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Sediment-Porewater Partitioning, Total Sulfur, and Methylmercury Production in Estuaries

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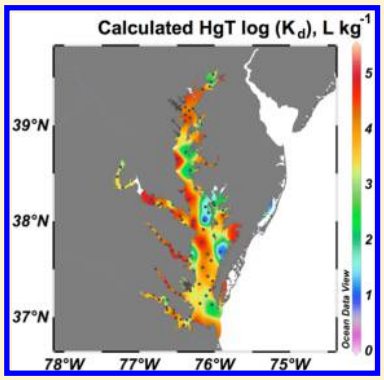
Supporting Information

ABSTRACT: Mercury (Hg) speciation and the activity of Hg(II)-methylating bacteria are responsible for the rate of methylmercury production and thus bioaccumulation in marine foodwebs. Factors affecting porewater partitioning (K_d) and methylation of Hg(II) were examined at 11 sites in sediment of 4 biogeochemically diverse estuaries in the Northeast U.S. In Long Island Sound, 88% of total mercury (HgT) log K_d variability was described by porewater dissolved organic carbon concentration and sediment total sulfur (S) content. Whereas across all estuaries, regression analyses showed that S alone drives about 70% of K_d variability and 50% of changes in methylation rates; and the inclusion of DOC and sulfides did not improve the prediction. Thus, we demonstrated that S is a better predictor of HgT log K_d than the sediment organic matter across multiple estuaries, and while organic matter and S are interchangeable in small-scale studies, on a larger scale, sediment S content is the simplest and most effective variable to measure.



INTRODUCTION

Methylmercury (MeHg) causes long-term developmental delays in children[1,2] and has been associated with cardiovascular health risks in adults.[3] MeHg is produced from inorganic mercury (Hg^{II}) primarily by sulfate and iron-reducing bacteria in aquatic sediment,[4−6] although the recent discovery of methylating genes suggests that this ability is more widespread.[7] Once formed, MeHg can enter the benthic foodweb or diffuse into the water column and bioaccumulate in the pelagic foodweb.

Methylation in estuarine environments is mediated by an array of in situ biogeochemical factors, which can be divided into two major groups: those that control bacterial activity and those that can alter Hg(II) bioavailability. Known factors affecting bacterial activity are temperature, salinity, substrate availability, and pH. A number of studies have focused on identifying the fraction of Hg(II) available for methylation,[8] and regardless of the method used, these studies suggest that only a small fraction of the sediment HgT is bioavailable. Bioavailable Hg(II) is often assumed to be associated with the porewater fraction, and thus with the bulk sediment—porewater distribution coefficient for total mercury (HgT log K_d, L kg^{-1}).[8] Sediment organic matter (OM) and inorganic sulfur species have been shown to correlate with Hg(II) methylation rates (k_{meth}), and HgT log K_d, although most of these studies have focused on a single ecosystem.[9−17]

By expanding our study area to 11 biogeochemically diverse sites in 4 estuaries, we showed that OM does not explain variations in K_d and Hg(II) methylation.[14] We propose that either the quality of sediment OM is of greater importance than quantity, and must vary substantially across systems, or that other factors besides OM, such as the amount of inorganic reduced sulfur, are also important.[18] Herein, we examined whether sediment total sulfur (S) content rather than OM can be used as a proxy for HgT log K_d.

In estuarine sediment, most of the S species are produced in situ from seawater sulfates, with the production of reduced S (S^{-II} and S^0) predominantly due to sulfate-reducing bacteria, which respire SO_4 during carbon (C) remineralization. In coastal marine sediment, sulfate respiration is responsible for 10 to 85% of C remineralization.[19−21] Sediment reduced S is mostly composed of inorganic phases, operationally defined as Acid-Volatile Sulfides (AVS), corresponding to FeS-type species and dissolved sulfides, and Chromium-Reducible Sulfides (CRS), which is composed of mostly pyrite.[22,23] The relative size of each pool varies from system to system, and even within a system. In some systems, elemental sulfur (S^0) can also be high, but analytically tends to be assessed as part of the CRS pools.[24] In marine sediment most of total S is composed of AVS + CRS, and organic S is often calculated by subtracting the inorganic species from total S. Organic S compounds are formed during the reaction of H_2S with OM; this reaction is called sulfurization and is thought to increase OM preservation by forming large macromolecules.[25,26]

Sulfur and OM have interwoven cycles;[27] a fraction of the OM is the substrate for sulfate reducing bacteria, and oxygen depletion creates anoxic conditions favorable to S accumulation. Moreover, Hg has an affinity for S, and even the strong interaction between Hg and OM is attributed to S-containing functional groups (e.g., thiol ligands) in OM.[28−32] Mercury speciation is also influenced by other S species, such as

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Table 1. Sediment Characteristics (Average for the 0−4 cm Depth Interval) at the Three Sampling Locations in Long Island Sound[a]

site	period	sediment (mmol g^{-1} dry wt.)			organic matter	C/N	C/S	porewater DOC[b]	$\delta^{13}C$
		C	N	S	(%LOI)	(mol/mol)	(mol/mol)	(μM)	(‰)
W	Aug.	2.25 (0.02)	0.20 (0.00)	0.21 (0.01)	8.2 (0.05)	11.2	10.6	792	−20.0 (0.4)
	Dec.	2.70 (0.2)	0.23 (0.02)	0.20 (0.01)	10.2 (1)	11.5	13.3	242	−18.7 (1)
	May	2.36 (0.02)	0.22 (0.00)	0.23 (0.02)	9.1 (0.2)	10.7	10.2	358	−19.1 (0.4)
C	May	2.17 (0.08)	0.24 (0.03)	0.14 (0.00)	9.0 (0.7)	9.0	9.0	402	
E	Aug.	0.36 (0.03)	0.05 (0.00)	0.03 (0.00)	2.2 (0.02)	7.3	14.0	54	−19.0 (0.3)
	Nov.	0.48 (0.02)	0.05 (0.00)	0.04 (0.00)	2.5 (0.04)	10.1	11.5	340	−18.6 (0.2)
	May	0.53 (0.00)	0.06 (0.00)	0.04 (0.00)	2.9 (0.4)	9.0	12.8	366	−18.7 (0.4)

[a]Standard deviations between cores are given in parentheses. [b]Porewater was pooled together from multiple cores. "−" Not measured.

dissolved sulfides,[5,33,34] pyrite,[35,36] amorphous FeS,[12,16,17,29,37−39] and polysulfides.[28,40,41] Moreover, marine sediment plays an important role in both C and S cycling; they are a major sink for S through the formation of sulfide minerals such as mackinawite (FeS), pyrite (FeS_2), and organic S compounds.[27] However, despite substantial evidence for S species being important in Hg cycling, the role of sediment as a sink for both S and C, and the analytical simplicity of total S measurements, sediment total S concentrations, which include all the S species mentioned above (pyrite may not be fully recovered), are rarely measured and evaluated in Hg studies.[13,16,17]

Therefore, using published field data from our lab and collaborators,[14,16,17] and newly measured ancillary parameters, we assessed the role of sediment total S content in HgT log K_d's variability and in Hg(II) methylation. We concluded that S, which correlates with OM within but not across multiple estuaries, was the single best variable to predict HgT distribution coefficients and methylation rates. We developed a statistical model and applied it to Chesapeake Bay sediment data, and found good agreement between measured and predicted HgT log K_d.

METHODS

Study Sites. Eleven sites were sampled in CT/NY, ME, NH, and NJ. More details on the systems are available in Schartup et al. (2013).[14]

Sampling. Long Island Sound (LIS) was sampled at two locations (sites W and E) on three occasions in the summer, late fall, and in the spring (Supporting Information, SI, Figure S1 and Table S1). A third location was sampled in the spring (site C) for sediment chemistry only. Sediment cores were obtained using a multicorer; a minimum of eight per station was used for bulk HgT, MeHg, and sulfide analysis. In July and August 2009, we sampled nine sites located in the pristine beach town of Wells Maine (ME), industrialized Portsmouth New Hampshire (NH), and contaminated Hackensack New Jersey (NJ).

Chemical Analyses. Duplicate cores were sectioned in a nitrogen filled glovebag within 12 h of collection at 1 or 2-cm intervals 10-cm down core, and sections were immediately frozen. A series of analyzes were performed on freeze-dried sediment. Organic matter content was measured by loss on ignition (LOI) at 550 °C. Sediment sulfur (S), carbon (C), and nitrogen (N) were measured with CNS analyzer (Fisons NA 1500 series 2), which was calibrated daily; every sample was analyzed in triplicates, complete S recoveries were checked using marine sediment reference material, PACS-2 (certified value for S of 1.29 ± 0.13 g/100g). We refer to S recovered by this method as total S. TC is strongly related to TOC as seen in SI Figure S2 $\delta^{13}C$ and $\delta^{15}N$ were measured using an elemental analyzer and a Finnigan model isotope ratio mass spectrometer. At least 4 cores from each site were sectioned in a nitrogen filled glovebag for porewater extractions. Porewater was extracted from 2-cm sediment subsections using direct vacuum filtration with acid-washed Nalgene polystyrene filter units and 0.2-μm cellulose nitrate filters.[16] Silty/Clay sediment was centrifuged prior to filtration for porewater extraction, and aliquots of porewater for HgT and MeHg analyses were frozen in Teflon bottles and acidified to 0.5% with optima grade HCl.[42] Aliquots of porewater for sulfide analysis were preserved in sulfide antioxidant buffer (2 M NaOH, 0.2 M Na_2EDTA, and 0.2 M ascorbic acid, in degassed deionized water) and analyzed immediately.[43] Dissolved Organic Carbon (DOC) concentrations were determined using a Shimadzu TOC analyzer. For methylation/demethylation assays, the stock solutions of $^{200}Hg(II)$ and $Me^{199}Hg$ ($^{200}Hg(II)$ purity of 96.41%, obtained from Oak Ridge National Laboratory, $Me^{199}Hg$ was synthetized using methylcobalamine[44] were diluted with filtered bottom water (0.22-μm) and equilibrated for an hour before injection.[11,16,45−47] Isotope injections were made into replicate intact sediment cores at 1-cm intervals 10-cm down core and into the overlying water, capped cores were incubated between 2 to 7 h at ambient bottom water temperature, sectioned, and immediately frozen. For stable isotope Hg(II) analysis, freeze-dried samples were homogenized, spiked with an enriched isotope internal standard ($^{201}HgCl$) and microwave digested in a 4:1 mixture of HNO_3/HCl for a total of five minutes, followed by an addition of BrCl and deionized water.[12] $^{200}Hg(II)$ was measured using a Perkin-Elmer ELAN DRCII ICP-MS with an attached Flow Injection Auto Sampler (FIAS). Sediment for $Me^{199}Hg$ analysis were processed and analyzed following standard distillation and ethylation protocols,[48] a Perkin-Elmer ELAN DRCII ICP-MS was used for detection.

The Hg(II)-methylation rate constant (k_{meth}) was estimated by measuring the excess $Me^{200}Hg$ formed from the injected $^{200}Hg(II)$, while the demethylation constant (k_{demeth}) was estimated using the loss in $Me^{199}Hg$.[47] In both cases, pseudo-first order kinetic reactions were assumed. The detection limits (DL) for k_{meth} were estimated to be 0.0001 day^{-1} for LIS samples and 0.0006 day^{-1} for all other sites,[49] and methylation rates were above the DL in all samples. The ratios of ambient Hg 200:202 in laboratory standards were found to have relative standard deviations of 3.8% over the course of analyses. Similar calculation yielded a detection limit for k_{demeth} of 0.01 d^{-1} and an RSD of 4.3% for 199:202 (n = 72).

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Data Analyses. Statistical and graphical analyses were done using the JMP software and Sigmaplot. Regressions were considered significant at p-values <0.05. The effects of all the variables measured in LIS on log K_d were screened. Since log K_d is log-transformed all independent variables were also log-transformed to maintain the linearity needed for linear regression analyses. Variables providing the best correlations with log K_d were then used in stepwise and best-subset regression analyses to identify the variables that best describe changes in log K_d. The variance inflation factors were maintained below 3 for all variables. Variables presenting significant correlations in LIS were measured in all the other study sites; all of the statistical tools used for LIS sediment were applied to the multiple estuary analysis (detailed reports are available in the SI).

RESULTS AND DISCUSSION

The results presented are for surficial sediment (0−4 cm) at the oxic-anoxic interface where the bulk of Hg(II)-methylation occurs.

Long Island Sound. An analysis of variance between the three locations in LIS was performed, using a student t test, to identify the variables that present a significant change from east to west regardless of seasonal variability. We found that sediment in the west, sites W and C, contain more organic matter than the eastern location E (Table 1). The C/N was greater at site W than site E; higher C/N values are indicative of larger wastewaters inputs[50] and autochthonous production, this is supported by a $\delta^{13}C$ within the range of those found in marine plankton. There was a significant difference in the $\delta^{13}C$ and DOC between eastern and western LIS (Table 1).

Only variables that presented significant differences between east and west of LIS were selected for regression analyses. Among those, S, porewater DOC and %LOI best predicted HgT log K_d. Subsequent regression analysis selected S and porewater DOC, which combined explained 87% of the variation in HgT log K_d for LIS (Figure 1). The partitioning coefficient was negatively related to porewater DOC and positively with S, similar trends have been found in streams.[8]

As porewater DOC concentrations increase, more Hg(II) partitions into porewater and thus decreases the log K_d. The ability of DOC to maintain Hg(II) in the aqueous phase has been demonstrated in a number of studies.[51−54] The accumulation and preservation of organic C in coastal sediment is determined by the extent of aerobic versus anaerobic degradation, which is primarily controlled by relative magnitude of the input of organic C and the rate of diffusion of oxygen into sediment. Sulfate reduction is the main anaerobic degradation pathway in coastal environments[19,20] and thus in regions of high organic C sedimentation and insufficient O_2 penetration, sulfide formation and incorporation of S into organic C dominates, and reduced S becomes the dominant control over HgT partitioning. Moreover, the formation of iron sulfides, such as mackinawite (FeS) and pyrite (FeS_2) in sediment can lead to the coprecipitation or adsorption of HgT to solids, to a higher HgT concentration in the bulk phase, and thus higher partitioning coefficients (Figure 1). Additionally, there is the potential for precipitation of HgS, although DOC can hinder this process by stabilizing colloidal and nanoparticulate HgS.[53,55−57] Higher sediment total S concentration could indicate the presence of higher levels of such reduced S species, and the dominance of sulfate reduction over aerobic respiration. In these environments, total reduced S is the major control over HgT partitioning and bioavailability, as discussed further below for multiple estuaries.

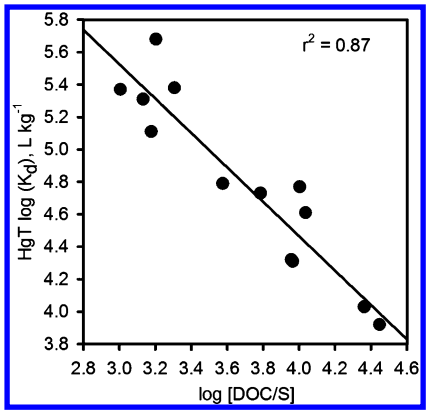

Figure 1. Log-transformed total Hg sediment porewater distribution coefficient (HgT log K_d) versus log-transformed ratio of porewater dissolved organic carbon (DOC) to the surficial sediment total sulfur content (S) in Long Island Sound. With HgT log K_d = 8.709 − (1.061 * log[DOC/S]), r^2 = 0.87, n = 13, p < 0.001.

Multiple Estuaries. To further examine the relationships found in LIS, data from LIS and estuaries in ME, NH, and NJ was combined. The data used is summarized in Table 2.

Sulfur has been shown to be an important sink for HgT in lakes through coprecipitation or sorption onto mackinawite (FeS)—the main constituent of AVS.[58] However, in estuarine sediment, the correlation between HgT log K_d and AVS is rarely found,[12] as pyrite formation provides another sink for HgT not found in most terrestrial environments. Thus, the relationship between K_d and S for coastal systems is not due exclusively to the formation of FeS, but also includes the increased S content of OM (lower C/S ratio) in reducing estuarine sediment.

We previously proposed that OM is not a good proxy of K_d, and the data presented here reinforce this notion.[14] While the correlation between K_d and OM is usually strong in smaller-scale studies,[12] it is less evident in large-scale studies covering multiple environmental locations.[14,16] We propose that this results from the correlation between C and S within site but not across multiple sites (Figure 2).

The variability in C/S ratios is demonstrated using the tabulated S and C data from Hollweg et al.[16,17] and this study (Figure 2). The correlations between S and C within each location were fitted with a least-squares linear regression line. The intercepts at origin are consistent with reduced S primarily being produced during C remineralization by sulfate reducing bacteria.[59] Chesapeake Bay sites and western LIS (W) had high relative S content when compared to the adjacent Shelf and Slope stations. Chesapeake Bay sites (Sta 1, 2, 3, and 4 in Figure 2) have an average C/S molar ratio comparable to the C/S measured in most marine sediment (C/S between 4.5 to 13.7 molar ratios).[60]

The high C/S of 35, measured at Sta 9 and the ME sites could be due to recent and historic factors influencing OM quality (especially the reduced S content). Indeed, OM from Sta 9 is believed to be old and refractory, thus less available to sulfate reducing bacteria, and representative of more recalcitrant humic material.[16,61] Moreover, fast burial rates are believed to preserve a larger fraction of more bioavailable OM, but result in lower C/S, thus higher C/S away from shore

Table 2. Sediment characteristics of New Hampshire, New Jersey and Maine sites (Average for the 0-4 cm Depth Interval)[a]

location	site	sediment (mmol g^{-1} dry wt.)			organic matter[b]	C/S	porewater DOC[c]
		C	N	S	(%LOI)	(mol/mol)	(μM)
New Hampshire (NH)	BB	2.92 (0.2)	0.26 (0.02)	0.29 (0.09)	10.0 (0.7)	11.3	787
	PNS	3.15 (0.6)	0.23 (0.04)	0.11 (0.00)	3.0 (1)	13.4	1105
	JEL	1.96 (0.2)	0.18 (0.02)	0.20 (0.02)	9.0 (1)	11.0	1107
New Jersey (NJ)	MC	2.28 (0.2)	0.16 (0.03)	0.27 (0.06)	8.3 (0.8)	14.1	168
	BC	1.51 (0.3)	0.11 (0.02)	0.13 (0.06)	11.6 (0.9)	13.8	
Maine (ME)	WD	0.50 (0.2)	0.05 (0.01)	0.02 (0.01)	2.2 (0.9)	10.2	
	WM	0.46 (0.04)	0.05 (0.01)	0.02 (0.01)	2.7 (0.3)	10.2	
	WH	0.08 (0.01)	0.01 (0.00)	0.02 (0.00)	7.5 (0.1)	7.4	

[a]Standard deviations between cores are given in parentheses. [b]From Schartup et al.[14] "–" Not measured. [c]Porewater was pooled together from multiple cores.

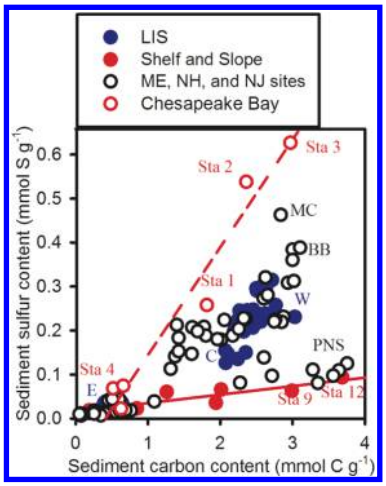

Figure 2. Sediment carbon and sulfur data from Hollweg et al.[16,17] in red and this study in blue and white (LIS, ME, NH, and NJ). Dotted red line is the linear regression for Chesapeake Bay (r^2 = 0.96, p < 0.001, n = 6) and the solid red line is for the Shelf and Slope adjacent to Chesapeake Bay (r^2 = 0.75, p = 0.012, n = 7).

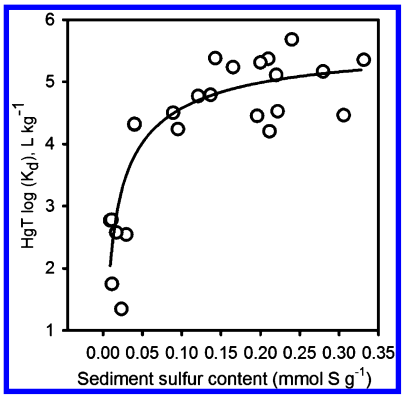

Figure 3. HgT log K_d plotted against sediment sulfur content from Maine, New Hampshire, New Jersey and Long Island Sound sites. The data are fitted by eq 1; HgT log $[K_d]$ = 5.38 − 0.15 * (ln $[S]$)^2, r^2 = 0.70 p < 0.001.

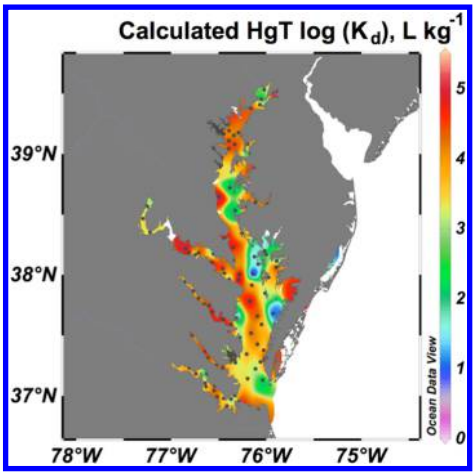

Figure 4. Calculated HgT log K_d for Chesapeake Bay using surficial sediment sulfur data collected and provided by the Maryland Geological Survey.[63,64]

can be indicative of slower burial rates.[61,62] Sampling sites in ME, NH, NJ, and LIS sites distribute between the two extremes (Figure 2).

When sampling in a small spatial area sediment C and S contents covary and are interchangeable as a proxy for HgT partitioning. However, with the multiestuarine approach, sites with same C content (Sta9 and Sta3) have very different S content. Since reduced S is an indicator of redox conditions and the extent of anaerobic degradation, S is a better proxy for HgT partitioning in sediment and the sediment's capacity to accumulate OM and reduced S species.

Test of HgT log K_d/S Method. Many approaches have been used to define a relationship between sediment characteristics and HgT partitioning and methylation. We obtained the best-fit eq 1 using the Table Curve 2D software (Figure 3):

$$\text{HgT log}[K_d] = 5.38 - 0.150^*(\ln[S])^2, \quad r^2 = 0.70 \quad p < 0.001 \tag{1}$$

To illustrate the relationship and how this impacts partitioning within one ecosystem, eq 1 and published S values[63,64] were used to construct a HgT log K_d distribution map for Chesapeake Bay (Figure 4). The strong agreement between the modeled and measured data[16,17] is illustrated in Figure 5, especially within the area of highest variability, at intermediate S concentrations <0.3 mmol g^{-1}(SI Figure S3).

Such relationships provide a simple method of estimating HgT bioavailability within sediment in contrast to porewater extractions and HgT analyses, which are expensive and time-consuming. We suggest using S as a proxy for HgT log K_d as this provides a higher resolution HgT log K_d map than actual measurements. Figure 4 highlights the heterogeneity of the system; this information is critical when calculating system wide fluxes of HgT and MeHg from sediment, and for understanding the distribution of Hg(II) methylation. Additionally, S

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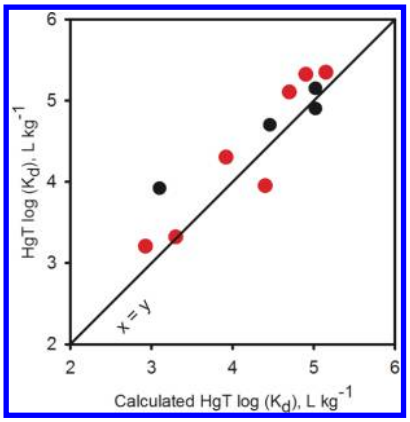

Figure 5. Actual HgT log K_d measured by Hollweg et al.[16,17] in Chesapeake Bay plotted against calculated log K_d using sediment sulfur data from Hollweg et al.[16,17] (red circles). The black symbols are for the actual HgT log K_d measured by Hollweg et al.[16,17] plotted against calculated log K_d using sediment sulfur data from the Maryland Geological Survey[63] (extracted from Figure 4). The solid line represents the 1:1 fit.

measurements can be easily performed during pilot studies to identify areas of interest and to plan future work when studying a new ecosystem.

Sulfur and Hg(II)-Methylation. Methylmercury production in sediment is regulated by the activity of methylating bacteria, the bioavailability of Hg(II), and MeHg demethylation rates. Demethylation rates did not correlate with any of the variables measured, including porewater sulfide concentrations and sediment bulk MeHg content, both of which have been found to correlate with k_{demeth}.[17,65] We show that for S concentrations above 0.03 mmol S g^{-1}, the methylation rate, k_{meth}, and total S content are inversely related (Figure 6 and SI Figure S4).[12,66]

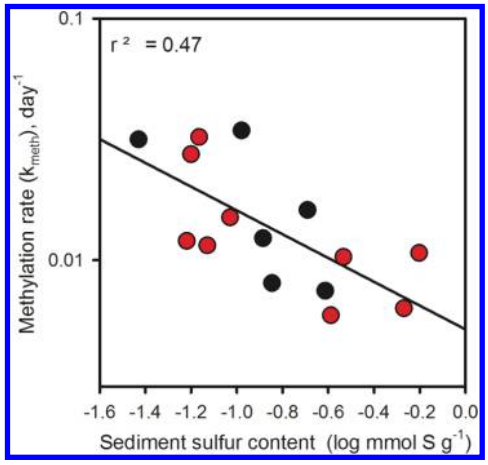

Figure 6. Methylation rate is plotted against log-transformed sediment sulfur content data obtained in this study (black symbols) and data published by Hollweg et al. (red symbols);[16,17] r^2 = 0.47, p = 0.0048, n = 15, log [k_{meth}] = −2.3 − 0.50*log [S].

Relationships between porewater sulfide and methylation have been previously proposed[10,17,34] and typically suggested a negative relation for porewater sulfide levels above a few micromolars. At lower levels, it was suggested that microbial activity, and specifically sulfate reduction rate, was limiting methylation and not Hg(II) bioavailability; our results are similar, but the change in k_{meth} is associated with the bulk measurement rather than dissolved species. The relationship between k_{meth} and sediment S below 0.03 mmol S g^{-1} is insignificant, p = 0.06, (SI Figure S5). More data are needed in the lower end of the sediment S content where k_{meth} ranges from 0.6% to 4.1% day^{-1}.

We Propose Three Possible Explanations for Our Observations.

(i) During the assays, the injected ^{200}Hg(II) isotope rapidly adsorbs onto solid FeS/FeS_2 and hence the decrease in the methylation rate. While, this seems to be the case for native porewater Hg(II), as evidenced by the relationship between HgT log K_d and S, this is an unlikely scenario during methylation assays. Laboratory experiments have shown that the kinetics of HgT adsorption to the strong binding sites are slower than most Hg isotope incubation periods (2 to 7 h).[39,67]

(ii) Sites with high sediment S content have higher porewater sulfides, and ^{200}Hg(II) and porewater sulfides form charged HgS species that are less bioavailable.[34] However, we found no relationship between porewater sulfides and methylation rates for these sites,[14] and the addition of sulfides to the regression model did not improve the prediction.

(iii) Finally, sites with higher S contain more organosulfides; these can quickly bind to Hg(II) and make it unavailable for methylation. This could explain the lack of relationship between S and k_{meth} when S content is under 0.03 mmol S g^{-1} (SI Figure S3). Low S content is characteristic of sediment with limited reducing conditions and low C preservation capacity,[62] both of which can inhibit the activity of sulfate reducers and the formation of organosulfides. We believe that (iii) is the most likely scenario.

While more work may be needed to establish whether the equation obtained in this manuscript can be applied "as is" to other systems, this multisystem approach enabled us to identify an important variable, total sulfur, that is seldom present in mercury related studies.

■ ASSOCIATED CONTENT

Supporting Information

Maps of sampling sites, tables with standard deviations, figures, and statistical reports referred to in this manuscript. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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