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INORGANIC MERCURY BINDING WITH DIFFERENT SULFUR SPECIES IN ANOXIC SEDIMENTS AND THEIR GUT JUICE EXTRACTIONS

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Abstract—To investigate the roles of different sulfur (S) species in controlling the partitioning and bioavailability of inorganic mercury (Hg) in anoxic sediments, we examined the differential binding of Hg with three key S species in anoxic sediment (mackinawite [FeS], pyrite [FeS_2], and S^{2-}) and then quantified their extraction by the gut juice of deposit-feeding sipunculans *Sipunculus nudus*. A sequential extraction method was simultaneously used to distinguish Hg sorption with different sediment components. All three S-containing sediment components could lead to a high binding of Hg in sediments, but most Hg was sorbed with FeS or FeS_2 instead of formation of Hg sulfide despite the presence of S^{2-} or humic acid. The gut juice extraction was relatively low and constant whenever FeS and FeS_2 were in the sediment, indicating that both FeS and FeS_2 controlled the Hg gut juice extraction and thus bioavailability. Mercury sorbed with FeS_2 had higher gut juice extraction than that with FeS, while Hg sulfide was not extracted, strongly suggesting that Hg sorbed with FeS_2 was more bioavailable than that with other S species. Mercury sorbed with FeS had very low bioavailability to sipunculans at a low Hg:S ratio in the sediment but was more bioavailable with increasing Hg:S ratio up to a maximum (~1:10, mole based). The present study showed that different S species (FeS, FeS_2) and Hg:S ratios significantly affected the binding and bioavailability of Hg in anoxic sediments.

Keywords—Anoxic sediment Mercury mackinawite Pyrite sulfide

INTRODUCTION

Mercury (Hg) is a highly toxic metal and poses great risk to organisms in aquatic systems. Inorganic Hg is the dominant form of Hg in sediments [1,2] and could be transformed to methylated Hg both in sediments and within the organisms [3; www.nap.edu/openbook.php?isbn=0309086256]. Although methylated Hg is a more toxic species and could be more readily bioaccumulated [4], most of the Hg accumulation in marine deposit-feeders like polychaetes could be due to inorganic Hg uptake because of its much higher concentration in the sediments [5]. The sorption of Hg with different sediment components greatly influences the binding and bioavailability of Hg under oxic conditions [6,7]. In oxic sediments with low Fe and Mn oxides content, clay and organic matter (humic or fulvic acid) controlled the binding and bioavailability of Hg to deposit-feeding sipunculans [7]. In contrast, the binding and bioavailability of Hg in anoxic sediments are not yet fully understood, and most studies on Hg bioavailability in anoxic sediments focused on the methylation of Hg by bacteria [3].

A number of studies have examined the behaviors of trace metals bound with acid volatile sulfide, including their bioavailability [3]. However, investigation on the sorption and bioavailability of Hg-sulfur (S) or Hg–acid volatile sulfide is rare, partly because methylated Hg is more bioavailable than inorganic Hg and draws more attention. In anoxic sediments, Hg can be adsorbed onto or coprecipitated (these two processes were considered together and mentioned as sorption in the present study) with the sulfide minerals [8,9]. It has been suggested that the S content in anoxic sediments plays a critical role in controlling the binding, speciation, and bioavailability of metals [3,10]. However, the S pool in anoxic sediments may be composed of several S-containing compounds, including mackinawite (FeS), pyrite (FeS_2), greigite, and dissolved sulfide species (e.g., S^{2-}, HS^-, and H_2S). Pyrite could be formed by the reaction of FeS with elemental S, hydrogen sulfide, or other oxidants. It is more abundant when high S^{2-} concentration favors FeS_2 formation [11,12] or in areas around the S^{2-}-S^{2-}–SO_4^{-2} boundary where FeS_2 has a very high thermodynamic stability while FeS is not formed [11]. Greigite is the product of FeS oxidation in the presence of trace oxygen [11] and is not considered in the present study. The variable composition of the S pool may influence the binding and bioavailability of trace metals in sediments if metals sorbed with different S species have different mobilities. No study has compared the binding of Hg with the different S species and the different bioavailability to deposit-feeders.

In the present study, several S species were specifically compared, i.e., FeS, FeS_2, and S^{2-} (which could exist as HS^- and H_2S in the dissolved phase, as shown later), as the key anoxic sediment components that influenced the binding and bioavailability of inorganic Hg in the sediments. Radioactive and stable Hg were spiked into the artificial anoxic sediments, which were composed of different components of FeS, FeS_2, S^{2-}, humic acid (HA), quartz, clay, and calcium carbonate. The five-step sequential chemical extraction method [13] was used to determine the Hg solid speciation in the sediments and thus the internal sorption of Hg with different sediment components. The bioavailability of Hg in sediments to deposit-feeders was quantified by gut juice extraction of sipunculans, which quantified the fraction of Hg solubilized by the gut juices from sediments [14]. Digestive solubilization of sediment-bound metals in the gut of deposit-feeders is a key process in metal assimilation from food and thus bioaccumulation [3], and the gut juice extraction method has been used

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frequently to assess the bioavailability of sediment-bound metals and organic pollutants, as well as in risk assessments [3,14,15]. Besides S speciation, we also examined the effects of the ratio between Hg and total S (based on the S in FeS, FeS_2, and S^{2-}) in anoxic sediments on the binding and gut juice extraction of Hg.

MATERIALS AND METHODS

Chemicals and gut juices

The FeS, silicon dioxide (quartz), montmorillonite (clay), sodium sulfide nonahydrate, and mercuric chloride ($HgCl_2$) were purchased from Sigma-Aldrich. The FeS_2 was purchased from Tongling Huaxin minerals industry (Anhui). The calcium carbonate was from Nacalai Tesque. The HA (Category No. 1S102H) was from the International Humic Substance Society. All particles were less than 100 μm in diameter. The gamma radioactive isotope ^{203}Hg ($t_{1/2}$ = 46.6 d, $^{203}HgCl_2$ in 0.1 N of hydrogen chloride, with an initial specific activity of 45.1 GBq/g) was purchased from Isotope Products Laboratories. The natural seawater (pH was ~8.0) was filtered through 0.22-μm nitrocellulose membranes (Millipore) before use. Sipunculans *Sipunculus nudus* (5–7 cm in body length), deposit-feeders living in the surface layers of sediments, were collected from Ting Kok, Hong Kong. All sipunculans (~100 individuals) were dissected immediately after being brought to the laboratory, and their gut juices were collected. The pooled gut juices containing sediment particles were centrifuged at 6,297 *g* for 20 min at 4°C to remove any particles and then stored at −80°C before being used as an extractant. Approximately 30 ml of gut juices were recovered from the dissected sipunculans. The pH of the gut juices was approximately 8.0.

Preparation of artificial sediments and radiolabeling

Twelve artificial sediments with four different groups (FeS group, FeS_2 group, mixed particle group, and HgS group) were used in the present study and spiked with the radioactive Hg isotope. For the FeS group, the FeS particles were spiked with Hg, S^{2-}, or HA: i.e., FeS (FeS was spiked with Hg only), FeS and S^{2-} (FeS, S^{2-}, and Hg were mixed at the same time, and then S^{2-} was added as sodium sulfide nonahydrate to reach 0.1 mmol/L as in other sediments except when specified), and FeS and HA (FeS, HA, and Hg were mixed at the same time, and then 50 mg/L of HA was added in the mixtures as in other sediments). For the FeS_2 group, the FeS_2 particles were spiked with Hg, S^{2-}, or HA, the same combination as the preceding FeS group, except FeS was replaced by FeS_2. For the mixed particle group, the control treatment contained 2.5% FeS, 2.5% FeS_2, 0.1 mmol/L of S^{2-}, HA, 55% quartz, 30% clay, and 10% calcium carbonate (all percentages of particles were based on dry weight). The other mixture treatments were omitted of a specific sediment component (i.e., $-S^{2-}$, −HA, −FeS, and −FeS-FeS_2). Finally, the HgS group was prepared by reacting Hg and S^{2-} at a 1:1 ratio.

In each treatment, 10 mg (dry weight) of sediment resuspended in filtered natural seawater were used. Mercury isotope was added into the mixtures, and the initial spiked Hg concentration calculated based on the specific activity of the Hg isotope was 2.69 μg of Hg per gram of dry weight. The pH of liquid in all treatments during the radiolabeling and gut juice extraction was approximately 8.0 and was not adjusted. The solid-to-liquid ratio during the radiolabeling (referred to the mixing of particles, S^{2-}, and HA with the Hg isotope in all treatments) was 10 mg to 1 ml. The radiolabeling lasted for 1 d in the dark with constant shaking at 600 rounds per min by a Thermolyne Maxi Mix III vortex mixer (the same was used later for all shaking), after which the mixture was centrifuged at 6,297 *g* for 20 min before sequential extraction and gut juice extraction. Although Hg binding in sediments could increase with contact time between Hg and sediments [6], 1-d contact time was chosen to minimize the extent of Hg methylation (usually less than 2% [16]). The radioactivity in the radiolabeled sediments and seawater were determined with a gamma detector (1480 Wallac WIZARD 3″ Automatic Gamma Counter). For all radioactive measurements, the counting time was set at a maximum of 5 min to minimize the counting error (less than 5% for most samples). All operations except the centrifugation and radioactivity measurements were conducted in a glove bag filled with nitrogen gas (99.995%). The seawater was bubbled with nitrogen gas overnight before use, and the dissolved oxygen concentration in the filtered seawater after deoxygenating was less than 0.1 mg/L.

Determination of Hg solid speciation in sediments

To distinguish sorption of Hg with different S species (e.g., FeS and FeS_2) in sediments, Hg in sediments was sequentially extracted by different extractants (10 mg of sediment per 1 ml of extractant, dry weight). Mercury in the sediments was separated into three geochemical phases [13,17]: organocomplexed (extracted by 1 N of potassium hydroxide, F3, including, e.g., Hg–organic complexes, methylated Hg, or Hg_2Cl_2), strongly complexed (extracted by 12 M of nitric acid, F4, including, e.g., element Hg, Hg_2Cl_2, Hg associated with amorphous organosulfur, or Hg in mineral lattice), and Hg sulfides (F5, solids remained after nitric acid extraction for F4). A rinse step by the same extractant was applied after each step of extraction, except for the final fraction (F5). Detail sequential extraction has been described in Bloom et al. [13]. Mercury in the water-soluble (F1) and stomach acid–soluble phases (F2) was not identified since the distribution of Hg in these two phases was very low (generally <5%) based on our preliminary experiments and previous studies [6,7,13,18,19]. The F3 extractant (1 N of potassium hydroxide) was bubbled with nitrogen gas before use to avoid oxidation during the sequential extraction. The radioactivity of the Hg isotope in each geochemical phase was quantified by a gamma detector, and the overall recovery rate (Hg in F3 + F4 + F5 per Hg in the sediments before the sequential extraction) was approximately 110% according to mass balance. Mercury distribution (%) in different geochemical phases was normalized to 100%. Mercury solid speciation in the present study mainly referred to the sorption of Hg with different sediment components (e.g., FeS or FeS_2).

Gut juice extraction

Gut juice extraction [14], which identifies the bioavailable metals as the fraction solubilized from sediments by gut juices, was used in the present study to assess the bioavailability of Hg in different artificial sediments. Mercury in sediments was extracted by the gut juices at a ratio of 25 mg/ml (sediment dry weight per gut juice volume, 10 mg of sediment in a 2-ml Eppendorf tube containing 0.4 ml of gut juices) for 4 h in the dark with constant shaking in glove bags filled with nitrogen gas. After that, the mixture was centrifuged at 6,297 *g* for

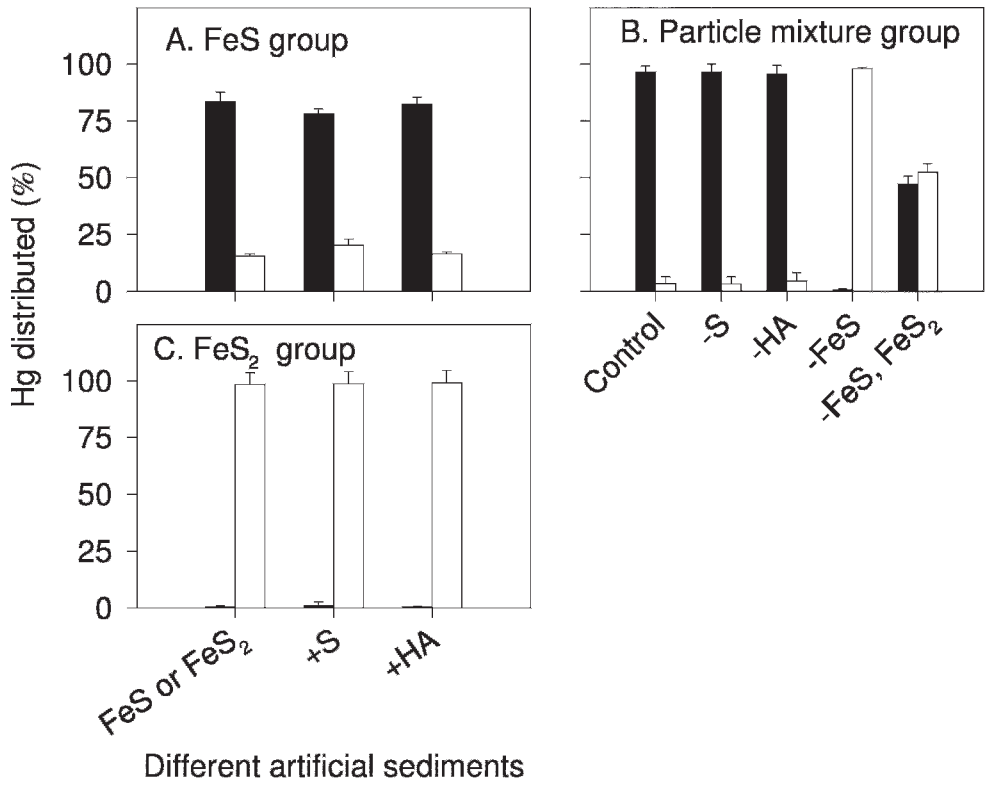

Fig. 1. Relative distribution of mercury in different geochemical phases quantified by the sequential chemical extraction (F3: organocomplexed, black bars; F4: strongly complexed, empty bars) in different groups of sediments (mackinawite or pyrite group sediments, mixed particles). Mean + standard deviation ($n = 2$).

20 min at 4°C and the radioactivity in the gut juices or sediments was measured.

Hg:S ratio

The present study tested the effects of the Hg:S ratio in sediments on the binding and gut juice extraction of Hg. Different concentrations of Hg (containing a constant amount of Hg isotope and different amounts of stable Hg) were spiked into three different artificial sediments with a fixed S content—FeS–quartz mixture, FeS_2–quartz mixture, and quartz—to result in different initial Hg:S ratios (mole added to mole in sediments). Quartz, the most common and dominant component of sediments, was coated with 1 g/L of HA for 1 d and washed before mixing with FeS or FeS_2 and spiking with Hg as described earlier. The initial Hg:S ratios (as the added Hg:S ratios, to be distinguished from the real Hg:S ratios in the artificial sediments after the radiolabeling and washing steps) were 0.000132, 0.1, 0.2, 0.5, 1, 2, 5, and 10. The calculated S content in the artificial sediments was 100 μmol/g. Procedures for radiolabeling and gut juice extraction (4 h) were as described earlier.

RESULTS

Hg binding and solid speciation in anoxic sediments

Despite the varied sediment composition (FeS, FeS_2, S^{2-}, or HA), the binding of Hg in sediments containing any of the three S-containing compounds was comparable and high, i.e., more than 98% of the radiolabeled Hg was sorbed with the sediment in most treatments. The solid speciation of Hg in different artificial sediments was also quantified by sequential extraction (Fig. 1) to distinguish Hg sorption with different sediment components. For the FeS group, most Hg was in the F3 phase (organocomplexed, >78%), and the presence of other components (S^{2-} or HA) had little effect on Hg solid speciation. In contrast, for the FeS_2 group, nearly all Hg was in the F4 phase (strongly complexed, >98%), despite of the presence of other components (S^{2-} or HA). For the particle mixtures, Hg was mostly in F3 in all treatments with FeS content (control, $-S^{2-}$, and −HA treatments), while the elimination of FeS led to a major distribution in F4. In the particle mixtures without FeS and FeS_2 but with S^{2-}, Hg was distributed in both the F3 and the F4 phases. Mercury sulfide, reacted by combining Hg and S^{2-} at a 1:1 ratio (mole basis), was in the F5 phase (Hg sulfides, not shown in the figure).

Hg extraction by gut juices

Gut juice extraction of sediment-sorbed Hg is shown in Figure 2. The percentages of Hg extracted by the gut juices (extraction efficiency) were calculated as the Hg in the gut juices after extraction per Hg in the sediments before extraction. Only the 4-h extraction data are presented in Figure 2. After 4 h, the extraction efficiencies leveled off. Mercury was hardly extracted when sorbed with FeS or reacted with S to form HgS, but the extraction efficiency was higher (7%) when Hg was sorbed with FeS_2. When FeS and FeS_2 were present in the sediment mixtures (control, $-S^{2-}$, and −HA treatments), the differences in extraction efficiencies were minor (12–14%). When FeS or both FeS and FeS_2 were eliminated from the mixture, the gut juice extraction efficiency increased to 20 to 23%.

Hg:S ratio in sediments

In the FeS–quartz mixture, the Hg concentration and Hg:S ratio in sediments after radiolabeling increased (the maximum value was ~1:10, mole basis) with added Hg until the added

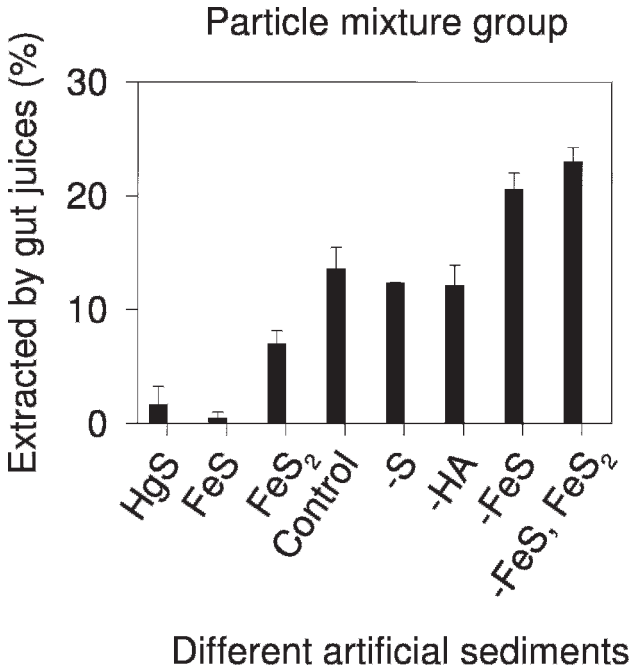

Fig. 2. Percentages of mercury extracted by gut juices of sipunculans from different artificial sediments. Mean + standard deviation ($n = 2$).

Hg:S ratio reached 1, after which the binding of Hg leveled off (Fig. 3, top panels). Both the Hg concentration and the Hg:S ratio reached in the artificial sediments after radiolabeling were much higher in the FeS–quartz mixture than in the FeS_2–quartz mixture or the quartz particles.

With an increase in Hg concentration and thus a higher Hg:S ratio in the FeS–quartz mixtures, the percentage of Hg extracted by gut juices increased to as much as 53% until the added Hg:S ratio was higher than 1 (Fig. 3). When the added Hg:S ratio exceeded 1:1, the gut juice extraction efficiency increased sharply from 27 to 50% and then became relatively constant despite a further increase in the Hg:S ratio. At the lowest Hg concentration, the gut juice extraction was more efficient in the FeS_2–quartz mixture (28%) or quartz (42%) than in the FeS–quartz mixture. The percentages of Hg extracted from the FeS_2–quartz mixture or the quartz particles at higher Hg:S ratios were not included in Figure 3 because the radioactivity in those sediments was too low to give a meaningful estimate.

DISCUSSION

Hg sorption and complexation in anoxic sediments

It was possible that FeS and FeS_2 could be changed to each other during the radiolabeling period or reacted with other ligands in the mixtures [11], which may potentially affect the interpretation of the exact S speciation in the artificial sediments. However, the distinct Hg solid speciation in the FeS and FeS_2 groups, as well as the constant distribution pattern of Hg in F3 or F4 despite of the presence of S^{2-} or HA, indicated the different sorption of Hg with these two S-containing compounds. Thus, it was likely that most FeS and FeS_2 remained unchanged within the short radiolabeling period (1 d). Besides, the organic matter (HA) used in most treatments may inhibit the reaction of FeS with H_2S to form FeS_2 [11]. Overall, these artificial sediments may be considered as mixtures of different S species and their reaction products but were dominated by certain S species (e.g., FeS or FeS_2). In addition, the dissolved FeS and FeS_2 in the seawater and the possible Hg sorption with these dissolved species was not directly measured, but it was assumed that nearly all Hg was present as the solid phase (>98% in most treatments).

The binding of Hg in artificial anoxic sediments was controlled by FeS, FeS_2, and S^{2-}, considering the high and comparable Hg binding in the sediments whenever any of the three S-containing compounds was presented. To distinguish

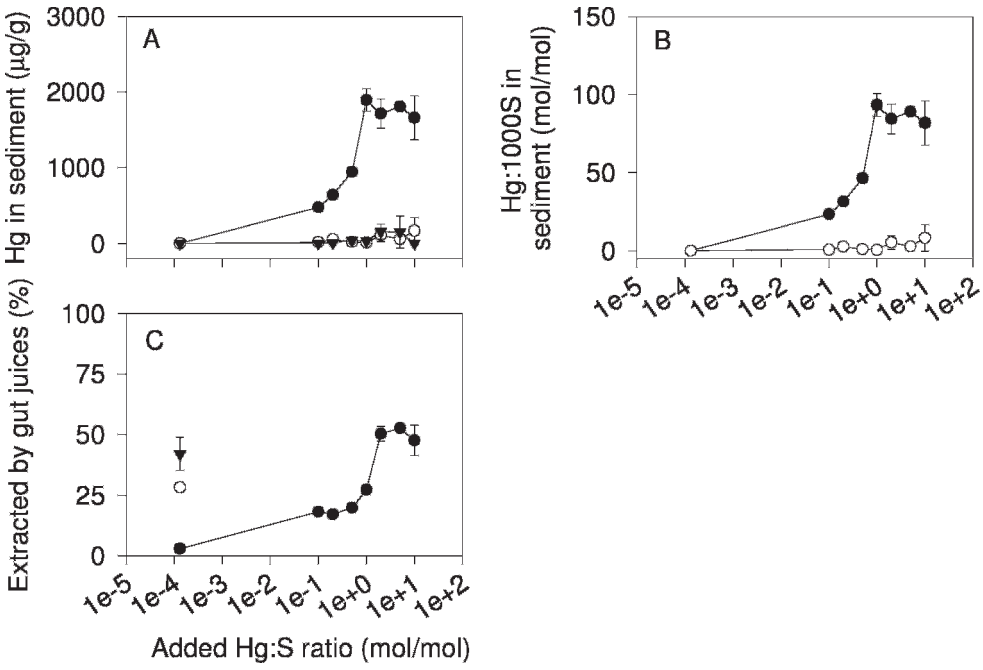

Fig. 3. Mercury (Hg) concentrations (**A**), Hg-to-sulfur (S) ratio (**B**), and percentage of Hg extracted by gut juices of sipunculans (**C**) in different artificial sediments with different added Hg:S ratios. Log scale on the *x* axis. Mean ± standard deviation ($n = 2$). ● = mackinawite + quartz; ○ = pyrite + quartz; ▲ = quartz.

the Hg sorption with different components (e.g., FeS, FeS_2, or the others) in the artificial sediments, the sequential extraction method was used to confirm the distinctive solid speciation of Hg sorbed with different S species. The sequential chemical extraction method has been used widely in recent years to indicate the Hg solid speciation and sorption with different solids within particles, soils, or sediments [6,7,17,18,20]. This method has some limitations, including its selectivity for different Hg species, the extraction of certain Hg species in several steps (e.g., Hg–organic matter complexes could be extracted in both F3 and F4), and the terminology of a certain phase that could include other species (e.g., Hg-organic matter; organocomplexed phase could also include inorganic Hg species like Hg_2Cl_2). However, the differential distribution of Hg in different phases based on this method may help us differentiate the Hg sorption with different solids.

Although the exact speciation of S in the artificial sediments was not known, it was possible to distinguish the sorption of Hg in the sediment mixtures dominated by certain S species (e.g., FeS or FeS_2) given their different distributions in F3 or F4. The desorption of Hg from FeS by potassium hydroxide (in F3) could be due to the increased dissolution of FeS in alkaline environment [21] and thus the release of Hg from solids, while the desorption of Hg from FeS_2 by nitric acid (in F4) may be caused by the oxidation of FeS_2 [11]. However, further studies should be carried out to investigate the reactions involved during sequential extraction. Based on the different distributions of Hg in different artificial sediments (e.g., Hg sorbed with FeS was mainly in F3, Hg sorbed with FeS_2 was mainly in F4, and Hg reacted with S^{2-} was mainly in F5), we found that Hg was mainly sorbed with FeS or FeS_2. The high and comparable percentages of Hg in F3 (in which Hg was less bioavailable than that in F4 [6]) in the FeS group, and in the mixed particle group with FeS presence suggested the strongest sorption ability of FeS with Hg among the studied components and that most Hg was sorbed with FeS instead of directly reacting with those dissolved S species like S^{2-}, HS^-, or H_2S to form HgS. Previous studies also suggest that FeS could be the major sink for metals including Hg during early diagenesis in anoxic sediments by adsorption and coprecipitation [22]. Similarly, for the FeS_2 group and mixed particle group with FeS_2 presence (but without FeS), nearly all Hg was distributed in the F4 phase despite of the presence of S^{2-} or HA, indicating that most Hg was sorbed with FeS_2 but not precipitated as HgS. A previous study also showed that Hg could be precipitated with FeS and FeS_2 in sulfidic sediments instead of existing as pure HgS [23]. The results of the present study suggest that a significant proportion of Hg could be sorbed with FeS_2, especially in those sediments with high FeS_2 and low FeS. In fact, FeS_2 usually contributed most to the total inorganic reduced S in sediments [11], and nonsilicate bound metals including Hg may coprecipitate with FeS_2 near the sediment–water interface [24].

It has been suggested that sulfide dominated organic matter in the competition for Hg sorption because of its stronger affinity for Hg [25]. Based on the Hg solid speciation quantified in the present study (most Hg was distributed in phases other than F5), we found that Hg did not exist as HgS in almost all of the treatments (except the Hg + S^{2-} treatment). Even in sediments added with S^{2-} (but without FeS or FeS_2), Hg was distributed in both the F3 and the F4 phases, which could be explained by the formation of complexes involving Hg, sulfide, and other ligands like organic matter [23,26–28] and the inhibition of HgS formation in the presence of organic matter and chloride [9,29]. Besides, the presence of organic matter like HA may inhibit the coagulation of HgS and the formation of HgS precipitates and may lead to the extraction of HgS (perhaps nanoparticles) in earlier phases (F3 or F4).

Hg bioavailability in anoxic sediments

The present study clearly showed that Hg extraction by gut juices (quantifying the bioavailability of Hg to deposit-feeders) from anoxic sediments was controlled by both FeS and FeS_2. Despite the presence of HA and S^{2-}, the extraction efficiency of Hg was comparable in particle mixtures with FeS and FeS_2, which could be explained because most Hg was sorbed with FeS or FeS_2 in the artificial sediments. The efficiencies of extracting Hg by gut juices from artificial anoxic sediments (0–23%) were generally lower than those from oxic sediments (7–61%) [6,7] since the presence of either FeS or FeS_2 decreased the extraction efficiency. The elimination of either component increased the Hg extraction by gut juices. Such an increase was more obvious when FeS was eliminated, indicating that Hg-FeS could be less bioavailable than Hg-FeS_2 at the experimental Hg:S ratio. Also, Hg sorbed with pure-phase FeS_2 had higher extraction efficiency than Hg with pure-phase FeS, partly due to the oxidation of FeS_2 and thus the release of Hg during the gut juice extraction [24]. Consequently, in anoxic sediments dominated by FeS_2 (e.g., high S^{2-} concentration, which favors FeS_2 formation [11,30]), the mobility and bioavailability of Hg could be higher than with high FeS content. In contrast to FeS and FeS_2, HgS was very refractory and resistant to gut juice extraction. Because little Hg existed as HgS, the reaction of Hg with S^{2-} (e.g., HS^- or H_2S in the dissolved phase) was not important in determining the Hg extraction efficiency from sediments in the presence of FeS or FeS_2. However, when both FeS and FeS_2 were eliminated from the sediments, the presence of S^{2-} led to high binding of Hg in sediments and greatly increased the gut juice extraction of Hg, which was presumably due to the simultaneous sorption of Hg with other solids or organic matter in the sediments besides sulfide in the absence of FeS and FeS_2.

Hg:S ratio in anoxic sediments

A wide range of Hg concentrations in sediments (~2–1,896 μg/g after radiolabeling) was used in this Hg:S ratio experiment to create different Hg:S ratios in the sediments. Although these high Hg concentrations are rare in real-environment settings (except in a few cases such as mining areas, where Hg concentrations can be as high as 30,000 μg/g) [31], the present study provides information on the changes in the binding of Hg and its bioavailability as a function of the Hg:S ratio in sediments and could be useful in conditions where S concentrations are relatively low. No previous study has reported the saturating ratio between Hg and S in anoxic sediments and its influence on Hg bioavailability, although a recent study quantified the Hg sorption with FeS at different Hg:FeS ratios [32]. In that study using FeS nanoparticles for Hg sorption [32], it was found that with the increase of the Hg:FeS ratio Fe(II) was released from FeS to form Fe hydroxides at the surface of FeS and inhibited the further formation of HgS while absorbing Hg.

At the lowest Hg:S ratio in the present study, the Hg-S interactions (probably Hg substituted Fe from FeS on particle surface) in FeS–quartz sediments led to an extremely low extraction of Hg by gut juices. At these low Hg:S ratios in

sediments (less than 1:10), Hg may be adsorbed on the FeS surface with Fe hydroxides (released from FeS [32]) as Hg_2Cl_2, which was consistent with the observations that most Hg with FeS was distributed in F3 (Hg_2Cl_2 could be distributed in F3 [13]). So, with an increasing Hg:S ratio in FeS–quartz sediments, more Hg was sorbed with Fe (hydro)–oxides and thus became more bioavailable. A linear relationship existed between gut juice extraction and Hg:S ratios reached in sediments at lower Hg:S ratios (less than the maximum value 1:10, $r^2 = 0.812$). With the further increase of added Hg:S ratios, Hg adsorption onto the FeS surface could become saturated, which explained the constant Hg:S ratios (1:10) in FeS–quartz mixtures despite of the increase of added Hg. Mercury extraction by gut juices increased sharply when the added Hg:S ratio was higher than 1:1, implying the spillover of Hg from stronger sorption sites on FeS particles to weaker ones on quartz particles, which increased the amount of bioavailable Hg.

CONCLUSION AND IMPLICATIONS

Although the composition of S in anoxic sediments was variable [11] and FeS could have higher affinity for Hg than FeS_2, both FeS and FeS_2 played predominant roles in Hg binding in anoxic sediment. Since FeS_2 was a major reservoir of reduced S in sediments [11], it should be clearly considered when investigating the binding of Hg in anoxic sediments, especially in those sediments with high FeS_2 contents. Both FeS and FeS_2 could decrease the bioavailability of Hg in anoxic sediments, but Hg sorbed with FeS_2 had a higher bioavailability as compared to Hg with FeS, indicating that Hg could be more bioavailable in anoxic sediments dominated by FeS_2. When most Hg was sorbed with FeS, the bioavailability of Hg depended on the ratio between Hg and S in the sediments. Although extraction of Hg by gut juices could increase with the Hg:S ratio in the sediments (until the ratio reached 1:10 in mole:mole), the bioavailability of Hg in anoxic sediments was low in most situations in view of the environmental concentrations of Hg in sediments. However, in heavily contaminated sites where Hg concentrations in sediments were high, Hg sorbed with FeS could be a mobile pool.

In view of the much stronger binding between Hg and S species than with other sediment components (e.g., organic matter or other inorganic particles), Hg could be accumulated in this anoxic layer of sediments at higher concentrations than in the oxic layers. The results of the present study showed that the partitioning of Hg from the oxic layers to anoxic layers in sediments could decrease its mobility and thus bioavailability. Anoxic sediments could be considered as a refractory Hg pool, decreasing the mobility of Hg and the extent of Hg uptake by aquatic organisms. During natural resuspension or dredging events, these S species can be oxidized, Hg may be released, and Hg could become more bioavailable.

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