quantitect SYBR green PCR kit (Qiagen, Valencia, CA) and 0.6 LM final primer concentration, with melting curves performed at the end of each reaction to ensure product integrity. Forty cycles were performed at the recommended temperatures and times, with one modification. The fluorescence was recorded after extension, followed by a post-extension heating step at recommended temperature. Quantitation standards were plasmids containing the gene of interest, and were prepared by cloning PCR products into the pcR2.1 plasmid using the Topo TA cloning kit (Invitrogen, Carlsbad, CA). All concentrations were normalized with respect to sediment dry weight.

2.4. Statistical correlations

Pearson's correlation coefficients and p-values were determined using the statistical software R version 3.0.3. Prior to running the correlations, normality of concentrations for each analyte by data set (PT, SQ, and both sites combined) was determined using ProUCL version 5.0. If the concentrations of an analyte for a given data set was not normal based on a 95% confidence interval, concentrations were natural log-transformed prior to running correlations. When solid-phase and pore-water depth intervals did not correspond in a data set, results were linearly interpolated between adjacent pore-water depth intervals prior to running correlations.

3. Results

The sediments at the two studied intertidal mudflats were periodically subject to mixing. The polychaete assemblages differed in the two sites. PT sediments were dominated by sand worms (*Nereis virens*), which are omnivorous scavengers and grazers that can burrow to depths of 45 cm (Creaser et al., 1983; Nielsen et al., 1995). In contrast, small red-gill mud worms (*Marenzelleria viridis*) and oligochaetes, both of which are deposit-feeders (Dauer, 1997; Rossi et al., 2001), dominated SQ sediments and had much less influence on the sediment structure. During visual inspection of sediment cores, oxidized burrows were observed at PT, and SQ cores were considerably darker in color with no visible oxidized burrows. For the duration of this study, no significant net sediment accretion or erosion was observed at PT. The peepers were deployed for a period of three weeks, and as such, the pore-water data are integrated over this time period. At SQ, the sediment accretion and erosion events (determined by changes in sediment-water interface location relative to peeper cells from the beginning to the end of the deployment interval) observed in June '10 and September '10, respectively, refer to the net sediment transport during peeper deployments. For August '08 and June '09 sampling, no net sediment transport was observed at SQ during the peeper deployment time. As a result, sediment mixing at PT was brought about by bioturbation by *N. virens*. Mixing at SQ was brought about by periodic sediment accretion and erosion episodes.

3.1. Inorganic mercury and methylmercury distribution

Fig. 1 shows the pore-water and solid-phase Hg_i and MeHg concentrations along the sediment column. The average solid-phase Hg_i concentration at PT ($2.79 \pm 0.83 \text{ nmol g}^{-1}$) was higher than that at SQ ($1.59 \pm 0.41 \text{ nmol g}^{-1}$). There were statistically significant trends ($p < 0.05$) with depth in solid-phase Hg_i concentrations in some of the cores.

A positive relationship ($p < 0.05$) was found between pore-water and solid-phase Hg_i for PT but not for SQ or when combining both sites (see Tables S1, S2, and S3 for correlation coefficients [r] and p-values). Peak pore-water Hg_i was observed close to the sediment-water interface at SQ in August '08 and May '09, at greater depths at SQ in June '10 (12 cm) and PT in August '08 (7.5 cm) and May '09 (7.5 cm) (Fig. 1c).

Average solid-phase MeHg concentrations were higher at SQ ($12.4 \pm 5.3 \text{ pmol g}^{-1}$) than at PT ($6.8 \pm 2.5 \text{ pmol g}^{-1}$). Solid-phase MeHg in SQ exhibited peaks close to the sediment-water interface except in September '10, where net sediment erosion was observed and the average solid-phase MeHg concentration was lower. At PT, a distinct solid-phase MeHg peak near the sediment-water interface was only observed in September '10, the only sampling event at the site where bioturbation was not apparent. SQ had a higher degree of temporal variability in solid-phase MeHg concentrations compared to PT (Fig. 1b). The average solid-phase MeHg concentrations in this study are similar to those from another study of Great Bay, NH (three intertidal sites in the estuary, including PT), but higher than those in the nearby more pristine Wells Estuary, ME, with concentrations that ranged between 0.19 and 2.56 pmol g^{-1} (Balcom et al., this issue).

A positive relationship was found between pore-water and solid-phase MeHg for PT and when combining both sites (Tables S1 and S2), but not for SQ (Table S3). The only instance with coincident pore-water and solid-phase MeHg peaks was at SQ in August '08 (Figs. 1b and 1d). At both PT and SQ, pore-water MeHg concentrations exhibited a high degree of temporal variability. Another recent study of the PT sediment found an average pore-water MeHg concentration of 1.38 pM in the top 6 cm (Balcom et al., this issue), within the range of the concentrations observed in this study.

3.2. Ancillary pore-water analyses

The ancillary pore-water constituents include S(–II), Fe(II), DOC (Fig. 2), alkalinity, and pH (Fig. S2). Samples for ancillary measurements were obtained in peepers placed adjacent to those for the Hg species.

At both sites, pore-water S(–II) concentrations were fairly uniform with depth (Fig. 2a). Two exceptions are a peak in S(–II) below 7.5 cm at both sites in August '08 and an increase from 1.5 cm to the sediment-water interface at PT in August '08 and September '10. No apparent S(–II) peaks were observed at depth in May '09 or September '10; however, sampling depth was limited in May '09. A significant positive relationship was found between pore-water S(–II) and alkalinity, and solid-phase MeHg:THg ratio, as well as between pore-water S(–II) and pore-water MeHg for PT, SQ, and when combining both sites (Tables S1-S3).

Pore-water Fe(II) concentrations were highest close to the sediment-water interface at both sites in August '08 and May '09 (Fig. 2b). In September '10, the increase in pore-water Fe (II) was observed deeper in sediment at both sites.

Pore-water DOC in all sampling events in SQ showed a consistent gradual increase with depth (Fig. 2c). In PT, however, the pore-water DOC was more variable. In August '08, May '09 and June '10, where PT sediment was subject to bioturbation, the pore-water DOC was generally $<10 \text{ mg L}^{-1}$ in the top 6 cm. In September '10, where bioturbation was not observed at PT, the pore-water DOC concentration showed a peak (26.3 mg/L) close to the sediment-water interface.

Pore-water EEMS measurements were taken for May '09 and June '10 samples to characterize the quality of DOC (Fig. 3). The EEMS data are classified into five components that represent peaks in the EEMS output data (1 and 2: humic-like, 3: fulvic-like, 4: humic- and fulvic-like, and 5: protein-like; Chen et al., 2003). The relative percentage was calculated as the peak intensity for a given component to the total EEMS intensity for that sample. In all samples, the protein-like component was significantly more abundant at PT ($27 \pm 21\%$ in May '09 and $11 \pm 10\%$ in June '10) than at SQ ($2 \pm 1\%$ in May '08 and $0.2 \pm 0.3\%$ in June '10). Pore-water DOC samples in SQ were dominated by the humic-like components (1 and 2) in all depths.

3.3. Ancillary solid-phase analyses

The ancillary solid-phase analyses were performed to determine the AVS and Fe(III) (Fig. 4), porosity and %LOI (Fig. S3), and ^7Be (Fig. S4). Porosity and %LOI were higher at SQ

compared to PT, and porosity was highest near the sediment-water interface at both sites (Fig. S3). The higher average porosity at SQ may be attributed to its higher sediment organic matter content.

The AVS concentrations showed a general increase with depth at both sites and were also higher at SQ than at PT (Fig. 4a). The exception was in June '10, where the top 10 cm of SQ sediment had lower AVS than PT, possibly due to accretion of fresh sediment at SQ. At both sites, AVS was the lowest in May '09. Significant positive relationships were observed between AVS and pore-water MeHg and between AVS and pore-water MeHg:Hg ratio when combining both sites and for SQ alone (Tables S1 and S3), but not for PT alone (Table S2).

Solid-phase Fe(III) concentrations were higher in PT than in SQ in August '08, May '09 and June '10, when bioturbation was observed in PT. In September '10, however, where no infaunal activity was observed in PT, the solid-phase Fe(III) concentrations were at or below the detection limit at this site. Sediment ⁷Be was analyzed only in May '09 samples and was detected to a greater depth at SQ compared to PT (Fig. S4).

3.4. Sediment microbial DNA

Sediment microbial DNA (i.e., total DNA, MCR, GEO, and DSR) was characterized in August '08 and May '09 sediments (Fig. 5 for MCR; Fig. S5 for others). Total DNA, MCR, GEO, and *mer-A* concentrations were significantly higher at SQ compared to PT. No significant difference was observed in DSR concentrations between sites. No trend in total DNA was observed with depth at either site. Total DNA was significantly higher at SQ than PT in both August '08 and May '09. At SQ, MCR (an indicator of the presence of methanogens) concentrations increased with depth, whereas concentrations did not show any trend with depth at PT. Average DSR concentrations were lower in August '08 compared to May '09 at both sites, while the opposite was true for GEO concentrations. A significant positive relationship was observed between GEO and pore-water MeHg (both sites combined, PT, and SQ) and between GEO and pore-water Hg_i (both sites combined and SQ; Tables S1-S3). A significant negative relationship was observed between DSR and pore-water MeHg (both sites combined, PT, and SQ) and between DSR and pore-water Hg_i (both sites combined and SQ). Average *mer-A* (the gene responsible for the reduction of inorganic Hg(II) to Hg(0); Barkay et al., 2003) concentrations were nearly two orders of magnitude higher at SQ than at PT. A *mer-A* peak at SQ was observed at 1.5–2 cm, coincident with a peak in Hg_i.

4. Discussion

4.1. Sediment mixing

Solid-phase ⁷Be was measured to determine the extent of sediment mixing at PT and SQ (Fig. S4). ⁷Be is a cosmogenic isotope with a half-life of 53 days, and physical mixing on the time scale of up to a few months is inferred if ⁷Be is found at depth (Sharma et al., 1987). Solid-phase ⁷Be was detected to a depth of 15.5 cm at SQ and 6.5 cm at PT,

indicating that sediments from both sites were vertically mixed on a relatively short time scale.

Several lines of evidence suggest that SQ and PT sediments were mixed by different mechanisms: (a) the presence of significantly-higher freshly-precipitated Fe(III) hydroxide at PT than at SQ (Fig. 4b); (b) visual inspection of sediment cores that showed Fe(III) precipitation down to ~10 cm in the sediment column in the presence of benthic infauna in PT (Fig. S6); and (c) the presence of significantly higher MCR concentrations at SQ than at PT. The role of polychaetes in creating an oxidizing environment in marine sediments that leads to the increase in sediment Fe(III) hydroxide has been shown previously (e.g., Ferro et al., 2003). The MCR indicates the presence of methanogens in a system, and, although methanogens can be resistant to transient exposures to oxygen of up to a few hours (Jarrell, 1985), the lack of MCR at PT suggests that the sediment at this site is subjected to frequent exposure of O₂. These lines of evidence point to bioturbation as the dominant sediment mixing mechanism at PT predominantly brought about by the polychaete *Nereis* spp. A previous study of Great Bay demonstrated that infaunal burrowing was more active at sites with higher salinity and less variation in salinity (Winston and Anderson, 1971), which is expected at PT due to its proximity to the mouth of the estuary. Burrowing polychaetes can transfer sediment to the surface, create substrate-rich fecal pellets, and expose fresh surfaces for microbial colonization (Kristensen, 2001). Polychaetes, including *Nereis* spp., cause bioirrigation that results in frequent pore-water flushing through the burrows and enhances exchange of O₂ and other chemicals, including reaction metabolites, with the overlying water (Aller, 1984; Polerecky et al., 2006).

Sediment collected at SQ was darker in color with no oxidized burrows and lower solid-phase Fe(III) concentrations (Fig. 4b) compared to PT. Sediment physical mixing at SQ was due to sediment transport, as evidenced by net accretion and erosion in June '10 and September '10, respectively. The average water velocity at SQ was $6.5 \pm 3.9 \text{ cm s}^{-1}$ at 25 cm above sediment on 19 August '09 during a full tidal cycle, compared to $2.9 \pm 3.9 \text{ cm s}^{-1}$ at PT on the same day (Swett, 2010).

The different sediment mixing modes at the two sites may have caused other differences in sediment geochemical characteristics. For example, the difference in %LOI between the two sites may be partly attributed to the fact that sediments populated by polychaetes are more efficient in organic carbon mineralization compared to defaunated sediments. This leads to an overall smaller pool of reactive organic carbon, the extent of which depends on the type of polychaetes (Kristensen, 2001). Hines and Jones (1984) observed a net removal of DOC from pore water in Great Bay sediment in the presence of infaunal polychaete activity. They also reported greater SRB activity by measuring SO_4^{2-} reduction rates at sites that were subject to bioturbation by polychaetes and attributed it to the enhanced transport of fresh DOC to depth. The fresh DOC serves as high quality substrate for the SRB that are believed to be the main agents for Hg methylation in estuarine sediments (Compeau and Bartha, 1985). In our study, an increase in DSR is only observed in our May '09 data at PT at 5–6 cm (Fig. S5), close to the depth where the freshly-precipitated Fe(III) hydroxide concentration decreases (Fig. 4b).

With an increase in SO_4^{2-} reduction rate at a bioturbated site (Hines and Jones, 1985), sediment AVS is expected to increase due to the production of dissolved S(-II). However, we observed higher AVS concentrations at the non-bioturbated, but otherwise mixed SQ sediment (Fig. 4a). Lower AVS at PT may be due to the continual introduction of O_2 due to bioirrigation in the sediment, resulting in the oxidation of $FeS_{(s)}$. Chemical equilibrium modeling showed that at both sites, and at all depths where dissolved Fe(II) and S(-II) could be measured, the pore water was saturated or slightly supersaturated with respect to amorphous $FeS_{(s)}$ and that precipitation would occur (Brown, 2010). In bioturbated PT sediment in August '08, pore-water Fe(II) ranged between approximately 90 to 200 μM in the top 7.5 cm, higher than the pore-water S(-II) concentrations (Fig. 2a), suggesting that Fe(II) controlled S(-II) concentration. In September '10, however, where no significant infaunal activity was observed in PT sediment, pore-water S(-II) accumulated and Fe(II) concentrations were significantly lower than those in the presence of infaunal activity in the top ~5 cm (Fig. 2b). This was similar to the Great Bay study by Hines and Jones (1985) in which dissolved Fe(II) was present and replenished by bioirrigation with continuous Fe redox cycling, removing S(-II) from the pore water as $FeS_{(s)}$.

The increase in pore-water alkalinity in estuarine sites may be attributed to SO_4^{2-} reduction (Merritt and Amirbahman, 2007). A greater increase in alkalinity with depth was seen at SQ compared to PT (Fig. S2), perhaps suggesting a higher SO_4^{2-} reduction rate at SQ. However, bioirrigation of PT sediment may have caused flushing of alkalinity out of the sediment pore water, equilibrating it with the alkalinity of the overlying water.

The EEMS data (Fig. 3) show that a greater percentage of DOC below the sediment-water interface at PT was fresh protein-like material, which is more labile than humic- and fulvic-like fractions that were dominant below the sediment-water interface at SQ. Fresh protein is a more reactive source of organic matter for microbes compared to more degraded humic and fulvic acids. This reactive DOC is a product of excretions and mucus secretions of the polychaetes along burrow walls (Kristensen, 2001). Therefore, higher quality DOC (i.e., less degraded) may have been transported to depth in the sediment at PT, as was also reported by Hines and Jones (1985), or excreted by the polychaetes. In contrast to the study by Hines and Jones (1985); Mitchell and Gilmour (2008) did not observe a correlation between overall microbial activity and the more labile DOC. Mitchell and Gilmour (2008) found a positive relationship between increasing Hg methylation rate constants and increasing molecular weight of DOC in their study of a Chesapeake Bay salt marsh. They attributed the increase in Hg methylation to the higher molecular weight DOC binding Hg, and increasing its bioavailability. Their observation was corroborated by Hollweg et al. (2009) in the Chesapeake Bay and mid-Atlantic continental margin sediment. Freshly-produced organic matter in sediment was hypothesized to be a reason for enhanced methylation in the Gironde Estuary, France (Schäfer et al., 2010). Further, protein-like DOC has been observed to enhance MeHg uptake by plankton compared to the humic-like DOC (Schartup et al., 2015). In contrast to sediment at PT, the percent of DOC as fresh proteins rapidly declined from above to below the sediment-water interface at SQ; with less degraded and more bioavailable pore-water DOC, Hg methylation at PT is expected to be enhanced compared to SQ.

4.2. Inorganic mercury(II)

Solid-phase Hg_i concentrations at PT and SQ (Fig. 1a) are typical of estuaries without a direct input of Hg from industry or mining (Fitzgerald et al., 2007). Solid-phase Hg_i concentration is not expected to change seasonally, as its origin is external and watershed related. Despite the lower %LOI at PT, sediment at this site contained higher solid-phase Hg_i concentrations, further suggesting that supply of Hg is higher at PT than SQ. The spatial variations in solid-phase Hg_i depth profiles at the two sites are possibly due to sediment heterogeneity and no trends are inferred from them.

Whereas solid-phase Hg_i concentrations and profiles were similar, pore-water Hg_i (Fig. 1c) profiles differed between PT and SQ. Pore-water Hg_i concentrations were lower at PT than at SQ, when PT sediment was subject to infaunal activity, even though solid-phase Hg_i concentrations were generally greater at PT. Significantly higher concentrations of *mer-A*, the gene responsible for the reduction of inorganic Hg(II) to Hg(0) (Barkay et al., 2003), were observed at SQ (Fig. 5b), where higher pore-water Hg_i concentrations were observed. We have not quantified elemental Hg concentrations in pore water; however, presence of *mer-A* has apparently not resulted in lower pore-water Hg_i concentrations at SQ. Instead, the lower concentrations at PT may be attributed to enhanced adsorption at this site, as described below.

Lower pore-water Hg_i concentrations at PT led to a significantly greater average $\log K_D$ (sediment-water partitioning coefficient, defined as a species' solid-phase:pore-water concentration ratio) for Hg_i compared to SQ in August '08 and June '10 (Fig. 6a). In May '09, pore-water Hg_i concentrations were below the detection limit to a depth of 5.5 cm at PT, and $\log K_D$ could not be calculated, but down to this depth, $\log K_D$ for PT would likely be significantly higher than that for SQ. In several studies (Bloom et al., 1999; Hammerschmidt and Fitzgerald, 2004; Hollweg et al., 2009), greater $\log K_D$ values were explained by the higher sediment organic matter content or AVS. This was contrary to our observations, where average %LOI and AVS were significantly higher at SQ than at PT, but $\log K_D$ values were higher at PT than at SQ.

Differences in $\log K_D$ values for Hg_i between the two sites studied here may be explained by sediment Fe(III) hydroxide concentrations. Indeed, the pore-water Hg_i concentrations for both sites are inversely correlated to the solid-phase Fe(III) concentrations (Table S1). Acidic hydroxylamine was used in this study to extract solid-phase Fe(III); this reductant has been shown to extract Fe(III) that is (a) most susceptible to microbial reduction and (b) poorly crystalline (Lovely and Phillips, 1987). The freshly-precipitated Fe(III) hydroxide is known to be amorphous and an efficient scavenger of trace metals (Dzombak and Morel, 1990). Amorphous Fe(III) hydroxide, for example, was shown to carry as much as half of the particulate total Hg load in an estuarine environment (Laurier et al., 2003). The freshly-precipitated Fe(III) hydroxide concentration at PT was significantly higher than that at SQ when benthic infauna were active at PT (August '08, May '09, and June '10), and the corresponding pore-water Hg_i concentrations (Fig. 1c) were significantly lower at PT than at SQ during the same times at depths where infaunal activity was expected. In May '09 and June '10, pore-water Hg_i concentrations increased at PT at depths lower than 6 and 10 cm,

respectively. These depths coincide approximately with depths where a decrease in solid-phase Fe(III) hydroxide was observed (Fig. 4b); the higher pore-water Hg_i mobilization at lower depths may be attributed to the low concentration of freshly-precipitated Fe(III) hydroxide.

The role of solid-phase Fe(III) hydroxide in Hg partitioning was also observed in Thau Lagoon, France (Muresan et al., 2007), where pore-water concentrations of Hg species were lower, and $\log K_D$ values were higher just below the sediment-water interface because of scavenging by Fe(III) and Mn(IV) (hydr)oxides. Low dissolved total Hg concentrations were also observed in sediments from the Gulf of Trieste and were attributed to the same effect (Koron and Faganeli, 2012). Fe(III) and Mn(IV) (hydr)oxides have been implicated in controlling solid-phase partitioning and mobility of Hg species in other coastal systems as well (Gagnon et al., 1997; Bloom et al., 1999; Covelli et al., 2008). Gobeil and Cossa (1993) and Bothner et al. (1980) showed that presence of Fe(III) hydroxide close to the sediment-water interface acts as a sink for Hg_i thereby limiting its flux. By removing pore-water Hg_i , also the availability of this species for methylation is diminished (Hammerschmidt and Fitzgerald, 2004).

However, the exact mechanism for pore-water Hg_i removal in iron-rich sediments is not clear. Using the existing stability constants (Table S4), pore-water Hg_i speciation is dominated by sulfide complexes (Fig. S7), and as such, direct interaction between Hg_i hydroxo or chloride species and the surface is unlikely. The sulfide complexes are kinetically stable (Morse and Luther, 1999) and are not known to readily adsorb to mineral surfaces; presence of trace-level S(-II) concentrations in oxic marine waters has been attributed to its stable metal complexes (Luther and Tsamakis, 1989). In iron-rich marine sediments direct reduction of Fe(III) hydroxide has been shown to be an important mechanism for oxidation of dissolved S(-II) (Canfield, 1989; Luther et al., 1992). However, the extent to which dissolved S(-II)-metal complexes, such as those of Hg(II), may be oxidized in the presence of Fe(III) hydroxide is not known. Formation of DOM-Hg-S(-II) complexes or partitioning of neutral Hg-S(-II) complexes into the DOM have been proposed by Miller et al. (2007); should these DOM complexes form, they are expected to interact with the surface of Fe(III) hydroxide.

Alternatively, model simulations show that solubility with respect to metacinnabar (β - $HgS_{(S)}$) is reached, or exceeded in the pore water for most of the sediment column (Fig. S7). $HgS_{(S)}$ precipitation rate may be considered a function of its degree of oversaturation (Meysman et al., 2003), and particle growth rate a function of DOC concentration and ionic strength (Deonaraine and Hsu-Kim, 2009). Laboratory studies have shown the formation of nanosized $HgS_{(S)}$ colloid clusters in the size range $< 0.2 \mu m$ (smaller than the protective filters used in our peepers) in the presence of organic ligands with thiol functional groups (Deonaraine and Hsu-Kim, 2009; Gerbig et al., 2011). As such, it is likely that nanosized $HgS_{(S)}$ colloids form in our system. Presently, however, equilibrium speciation models that are based on the dissolved phase do not represent the thermodynamics of the nanoparticulate phase well (Gilbert and Banfield, 2005). Present equilibrium Hg speciation models also do not account for the formation of nanoparticulate $HgS_{(S)}$ in a ternary Hg(II)-S(-II)-DOC system.

Organic ligands serve to stabilize and mobilize colloids in aqueous solutions by adsorbing to the surface and altering the surface potential (Ryan and Elimelech, 1996); negatively-charged ligands, such as DOM, depress the isoelectric point. Thiol-containing ligands have been shown to stabilize nanosized $\text{HgS}_{(\text{s})}$ colloids via the same mechanism, with colloid stability decreasing with decreasing pH and increasing ionic strength (Gondikas et al., 2010). Regardless of the surface charge characteristics of bare $\text{HgS}_{(\text{s})}$ colloids, the organic coating imparts an overall negative charge on the surface of these colloids at pH values relevant to this study.

Surface complexation modeling (Dzombak and Morel, 1990) shows that freshly-precipitated Fe(III) hydroxide has a point of zero charge of ~ 8 and a total reactive site concentration in the order of 14 mmol L^{-3} in the pH range of 7–8 in our system (Fig. S8). It is expected that some of the surface groups are covered by background ions and DOM, and are therefore, uncharged or negatively charged. Nevertheless, this relatively large concentration of reactive sites on the sediment surface and a high ionic strength can result in favorable surface-colloid interactions (Ryan and Elimelech, 1996) and attachment of $\text{HgS}_{(\text{s})}$ colloids to the Fe(III) hydroxide surface.

4.3. Methylmercury

Solid-phase MeHg concentrations at PT and SQ are typical of estuaries without direct Hg industrial or mining input (Fitzgerald et al., 2007). In SQ (August '08, May '09 and June '10) and in PT (September '10 only, where no infaunal activity was observed), maximum MeHg concentrations were observed close to the sediment-water interface, as commonly detected in coastal sediments that are not significantly affected by bioturbation (e.g., Bloom et al., 1999; Sunderland et al., 2004; Merritt and Amirbahman, 2008; Covelli et al., 2008; Hollweg et al., 2009). In September '10, where the top ~ 5 cm of sediment had been eroded prior to sampling at SQ, no peak in MeHg was observed (Fig. 1b), suggesting that sediment erosion and resuspension may be a more important source of MeHg than diffusion to the overlying water in physically dynamic sites (Gagnon et al., 1997).

In August '08, May '09, and June '10, where infaunal activity was observed at PT, a MeHg peak was not observed close to the sediment-water interface; however, increase in pore-water MeHg was observed lower in the sediment column for August '08 and May '09 samples (Fig. 1d). Deeper peaks in MeHg with depth have been previously observed at sediments with a high degree of bioturbation in Boston Harbor (Benoit et al., 2006). Methylmercury production is sensitive not only to the redox environment but also to the availability of Hg_i for methylation by microbes (Jonsson et al., 2012), which is controlled by its partitioning to the solid phase. We propose that low Hg_i concentrations in shallower depths of bioturbated PT sediments, resulting from its partitioning to freshly-precipitated Fe(III) hydroxide, may lead to the lower MeHg concentrations at these depths. Alternatively, a lack of solid-phase MeHg accumulation in the bioturbated zone at PT may be due to its release into the overlying water by bioirrigation; greater MeHg flux and lower solid-phase MeHg concentrations with increased bioirrigation have indeed been observed (Benoit et al., 2009). We also propose that the increase in solid-phase MeHg concentration below the

bioturbation zone may be due to (a) the lower solid-phase Fe(III) hydroxide concentration and (b) the presence of higher quality DOC, as shown by EEMS (Fig. 3).

The log K_D values for MeHg (Fig. 6b) were statistically similar at the two sites in August '08 ($p = 0.658$) and May '09 ($p = 0.465$). In June '10, however, the log K_D values were significantly higher in PT than in SQ ($p = 0.001$), despite the higher %LOI and AVS at SQ.

4.4. MeHg:Hg_i ratio

The MeHg:THg ratios for solid phase and pore water are shown in Fig. 7. This ratio has been used as a proxy for methylation potential in some coastal sediments (e.g., Sunderland et al., 2004; Drott et al., 2008), provided that the produced MeHg is not significantly lost to the overlying water or via other mechanisms (Ogrinc et al., 2007; Hammerschmidt and Fitzgerald, 2008). Solid-phase MeHg:THg ratios at PT ranged from 0.001 to 0.003 along the depth with no significant trends with depth and time of sampling. These ratios are similar to those from another study of Great Bay, NH, but significantly lower than ratios at the nearby Wells Estuary, ME, that ranged between 0.018 and 0.027 (Balcom et al., this issue). In September '10, where no infaunal activity was observed at PT, a peak of 0.01 was observed close to the sediment-water interface, suggesting a higher methylation efficiency, as shown for similar sediments (e.g., Sunderland et al., 2004; Hammerschmidt and Fitzgerald, 2006).

Solid-phase MeHg:THg ratios show a positive relationship with both pore-water S(–II) and alkalinity at PT, SQ, and when combining both sites (Tables S1–S3). Increased pore-water S(–II) and alkalinity both suggest higher SRB activity that enhances MeHg production. Solid-phase MeHg:THg ratios at SQ were significantly higher than the ratios at PT. Ogrinc et al. (2007) observed that methylation potential was inversely related to log K_D for THg in marine and coastal sediments; the lower range of solid-phase MeHg:THg ratios at PT may be attributed to the generally higher log K_D at this site than at SQ. Furthermore, at SQ, the solid-phase MeHg:THg ratios were significantly higher at the top 6 cm than at lower depths in August '08 and June '10, suggesting higher methylation efficiencies close to the sediment-water interface. In May '09, there are observed peaks at 3.5 and 9.5 cm. In September '10, where sediment top ~5 cm was eroded, there was no significant change in the solid-phase MeHg:THg ratios with depth.

The trends in the pore-water and solid-phase MeHg:THg ratios, however, are different. In August '08, pore-water ratios are higher in PT than other times, even though this is not observed in the solid-phase ratios at PT. Also, in May '09, the pore-water ratios at PT are expected to be significantly higher, since pore-water Hg_i was not detected at this time. We attribute the variations in pore-water MeHg:THg ratios at PT to potentially variable advective flux due to bioirrigation by the polychaetes.

An inverse relationship between pore-water MeHg:THg ratios and pore-water S(–II) concentrations have been previously observed (Hines et al., 2006). Inverse relationships between pore-water MeHg:THg and pore-water S(–II) or sediment AVS were not observed at PT, SQ, or when combining both sites (Tables S1–S3). Higher pore-water MeHg:Hg_i at PT may be due to Hg_i removal from the dissolved phase by Fe(III) hydroxide and enhanced Hg methylation due to transport of more labile DOC to depth with bioirrigation, as

evidenced in the significant inverse relationship between pore-water MeHg:Hg_i and solid-phase Fe(III) hydroxide (Table S1).

Fig. 7 shows MeHg:Hg_i ratios > 1 at PT in August '08 and SQ in June '10; pore-water studies of similar estuaries generally show ratios <1. MeHg is in general more mobile than Hg_i, as manifested in its lower log K_D than Hg_i (Fig. 6). In August '08, PT sediment had high Fe(III) concentrations (Fig. 4b), and in June '10, the SQ sediment had high AVS concentrations (Fig. 4a) at depths where MeHg:Hg_i ratios >1 were observed. These surfaces may remove Hg_i preferentially.

4.5. Conclusions

In summary, the two mudflats whose top sediments were physically mixed via different mechanisms showed different characteristics with respect to Hg dynamics. The sediments at PT that were mixed by the benthic infauna possessed lower MeHg concentrations at the depths where the infaunal bioirrigation had resulted in significant concentrations of oxidized iron. Immediately below this depth, however, MeHg concentrations increased suggesting that the observed increased sediment MeHg efflux in bioirrigated sediments may originate from deeper in the sediment; alternatively, the MeHg efflux in the bioirrigated zone may have lowered the MeHg concentration in that zone. In the bioirrigated sediments, higher log K_D values for Hg_i were not related to the sediment organic content, but the oxidized iron. In sediments at SQ where mixing was by erosion and sedimentation, MeHg distribution was extended deeper into the sediment column, rather than a peak close to the sediment-water interface. Even though sediment resuspension has not been shown to mobilize dissolved Hg species, the resuspended sediment leads to net Hg mobilization and transport efflux from the estuary. At both sites, where no sediment mixing was detected during sampling time, a MeHg peak close to the sediment-water interface was observed, similar to unmixed sediments in most other studies. At neither site was sediment total Hg a good predictor for MeHg. These findings indicate that the degree and type of sediment disturbance greatly impacts the biogeochemistry of MeHg in estuarine ecosystems and that these conditions can vary greatly within a system both spatially and temporally.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.
Solid-phase and pore-water Hg_i and MeHg for Portsmouth (left panels) and Squamscott (right panels) mudflats. The dashed line represents the sediment-water interface.

Fig. 2. Pore-water S(-II) (μM), Fe(II) (μM), and DOC (mg/L) concentrations for Portsmouth (left panels) and Squamscott (right panels) mudflats. The dashed line represents the sediment-water interface.

Fig. 3. Pore-water EEMS for Squamscott and Portsmouth mudflats. Peaks in the EEMS output were classified into five different components: 1 and 2: humic-like DOC, 3: fulvic-like DOC, 4: humic- and fulvic-like DOC, and 5: protein-like DOC (Chen et al., 2003).

Fig. 4. Sediment AVS and Fe(III) concentrations for Portsmouth (left panels) and Squamscott (right panels) mudflats. The dashed line represents the sediment-water interface.

Fig. 5.

(a) Sediment methyl coenzyme methyl M reductase (mcr) for Portsmouth (left panel) and Squamscott (right panel) mudflats, and (b) sediment mercury reductase (mer-A) for August 2008 for both mudflats. The dashed line represents the sediment-water interface.

Fig. 6. Hg_i and MeHg sediment-water partitioning coefficients ($\log K_D$) for Portsmouth (left panels) and Squamscott (right panels) mudflats. The dashed line represents the sediment-water interface. $\log K_D$ for Hg_i could not be calculated above 6.5 cm at Portsmouth in May 2009 because Hg_i concentration was below the detection limit.

Fig. 7.
Solid-phase and pore-water MeHg:Hg_i ratios for Portsmouth and Squamscott mudflats.