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Importance of organic matter lability for monomethylmercury production in sulfate-rich marine sediments

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ABSTRACT

Sediment cores were collected from two shallow sites in the Venice Lagoon, Italy, in order to study the lability of organic matter and the methylation rate of inorganic Hg(II). Measurements were made of concentrations of total Hg and monomethylmercury (MMHg), Hg(II) methylation rates, concentrations of total organic carbon and total nitrogen in the sediments, and dissolved sulfate, sulfide, and alkalinity in sedimentary pore waters. A positive linear relationship was detected between the specific Hg(II) methylation rate constant and the fraction of total Hg comprised of MMHg (%MMHg/Hg), indicating that short-term Hg(II) methylation rate reflects a long-term accumulation of MMHg in sediment. In addition, the %MMHg/Hg and specific Hg(II) methylation rate constant in sediment increased with decreasing ratios of total organic carbon to total nitrogen (C/N), whereas concentrations of dissolved sulfate, sulfide, and alkalinity in pore water remained constant. This result suggests that the Hg(II) methylation rate was affected by lability of organic matter. In particular, surface sediments, which contained large fractions of fresh algal organic material (C/N = 5.8–7.8), showed higher Hg(II) methylation rates than did deeper sediments (C/N > 10). Our results indicate that the C/N ratio can be used as a proxy for the lability of organic matter that influences Hg(II) methylation rate in sulfate-rich marine sediments.

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1. Introduction

Monomethylmercury (MMHg) is a highly toxic form of Hg that results in neurotoxicity in humans, particularly in the developing brain of fetuses and infants (Oken et al., 2005). The major route of MMHg exposure to humans is through consumption of seafood that accumulates MMHg via the benthic and pelagic food chains (Al-Reasi et al., 2007; Chen et al., 2009; Kim et al., 2004). In coastal food chains, anoxic sediments appear to be major sources of MMHg (Compeau and Bartha, 1985; King et al., 2000; Pak and Bartha, 1998). For example, in Chesapeake Bay and its adjoining shelf area, the minimum contribution of MMHg from coastal shelf sediments to the water column (8 mol $year^{-1}$) was of the same order as other major inputs to the system (28 mol $year^{-1}$ from the bay and 3.5 mol $year^{-1}$ from atmospheric deposition; Holloway et al., 2009). Predicting and understanding MMHg production in sediments is therefore crucial for evaluating the risk of Hg contamination in coastal systems.

One of the most important geochemical processes governing methylation of inorganic Hg, Hg(II), is the decomposition of organic matter by sulfate-reducing bacteria (SRB; Compeau and Bartha, 1985; Gilmour et al., 1992; King et al., 2000). Several studies have reported that depth profiles of bacterial sulfate reduction rate (SRR) and Hg(II) methylation rate (MMR) in lake sediments show similar trends (Gilmour et al., 1992, 1998). In marine sediments, SRR also appears to be the most important factor in the prediction of MMR (King et al., 2000). Sulfate, an electron donor, is well known to promote bacterial activity (Jørgensen et al., 2004; King et al., 2000). In contrast, dissolved sulfide, the product of sulfate reduction, inhibits bacterial growth and activity (Icgen and Harrison, 2006; Reis et al., 1991) and also decreases bioavailability of Hg(II) (Benoit et al., 2001). A few studies have suggested that dissolved sulfide in pore water is the primary regulator of MMR in sediment (Benoit et al., 2001; Gilmour et al., 1998; Holloway et al., 2009). In the Chesapeake Bay and the mid-Atlantic continental margin, sulfate concentration increased (from 7 to 25 mM) from the bay to the slope, while SRR (from 56 to 6 nmol cm^{-3} h^{-1}) and dissolved sulfide (557 to 0.8 μM) decreased (Holloway et al., 2009). In the same sites, MMR increased from the bay to the slope sediment, suggesting that dissolved sulfide decreases the *in situ* methylation rate of Hg(II) (Holloway et al., 2009). A similar inverse correlation between dissolved sulfide concentration and MMR was reported in northern Everglades sediments (Gilmour et al., 1998).

The solubility of Hg was suggested as another important factor governing MMR, because inorganic Hg(II) is the substrate for bacterial MMHg production. In the Long Island Sound coastal sediment, MMR was

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regulated by the partitioning of Hg(II) between sediment particles and pore water, which in turn was influenced by solid organic matter and acid-volatile sulfide contents (Hammerschmidt and Fitzgerald, 2004). In the same sites, MMR varied inversely with the K_d (particle–water distribution coefficient) of Hg and positively with the concentration of HgS^0 in pore water (Hammerschmidt and Fitzgerald, 2004). Concentrations of neutral Hg sulfide species (i.e., $Hg(SH)_2^0$ and HgS^0) were also correlated with the specific MMR in brackish and freshwater sediments, which suggests that neutral Hg sulfide species are bioavailable form of Hg(II) for Hg(II) methylating microorganisms (Benoit et al., 2001; Drott et al., 2007).

If the concentrations of sulfate, sulfide, and solid organic matter are fairly constant (e.g., in pristine coastal sediments: sulfate = ~27 mM, sulfide <0.1 mM, and organic carbon: 0.5–1%), the quality of organic matter is predicted to have primary significance for MMR (Drott et al., 2007; Lambertsson and Nilsson, 2006). In marine sediments of similar sulfate levels, MMR can vary over a large range, approximately several orders of magnitude, in response to the amount and lability of organic matter undergoing bacterial decomposition (Westrich et al., 1984). Laboratory experiments have also demonstrated that the reactivity or lability of organic matter controls sediment bacterial activity (Pallud and Van Cappellen, 2006). In general, organic matter of terrestrial origin, on a per carbon basis, is less easily degraded than is material of marine origin, due to the presence of recalcitrant biopolymeric materials (e.g., lignin and cellulose) (Freudenthal et al., 2001). Nevertheless, few studies have yet explored the relationship between lability of organic matter and Hg(II) methylation potential (Drott et al., 2007; Kainz et al., 2003).

In the present study, we evaluated the importance of the lability of sediment organic matter in the control of Hg(II) methylation potential in sulfate-rich marine sediments. To equalize the control of sulfate, sulfide and solid organic matter over MMR, sediment cores were selected from two shallow coastal sites characterized by similar concentrations of sulfate (27 ± 1 mM), sulfide (<0.1 mM), and organic matter (0.87 ± 0.4%). Mercury methylation potential was determined by anaerobic incubation of stable isotopes of Hg(II) and the total organic carbon to total nitrogen (C/N) ratio was used as an indicator of lability of sediment organic matter. The overall aim of our study is to understand the biogeochemical factors important for Hg(II) methylation rate in pristine coastal sediments that have comparable levels of sulfate, sulfide and solid organic matter.

2. Methods and materials

2.1. Study areas

The Venice Lagoon, located in the northern part of the Adriatic Sea, is the largest lagoon in the Mediterranean. It has an average depth of 1 m and a surface area of 549 km^2, 40% of which consists of tidal marshes, islets, and fish farms (Bloom et al., 2004; Han et al., 2007). Industrially discharged Hg from the petrochemical zone of Porto Marghera from 1950s to 1980s is widely distributed in the sediments of the northern basin (Bloom et al., 2004; Pranovi et al., 2003). The study area consists of two sites (SS1 and S2) in the northern lagoon that have approximate water depths of 1.4 m. Surface sediment of site SS1 contains less organic C (0.4–0.8%) and more sand (silty–clayey sand) compared with that of S2 (1.1–1.2% organic C and clayey–sandy silt) (Han et al., 2007).

2.2. Sample collection

Sediment samples were collected in acid-cleaned polypropylene cores (10 cm diameter and 30 cm long) in May and November 2006. All sediment cores were collected with sufficient overlying water to allow recovery of the actual surface sediment. Within 24 h after collection, cores were extruded and sectioned in an N_2-filled glove box at intervals of 2.5 cm for the 0 to 10 cm layer, and 5 cm for the 10 to 20 cm layer. Approximately half of the sediment slices were sealed in amber glass vials under N_2 and transported to the laboratory in a portable electric cooler (~4 °C) for Hg(II) methylation rate experiments. Mercury methylation experiments were carried out within several days of the sampling date. The remaining sediment slices were stored frozen for analyses of sedimentary Hg and MMHg. After extrusion and sectioning in the glove box, pore water was extracted by centrifugation at approximately 5000 rpm. After filtration (0.45 μm) of pore water under anaerobic conditions, approximately 20 cm^3 of the filtered pore water sample was used for analyses of dissolved sulfide, sulfate, alkalinity, and total Hg.

2.3. Sample analyses

For the analyses of total Hg in sediments, approximately 1 g of sediment was digested overnight in Teflon® bottles at room temperature with 8 cm^3 of 12 N HCl and 2 cm^3 of 14 N HNO_3 then diluted in 500 cm^3 Milli-Q water (Choe et al., 2004). Only aliquots of sediment digests (0.1–0.3 cm^3) were used to quantify total Hg concentrations. Overall precision and accuracy are presented in Table S1 (Supplemental Information). Water content of sediments was determined separately to transform the concentrations of Hg and MMHg expressed as g-wet sediment to g-dry sediment. For the analyses of total Hg in pore water, acid-preserved (0.5% HCl solution) samples were oxidized using ultraviolet (UV) irradiation (eight lamps of 15 W each) for 24 h prior to quantification by cold vapor atomic fluorescence spectrometry (CVAFS) (Choe et al., 2004; Gill and Bruland, 1990).

Monomethyl Hg in sediments was extracted as described in Choe et al. (2004). Approximately 1 g wet sediment was mixed with 5 cm^3 acidic KBr solution, 1 cm^3 of 1 M $CuSO_4$ solution, and 10 cm^3 of CH_2Cl_2. After a 2 h reaction at room temperature, samples were vigorously shaken for an additional hour on a mechanical shaker. After centrifugation for 20 min at 3000 rpm, a 2 cm^3 aliquot of the CH_2Cl_2 layer was pipetted into acid-cleaned 60 cm^3 Teflon distillation vials, and then 40 cm^3 of Milli-Q water was added to each vial. Distillation vials were placed into a heating block held at 45 °C and solutions were purged with N_2 until complete volatilization of CH_2Cl_2 had occurred. Monomethyl Hg extracted from sediment samples was quantified by cold vapor atomic fluorescence spectrometry following the aqueous phase ethylation using sodium tetraethylborate and GC separation (Choe et al., 2004). The matrix spike recovery and the certified reference material recovery are presented in Table S1, Supplemental Information.

The determination methods of alkalinity, sulfate, and sulfide were performed as described by Gieskes et al. (1991). Briefly, alkalinity was determined based on an electrometric titration of pore water samples with dilute 0.1 M HCl. The nephelometric method was used for the determination of dissolved sulfate, and sulfide was determined by a colorimetric method (Gieskes et al., 1991).

The Hg(II) methylation assay used a tracer incubation method using Hg stable isotopes with a cold vapor generation system interfaced to an inductively coupled plasma–mass spectrometer, as described in Hammerschmidt and Fitzgerald (2004). In our method, a ^{200}Hg working solution, diluted from $^{200}Hg(NO_3)_2$ with filtered overlying water, was added to sediment samples at concentrations of 2 ng ^{200}Hg g^{-1} wet sediment under a N_2 saturated atmosphere. This concentration range corresponds to 0.5% to 2% of the natural Hg concentrations in Venice Lagoon sediments. The sediment samples were incubated under anoxic conditions for 4 h at field temperatures, after which sediment samples were frozen at −80 °C. The concentration of $MM^{200}Hg$ in incubated sediment was determined using an inductively coupled plasma–mass spectrometer interfaced to a cold vapor generation system. The MMR was calculated as the amount of Hg methylated per hour, using Eqs. (1) and (2). More details

regarding the theoretical calculation are available in Hintelmann et al. (1995).

$$\mathrm{MMR}\left(\%\mathrm{h}^{-1}\right) = \sum \mathrm{MM}^{200}\mathrm{Hg}_{sp} \times 100 / \left({}^{200}\mathrm{Hg}_{sp} \times \text{hours of incubation}\right) \quad (1)$$

$$\begin{aligned}\sum \mathrm{MM}^{200}\mathrm{Hg}_{sp} &= \mathrm{MM}^{200}\mathrm{Hg}_{sp} / \mathrm{A}_{200} \\ &= \left(\Sigma\mathrm{MM}^{198}\mathrm{Hg} - \Sigma\mathrm{MM}^{200}\mathrm{Hg} \times \mathrm{R}_n\right) / \left(\mathrm{R}_{sp} - \mathrm{R}_n\right) \times \mathrm{A}_{sp}\}\end{aligned} \quad (2)$$

where $MM^{200}Hg_{sp}$ is the newly produced MMHg from the spike injection, $^{200}Hg_{sp}$ is the amount of $^{200}Hg(II)$ spiked in the sediment sample, A_{200} is the abundance of isotope ^{200}Hg in the spike solution, $\Sigma MM^{198}Hg$ is the total concentration of $MM^{198}Hg$ (the sum of $MM^{198}Hg$ originally present in the sediment and $MM^{198}Hg$ newly produced from the spike injection), and $\Sigma MM^{200}Hg$ is the total concentration of $MM^{200}Hg$ (the sum of $MM^{200}Hg$ originally present in the sediment and $MM^{200}Hg$ produced from the spike injection). The R_{sp} is the isotope ratio of the newly produced MMHg, which is calculated from the inorganic Hg isotope ratio measurement in the tracer solution used for spiking (Eq. (3)). The R_n represents the isotope ratio of the unspiked sediment sample (Eq. (4)).

$$\mathrm{R}_{sp} = \mathrm{MM}^{198}\mathrm{Hg}_{sp} / \mathrm{MM}^{200}\mathrm{Hg}_{sp} \quad (3)$$

$$\mathrm{R}_n = \mathrm{MM}^{198}\mathrm{Hg}_n / \mathrm{MM}^{200}\mathrm{Hg}_n. \quad (4)$$

The detection limit of $MM^{200}Hg$ produced is a function of the ambient MMHg concentration (~0.5 ng MMHg g^{-1} dry sediment), the natural abundance of ^{200}Hg, and the precision of the measurement of $^{198}Hg/^{200}Hg$. In this study, the detection limit averaged 1.3 pg g^{-1} with 1.1% coefficient of variation (CV) in the measurement of $^{198}Hg/^{200}Hg$. In most cases, the calculated concentrations of $MM^{200}Hg$ were greater than the detection limit; otherwise, methylation rate was considered as 0% h^{-1}. The precision of the method was 32% CV ($n = 19$) based on duplicate analysis. The MMR determined using Eqs. (1) and (2) should be considered as the Hg(II) methylation potential because we assumed that MMR determined from short-term incubation of Hg(II), namely the initial rate of Hg(II) methylation reaction, represents the net Hg(II) methylation rate. In order to compare the MMR to literature data, the specific Hg(II) methylation rate constant, K_m, was calculated using first-order reaction kinetics: K_m (day^{-1}) = $[MM^{200}Hg]/([^{200}Hg]t)$, where t is incubation time in days (Drott et al., 2007). The extraction method for MMHg from sediment to an aqueous phase and a correction method for carry-over of $^{200}Hg(II)$ during the MMHg extraction process are described in Hammerschmidt and Fitzgerald (2004).

For the measurement of total organic carbon and total nitrogen in sediment, approximately 2 g of sediment was lyophilized overnight in acid-cleaned glass bottles. Approximately 0.2 g of dry sediment was weighed into silver capsules placed in a microtiter plate, and the accurate weight of each sample was recorded. A small amount of dilute HCl was added repeatedly until the release of CO_2 was complete, then the sediment samples were dried at 60 °C, and carefully crimped silver capsules were shipped to the UC Davis Stable Isotope Facility (Davis, CA). At that facility, the carbon and nitrogen mass in dried sediments was measured using an elemental analyzer.

3. Results and discussion

3.1. The depth profiles of organic carbon to nitrogen ratio

When the top 2.5 cm of sediment was compared between SS1 and S2, a greater marine influence was seen in SS1, located close to the Adriatic Sea, as indicated by the lower C/N ratio (mean C/N for SS1: 6.5 and for S2: 7.1; Fig. 1). The C/N ratio characterizes sources of organic matter because the C/N ratio is typically higher in terrestrial vascular plants than in marine algae (Kainz et al., 2003; Meyers and Ishiwatari, 1993). The increase in continental deposition, likely related to the higher silt fraction in S2, seems to affect the C/N ratio of S2 organics. Literature values for the C/N ratio of autochthonous organic matter are similar to those shown here, ranging between 6 and 11, while a larger C/N ratio has been reported for allochthonous organic matter (Liu et al., 2007), which suggests that the sources of SS1 and S2 organic matter were predominantly of marine origin.

Early diagenesis of organic matter mediated by aerobic and anaerobic bacteria modifies the C/N ratio because different components of organic matter degrade at different rates (Lehmann et al., 2002; Meyers and Ishiwatari, 1993). In general, a more rapid degradation occurs for organic matter containing N-rich compounds than for N-poor organic matter, which explains the increasing C/N ratio with depth, as shown in Fig. 1. The overall organic matter content was generally higher in S2 than in SS1 (Table S2, Supplemental Information), but organic matter was more labile in SS1 than in S2, and also more labile in surface than in subsurface layers.

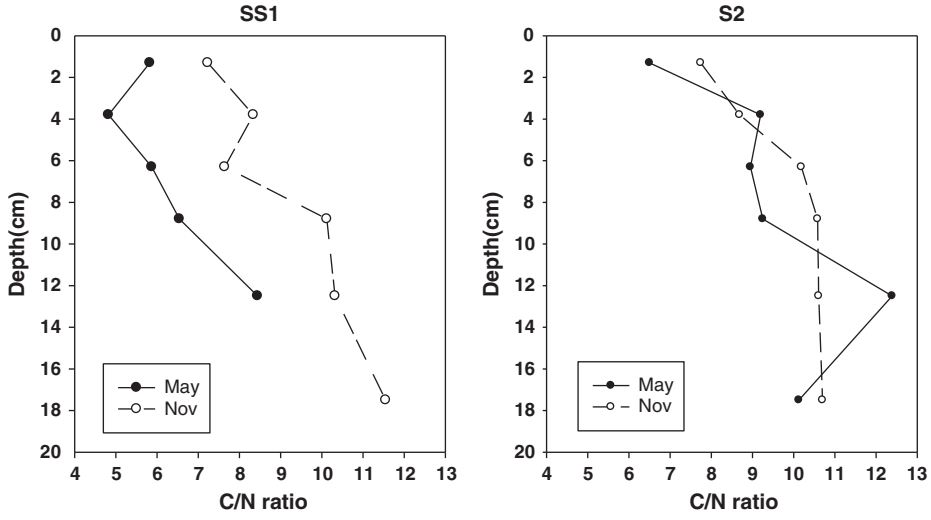

Fig. 1. Depth profiles of total organic C to N ratio in sediments of SS1 and S2.

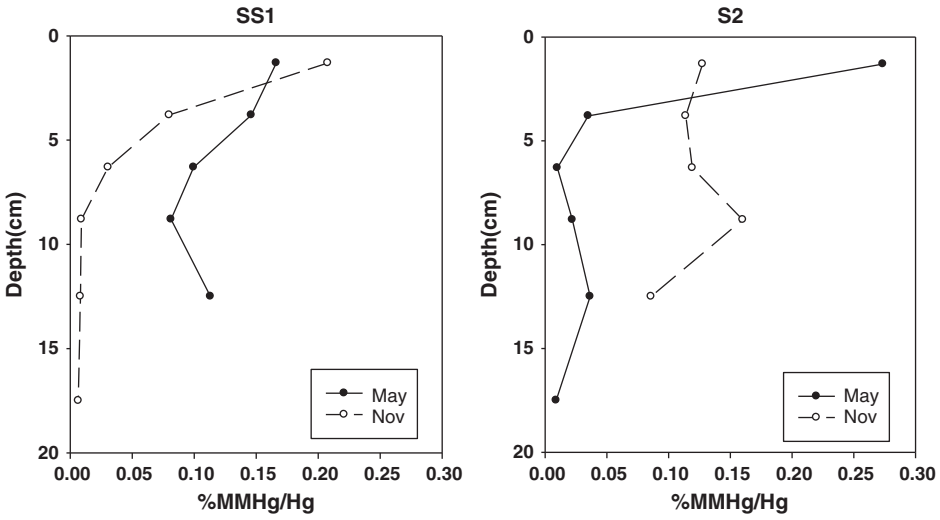

Fig. 2. Depth profiles of %MMHg/Hg in sediments of SS1 and S2.

3.2. The depth profiles of K_m and %MMHg/Hg

Figs. 2 and 3 illustrate the vertical distributions of %MMHg/Hg and the specific MMR constant found in two shallow sites in the Venice Lagoon. In the top sediments, MMHg made up a fraction of total Hg (% MMHg/Hg) that was consistent with values reported for other coastal sediments (0.06–0.7%). Total Hg concentrations (300 ± 123 ng g^{-1}, Table S2, Supplemental Information) were larger than the typical Hg values reported for uncontaminated marine sediments (20–100 ng g^{-1}; Fitzgerald et al., 2007). In a recent review paper by Fitzgerald et al. (2007), %MMHg/Hg was shown to vary in a relatively narrow range, mostly from 0.1% to 0.7%, while total Hg in marine sediments ranged widely from 20 to 5200 ng g^{-1}. Fig. 3 shows that the determined specific MMR constant was in agreement with literature values (e.g., 1.0×10^{-3} day^{-1} to 5.0×10^{-2} day^{-1}, Drott et al., 2007; Sunderland et al., 2004).

In general, specific MMR constants and %MMHg/Hg showed decreasing trends with depth (Figs. 2 and 3), which is consistent with the fact that short-term MMR reflects a long-term accumulation of MMHg (Drott et al., 2008; Mitchell and Gilmour, 2008). Indeed, a significant positive correlation between the specific MMR constant (K_m, day^{-1}) and the %MMHg/Hg was observed in cores collected from both sites (Fig. 4). The *in situ* MMR has been previously reported to be affected by a variety of geochemical factors, mainly availability of dissolved Hg(II) and microbial activity (Gilmour et al., 1998; Hammerschmidt and Fitzgerald., 2004; Han et al., 2008). While the specific MMR constants were mostly higher in the 0–2.5 cm layers (Fig. 3), the dissolved Hg concentrations were generally higher in the subsurface layers (2.5–7.5 cm; Table S3, Supplemental Information). Therefore, microbial activity appears to be associated with high MMR in the surface sediment. This explanation would be reasonable if total Hg in pore water represents mostly inorganic Hg(II) instead of MMHg. Indeed, MMHg content in pore water constituted a minor fraction of total Hg in estuarine and coastal sediments: approximately 10% in the Chesapeake Bay and a nearby slope (Holloway et al., 2009); 19 ± 21% in the San Francisco Bay (Choe et al., 2004); and 30 ± 10% from the New England continental shelf (Hammerschmidt and Fitzgerald, 2006). In Venice Lagoon sediments, MMHg concentration was reported to be approximately 10% of the total Hg in pore water (Han et al., 2007).

Even though we found an overall linear relationship between the MMR and %MMHg/Hg, the moderate nature of the correlation factor ($r^2 = 0.54$) indicates that additional information (e.g., demethylation rate) may be needed for correct prediction of the steady-state MMHg concentration (or %MMHg/Hg). According to King et al. (1999, 2000), Hg methylation and demethylation reach equilibrium conditions in 12

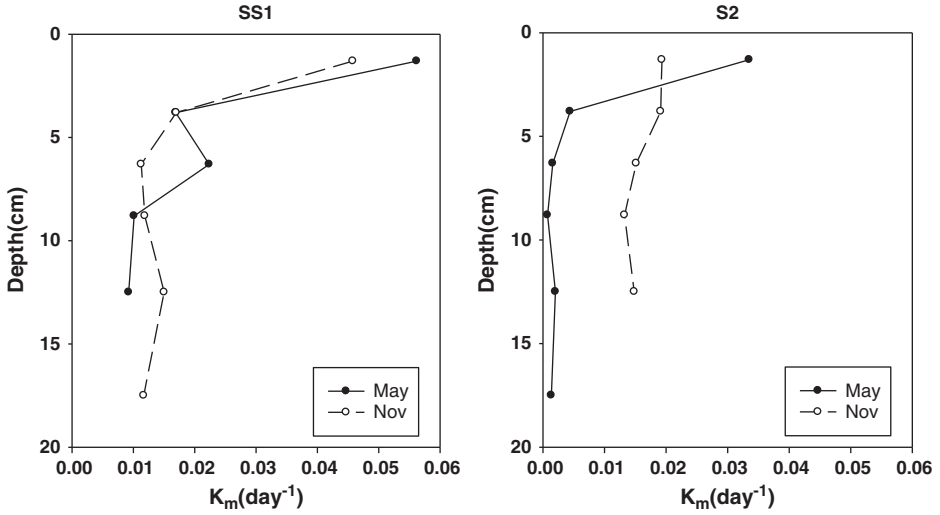

Fig. 3. Depth profiles of specific Hg(II) methylation rate constant (K_m) of SS1 and S2.

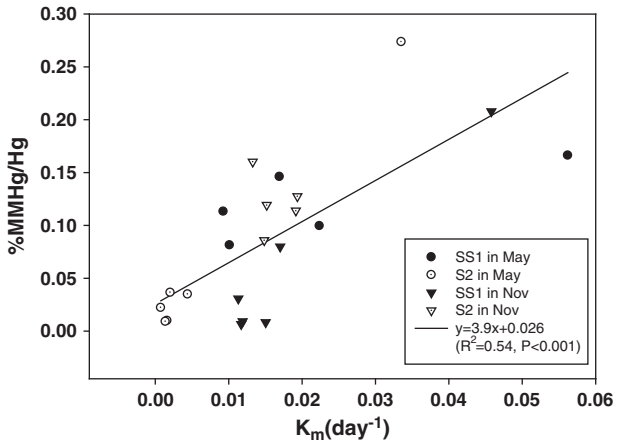

Fig. 4. The relationships between %MMHg/Hg and specific Hg(II) methylation rate constant (K_m) in SS1 and S2 cores.

to 24 h at room temperature; consequently, our measurement only provides the initial rate of Hg(II) methylation reaction. However, we argue that the initial MMR might be a useful proxy for the steady-state MMHg concentration, because site and depth differences of ambient MMHg concentrations were mainly determined by MMR rather than demethylation rate in river and marine sediments (Hines et al., 2000; Warner et al., 2003). For example, consistent demethylation rate constants were detected from Mobile Alabama River Basin sediments dominated by different electron accepting processes (Warner et al., 2003). In the Gulf of Trieste, the demethylation rates exhibited similar values between each site, while MMR and ambient MMHg concentration showed large variations (Hines et al., 2000). On the other hand, demethylation rate constants for Hg-contaminated sites were 20 times higher than those for pristine sites and %MMHg/Hg were lower in the contaminated sites, indicating that demethylation rate is important in control of ambient MMHg concentration in Hg-contaminated sites (Schaefer et al., 2004). In the current study, none of the sampling sites showed notably different Hg levels between SS1 and S2 and between each depth layer (Table S2, Supplemental Information); therefore, we argue that demethylation rates may not be extremely different between each site and depth layer.

3.3. The relationship between %MMHg and C/N ratio

We found a significant negative linear relationship between %MMHg/Hg and C/N ratio (Fig. 5a), and between the specific Hg(II) methylation rate constant and the C/N ratio (Fig. 5b). To our knowledge, this is the first observation of any direct correlation between the quality of organic matter and the MMR in coastal sediments, although indirect results have been previously reported by Drott et al. (2007) and Kainz et al. (2003). Drott et al. (2007) reported that potential Hg(II) methylation rate is a function of a neutral Hg sulfide species (e.g., $Hg(SH)_2$ and HgS), and that the slope of the linear regression model between Hg(II) methylation rate and the concentration of neutral Hg sulfide species increases with decreasing C/N ratio. The highest slope of the linear regression model was found from high-productivity freshwater sediment that had the lowest C/N ratio (Drott et al., 2007), which agrees with the experimental results in the present paper. In addition, Kainz et al. (2003) used source-specific fatty acid biomarkers to identify the quality of organic matter and demonstrated that MMHg concentration is larger when labile organic matter (i.e., algal and bacterial organic matter) is abundant in sediment. In the same literature, the amount of recalcitrant organic matter was found to be unrelated to MMHg concentration in sediments (Kainz et al., 2003).

In addition to microbial activity, microbial structure is known to affect MMHg production (Holloway et al., 2009; Macalady et al., 2000). For example, PLFA (phospholipid fatty acid) biomarkers analyzed in Clear Lake sediments demonstrated that the proportion of *Desulfobacter*-like bacteria among SRB covaried with the MMHg fraction (Macalady et al., 2000). Similarly, MMHg formation in watershed sediments near an Hg mining area was strongly correlated with nutrients and soil moisture concentrations, which affect microbial structure (Holloway et al., 2009). Therefore C/N ratio could possibly be associated with the structure of microbial community as well as the activity.

The amount of total N would be positively correlated to the MMR, if total N content represents the amount of labile N-rich organic matter in sediments and if absolute amount of labile organic matter is an important factor governing MMR. In order to test this possibility, we correlated the MMR constant and %MMHg/Hg to the total N content (Fig. S1, Supplemental Information): no significant correlation was found either between bulk N content and MMR constant or between bulk N content and %MMHg/Hg. Indeed, the depth variability of total N content was not sufficiently large to support the depth variability of MMR. In addition, we found no significant correlation between the MMR (and %MMHg/Hg) and the total organic C content (Fig. S2, Supplemental Information). It appears that the use of organic C to N ratio to predict MMR is more detailed and informative than the use of absolute amount of total N or total organic C. This is perhaps because bacteria use only a small fraction of bulk organic matter.

The negative correlation between C/N ratio and MMR (and %MMHg/Hg) shown in Fig. 5 was demonstrated in SS1 and S2 sediments with constant sulfide and sulfate content. We speculate that the same

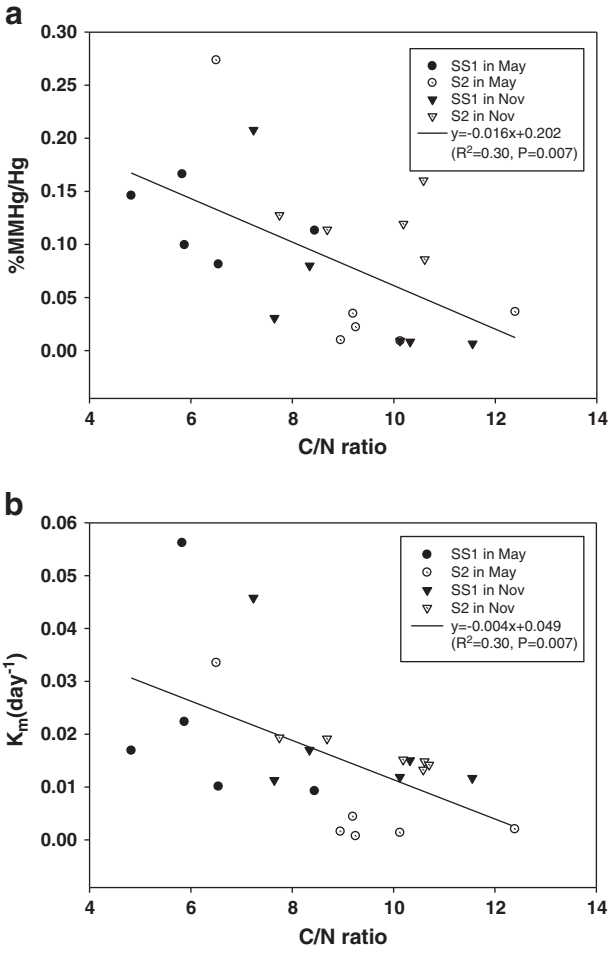

Fig. 5. (a) The relationships between total organic C to N ratio and %MMHg/Hg, and (b) specific Hg(II) methylation rate constant (K_m) in SS1 and S2 cores.

correlation would not be found in sediments with variable sulfate and sulfide content, because MMR is primarily controlled by sulfate and sulfide gradients in sediment pore waters (Benoit et al., 2001; Drott et al., 2007; Holloway et al., 2009). Support for this speculation is shown in Fig. S3, Supplemental Information: the correlation between MMR constant (and %MMHg/Hg) and C/N ratio was not significant for the V1 and V2 sites that have variable levels of dissolved sulfide and sulfate (Table S4, Supplemental Information).

Finally, our detection method for dissolved sulfide has a relatively large detection limit (0.1 mM); therefore, we were not able to discriminate micro-molar level changes in dissolved sulfide in pore water. This caveat should be carefully tested in further studies in order to guarantee that the C/N ratio is consistently associated with the MMR in low sulfide and high sulfate coastal sediments.

4. Conclusion

The organic C to N ratio was negatively correlated with the %MMHg/Hg and specific Hg(II) methylation rate constant in marine sediments (0–20 cm) when the availability of sulfate and sulfide in sediment pore water was maintained at a constant level. The lability of organic matter, determined by its source and level of microbial degradation, is therefore strongly associated with the Hg(II) methylation rate. Fresh organic matter of algal origin that shows lower C/N ratio results in a higher Hg(II) methylation rate when compared to refractory organic matter with a higher C/N ratio. Overall, the C/N ratio appears to be a useful proxy for prediction of Hg(II) methylation rates in sulfate-rich marine sediments.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.scitotenv.2010.10.050.

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