Methylmercury Cycling in Sediments on the Continental Shelf of Southern New England

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Abstract

Exposure of humans to monomethylmercury (MMHg) occurs primarily through consumption of marine fish, yet there is limited understanding concerning the bioaccumulation and biogeochemistry of MMHg in the biologically productive coastal ocean. We examined the cycling of MMHg in sediments at three locations on the continental shelf of southern New England in September 2003. MMHg in surface sediments is related positively to inorganic Hg (Hg(II) = total Hg − MMHg), the geographical distribution of which is influenced by organic material. Organic matter also largely controls the sediment−water partitioning of Hg species and governs the availability of dissolved Hg(II) for methylation. Potential gross rates of MMHg production, assayed by experimental addition of ^{200}Hg to intact sediment cores, are correlated inversely with the distribution coefficient (K_D) of Hg(II) and positively with the concentration of Hg(II), most probably as HgS^0, in 0.2-μm filtered pore water of these low-sulfide deposits. Moreover, the efflux of dissolved MMHg to overlying water (i.e., net production at steady state) is correlated with the gross potential rate of MMHg production in surface sediments. These results suggest that the production and efflux of MMHg from coastal marine sediments is limited by Hg(II), loadings of which presumably are principally from atmospheric deposition to this region of the continental shelf. The estimated diffusive flux of MMHg from the shelf sediments averages 9 pmol m^{-2} d^{-1}. This flux is comparable to that required to sustain the current rate of MMHg accumulation by marine fish, and may be enhanced by the efflux of MMHg from near-shore deposits contaminated more substantially with anthropogenic Hg. Hence, production and subsequent mobilization of MMHg from sediments in the coastal zone may be a major source of MMHg to the ocean and marine biota, including fishes consumed by humans.

1. Introduction

Humans are exposed to monomethylmercury (MMHg) principally by the consumption of fish (Fitzgerald and Clarkson, 1991), most (> 60%) of which are from marine systems (U.S. EPA, 2002). Moreover, the coastal zone supports greater than 75% of marine fish productivity (Ryther, 1969). This means that the biogeochemistry and bioaccumulation of MMHg in near-shore and continental shelf areas may be major factors affecting the exposure of humans to MMHg. However, and unfortunately, little is known about the production and cycling of MMHg in coastal marine systems and the open ocean, where most of the MMHg in biota has been hypothesized to result from production in deep sea sediments and/or hydrothermal systems (Kraepiel et al., 2003).

We have investigated the biogeochemistry (Hammerschmidt and Fitzgerald, 2004; Hammerschmidt et al., 2004; Balcom et al., 2004) and bioaccumulation (Hammerschmidt, 2005) of MMHg in Long Island Sound (LIS), a large and biologically productive coastal embayment in the northeastern United States. These studies have shown that (1) sedimentary production of MMHg is influenced strongly by the availability of dissolved (i.e., < 0.2 µm) inorganic Hg, most likely as HgS^0, to methylating bacteria, (2) partitioning with sedimentary organic matter largely controls pore water concentrations of inorganic Hg, (3) bioturbation can enhance Hg methylation, (4) *in situ* benthic production is the principal source of MMHg to the Sound, and (5) most of the MMHg in lower trophic levels of LIS can be attributed to production and mobilization from underlying sediments. Also, the results from LIS suggest that the diffusive efflux of MMHg from sediments on the continental shelf would approach that required to account for its accumulation in near-shore and pelagic fish (Hammerschmidt et al., 2004).

We tested this hypothesis and examined sedimentary cycling of MMHg in sediments at three locations on the continental shelf of southern New England. The sampling locations were selected to span ranges in water depth and sedimentary characteristics (e.g., organic matter, total Hg) that are typical of other shelf deposits. Here, we show that the processes and mechanisms affecting the cycling of MMHg in sediments on the continental shelf are comparable to those in the sedimentary environs of LIS. Thus, and most importantly, organic matter, through its control of inorganic Hg in pore water, is a major influence on the production and distribution of MMHg in low-sulfide coastal marine sediments. Further, this study suggests that deposits on the continental shelf are a potentially significant source of MMHg to oceanic systems, including fishes for human consumption.

2. Materials and methods

2.1. Sampling

Sediments were collected with a box corer (0.06 m^2, Ocean Instruments, San Diego, CA) from three stations (71north, 71central, and 71south) on the continental shelf of southern New England, northwestern Atlantic Ocean, on September 24–25, 2003 (Fig. 1). The sampling locations were selected to span ranges in both water depth and sediment grain size, which had been surveyed previously (Twitchell et al., 1981). Grain size of coastal marine deposits often is correlated with organic matter and inorganic Hg (e.g., Varekamp et al., 2000), factors that can affect the biogeochemistry of MMHg (Hammerschmidt and Fitzgerald, 2004). Fine-grained material ($\leq$ 63 µm; silt + clay) comprised about 20% of the sediment mass at station 71north, 98% at 71central, and 50% at 71south. Collection of intact sediment cores with overlying water

from sandy environs, such as station 71north, is challenging and can be aided by applying additional lead weight to the box corer and allowing it to free fall through the water column. Water depths at our sampling locations were 59 m (71north), 81 m (71central), and 131 m (71south). Sediments were sampled in September, when the temperature of water and sediment was near its seasonal maximum, because rates of Hg methylation increase with temperature (Winfrey and Rudd, 1990; Hammerschmidt and Fitzgerald, 2004). The temperature of water overlying sediments at these locations was about 21 °C at 71north and about 12 °C at stations 71central and 71south. Bottom water salinity was comparable among sites, ranging from 33.6 at station 71north to 34.4 at 71south. In addition to sediment, surface water (1 m depth) and water below the seasonal thermocline (30 m) were sampled at each station for analysis of dissolved (< 0.2 µm filtered) and particulate MMHg (> 0.2 µm). Water samples were collected at each station with a Teflon coated Go-Flo^{TM} bottle suspended from a Kevlar line prior to sediment sampling. MMHg was not measured in water collected with the box corer.

Nine cylindrical, intact sub-cores of sediment were sampled from two box-cores taken at each station. Box-cored sediments and overlying water were subsampled with polycarbonate tubes (6.4 cm inner diameter). Four sub-cores were collected from the first box of sediment and overlying water; one was used for Hg speciation in both the solid and pore water phases, another for the determination of acid-volatile sulfide (AVS), grain size, and dissolved sulfide and oxygen, and the other two were used for assays of Hg methylation potentials with an isotopic tracer (^{200}Hg). Five sub-cores were collected from the second box of sediment; two were used for Hg speciation in surface sediment only (upper 3 cm), and the other three for analysis of benthic macrofauna. Macrofauna cores were sieved through a 300-µm mesh screen within 12 h

of collection, and the retained material was preserved with 70% ethanol until identification and

enumeration of the organisms. Sediment cores for chemical analysis were stored in the dark at 5

°C until sectioning. Cores for the determination of [200]Hg methylation potentials from station

71north were kept at 22 ± 1 °C both prior to and during incubations in darkened containers on

the deck of the research vessel, and those from stations 71central and 71south were incubated

similarly, but at 14 ± 3 °C.

Sediment cores for chemical analyses were sectioned within 4−8 h of collection

(Hammerschmidt et al., 2004). Cores were placed inside a low−O_2 (evacuated, N_2−flushed)

glovebox before overlying water was removed carefully with a syringe. Sediments were

sectioned with plastic tools in 1-cm vertical intervals. Pore waters were extracted from

sediments by centrifugation and vacuum filtration of the supernatant through 0.2-µm

polycarbonate filters inside the glovebox (Mason et al., 1998). Acid-cleaned filters were rinsed

with deoxygenated reagent-grade water (nominal resistivity, 18.2 MΩ−cm) immediately prior to

sample filtration. Filtered pore water, containing both dissolved and colloidal size fractions, was

acidified to about 0.5% with HCl and stored frozen (≤ -20 °C) until analysis. Sediments were

frozen promptly after removal from the glovebox.

2.2. Hg Methylation potentials

Gross potential rates of MMHg production were assayed by adding isotopically enriched

[200]Hg (96.41% [200]Hg; Oak Ridge National Laboratory) to two intact sediment cores from each

station. Our methods for spike preparation, sediment incubation, MMHg extraction, and isotopic

Hg analysis by inductively coupled plasma mass spectrometry (ICPMS) are detailed in

Hammerschmidt and Fitzgerald (2004). Briefly, a stock solution of enriched $^{200}Hg(NO_3)_2$ was diluted with water overlying the sediments, and $^{200}Hg^{2+}$ was allowed to react with natural ligands for 1−2 h before aliquots of the dilution were added to sediment cores in 1-cm vertical increments by injection through silicone septa. Added ^{200}Hg increased the ambient Hg burden in sediments 8−12%. The relative degree of enrichment with ^{200}Hg was greater than that used in a similar assessment of LIS sediments, which have about 10-fold more ambient Hg (Hammerschmidt et al., 2004), but it was necessary to ensure that a quantifiable amount of $CH_3^{200}Hg$ was produced. Measured rates of ^{200}Hg methylation are considered *methylation potentials* because the added Hg, having undetermined chemical speciation and sediment−water partitioning, may be more available for methylation than ambient inorganic Hg (Benoit et al., 2003). Cores were incubated for 6 h in the dark at *in situ* temperatures before termination by sectioning of the cores and freezing the sediment sections. A 6-h incubation period was used to minimize potential *in situ* demethylation of $CH_3^{200}Hg$ product. MMHg was extracted from lyophilized, incubated sediments with acid and CH_2Cl_2 (Bloom et al., 1997; Hammerschmidt and Fitzgerald, 2004), and the fraction of added ^{200}Hg transformed to $CH_3^{200}Hg$ was measured by continuous-flow cold vapor generation with a Finnigan Element2 magnetic sector ICPMS (Klaue and Blum, 1999; Hammerschmidt and Fitzgerald, 2004). Methylation of added ^{200}Hg was quantified as the excess concentration of ^{200}Hg versus ^{202}Hg in sample extracts (Hintelmann and Evans, 1997). The method detection limit (MDL) of these analyses is a function of ambient MMHg concentration, natural abundance of ^{200}Hg (23.13%), and precision of our $^{200}Hg/^{202}Hg$ ratio measurements (Hintelmann and Evans, 1997), which averaged 0.93% relative standard

deviation (RSD) for 11 independent analyses of internal MMHg standards. The average MDL

for our analyses corresponds to a ^{200}Hg methylation potential of about 0.2% d^{-1}.

^{200}Hg methylation potentials were corrected for "carry-over" of Hg^{2+} in the CH$_2$Cl$_2$ phase

during extraction (Hammerschmidt and Fitzgerald, 2004). In natural waters and in our

extraction procedure, Hg^{2+} can form complexes that make it relatively hydrophobic (e.g.,

Hg–organic, HgS^0, HgCl$_2^0$) and soluble in the CH$_2$Cl$_2$ phase of our extraction. Such "carry-

over" Hg is interpreted as MMHg by our methodology, which assumes that all Hg partitioning

into CH$_2$Cl$_2$ is MMHg. We accounted for the potential transfer of ^{200}Hg^{2+} by adding

^{201}Hg(NO$_3$)$_2$ (Oak Ridge National Laboratory, 98.11% ^{201}Hg) to lyophilized sediments before

extraction (about 25% of total samples analyzed). The amount of ^{201}Hg added was comparable

to the quantity of ^{200}Hg added to whole sediment prior to incubation. Transfer of added ^{201}Hg^{2+}

to analytical extracts was evaluated as the excess concentration of ^{201}Hg versus ^{202}Hg

(Hintelmann and Evans, 1997). Carry-over of ^{201}Hg^{2+} averaged 0.15% (1 SD, 0.07%; $n = 15$) of

the nominal mass added prior to extraction. This fraction was comparable to the amount of

^{201}Hg^{2+} carried over in LIS sediments extracts (mean, 0.12%; 1 SD, 0.03%; $n = 12$;

Hammerschmidt and Fitzgerald, 2004). We corrected the measured quantity of CH$_3^{200}$Hg for

0.15% transfer of ^{200}Hg^{2+} added for the incubation assay. Although ambient Hg^{2+} also was

carried over during the acid/CH$_2$Cl$_2$ extraction, it has no effect on our determination of ^{200}Hg

methylation potentials, assuming that ambient Hg in the shelf sediments has natural isotopic

abundance and that individual isotopes are transferred in proportion to their atomic mass

fraction.

Sediment sections from at least one whole core from each site were analyzed for ^{200}Hg methylation. The precision (relative percent difference, RPD) of ^{200}Hg methylation potential measurements averaged 20% ($n = 13$), based on analyses of methodically replicated subsamples. Additional sections from a second core were selected randomly for analysis. Agreement between samples from the same depth of the two cores is shown by the error bars ($\pm$ 1 SE) in Figure 10.

2.3. Determination of Hg species

Total Hg and MMHg were measured in 0.2-µm filtered pore waters and lyophilized sediments. Total Hg and MMHg in the solid phase of sediment were defined operationally as the fraction of each species remaining after pore water removal. Total Hg in pore water was quantified by dual Au-amalgamation cold vapor atomic fluorescence spectrometry (CVAFS; Fitzgerald and Gill, 1979; Bloom and Fitzgerald, 1988) after acid digestion and BrCl oxidation of the samples (Hammerschmidt and Fitzgerald, 2004). Total Hg in the solid phase was quantified with a Milestone DMA-80 pyrolytic Hg analyzer. MMHg was extracted from sediment and pore water by aqueous distillation (Hammerschmidt and Fitzgerald, 2001) and measured with flow-injection gas chromatographic CVAFS (Bloom, 1989; Tseng et al., 2004). We define the difference between total Hg and MMHg in pore water and solid phases as Hg(II). Thus, Hg(II) represents the sum of all Hg^{2+} species that are complexed with inorganic and organic ligands.

MMHg was measured in filtered seawater after quantitative extraction with CH$_2$Cl$_2$. Seawater samples were filtered through 0.2-µm pore size polycarbonate membranes within 6 h

of sampling, and the filtrate was frozen promptly without chemical preservative. The filters also were stored frozen, and were analyzed for particulate MMHg after leaching with dilute HNO_3 (Hammerschmidt and Fitzgerald, 2005). Frozen samples of filtered seawater were thawed overnight in the laboratory, and 200 mL were transferred to a 250-mL Teflon bottle (extraction bottle). Ten mL of CH_2Cl_2 were added to seawater in the extraction bottle, and it was capped and shaken vigorously by hand for 12 min. CH_2Cl_2 extracts MMHg, most likely as a hydrophobic organo- or chloro-complex, by solubility from the polar seawater matrix, which contains potential analytical interferences (e.g., Cl^-). After shaking, the organic phase containing sample MMHg was transferred to a different bottle (back-extraction bottle) containing 100 mL of reagent-grade water. MMHg was extracted from each seawater sample twice more with the same method, resulting in 30 mL of CH_2Cl_2 in the back-extraction bottle. MMHg in the CH_2Cl_2-phase of the back-extraction bottle was transferred into reagent-grade water by evaporating the CH_2Cl_2 in a 70 °C water bath with continuous N_2 purging (Safety note: All manipulations with CH_2Cl_2 should be done inside a fume hood). Residual quantities of CH_2Cl_2 interfere with MMHg analysis, so all of the CH_2Cl_2 must be evaporated. MMHg in the seawater extracts was determined by gas chromatographic CVAFS with the methods described above for sediments and pore water. The estimated detection limit for a 200-mL seawater sample was about 0.02 pM.

2.4. Estimated sediment−water fluxes of MMHg

Diffusive fluxes of MMHg from sediments on the continental shelf were estimated similarly to those from LIS (Hammerschmidt et al., 2004) and Lavaca Bay (Gill et al., 1999).

Sediment−water fluxes of dissolved MMHg (< 0.2 µm), presumably as CH_3HgSH^0 (Dyrssen and Wedborg, 1991), were calculated from the concentration gradient between pore waters of surface sediments and water sampled below the seasonal thermocline (30 m) at each location, which ranged between 0.17 pM and 0.44 pM. MMHg was measured in filtered pore water of surface sediment in three cores from each station. The mean concentration of dissolved MMHg between the 0−1 cm and 1−2 cm sediment horizons was used for the pore water value, and the mean concentration was applied to 1.0 cm depth for the flux calculation. Averaging the pore water concentration in this manner minimizes the potential effect of MMHg dilution in the 0−1 cm section by inclusion of overlying water, though perceived to be minimal during sediment sectioning, and establishes a defined length (1 cm) for the flux estimate. Diffusional flux estimates derived from interfacial pore-water concentration gradients provide a reasonable estimate for scaling purposes and comparison within and among systems, although they commonly underestimate the actual flux of MMHg (Choe et al., 2004). Factors such as scavenging and demethylation at the sediment−water interface as well as bioirrigation of pore fluids can result in considerable differences between estimated diffusional and actual benthic fluxes.

2.5. Ancillary geochemistry of sediment

Several geochemical properties of sediment were measured to assess their relationship to Hg speciation and methylation potential. Standard gravimetric techniques were used to measure the organic content (loss on ignition, LOI) and density of lyophilized sediments (Heiri et al., 2001). The fraction of sediment with a diameter ≤ 63 µm (silt + clay) was determined

gravimetrically after sieving. Dissolved sulfide and oxygen were profiled electrochemically

within 1 h of sediment sampling (Visscher et al., 1992). Dissolved sulfide was less than the

detection limit (about 10 µM) in the upper 8 cm of sediment at each site. Dissolved oxygen at the

sediment−water interface was comparable to that in overlying water and penetrated no deeper

than 0.8 cm in all sediment cores. AVS was measured with colorimetric techniques (Trüper and

Schlegal, 1964).

2.6. Quality assurance of Hg dterminations

Trace-metal clean procedures were employed throughout collection, processing, and

analysis of sediment and water samples (Gill and Fitzgerald, 1985). All equipment was cleaned

rigorously with acid and rinsed with reagent-grade water. Chemical reagents were suitable for

each analysis (Trace Metal or ACS grade). Analyses of total Hg in pore water were calibrated

with aliquots of Hg^0 taken from the headspace over pure liquid (Gill and Fitzgerald, 1987) and

verified by comparison to analyses of aqueous Hg^{2+} standards traceable to the U.S. National

Institute of Standards and Technology (NIST). Recovery of aqueous Hg averaged 103% (range,

96−108%) compared to Hg^0 standards. Analyses of total Hg in sediments with the DMA-80

were calibrated with the same aqueous Hg^{2+} standard. Sample MMHg was measured after

calibration with aliquots of a MMHg standard solution, which was calibrated before each use

against Hg^0 standards and a NIST-traceable aqueous Hg standard.

The precision and bias of our measurements of total Hg and MMHg were estimated by

analyses of (1) procedural blanks taken through the digestion or distillation process, (2) certified

reference materials for total Hg in marine sediment (MESS-3 and PACS-2; National Research

Council of Canada), (3) replicate subsamples of sediment and pore water, and (4) spiked

subsamples of sediment and pore water (MMHg only). All analyses of total Hg in both reference

materials were within their respective certified ranges. The precision of total Hg measurements

averaged 6.3% RSD (range, 0.1−13.3%) for sediments and pore waters combined. The precision

of MMHg determinations averaged 6.8% RSD (range, 0.3−20.5%) for pore water and sediment

determinations. The mean recovery of MMHg was 104% (95% confidence interval, 100−108%)

from 17 procedurally spiked distillates. Estimated detection limits (pmol g^{-1} dry weight) for a

0.5-g sample were about 1 for total Hg and 0.02 for MMHg. Detection limits for 5-mL aliquots

of pore water were about 2 pM for total Hg and 1 pM for MMHg.

3. Results and discussion

3.1. Hg in surface sediments

Surface sediments (upper three cm) on the continental shelf of southern New England

have relatively low concentrations of Hg(II) and MMHg (Table 1). Hg(II) ranges from 32 to 169

pmol g^{-1} dry weight and MMHg ranges 0.05−1.55 pmol g^{-1} among our sampling locations.

These concentrations are 2−3 fold less than those in sandy, low-organic deposits of central LIS

(i.e., ELIS site; Hammerschmidt and Fitzgerald, 2004) and 10−100 times less than those in

western LIS (Hammerschmidt et al., 2004) and many other near-shore marine sediments (e.g.,

Mason and Lawrence, 1999; Bloom et al., 1999; Mikac et al., 1999; Conaway et al., 2003; Choe

et al., 2004; Stoichev et al., 2004). Rivers, including Hg that is atmospherically deposited and

subsequently leached from the watershed, and industrial/municipal wastewater discharges are

major sources of Hg to coastal embayments (Mason et al., 1999; Balcom et al., 2004). The

relatively low levels of Hg(II) in the shelf sediments reflect their distance from these sources and the efficient scavenging of Hg(II) by particles in near-shore waters.

We assessed the spatial heterogeneity of Hg species in the solid and pore water phases of surface sediments at each of the three sampling locations (Table 1). Three sediment cores for Hg analysis were collected at each station; one of the cores was sampled from a separate box core. There is little variation in solid-phase MMHg and Hg(II) among replicate cores at each station (Table 1); the RSD of Hg concentrations ranges from 10% to 13% for MMHg and 4−14% for Hg(II). Differences in solid-phase Hg concentrations among cores at each station are only slightly greater than the average analytical precision of our measurements (i.e., about 7% RSD). Moreover, levels of MMHg and Hg(II) in sediment are often closely related to the organic content of coastal marine surface sediments (Varekamp et al., 2000; Hammerschmidt and Fitzgerald, 2004), and some of the variability in the concentration of Hg species among cores at each location may be attributed to differences in organic content (Table 1). MMHg and Hg(II) in pore water are more variable than levels in the solid phase among cores at each station, and range from 6% to 42% RSD (Table 1), comparable to the variation observed in surface sediments at sites in Lavaca Bay, Texas (Bloom et al., 1999).

The distribution of solid-phase Hg species is correlated strongly with organic matter in surface sediments (upper 3 cm) on the continental shelf of southern New England (Fig. 2). The error associated with these measures averages 2% RSD of the mean for LOI and, as noted, 6−7% RSD for Hg species. Although the relationships in Figure 2 are limited in spatial coverage (i.e., no samples in 3−5% LOI range), we have observed comparable correlations between concentrations of Hg species and organic matter in surface sediments of LIS (Hammerschmidt

and Fitzgerald, 2004). Slopes of the relationships in LIS (175 ± 10 for Hg(II) and 1.40 ± 0.13 for MMHg), however, are about 10-fold greater than in the shelf sediments (Fig. 2), and differences in slope values between the two study areas likely reflect the proximity of LIS deposits to pollution sources of Hg, rather than differences in the affinity of Hg species for sedimentary organic material (discussed below). The affinity of Hg(II) for organic matter is well known, both in coastal waters (e.g., Coquery et al., 1997; Lamborg et al., 2004) and sediments (e.g., Lindberg and Harriss, 1974; Hammerschmidt et al., 2004), and the relation in Figure 2a results from scavenging of Hg(II) in the water column by organic particles. Similarly, the relationship in Figure 2b likely results from sedimentary organic matter scavenging MMHg produced within the sediment, although the potential for MMHg accumulation through deposition to the seafloor cannot be discounted. The *y*-intercept values in Figure 2 indicate that nearly all of the Hg(II) and MMHg is associated with organic material.

MMHg is related positively to Hg(II) in sediments on the continental shelf (Fig. 3), as might be expected given the covariation of Hg species with organic matter (Fig. 2). Although levels of both MMHg and Hg(II) in sediments on the shelf are much less than those in LIS, the average ratio of MMHg to Hg(II) is comparable between the two study areas; the slope of the regression for shelf sediments is 0.0076 ± 0.0006 (Fig. 3) and the mean MMHg:Hg(II) concentration ratio in LIS sediments is 0.0083 ± 0.0005 (Fig. 9 in Hammerschmidt and Fitzgerald, 2004). Moreover, and although levels of MMHg and Hg(II) can vary $10–10^2$ within a particular system, Figure 4 shows that *mean* MMHg:Hg(II) concentration ratios in surface sediments are constrained to a relatively narrow range among these and other coastal marine systems having considerable differences in climatology, geography, and Hg contamination. The

slope of Figure 4 indicates an average MMHg:Hg(II) ratio of 0.005, or about 0.5% MMHg. This

extended perspective of average MMHg:Hg(II) concentration ratios suggests a similar and

ubiquitous mechanism may influence the solid-phase concentration of MMHg relative to Hg(II)

in surface sediments of coastal marine systems. We have posited that nearly constant sediment

MMHg:Hg(II) concentration ratios *within* a coastal marine system result from proportional

sediment−water partitioning and solid-phase retention of the two Hg species, and that organic

matter largely controls the partitioning (Hammerschmidt and Fitzgerald, 2004). The relationship

in Figure 4 suggests this hypothesis may have broader applicability, although MMHg:Hg(II)

concentration ratios can be very different in non-marine and highly contaminated systems.

3.2. Sediment−water partitioning of Hg species

We have shown that organic matter exerts a primary control on the sediment−water

partitioning of Hg species in LIS sediments, and by extension, other comparable coastal marine

deposits (Hammerschmidt and Fitzgerald, 2004; Hammerschmidt et al., 2004). In this study,

distribution coefficients (K_D, L kg^{-1}) for both MMHg and Hg(II) are related positively to the

organic content of sediments on the continental shelf (Fig. 5). Data for LIS sediments

(Hammerschmidt et al., 2004) also are presented in Figure 5. These relationships are very robust

as they include samples from different study areas, sampling locations and periods, sediment

depths (up to 15 cm), and widely varying Hg concentrations in solid and pore water phases of

sediment. With data from both this study and LIS combined, the relation between the K_D of

Hg(II) ($K_{D(HgII)}$) and organic content of sediments (% LOI) is described by the regression

equation ($r^2 = 0.75$, $n = 102$)

$$\log K_{D(HgII)} = (3.13 \pm 0.05) + (0.15 \pm 0.01)[\%LOI] \tag{1}$$

Similarly, the relationship between the K_D of MMHg ($K_{D(MMHg)}$) and organic content of sediment

is described by the equation ($r^2 = 0.75$, $n = 105$)

$$\log K_{D(MMHg)} = (1.55 \pm 0.05) + (0.13 \pm 0.01)[\%LOI] \tag{2}$$

These strong relationships, across a wide range of physicochemical sedimentary characteristics,

show clearly the predominant role of organic matter in influencing the sediment−water

partitioning of Hg species in coastal marine sediments. Additionally, and given the similarity of

Hg species partitioning with organic matter between these systems, it appears that the Hg-

complexing quality of organic matter in LIS deposits is comparable to that in more distant

regions on the continental shelf, where organic material is presumed to be entirely

autochthonous. This suggests that much of the sedimentary organic matter in LIS also may be

derived from marine plankton.

Sediment−water partitioning of Hg species is controlled largely by the concentration of

sedimentary organic matter (Fig. 5), and the slope of the relationship between the log K_D of

MMHg and sedimentary organic content is comparable to that for Hg(II) (equations 1 and 2).

This means that the affinity of MMHg for sedimentary organic matter is proportional to that of

Hg(II), and suggests that the concentration of MMHg in the solid phase of sediment should be

proportional to Hg(II) at steady state. Thus, the relatively constant MMHg:Hg(II) concentration

ratios observed in surface sediments within (Fig. 3, this study; Fig. 9 in Hammerschmidt and

Fitzgerald, 2004) and among (Fig. 4) coastal marine systems may be related to proportional

sediment−water partitioning of the Hg species (Fig. 5).

3.3. Hg methylation

Potential gross rates of [200]Hg methylation in shelf sediments are related positively to the concentration of Hg(II) in 0.2-µm filtered pore waters (Fig. 6), which includes both dissolved and colloidal Hg(II). In contrast, [200]Hg methylation potentials are unrelated, if not inversely related, to solid-phase Hg(II) ($r = -0.56$, $p = 0.002$). It is presumed that Hg(II) must be dissolved to enter a bacterial cell and be methylated, and that Hg(II) most likely enters by passive diffusion through the cellular membrane as a dissolved, neutrally charged complex (Benoit et al., 1999*a*). Sulfide controls the speciation of dissolved Hg–S complexes, and HgS^0 is presumed to be the Hg–S complex most available to bacteria in pore water (Benoit et al., 1999*a*, 1999*b*, 2001). We infer from the chemical speciation model of Benoit and coworkers (1999*b*) that HgS^0 is a major complex of dissolved Hg(II) in sediments on the continental shelf, where dissolved sulfide is less than 10 µM (detection limit). Accordingly, a positive relationship might be expected between [200]Hg methylation and Hg(II) in pore water if HgS^0 were the limiting reactant and a relatively constant or major fraction of dissolved Hg(II). We have found comparable relationships between [200]Hg methylation and the concentration of Hg(II) in 0.2-µm filtered pore water of LIS sediments having less than 10 µM dissolved sulfide (Hammerschmidt and Fitzgerald, 2004). This suggests there is excess methylating potential in these coastal marine deposits, and MMHg production is limited by the availability of dissolved Hg(II) (i.e., HgS^0) to methylating bacteria. This means that environmental factors that affect the level of HgS^0 in sediment pore water will influence the gross rate of MMHg production. These factors can include loadings of Hg(II), the concentration of dissolved sulfide (controlling the speciation of dissolved Hg–S complexes), and sedimentary organic content. Indeed, potential rates of [200]Hg

methylation in shelf sediments are related inversely with the K_D of Hg(II) (Fig. 7), which is

governed largely by the organic content of sediments (Fig. 5). Thus, sediments with less organic

matter have proportionately more Hg(II) in the dissolved phase (i.e., lower K_D) and the potential

 for Hg methylation is enhanced (Fig. 7). Comparable relationships between ^{200}Hg methylation

potential and the K_D of Hg(II) were observed in LIS (Hammerschmidt and Fitzgerald, 2004).

3.3.1. Gross Hg methylation and sediment MMHg

Solid-phase concentrations of MMHg in sediments often are correlated with gross Hg

methylation potentials assayed with short-term incubation experiments (e.g., Benoit et al., 2003;

Sunderland et al., 2004; Heyes et al., 2004). Hg(II) is the substrate for MMHg production, and

because Hg(II) varies among locations and sediment depths, potential relationships between

sediment MMHg and Hg methylation potentials should be evaluated by normalizing either the

methylation rate or the ambient MMHg concentration for the level of Hg(II). Figure 8a shows a

modest ($r = 0.58$), but significant ($p < 0.001$), correlation between ambient MMHg concentration

and MMHg production potential in sediments on the continental shelf. MMHg production

potentials in Figure 8a (pmol MMHg g^{-1} dry sediment h^{-1}) are calculated as the product of the

potential gross rate of ^{200}Hg methylation (% d^{-1}) and the ambient concentration of Hg(II) in the

solid phase (pmol g^{-1} dry weight). This normalizes the ^{200}Hg methylation potential for

differences in ambient Hg(II) among samples, and assumes that ambient Hg(II) has the same

availability as added ^{200}Hg. Assays of Hg methylation with added isotopes, however,

overestimate the production of MMHg from ambient Hg(II) because added Hg is more available

for methylation (Benoit et al., 2003). This is apparent for surface sediments on the continental

shelf where estimated hourly MMHg production potentials are a substantial fraction of the ambient MMHg concentration (Fig. 8a).

Sediment MMHg also is not correlated strongly with gross Hg methylation potentials in continental shelf sediments when the concentration of MMHg is normalized for the level of Hg(II) (Fig. 8b). Although the relationship was significant ($p < 0.001$), solid-phase MMHg:Hg(II) concentration ratios are correlated weakly ($r = 0.53$) with ^{200}Hg methylation potentials (% d^{-1}; Fig. 8b) in the same sediment samples shown in Figure 8a. The relatively low correlation coefficients for the relationships in Figures 8a and 8b suggest that the gross rate of Hg methylation is not a major factor influencing solid-phase MMHg concentrations in sediments on the continental shelf. The absence of a strong relationship between these two variables might be expected given that ^{200}Hg methylation potentials can vary widely (e.g., Fig. 6) and that MMHg:Hg(II) concentration ratios in the solid phase are relatively constant (Fig. 3). We have observed previously that potential rates of Hg methylation are unrelated to MMHg:Hg(II) concentration ratios in the upper four cm of LIS deposits (Hammerschmidt and Fitzgerald, 2004). As hypothesized, this was attributed to proportional sediment−water partitioning of Hg species (e.g., Fig. 5), and to particle sorption being a minor sink for MMHg relative to its diffusional efflux to overlying water.

3.3.2. Gross Hg methylation and sediment−water MMHg flux

If mobilization to overlying water were a major sink for MMHg produced in sediments, then a positive relationship might be expected between the gross potential rate of MMHg production in surface sediment and its efflux to overlying water. Mean diffusive sediment−water

fluxes of MMHg from deposits on the continental shelf (pmol m^{-2} d^{-1}, ± 1 SE) are 6.6 ± 0.6 at

71north, 12 ± 1.0 at 71central, and 8.2 ± 1.7 at 71south, based on three replicate cores at each

location. Figure 9 shows that sediment–water fluxes of MMHg are related positively to average

gross MMHg production potentials in the upper two cm of sediment among the three sampling

locations on the continental shelf and three stations in LIS in August 2001 and March 2002.

Previously published fluxes (Hammerschmidt et al., 2004) and methylation rates

(Hammerschmidt and Fitzgerald, 2004) are combined for the LIS dataset in Figure 9. Potential

rates of MMHg production in Figure 9 are estimated as the product of the potential rate of ^{200}Hg

methylation (% d^{-1}) and the ambient concentration of Hg(II) in the solid phase (pmol g^{-1} dry

weight). The upper two cm of sediment were used to calculate the average MMHg production

potential in surface sediment because this is the same depth interval used for the flux estimate

(Section 2.4).

The relationship in Figure 9 suggests a direct connection between gross rates of MMHg

production in coastal marine sediments and its efflux to overlying water, although estimates of

gross MMHg production overestimate the methylation of ambient Hg(II). The flux of MMHg

increases with its estimated production potential in surface sediments on the continental shelf

and in LIS, and seasonal variations in MMHg flux correspond to differences in MMHg

production among the three locations in LIS (Fig. 9). Moreover, the *y*-intercept of this

relationship indicates little or no MMHg efflux without active production (Fig. 9). This

relationship is striking because the flux of MMHg from sediments may be interpreted as a proxy

of *net* MMHg production at steady state (i.e., gross Hg methylation after losses to

abiotic/biological demethylation, bioaccumulation, and particle adsorption). However, and

given the uncertainty associated with the fraction of ambient Hg(II) that is available for

methylation, the difference between MMHg production potential (i.e., gross production) and its

flux from sediment (net production) does not allow quantitative evaluation of the rate of loss to

these sinks. Nevertheless, environmental factors that affect the sedimentary accumulation of

Hg(II) and/or its gross rate of methylation may influence the net production and mobilization of

MMHg from coastal marine deposits. We hypothesize that there is excess methylating potential

in coastal marine sediments based on observed relationships between [200]Hg methylation potential

and the level of Hg(II) in pore water on the continental shelf (Fig. 6) and in LIS (Fig. 8 in

Hammerschmidt and Fitzgerald, 2004). Accordingly, loadings of Hg(II) may be an important

control on net MMHg production, and this should be assessed by quantification of

sediment−water fluxes in addition to solid-phase accumulation of MMHg, which as noted, may

be influenced strongly by geochemical properties of sediment particles, namely the concentration

of organic matter.

3.4. Stratigraphy of Hg species

The vertical stratigraphy of Hg species and associated sedimentary geochemical

parameters at the three stations are presented in Figure 10. Although solid-phase Hg(II) varies

considerably among sampling locations (e.g., Table 1), it is homogeneous throughout the upper

10 cm of sediment at each site and decreases at depths greater than 10 cm at stations 71central

and 71south (Fig. 10b,c). Similar uniformity of Hg(II) or total Hg in the upper 10 cm of

sediment has been observed in other coastal systems (Varekamp et al., 2000; Hammerschmidt et

al., 2004; Sunderland et al., 2004; Choe et al., 2004), and, in many cases, it can be attributed to

the mixing and homogenization of sediment particles by the within-sediment migration of benthic infauna (Benninger et al., 1979). Profiles of Hg(II) in filtered pore water were less homogeneous, but measured concentrations and the K_D of Hg(II) varied by only 2-fold or less with depth at each station (Fig. 10). Vertical uniformity in the K_D of Hg(II) also has been observed in sediments of LIS (Hammerschmidt et al., 2004) and other coastal marine embayments (Bloom et al., 1999; Choe et al., 2004). This may be attributed to organic matter, a major control on sediment–water partitioning of Hg species (Fig. 5), having a relatively constant concentration in the upper 10 cm of coastal marine sediments (Hammerschmidt et al., 2004). A marked peak in the profile of dissolved Hg(II) at station 71south corresponded with depth horizons of maximum MMHg concentrations in the solid and pore water phases (Fig. 10c).

MMHg varies with sediment depth at each location (Fig. 10). Solid-phase concentrations of MMHg are maximum 3−6 cm below the sediment–water interface, and decrease gradually with increasing depth. Profiles of MMHg in filtered pore water are comparable to those in the solid phase at stations 71central and 71south, but not at 71north. MMHg averages 27% of total Hg (range, 7−62%) in pore water among all stations and sediment depths, a fraction much greater than that in the solid phase of sediment (mean, 0.66%).

Hg is actively methylated throughout the upper 10 cm of sediment on the continental shelf (Fig. 10). Profiles of [200]Hg methylation potential exhibit four characteristics that are common among all or most of the locations: (1) profiles of [200]Hg methylation potentials show a broad subsurface maximum, generally between 3 and 6 cm depth, and a gradual decline with increasing depth; (2) the depths of [200]Hg methylation maxima coincide generally with those of peak MMHg concentrations in the solid phase; (3) potential rates of [200]Hg methylation are

reduced at sediment depths where AVS was relatively enhanced (stations 71north and 71central

only); and (4) peaks in ^{200}Hg methylation potentials correspond with maximal values in the

bioturbation index (station 71north and 71south only). The *bioturbation index* (Hammerschmidt

et al., 2004) is a geochemical measure of non-local physical disturbance of the sedimentary

column, presumably by benthic infauna, that indicates the relative degree of change in organic

content between vertically adjacent sections of sediment. Accordingly, relatively large changes

in the organic content of adjacent sedimentary horizons are indicated by greater bioturbation

index values.

Bioturbation may enhance MMHg production in sediments on the continental shelf.

Bioturbation index values > 0.1 generally are indicative of non-local sediment disturbance

(Hammerschmidt et al., 2004). The greatest potential rates of ^{200}Hg methylation at 71north are

in the upper 6 cm of sediment, a zone that also had bioturbation index values greater than 0.1

(Fig. 10a). Moreover, the profile of ^{200}Hg methylation at 71south is irregular in shape; it has a

subsurface maximum in the 10−12 cm depth horizon that was observed in both of the cores

assayed for Hg methylation potentials (Fig. 10c). This peak in ^{200}Hg methylation, as well as the

broad one at 4−6 cm depth, coincides with maxima in the bioturbation index at 71south (Fig.

10c). The zoobenthic community at 71north is dominated by polychaete worms and amphipod

crustaceans, whereas brittle stars, *Axiognathus squamatus* and *Amphioplus abdius*, are the most

abundant macrofauna at 71south. The potential effect of non-local sediment disturbance on Hg

methylation is supported by profiles at 71central where bioturbation index values are low (< 0.1)

and ^{200}Hg methylation potentials are relatively low with no anomalous subsurface peaks (Fig.

10b), as well deeper sediments at 71north, where bioturbation index values and potential rates of

Hg methylation are less than those nearer the surface (Fig. 10a). Hence, physically disturbed

sediments, as indicated by the bioturbation index, may be more conducive for active Hg

methylation, although the reason for this is unknown (Hammerschmidt et al., 2004). We have

previously observed relationships between maxima in the bioturbation index and enhanced Hg

methylation potentials in sediments of LIS (Hammerschmidt et al., 2004), and Sunderland and

coworkers (2004) noted enhanced MMHg production in deposits disturbed by tidal currents in

the Bay of Fundy.

3.5. Sediment−water flux of MMHg

Estimated diffusive fluxes of MMHg from sediments on the continental shelf are

relatively low compared to those from sediments nearer to shore and fluvial sources of

anthropogenic Hg. As noted, the mean sediment−water fluxes of MMHg (pmol m^{-2} d^{-1}, ± 1 SE;

$n = 3$) are 6.6 ± 0.6 at 71north, 12 ± 1.0 at 71central, and 8.2 ± 1.7 at 71south. These fluxes are

$10–10^2$ less than those estimated or measured for sediments in near-shore embayments, including

LIS (basin-wide mean, 47 pmol m^{-2} d^{-1}; Hammerschmidt et al., 2004), Lavaca Bay (mean, 210

pmol m^{-2} d^{-1}; Gill et al., 1999), and a site in the Gulf of Trieste, northern Adriatic Sea (2300

pmol m^{-2} d^{-1}; Covelli et al., 1999). Direct atmospheric deposition is the presumed primary

source of Hg(II) to sediments at our sampling locations on the continental shelf, whereas

sediment Hg loadings in LIS, Lavaca Bay, and the Gulf of Trieste are enhanced by fluvial

sources of Hg, both from atmospheric deposition and anthropogenic activities in the watershed

(Covelli et al., 1999; Gill et al., 1999; Hammerschmidt et al., 2004).

Given the substantial sedimentary efflux of MMHg in LIS, we hypothesized previously

that diffusion from sediments in the coastal zone may be a significant source of MMHg to biota

in the ocean (Hammerschmidt et al., 2004). This is in contrast to the hypothesis that most of the

MMHg in marine fish results from potential methylation sources in the deep ocean such as

hydrothermal systems and sediments (Kraepiel et al., 2003). Although the source of MMHg in

marine fish is largely unknown, Rolfhus and Fitzgerald (1995) estimated that an annual flux of

about 0.2 Mmol MMHg to the ocean is required to sustain the average concentration in marine

fish (~0.2 μg g^{-1} wet weight). If sediments of the coastal zone, which is about 10% of the area

of the global ocean, were the primary source of MMHg, then we estimate that a flux of about 15

pmol m^{-2} d^{-1} is required to sustain this bioaccumulative uptake. The average diffusional flux of

MMHg from sediments at our sampling locations on the continental shelf averages 9 pmol m^{-2}

d^{-1} at a mean sediment temperature of 15 °C. This flux, estimated from just three stations on the

shelf of the northwestern Atlantic, is within a factor of two of that needed to sustain that annual

bioaccumulative uptake of MMHg by marine fish (i.e., 15 pmol m^{-2} d^{-1}). Moreover, the benthic

flux of MMHg from the coastal zone may be enhanced considerably by mobilization from

sediments that are impacted more severely by anthropogenic Hg. For example, and as noted,

fluxes of MMHg from deposits in LIS, Lavaca Bay, and the Gulf of Trieste are considerably

greater than those estimated for the shelf sediments sampled in this study.

3.6. MMHg in continental shelf water

The geographical and vertical distribution of MMHg in water on the continental shelf of

southern New England also suggests that *in situ* sedimentary production may be an important

source of MMHg to the shelf and possibly the open ocean. Levels of dissolved (< 0.2-µm filtered) and particle-associated MMHg in surface water (1 m), and water sampled below the seasonal thermocline (30 m), increase with distance from shore and total water column depth among stations (Fig. 11). That is, MMHg in surface and sub-thermocline water is considerably greater at 71south (131 m water depth) than at 71north (59 m). MMHg in the dissolved phase is a consistent fraction of total MMHg among the six samples (mean, 85%; range 80−89%). The trends in Figure 11 are inconsistent with rivers or estuaries being a major source of MMHg to these waters on the shelf and indicate that there is a significant *in situ* source of MMHg. Moreover, levels of dissolved and particulate MMHg are enhanced in water below the seasonal thermocline compared to surface water at each station (Fig. 11), suggesting that mobilization from sediments may be the major source of MMHg. Finally, concentrations of dissolved MMHg in shelf waters are much greater than those in the mixed layer of the open ocean (≤ 0.05 pM; Mason and Fitzgerald, 1993; Mason et al., 1995), and are thereby a source of MMHg. This is consistent with our hypothesis that sediments in the coastal zone, including those on the continental shelf, may be a potentially significant source of MMHg to the ocean and its biota.

4. Summary

The biogeochemical cycling of MMHg in sediments on the continental shelf is similar to that in near-shore systems such as LIS, although levels of Hg species in shelf deposits are considerably less. The concentration of Hg(II) in pore water, presumably as HgS^0 in low-sulfide sediments on the continental shelf and LIS, is a major factor influencing gross potential rates of Hg methylation, suggesting that MMHg production is limited by the availability of Hg(II) in

coastal marine deposits. Moreover, the diffusional benthic efflux of MMHg (i.e., net production) is related positively to its gross potential rate of production. This suggests that loadings of Hg(II), most of which are presumably from atmospheric deposition on the continental shelf and in near-shore environs like LIS (Balcom et al., 2004), may be an important factor influencing the gross and net production of MMHg and its flux to overlying water. Although anthropogenic sources have increased loadings of Hg(II) to near-shore deposits (Balcom et al., 2004), it is unclear if shelf sediments more distant from human and fluvial sources have been impacted similarly. Atmospheric deposition is the principal source of Hg in remote locations (Fitzgerald et al., 1998), and atmospheric Hg loadings have increased 2–4 fold globally since the Industrial Revolution (Lamborg et al., 2002). If atmospheric deposition were the primary source of Hg to continental shelf sediments, then it is likely that the production, sedimentary mobilization, and accumulation of MMHg in marine biota have increased proportionately. This is of particular human toxicological significance, given that most of the fish consumed by humans is of marine origin and that about 75% of marine fish productivity is supported by the coastal zone.

Acknowledgments

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Table 1. Mean characteristics of surface sediments (upper three cm) at the three sampling

stations on the continental shelf of southern New England. The relative standard deviation (%)

among cores at each station ($n = 3$) is given in parentheses.

Station	Organic content (%LOI)	Sediment (pmol g^{-1} dry weight)		Pore water (pM)	
		MMHg	Hg(II)	MMHg	Hg(II)
71north	1.9	0.36	43.0	3.62	17.2
	(11.3)	(10.3)	(14.2)	(5.6)	(41.7)
71central	6.8	1.13	158	3.49	8.6
	(4.8)	(10.3)	(4.0)	(21.8)	(22.9)
71south	5.8	0.74	96.6	4.41	15.5
	(8.3)	(12.5)	(5.2)	(16.0)	(18.6)

Figure captions

Figure 1. Location of sediment sampling sites on the continental shelf of southern New

England, northwestern Atlantic Ocean (71north, 40°44.20' N, 71°00.00' W; 71central,

40°28.00' N, 71°00.00' W; 71south, 40°12.00' N, 71°00.00' W).

Figure 2. Relation between the concentration of Hg species and organic content of surface

sediments (upper three cm) on the continental shelf of southern New England.

Figure 3. MMHg versus Hg(II) in the upper ten cm of sediment at three locations on the

continental shelf of southern New England.

Figure 4. Relation between reported average concentrations of MMHg and Hg(II) in surface

sediments of different coastal marine systems. Hg(II) was presumed equal to total Hg for

locations where Hg(II) was not reported; open circle (continental shelf of southern New

England; this study); closed circles (South China, Bering, and Baltic Seas; Kannan and

Falandysz, 1998); open square (Lagoon of Bizerte, Tunisia; Mzoughi et al., 2002); closed

square (Patuxent River estuary, Maryland; Benoit et al., 1998); open triangle up (Bay of

Biscay, France; Stoichev et al., 2004); closed triangle up (Long Island Sound,

Connecticut/New York; Varekamp et al., 2000; Hammerschmidt and Fitzgerald, 2004);

open dotted square (Gironde River estuary, France; Tseng et al., 2001); open triangle

down (San Francisco Bay, California; Conaway et al., 2003); closed triangle down

(Lavaca Bay, Texas; Bloom et al., 1999); open diamond (Chesapeake Bay, Maryland;

Mason and Lawrence, 1999); closed diamond (Seine River estuary, France; Mikac et al.,

1999); open hexagon (Saguenay Fjord, Quebec; Gagnon et al., 1997); closed hexagon

(New York/New Jersey Harbor; Hammerschmidt, 2005); dotted open circle (estuarine

section of Guanabara Bay, Brazil; Kehrig et al., 2003).

Figure 5. Variation of the distribution coefficients (K_D) of MMHg and Hg(II) with organic

content of sediments, measured as percent loss-on-ignition (%LOI), on the continental

shelf of southern New England and Long Island Sound (LIS). LIS data are from

Hammerschmidt et al. (2004).

Figure 6. Correlation between [200]Hg methylation potentials and levels of Hg(II) in pore water of

sediments on the continental shelf of southern New England.

Figure 7. [200]Hg methylation potential versus the distribution coefficient (K_D) of Hg(II) in

sediments on the continental shelf of southern New England.

Figure 8. Correlations between solid-phase MMHg and its potential gross rate of production in

the upper 12 cm of sediment on the continental shelf of southern New England: a)

ambient MMHg concentration versus potential MMHg production estimated from

ambient Hg(II) and incubations of added [200]Hg, and b) solid-phase concentration ratio of

ambient MMHg:Hg(II) versus [200]Hg methylation potential.

Figure 9. Relation between estimated diffusive fluxes of dissolved MMHg (< 0.2-µm filtered)

and gross potential rates of MMHg production in the upper two cm of sediment among

sampling locations on the continental shelf and in Long Island Sound (LIS) in August

2001 and March 2002 (Hammerschmidt and Fitzgerald, 2004; Hammerschmidt et al.,

2004). Error bars are $\pm$ 1 SE of the mean. The uncertainty of LIS flux estimates was not

determined. Data for LIS in June 2002 were not included because Hg methylation

potentials were inhibited and MMHg fluxes enhanced by a seasonal change in sediment

biogeochemistry following a spring plankton bloom.

Figure 10. Profiles of solid-phase and pore water Hg species, [200]Hg methylation potentials, and

ancillary sediment biogeochemistry at three stations on the continental shelf of southern

New England. Hg speciation profiles do not include results from the two surface

sediment cores (upper 3 cm only) at each station. Error bars represent $\pm$ 1 SE of the

mean.

Figure 11. Trends of increasing dissolved (diss; < 0.2-µm filtered) and particle-associated (part;

> 0.2 µm) MMHg with increasing water column depth in surface (1 m depth) and sub-

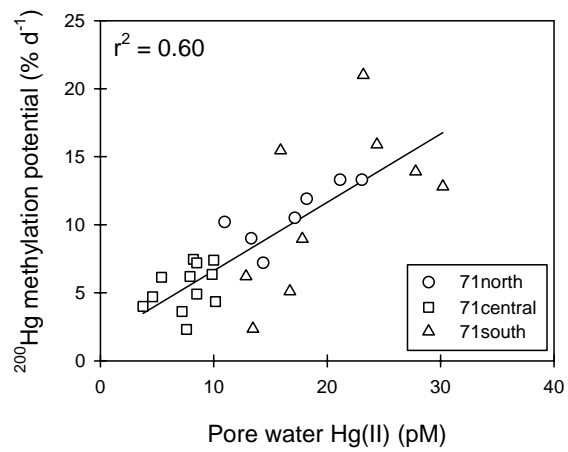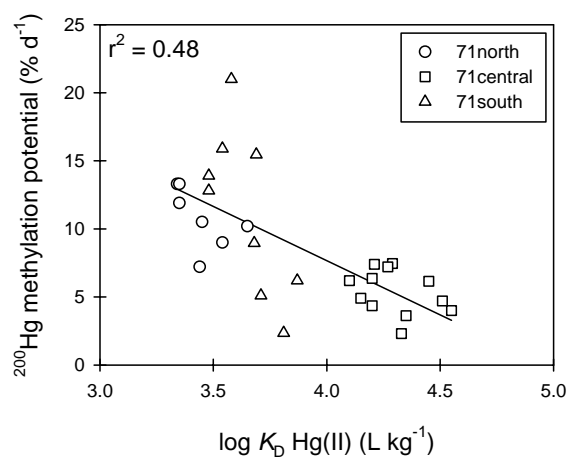thermocline (30m) water on the continental shelf of southern New England.

Figure 1. Hammerschmidt & Fitzgerald
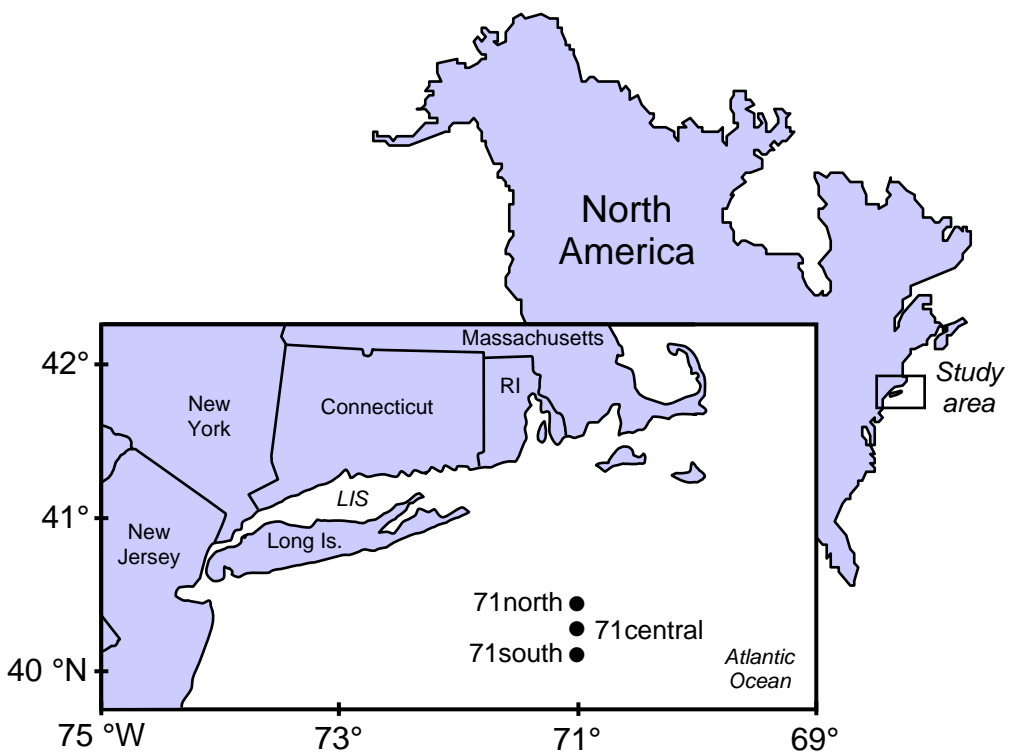
Figure 2. Hammerschmidt & Fitzgerald

(2a) Hg(II)
$r^2 = 0.83$

Hg(II) = (1.8 ± 9.7) + (20.2 ± 1.8)[%LOI]

(2b) MMHg
$r^2 = 0.74$

MMHg = (0.08 ± 0.09) + (0.14 ± 0.02)[%LOI]

Hg concentration (pmol g^{-1} dry weight)

Organic content (% LOI)
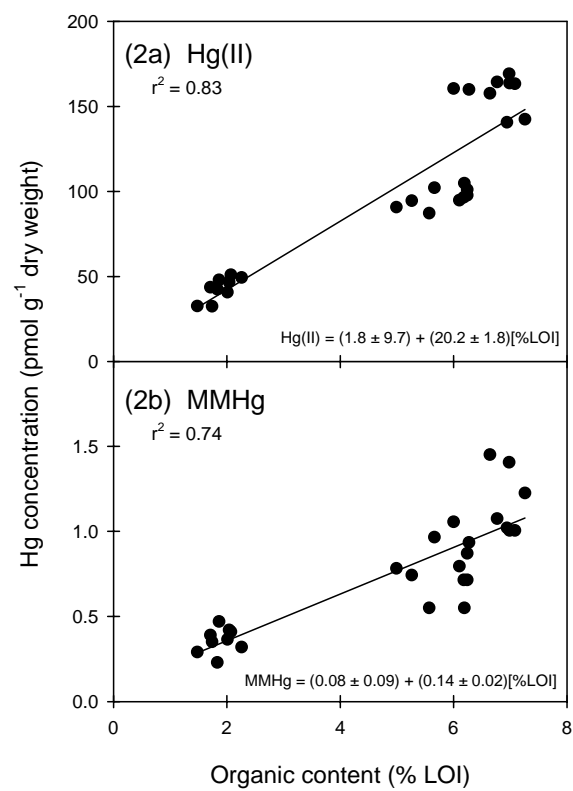
Figure 3. Hammerschmidt & Fitzgerald

MMHg = (0.006 ± 0.063) + (0.0076 ± 0.006)[Hg(II)]
$r^2 = 0.86$

MMHg (pmol g^{-1} dry weight)

Hg(II) (pmol g^{-1} dry weight)
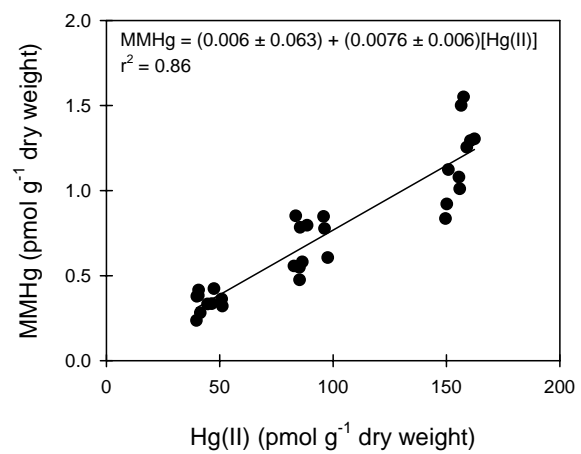
Figure 4. Hammerschmidt & Fitzgerald

Mean MMHg (nmol g^{-1} dry weight)

Slope = 0.0050 ± 0.0003
r^2 = 0.95

Mean Hg(II) (nmol g^{-1} dry weight)
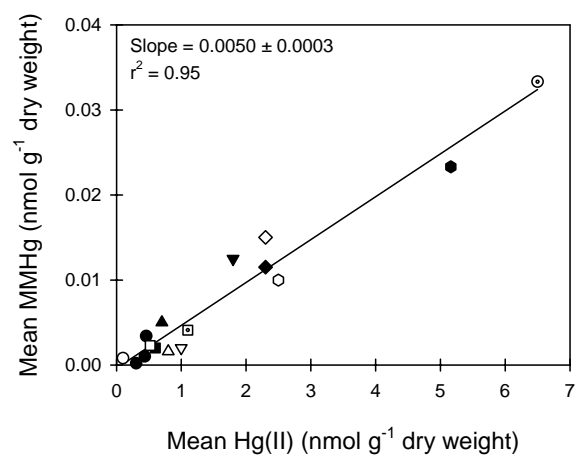
Figure 5. Hammerschmidt & Fitzgerald
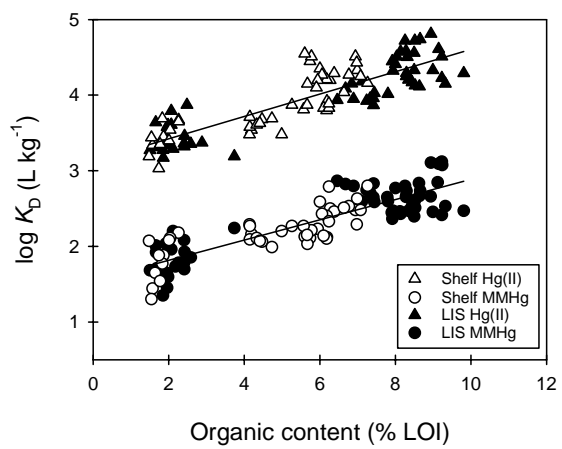
Figure 6. Hammerschmidt & Fitzgerald

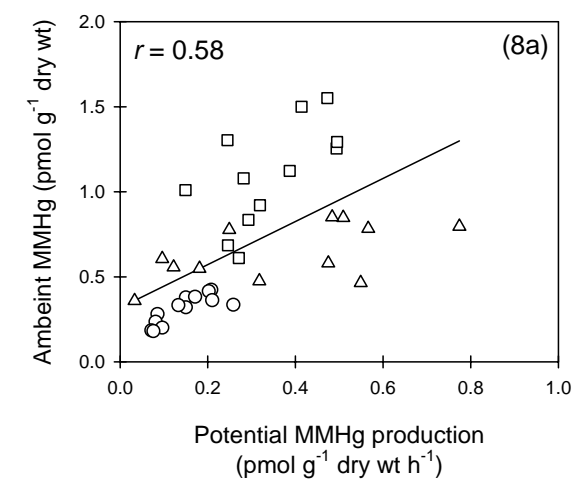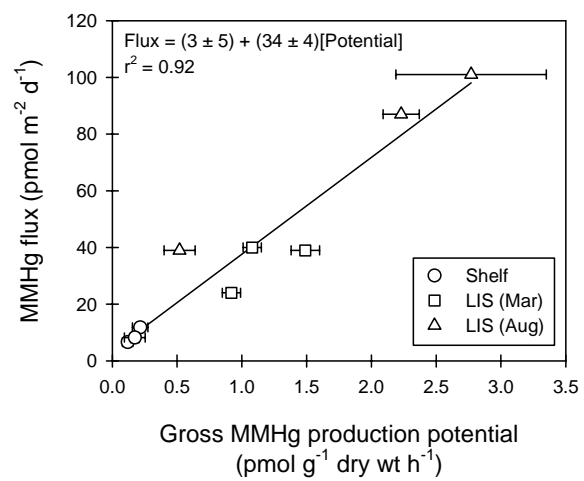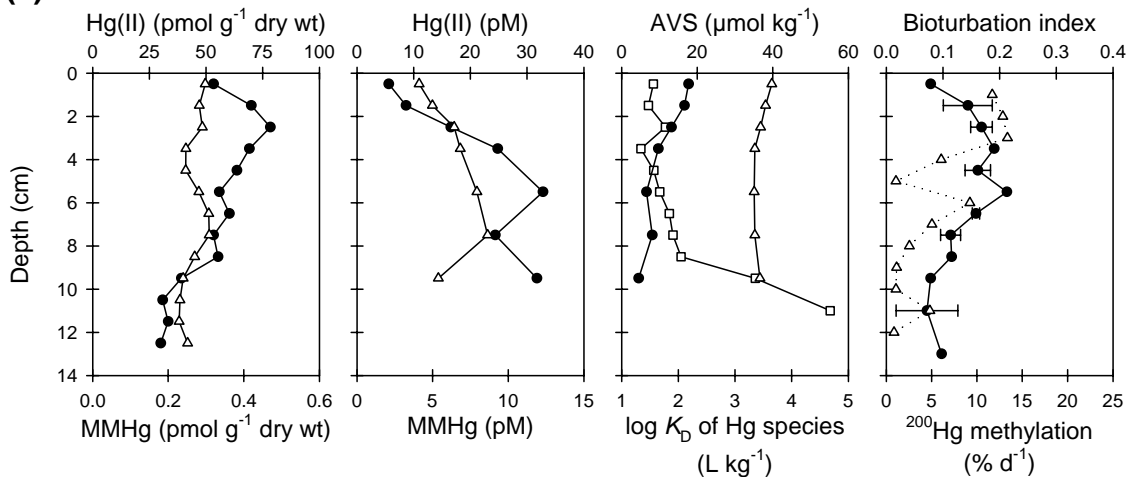Figure 7. Hammerschmidt & Fitzgerald

Figure 8. Hammerschmidt & Fitzgerald

Potential MMHg production
(pmol g^{-1} dry wt h^{-1})

^{200}Hg methylation potential (% d^{-1})
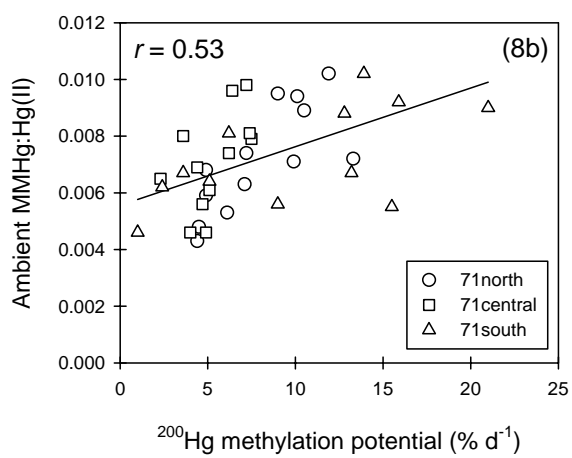
Figure 9. Hammerschmidt & Fitzgerald

Figure 10. Hammerschmidt & Fitzgerald

(a) 71north
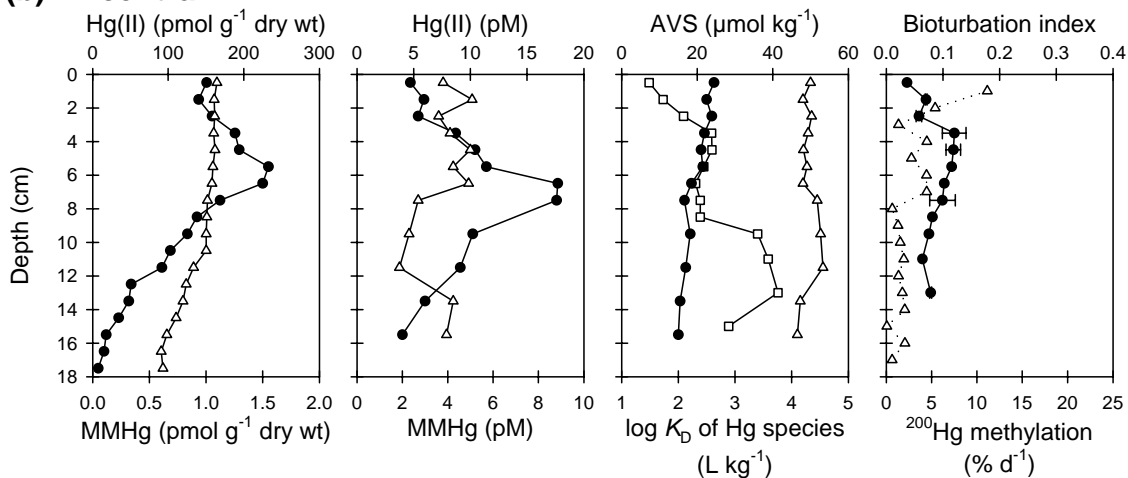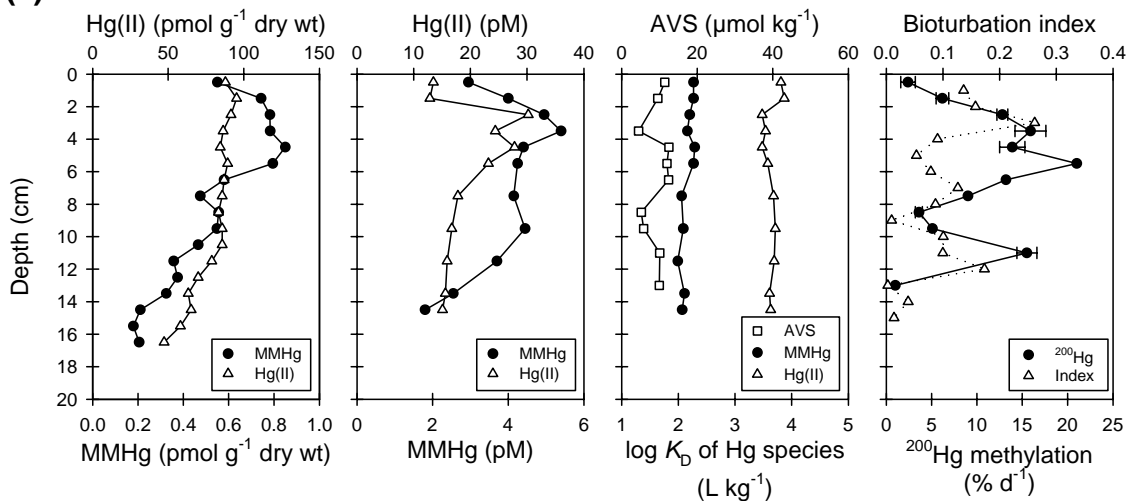

(b) 71central

(c) 71south

Figure 11. Hammerschmidt & Fitzgerald