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Effects of Acid Volatile Sulfides on the Use of Hydrochloric Acid for Determining Solid-Phase Associations of Mercury in Sediments

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The use of dilute HCl for the selective extraction of mercury from suboxic and anoxic sediments has been evaluated. The effect of acid concentration (1–6 M HCl) on the extraction of Hg and on the recovery of aqueous Hg preextraction spikes from sediments containing various amounts of AVS has been studied. The results obtained by using 1 M HCl as extractant (∼90% of added Hg was recovered in the solid phase after extraction) indicated that acid-soluble Hg may react with H_2S released from AVS phases (e.g. FeS, MnS) and precipitate in the form of HgS. The modeling of Hg speciation in HCl solutions in the presence of sulfide predicted the HgS(s) precipitation in 1 M HCl, observed experimentally. The precipitation of HgS(s) was found to be considerably lower when greater (2–6 M) HCl concentrations were used for Hg extraction. The modeling calculations confirmed that the extent of HgS(s) formation in the solution was controlled by the applied HCl concentration. The difference between HCl-soluble Hg fraction in an estuarine sediment core extracted by 1 M (1–5% of Hg_{tot}) and 6 M (50–60% of Hg_{tot}) HCl was consistent with the model experiments. These results suggest that the use of 1 M HCl extraction procedures must be questioned for methodological artifacts and that 6 M HCl could advantageously replace 1 M HCl for extracting Hg in the presence of AVS.

Introduction

The form of mercury present in sediment is of environmental concern, particularly since the availability of inorganic Hg is one of the main factors controlling the methylation of Hg in sediment. Methylmercury (MeHg) is the Hg species that is most toxic and bioaccumulates most efficiently, resulting in Hg biomagnification in the aquatic food chain (*1*). It was recently hypothesized (*2*) that HgS(aq) is the form available for methylation in sulfidic porewaters and that its concentration depends on the form of Hg in the sediment. Previous studies investigating the solid-phase associations of Hg in sediments using sequential extraction and other techniques have indicated that further work is needed to adequately characterize these associations.

Sequential extraction procedures involve the use of a single or several sequentially applied extractants to release metals associated with particular sediment phases. A frequently used extractant for estimating the metal fraction is dilute HCl which dissolves both oxidized different iron and manganese phases (e.g. oxyhydroxide and carbonate phases) from the sediment together with trace metals associated with these phases (*3*, *4*), while for anoxic sediments, iron monosulfide phases are also extracted. The partial extraction of Hg by cold HCl has been used for a number of purposes. Gagnon et al. (*5*) and Cossa et al. (*6*) used dilute HCl (0.1–1 M) to extract Hg associated with Fe and Mn oxides and to demonstrate the involvement of Hg in the iron oxidation–reduction cycle in coastal sediments. Huerta-Diaz and Morse (*4*) investigated, for a number of metals including Hg, the degree of trace metal pyritization in anoxic marine sediments, by using 1 M HCl for the extraction of FeS and associated trace metals. Morse (*7*) studied the remobilization of Hg, As, and Cu from pyrite after exposing anoxic sediment to oxidized seawater, by following the change in extractable Hg associated with the reactive (1 M HCl − extractable) iron. Di Toro et al. (*8*) suggested that the bioavailability and potential toxicity of certain heavy metals can be predicted in anoxic sediments by determining the ratio of acid volatile sulfide (AVS − sulfide extracted from the sediment using cold HCl, primarily FeS) to simultaneously extracted metals (SEM − the metals extracted by dilute HCl concurrently with the AVS). For sediments where the SEM is greater than AVS, and in the absence of other binding phases, environmentally significant porewater concentrations may exist. Metals that are expected to fit this model (in decreasing order of metal-sulfide solubility) include Ni, Zn, Cd, Pb, Cu, and Hg (*8*).

The determination of SEM by extracting sediments with 1 M HCl has recently been questioned for metals forming very insoluble sulfides such as Cu (*9*, *10*), Ni (*11*), and Hg (*12*). For a variety of sediment types recoveries of preextraction spikes were found to be variable and much lower for Hg and Cu, than for Cd, Ni, Pb, and Zn. It was concluded that binding of Hg and Cu with sulfides was sufficiently strong so that 1 M HCl would not necessarily keep the spiked metal in the dissolved state. However, because of insufficient data gaps for Hg (*12*), earlier studies have been unable to adequately assess the correlation of spike recovery of Hg with sediment characteristics and propose a more suitable method for estimating Hg associated with AVS or other easily extractable sediment phases. Moreover, extraction techniques using cold HCl to measure the concentration of trace metals associated with sulfide minerals were recently questioned (*13*), as it was demonstrated that Cu, Ni, and Hg sulfides were poorly soluble in 1–6 M HCl.

In the present study, the use of dilute HCl for extraction of soluble or easily released Hg from suboxic and anoxic sediments is evaluated. The work was performed by studying the effect of acid concentration (1–6 M HCl) on the extraction of Hg and the recovery of aqueous Hg preextraction spikes from sediments containing various amounts of AVS. The results obtained are used to describe conditions under which the extraction with dilute HCl is a reliable procedure for the determination of solid-phase associations of Hg in sediments containing AVS.

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Methods

Sediment Sampling and Extraction. Sediment cores were collected by box corers in the Seine river estuary at marine and estuarine locations (*14*, *15*). Cores were subsampled, onboard, at various depth intervals in a N_2-filled glovebag and placed in polycarbonate centrifuge tubes. In the laboratory, porewater from each subsample was separated by centrifugation, and the residual sediment was dried under a nitrogen atmosphere at a room temperature, ground, and sieved through a 63-pine sieve. Sediments from various depths (containing different amounts of AVS) were used for the extraction experiments. All sediment samples had similar characteristics (50–60% water; 90–99% clay; 2–3% org. C; 20–30 mg/g Fe (*14*, *15*)) but differed in the content of AVS. The same extraction procedure was used in all experiments, except the concentration of HCl and extraction time were varied. Dry sediment (0.2 g) was placed into 20 mL Teflon vials, and 10 mL of HCl (1, 2, 3 or 6 M) was added. Sediments were spiked by addition of standard Hg solution (in Milli-Q water) to the sample just prior to the HCl addition. Extractions were performed on a mechanical shaker for a period of 1, 5, or 24 h. At the completion of the extraction time the sample was filtered through a 0.45 μm filters (cellulose acetate membrane) using a plastic syringe, and 1% HNO_3 was added to stabilize Hg(II) in solution. The remaining sediment was quantitatively transferred into Teflon vials for the solid-phase Hg determination.

Sediment Extraction Experiments. For the evaluation of Hg extraction with 1 M HCl, two experiments were performed: (1) increasing quantities of Hg (50–200% in excess of the total Hg naturally present in the sample) were added to anoxic sediments containing 40 μmol/g of AVS and extracted using 1 M HCl for 5 h and (2) sediments containing various amounts of AVS (0.4–50 μmol/g) were extracted by 1 M HCl for 24 h. To compare the extent of Hg extraction by 1–6 M HCl, two experiments were performed: (1) a sediment containing 40 μmol/g of AVS and 1280 ng/g of the total Hg was extracted with 1, 2, 3, and 6 M HCl for 1, 5, and 24 h, without and with Hg spiking and (2) two sediments containing high (46 μmol/g) and low (0.4 μmol/g) AVS contents were extracted for 5 h with 1, 2, 3, and 6 M HCl without and with Hg spiking.

Analyses. For the total Hg determination in sediment, samples were digested in 5 mL of concentrated HNO_3 for 4 h at 140 °C. For the total Hg determination in the HCl extract, samples were treated with 0.5% BrCl for several hours in order to oxidize the residual sulfide in solution (if present) and to decompose nonlabile Hg complexes. Mercury was detected by cold vapor atomic fluorescence spectroscopy (CV AFS) after $SnCl_2$ reduction. Configuration includes a vapor generator (PSA 10.003), a gold platinum trap (PSA 10.501 Galahad), and fluorescence detector (PSA 10.023 Merlin) and is described in detail elsewhere (*16*). Iron and other trace metals in leachates were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Varian). Acid volatile sulfides (AVS) were isolated by acid distillation of wet sediment samples using cold 6 M HCl and determined quantitatively as CuS precipitate (*15*).

Results and Discussion

Evaluation of the Extraction Capacity of 1 M HCl. Extraction of a sediment rich in AVS (40 μmol/g) with 1 M HCl (Figure 1) showed that almost all added Hg (regardless of the added quantity) was recovered in the solid phase (89–92%), whereas less than 1% was found in solution. The overall recovery of added Hg was less than 100% (usually 90–95%), probably due to adsorption losses of added Hg onto container walls. Experiments on the recovery of Hg standard (without sediment) confirmed that in 1–3 M HCl some Hg (5–10%)
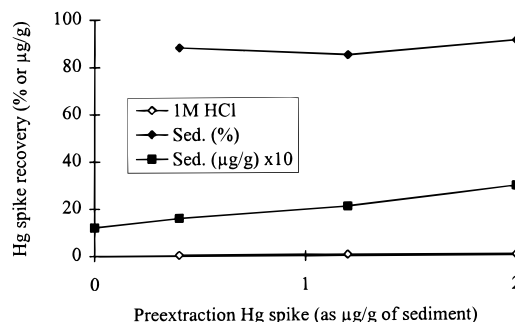

FIGURE 1. Recovery of preextraction Hg spike in solution and in residual sediment after the extraction of a sediment rich in AVS (40 μmol/g) with 1 M HCl for 5 h.
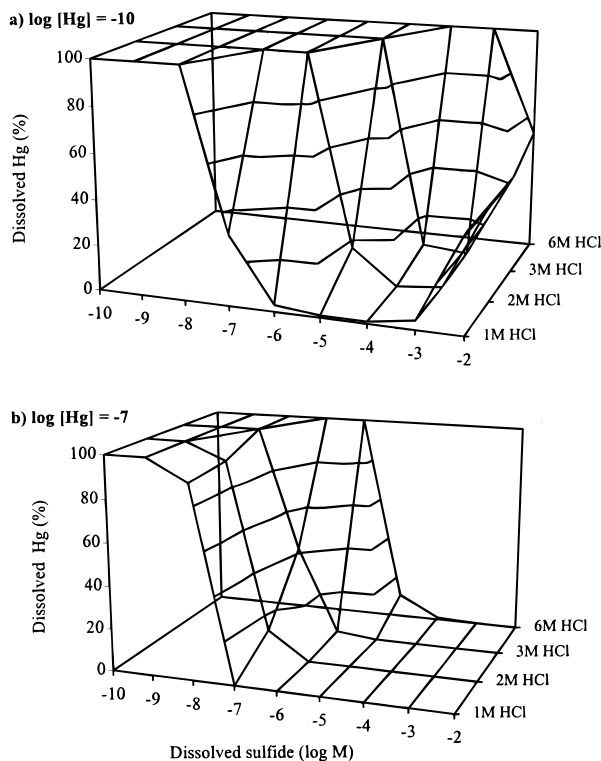

FIGURE 2. Calculated values of dissolved Hg (presented as percentages of total Hg) in 1, 2, 3, and 6 M HCl as a function of dissolved sulfide concentration.

was lost from the solution during extraction. A probable explanation for results obtained would be the precipitation of HgS(s) formed by the reaction of added Hg and H_2S released from the sediment during AVS and SEM dissolution. Two requirements should be fulfilled for a Hg spike to precipitate as HgS(s) in the residual sediment after extraction. The chemical conditions in the solution should be such that HgS is formed in the solution and the precipitated HgS(s) must not be soluble in dilute HCl. Formation of HgS in HCl depends on the competition between chloride and sulfide ions for Hg(II), since Hg(II) forms very strong chloride complexes which may prevent its reaction with H_2S (*17*).

The speciation of Hg in HCl solution in the presence of sulfide was modeled by using the MINEQL (Figure 2 a,b). The concentrations of Hg and sulfide in HCl used for modeling were calculated under the presumption that the content of Hg and AVS from 0.2 g of sediment was dissolved in 10 mL of HCl. The two Hg concentrations used for modeling (Figure 2a,b) correspond to (a) 1% dissolution of a sediment containing 100 ng/g and (b) total dissolution of a sediment containing 1000 ng/g Hg. These concentrations simulated
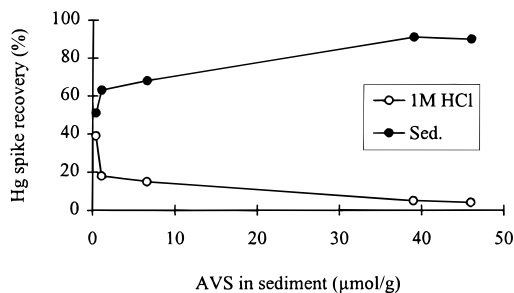
FIGURE 3. Recovery of preextraction Hg spike (500 ng) in solution and in residual sediment versus sediment AVS content after the extraction of sediments with 1 M HCl for 24 h.

sediments for which lower and higher amounts of Hg are extracted from natural sediments. The higher concentration corresponds roughly to a Hg concentration in HCl used in our experiments (10^{-7} mol/L). Sediment AVS concentrations of $0.1-200$ μmol/g will give dissolved sulfide in HCl of about $10^{-6}-10^{-2}$ mol/L; however, since H_2S is formed under acidic conditions, these concentrations may decrease through volatilization of H_2S from the solution. For this reason calculations were performed also for much lower (up to 10^{-10} mol/L) sulfide concentrations.

The dissolved Hg values calculated are presented as percentages of total Hg, where dissolved Hg comprises Hg–Cl species $HgCl_4{}^{2-}$, $HgCl_3{}^-$ and $HgCl_2(aq)$, and Hg–S species $Hg(HS)_2(aq)$ and $HgS(s)$ is the only solid phase. From Figure 2 (parts a and b) it is evident that in 1 M HCl, Hg is present entirely in the form of $HgS(s)$ for sulfide concentrations grater than 10^{-6} and 10^{-7} mol/L, for both the lower and higher Hg concentrations, respectively. Dissolution of AVS for the sediment described for Figure 1 will give about 10^{-3} mol/L of sulfide in HCl, where according to model calculations (Figure 2b) all Hg should be in the form of $HgS(s)$. Therefore, the modeling calculations predict the $HgS(s)$ precipitation (in 1 M HCl) observed.

When sediments containing different AVS concentrations ($0.4-50$ μmol/g) were extracted with 1 M HCl, increased concentrations of Hg in the solid phase are observed for sediments with greater AVS concentrations (Figure 3), again supporting the notion of $HgS(s)$ precipitation. The agreement with model calculations is good for higher AVS concentrations (which correspond to about 10^{-3} mol/L of sulfide), where all Hg is predicted to be in the form of $HgS(s)$ (Figure 2b). However, for lower sediment AVS concentrations (10^{-5} mol/L sulfide), significantly more Hg was measured in solution (about 40%) than predicted by the model (0%, Figure 2b). This is most likely due to the actual concentration of sulfide in HCl being much lower (due to a loss of H_2S by volatilization) than calculated from the sediment AVS content (according to modeling it should be about 10^{-8} mol/L; Figure 2b).

Preextraction Hg spikes simulate the behavior of mercury dissolved from sediment upon reaction with HCl. The results obtained indicate that reactive Hg (released from sediment by HCl) may precipitate during extraction by reaction with H_2S released from AVS phases (e.g. FeS, MnS), resulting in a lower concentration of acid-soluble Hg. Therefore, neither the HCl-insoluble Hg fraction in the form of HgS (13), nor the HCl-soluble Hg fraction are extractable by 1 M HCl. Consequently, the extraction with 1 M HCl suffers from two potential artifacts which preclude its use for partial extraction of Hg in sulfidic sediments. Recently, different authors suggested that formation of pure trace metal sulfides (11), especially HgS (2, 13, 17), may not occur even in sulfidic aquatic sediments. Luther and Morse (17) concluded that a strong Hg complexation with chloride and its high hydrolysis constant would retard Hg reactivity with sulfide and prevent formation of discrete HgS phases. Benoit at al. (2) suggested
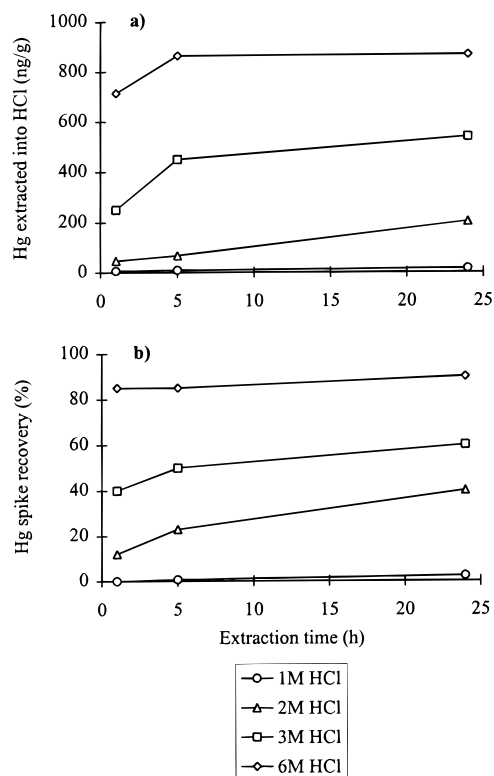

FIGURE 4. (a) Natural Hg extracted from sediment into HCl and (b) recovery of preextraction Hg spike (100 ng) in solution after the extraction of a sediment rich in AVS (40 μmol/g) with 1, 2, 3, and 6 M HCl for 1, 5 and 24 h.

that the existence of pure $HgS(s)$ in sediments is doubtful, as a solubility model of pure HgS failed to reproduce the observed concentration of dissolved Hg in porewater. In contrast, both iron monosulfide (18) and pyrite (19, 20) were shown to be good adsorbents for Hg(II). Therefore, if HgS is not a principal Hg form in sulfidic sediments, it is of crucial importance to develop leaching methods applicable to the extraction of all Hg-phases or selective extraction of known individual phases.

Evaluation of the Extraction Capacities of 2–6 M HCl. Different concentrations of dilute HCl have been used for the extraction of FeS (both for reactive iron and AVS determination) and metals associated with this sediment phase (reactive metals or SEM). Levental and Taylor (21) have shown that 1 M (24 h), 6 M (5 or 24 h), and 12 M HCl (hot, 1 min) leached comparable amounts of iron from sediments and proposed the use of 1 M HCl. Cornwell and Morse (22) found that $1-6$ M HCl completely dissolved amorphous FeS but did not release sulfur from pyrite. Consequently, although the most frequently utilized HCl concentration is 1 M (10, 11, 23), also other HCl concentrations have been used for AVS and SEM extraction: 0.5 M HCl (8), 3 M HCl (12), and 6 M HCl (24). In contrast to FeS, different HCl concentrations do not, however, give comparable results for all metals defined in the SEM fraction. For example, it was shown that 1 and 6 M HCl extract similar amounts of Zn, Cd, and Pb from sediments containing AVS, but much higher amounts of Ni and Cu are extracted by 6 M HCl (24).

When a sediment rich in AVS (40 μmol/g) was extracted with $1-6$ M HCl (Figure 4 a,b), increasing percentages of Hg extracted (or Hg-spike recovered) were measured for increasing HCl concentrations: <1% in 1 M HCl, up to 15 (30)% in 2 M HCl, up to 45 (60)% in 3 M HCl, and up to 70 (90)% in 6 M HCl. The almost quantitative recovery of Hg spikes in 6 M HCl suggested that the precipitation of HgS in
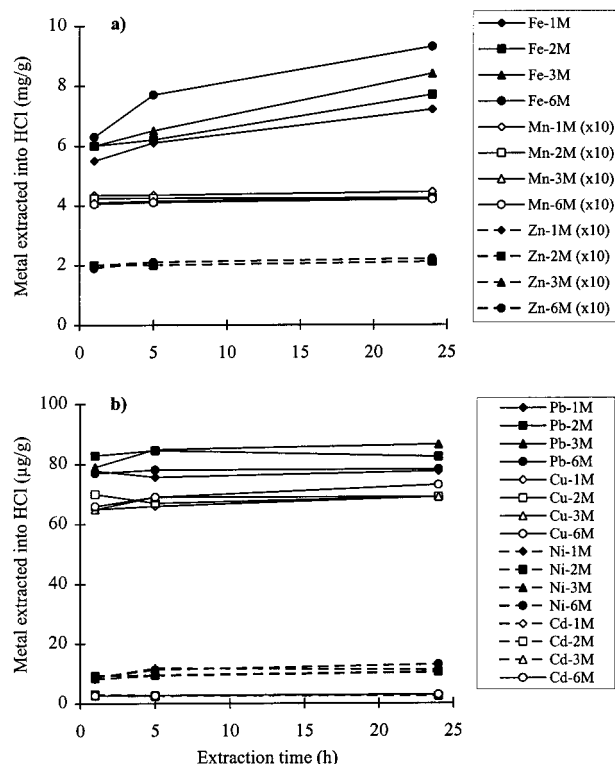
FIGURE 5. (a) Fe, Mn, and Zn and (b) Cd, Ni, Cu, and Pb extracted simultaneously with Hg from sediment into HCl during the experiment presented in Figure 4a.

6 M HCl was of minor importance. For the sulfide concentrations calculated from the sediment AVS content used in experiment presented in Figure 4 (10^{-3} mol/L), the precipitation of HgS in 6 M HCl predicted by modeling (Figure 2b), differs from experimentally obtained results. Again, modeling suggests that the actual concentration of sulfide in HCl must be significantly lower (10^{-6} mol/L) than that calculated from AVS dissolution. The important conclusion which can be drawn from the calculations (Figure 2a,b) is that precipitation of HgS is considerably less at greater HCl concentrations. Consequently, 10^3-10^5 times higher sulfide concentrations (depending on the Hg concentration in HCl, Figure 2 a,b) are required in 6 M than in 1 M HCl for Hg to be precipitated as HgS.

The concentrations of metals Fe, Mn, Zn, Cd, Ni, Cu, and Pb extracted during the same experiment were also determined (Figure 5 a,b). For all these metals similar amounts were extracted with all HCl concentrations investigated (80–90% for Cu, 70–80% for Zn, and Mn and 20–30% for Fe of the total metal content in the sediment). Comparable concentrations of Fe and Mn extracted by 1–6 M HCl suggest these HCl concentrations extract the same sediment phases. The extracted amount of Fe (100–150 μmol/g) is 2–3 times higher than the content of AVS (40 μmol/g), indicating that, in addition to FeS, the fraction extracted may comprise also Fe-oxide and carbonate phases. Hence, a difference in Hg extracted by various acid concentrations could not be a consequence of extraction of different sediment phases. In addition, as HgS is poorly soluble in HCl up to 6 M (13), higher amounts of Hg extracted by 2, 3, and 6 M HCl are unlikely to be attributable to an increased dissolution of HgS. This supports the hypothesis of Hg precipitation during extraction, where, for the same Hg and AVS levels, the extent of HgS(s) formation is controlled by the applied HCl concentration.

When extractability of Hg with 1–6 M HCl, for sediments of different AVS concentrations (46 μmol/g — Figure 6a and
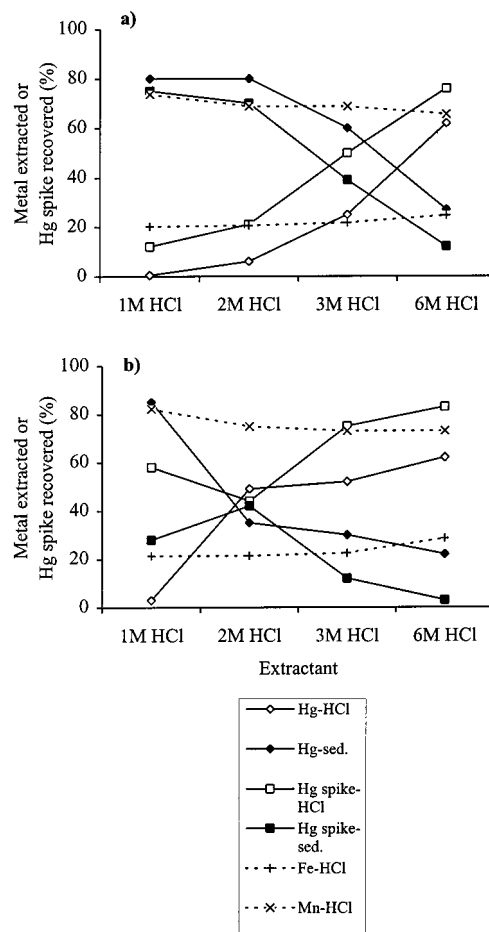

FIGURE 6. Hg, Fe, and Mn extracted from sediment and recovery of preextraction Hg spike (500 ng) after the extraction of (a) a sediment rich in AVS (46 μmol/g) and (b) a sediment poor in AVS (0.4 μmol/g) with 1, 2, 3, and 6 M HCl for 5 h (Hg-HCl: natural Hg extracted into HCl; Hg-sed.: natural Hg in residual sediment; Hg spike-HCl: recovery of Hg spike in HCl; Hg spike-sed.: recovery of Hg spike in residual sediment; Fe-HCl: Fe extracted into HCl; Mn-HCl: Mn extracted into HCl). Amounts of Hg, Fe, and Mn extracted are expressed as percentages of the total metal concentration in sediment.

0.4 μmol/g — Figure 6b) was evaluated, similar amounts of Hg extraction as previously (Figure 4) was observed for sediments rich in AVS. The observation that 10–80% of the Hg-spike was recovered in the solid phase confirmed that partial precipitation of Hg spikes was taking place in acid concentrations higher than 1 M HCl. Even for 6 M HCl, a small percentage (~10%) of added Hg was found in the residual solid phase fraction. These results indicated that for sediments rich in AVS, precipitation of HCl-soluble Hg may occur even in 6 M HCl, but it will be of minor importance compared with precipitation in 1 M HCl. Parallel curves for Hg-spikes recovery and Hg extracted from sediment indicate that Hg released from sediment behaves similarly to Hg spikes and confirms that the experimental design was suitable for testing the applicability of this extraction method. For sediment with a 100-fold lower AVS content (Figure 6b) a low Hg percentage was extracted by 1 M HCl, whereas a similar but higher percentage (~60%) was extracted with 2–6 M HCl. For this sediment, recovery of the Hg spike in the solution was significant for 1 M HCl (~30%) and high (80%) in 3 M HCl, and in 6 M HCl the precipitation of Hg spike was negligible (<1%). Therefore, for sediments with lower AVS concentrations, Hg precipitation artifacts become
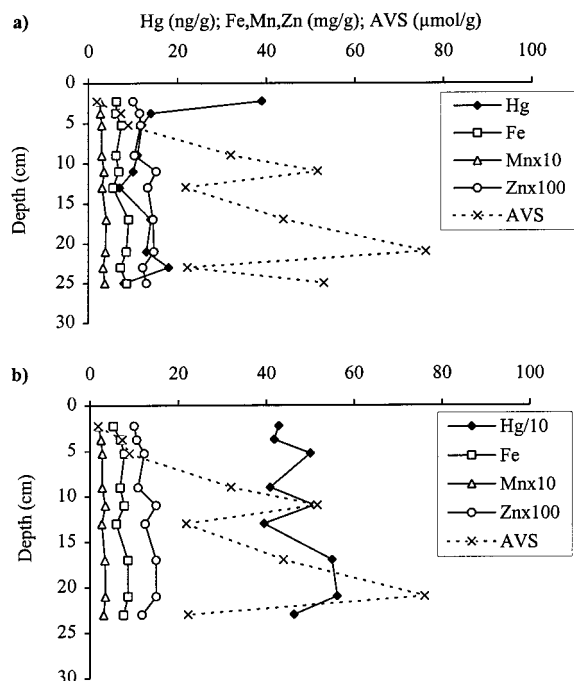
a)

Hg (ng/g); Fe,Mn,Zn (mg/g); AVS (µmol/g)

b)

FIGURE 7. Depth profiles of HCl extracted metals (Hg, Fe, Mn, and Zn) and AVS content in sediments from the Seine Estuary obtained after the extraction of sediment with (a) 1 M HCl for 24 h and (b) 6 M HCl for 5 h.

less significant for all HCl concentrations and acceptable recoveries are observed for 3 M HCl.

Comparison of 1 and 6 M HCl for Determination of HCl-Extractable Hg. The comparison was performed on a sediment core taken from the Seine estuary (Figure 7 a,b). According to the depth profiles of Fe and sulfate in porewater (*14, 15*), the sediment was suboxic from its surface (1.5 µmol/g AVS in the 0−2 cm layer) and anoxic below a depth of 10 cm. The concentration of AVS increases considerably with depth up to a level of 80 µmol/g. Amounts of Fe, Mn, and Zn extracted by 1 and 6 M HCl were comparable and did not change significantly with depth. The composition of this reactive Fe fraction could be assessed from a difference of the total HCl-soluble Fe and HCl-soluble Fe associated with AVS, where percent AVS-Fe provides a measure of the degree of sulfidization of the iron oxide minerals (*25*). In the analyzed sediment core, "oxidized" iron prevailed up to the depth of 5 cm (% AVS−Fe = 2−5), whereas at greater depths "sulfidized" iron became a more significant fraction (% AVS−Fe = 20−50) of the HCl-soluble iron pool. In contrast to Fe, Mn, and Zn, much lower amounts of Hg were extracted by 1 M HCl (1−5% of Hg_{tot}) than by 6 M HCl (50−60% of Hg_{tot}). The observed difference in HCl-soluble Hg profiles obtained by 1 and 6 M HCl is consistent with previously presented model experiments. The depth profile of 6 M HCl-extractable Hg was comparable with profiles of Fe, Mn, and Zn. Moreover, the highest amounts of Hg were extracted in layers containing peak AVS concentrations (Figure 7b), indicating Hg association with AVS. It is well-known that iron sulfides serve as a temporary sink for many trace metals during early diagenesis in anoxic sediments (*18*). Gagnon et al. (*5*) suggested that AVS may represent the principal Hg sink in the anoxic sediments of the Saguenay fjord. A good correlation between MeHg and AVS found in sediments of the Elbe river imply a coupling between MeHg and sulfide minerals in freshwater sediments (*26*).

Implications for Existing Sediment Extraction Procedures. The use of 1 M HCl extraction procedures for determining sulfide associated Hg must be questioned for

methodological artifacts. The low concentrations of Hg extracted by this procedure would underestimate the amount of Hg associated with AVS (FeS). This was the observation of two previous studies (*4, 27*) investigating the degree of trace metals pyritization (DTMP) in anoxic sediments by using 1 M HCl to extract metals associated with iron monosulfides. Low concentrations of Hg were found in the fraction extracted by HCl and high concentrations in the fraction extracted by HNO_3 (pyrite fraction). On the basis of these data, the authors suggested essentially complete incorporation of Hg into pyrite fraction. However, if the fraction of metal associated with FeS is low due to the artifact of the method used, then the calculated DTMP was too high. It is also possible that a portion of the Hg precipitated as HgS(s) during HCl extraction will be recovered in the fraction leached with HNO_3 (pyrite fraction) and give an even higher DTMP for Hg. Therefore, previous DTMP values for Hg should be reevaluated by using 6 M HCl (or some other validated method) to extract the reactive Hg fraction.

A significant increase in the 1 M HCl extractable Hg, As, and Cu fraction of anoxic sediments after exposing them to oxidized seawater was interpreted as a result of metal release upon partial pyrite oxidation (*7*). However, an increased amount of 1 M HCl-extractable Hg in sediments after resuspension could be also a consequence of much lower AVS content in these sediments. To verify if the 1 M HCl extraction has the same performance for sediments both before and after oxidation, a Hg spike recovery in 1 M HCl should be checked.

The use of simultaneous extraction of Hg, Fe, and Mn by 1 M HCl, for illustration of involvement of Hg in Fe and Mn cycling in surficial sediments, could also be questionable. Namely, if the extraction efficiency of Hg depends on the sulfide level in the sediment, a decrease in the amounts of extracted Hg with sediment depth (especially between oxic and suboxic layers) might be expected. In this case the simultaneous extraction of high levels of Hg, Fe, and Mn in the upper layer of sediment and subsequent decreased extraction of Hg with depth does not necessarily indicate the coupling between Hg and Fe cycling, as suggested by Gagnon et al. (*5*). For such a purpose it would be better to use a method which dissolves specifically Fe and Mn oxides, for example hydroxilamine−acetic acid which was used with sediments of the Laurentian Trough by Gobeil and Cossa (*28*).

Therefore, we propose that conclusions based on Hg extraction from anoxic sediments by 1 M HCl should be reevaluated. Results of this work suggest that if cold HCl is used for extraction than 6 M HCl could replace 1 M HCl for extracting Hg in the presence of AVS. Further experiments are required to elucidate the exact nature of the Hg phases (and probably other metals forming sulfides not soluble in 1 M HCl) extracted by 6 M HCl and to relate the extracted metal fraction to the reactivity and bioavailability of these metals in anoxic sediments.

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