Influence of Acid Volatile Sulfides and Metal Concentrations on Metal Partitioning in Contaminated Sediments

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The influence of acid volatile sulfide (AVS) on the partitioning of Cd, Ni, and Zn in porewater (PW) and sediment as reactive metals (SEM, simultaneously extracted metals) was investigated in laboratory microcosms. Two spiking procedures were compared, and the effects of vertical geochemical gradients and infaunal activity were evaluated. Sediments were spiked with a Cd–Ni–Zn mixture (0.06, 3, 7.5 μmol/g, respectively) containing four levels of AVS (0.5, 7.5, 15, 35 μmol/g). The results were compared to spiked sediments with four levels of Cd–Ni–Zn mixtures at one AVS concentration (7.5 μmol/g). A vertical redox gradient was generated in each treatment by an 18-d incubation with an oxidized water column. AVS vertical redox gradient was generated in each treatment.

Zn mixtures at one AVS concentration (7.5 μmol/g, respectively) containing four levels of AVS (0.5, 7.5, 15, 35 μmol/g). The results were compared to spiked sediments with four levels of Cd–Ni–Zn mixtures at one AVS concentration (7.5 μmol/g). A vertical redox gradient was generated in each treatment by an 18-d incubation with an oxidized water column. AVS vertical redox gradient was generated in each treatment.

Introduction

Most metals in aquatic environments are concentrated in the particulate phase, particularly in sediments. Once associated with sediments, metals undergo various biogeochemical transformations during diagenetic reactions. Metals can be mobilized from or immobilized to sediments, partly depending upon redox conditions. They can also be exchanged with overlying water, depending upon conditions that influence desorption or concentration gradients between porewater (PW) and overlying water. Geochemical forms within contaminated sediments and processes affecting geochemical partitioning between sediments and PW are particularly critical to the fate and bioavailability of metals (1–6).

Important sediment phases that bind metals, include iron oxides, manganese oxides, various organic phases, and iron sulfides (7–10). Sulfides, particularly acid volatile sulfide (AVS, which consists largely of iron sulfides), have received considerable attention in recent years as major reactive phases for metals such as Ag, Cd, Cu, Ni, Pb, and Zn in anoxic sediments (11–13). Recent studies addressing metal–sulfide geochemistry suggest that PW metal concentrations will be insignificant when [AVS] exceeds concentrations of metals simultaneously extracted with AVS (SEM) (14, 15). These studies also suggested that toxicity to bentic invertebrates would not occur when there is sufficient AVS to complex all the SEM in sediments.

Two interfaces are chemically and biologically the most active boundaries in sediments: that between sediment and overlying water and that between oxic and anoxic conditions (16, 17). Multiphysical, chemical, and biological processes coupled dynamically influence both AVS and PW metal concentration at these boundaries. Few of these processes have been considered in detail in previous studies concerned with AVS concepts (18, 19). For example, depth-variation of [AVS] in sediments could affect not only the vertical profile of metals in PW (20) but also the flux of metals to overlying waters (5, 13, 21). Most previous AVS studies also manipulated [SEM – AVS] by spiking variable amounts of metals to sediments containing a single (AVS). This approach requires the addition of high metal concentrations to achieve the desired range of [SEM – AVS] and co-varies [SEM] and [SEM – AVS].

In the present paper our objective is to test the influence of spiking procedures and vertically complicated redox profiles (like those in nature) on subcentimeter distributions of Cd, Ni, and Zn in PW, in the presence and absence of animals, and to test the influences of initial [AVS], initial [SEM], and AVS oxidation in surficial sediments on PW metal concentrations and their relationship with [SEM – AVS]. Concurrent bioaccumulation study is reported in the following paper (22). Here, we introduce an approach for varying [AVS] in sediments containing a constant [SEM] and compare the results with the more commonly used method where [SEM – AVS] is controlled by varying [SEM]. Varying [AVS] allows us to test the effects of [AVS] and to do so with environmentally realistic metal concentrations. We also investigate the influence of spiked metal concentrations on the oxidation of AVS and effects of AVS on extractability of metals in sediments. Finally, we analyze how different experimental conditions such as spiked metal concentrations and equilibration time could affect partitioning of metals between porewater and sediments and compared those effects with the data from the existing literature.

Experimental Methods

Two series of experiments were designed to evaluate effects of [AVS] on metal partitioning in sediments and subsequent metal bioaccumulation by marine invertebrates. In the first series (variable SEM series), [SEM – AVS] was manipulated by spiking four levels (M1, M2, M3, and M4) of a Cd–Ni–Zn mixture to sediments having the same nominal [AVS] (S2 level). In the second series (variable AVS series), [SEM – AVS] was controlled by [AVS] (S1, S2, S3, and S4) while keeping
M2 treatments (variable SEM series) were prepared by mixing the respective metal stock solutions with the same volume of previously prepared sediment slurry containing the S2 level of AVS in a poly(vinyl chloride) bag held in a bucket.

The nominal metal concentrations in M1 treatment were 0.02 μmol Cd/g, 0.6 μmol Ni/g, and 2.0 μmol Zn/g, and those in M2, M3, and M4 were 3×, 5×, and 7× metal concentrations in M1, respectively. Similarly, the sediments for the variable AVS series was made by mixing the M2 level stock solution with the sediments containing S1–S4 AVS levels. The mixture in the bag was equilibrated for 4 d under N2 and mixed vigorously several times daily. Following the 4-d equilibration, the sediment mixture was allowed to settle for 2 d. Then the overlying water was siphoned out, and about 4-L aliquots of the sediment in the bag were transferred to duplicate 6-L experimental polycarbonate containers (20 × 20 × 15 cm) and maintained at 15 °C. These sediments were allowed to consolidate for 1 wk. Then 90% of the 2-L of overlying water was replaced and left for another day; daily replacement of overlying water was repeated three times. Two replicate sediment samples per container were taken after the 10-d of consolidation at a depth of 1–3 cm using 30-ml polypropylene syringes to determine initial [AVS] and [SEM] (Table 1). Following the sediment sampling, test animals were introduced into the experimental sediments and incubated for 18 d. During the biological exposure, the overlying seawater was aerated continuously, and half of the 2-L overlying water was changed every other day.

**TABLE 1. Mean AVS and SEM Concentrations (μmol/g) in Sediment from All Treatments at the Beginning (t = 0 d) and the End of the Incubation (t = 18 d)**

<table>
<thead>
<tr>
<th>Treatment</th>
<th>t = 0 d</th>
<th>t = 18 d</th>
<th>SEM (μmol/g)</th>
<th>AVS (μmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>surface</td>
<td>deep</td>
<td>surface</td>
<td>deep</td>
</tr>
<tr>
<td>control</td>
<td>5.0 (0.1)</td>
<td>0.4 (0.4)</td>
<td>4.5 (0.3)</td>
<td>0.002 (0.2)</td>
</tr>
<tr>
<td>M1</td>
<td>5.8 (0.4)</td>
<td>0.3 (0.1)</td>
<td>4.7 (0.1)</td>
<td>0.017 (0.6)</td>
</tr>
<tr>
<td>M2</td>
<td>6.2 (0.9)</td>
<td>1.3 (0.2)</td>
<td>5.7 (0.4)</td>
<td>0.050 (2.7)</td>
</tr>
<tr>
<td>M3</td>
<td>7.1 (0)</td>
<td>2.0 (0)</td>
<td>6.0 (0)</td>
<td>0.086 (4.0)</td>
</tr>
<tr>
<td>M4</td>
<td>7.2 (0.1)</td>
<td>2.1 (0.1)</td>
<td>7.1 (0.6)</td>
<td>0.180 (6.0)</td>
</tr>
<tr>
<td>S1</td>
<td>0.6 (0.2)</td>
<td>0.2 (0.2)</td>
<td>0.6 (0.1)</td>
<td>0.058 (2.8)</td>
</tr>
<tr>
<td>S2</td>
<td>6.2 (0.9)</td>
<td>1.3 (0.4)</td>
<td>5.7 (0.4)</td>
<td>0.050 (2.7)</td>
</tr>
<tr>
<td>S3</td>
<td>14.9 (0)</td>
<td>4.1 (0)</td>
<td>13.3 (0)</td>
<td>0.056 (2.8)</td>
</tr>
<tr>
<td>S4</td>
<td>35.4 (1.0)</td>
<td>8.8 (0.7)</td>
<td>31.5 (1.1)</td>
<td>0.058 (2.6)</td>
</tr>
<tr>
<td>No-animal</td>
<td>6.5 (0.0)</td>
<td>1.0 (0.6)</td>
<td>5.4 (0.5)</td>
<td>0.050 (2.6)</td>
</tr>
</tbody>
</table>

* Values from 0 to 0.5 cm section. ‡ Depth-averaged from 0.5 to 7.5 cm sections. Values in parentheses are concentration differences between two replicates. ‡ Represents the treatment without animals.

**Manipulation of Experimental Sediment.** Sediments were obtained from a mudflat near Palo Alto in San Francisco Bay, U.S.A. (28). Dark AVS-rich anoxic sediment (–30 μmol AVS/g) was collected from 5 to 15 cm depth after surface oxic sediment was removed. Sediment was sieved through 1-mm fiber-glass mesh at the collection site, covered, and transferred directly to the laboratory, where it was homogenized extensively in a large container and then divided into two containers. One portion of sediment was mixed with 0.22-μm filtered salinity 25-ppt water, and the sediment slurry was oxidized by bubbling continuously with air for 3 d. Following aeration, the AVS in the oxidized sediment decreased to ~0.5 μmol/g. Deionized water was then added to adjust the salinity of the sediment mixture to 25 ppt. The second portion of AVS-rich sediment was maintained by mixing the sediment with deoxygenated seawater in a sealed container and purging continuously with N2 gas. After this process, the AVS of the anoxic sediment was increased from ~30 to ~35 μmol/g. The oxidized and anoxic sediments were mixed at appropriate ratios to achieve four nominal AVS levels of 0.5, 7.5, 15, and 35 μmol/g for S1, S2, S3, and S4 treatments, respectively. TOC analyzed by a carbon analyzer after acid pretreatment was 0.8% for both oxic and anoxic sediments. Particle size was analyzed by pipetting and a dry sieve method (29). Both sediment types had a mean particle size of 6.3 μm.

The metal stock solutions for spiking experimental sediments were made by dissolving appropriate amounts of reagent grade CdCl2, NiCl2·6H2O, and ZnSO4·7H2O in deoxygenated water at a salinity of 25% for the sediments for the variable SEM series (28). Two replicate cores were taken from each container using 140-ml syringe cores (5-cm diameter). The cores were immediately transferred into a glovebag under N2 atmosphere and sectioned to 5 depth intervals (0.5–1.5 cm). Extra care was taken to minimize disturbance of surface sediment and smearing during coring and sectioning processes. Sediment sections from the same depth intervals from the three cores in each experimental container were homogenized into one pooled sample in a deoxygenated glass jar. An aliquot of sediment (~20 g) was taken from this jar for PW analysis and transferred to a deoxygenated 50-ml polycarbonate centrifuge tube in a glovebag. The remaining sediment was tightly sealed in the jar and kept at 4 °C until AVS and SEM analysis. The sediment in the tube was centrifuged for 30 min at 3600g, and the supernatant was filtered with a 0.45-μm syringe filter into a 20-ml precleaned glass vial. The pH of the PW was adjusted.
AVS series treatments (S1 and M1 (Table 1). [SEM] for all three metals also changed little over the
in the S1 replicates. S2 and M2 is an identical treatment. The error bar represents the concentration difference between two
replicates. S2 and M2 is an identical treatment.

Ni will be noted as Throughout the text, the effect of the different metals on Cd,
whose solubilities are lower than the metal of interest (AVS evaluation should include the concentrations of the metals
-
AVS-SEM. Therefore, [AVS] and [SEM] were determined by the cold-acid (1N HCl) purge and trap technique described by Boothman and Helmstetter (31). The [SEM] and 
extractable metals were determined by (CAP-AES, GF-AAS, or ICP-MS (see Supporting Information). Solubility products for the formation of metal sulfides decreased in the order of Ag < Cu < Pb < Cd < Zn ≤ Ni < Fe < Mn (4, 12, 32). When multiple metals are employed in experiments, the SEM used for [SEM − AVS] evaluation should include the concentrations of the metals whose solubilities are lower than the metal of interest (15).
Throughout the text, the effect of the different metals on Cd, Zn, and Ni will be noted as $\Sigma_{SEM}^{Cd}$, $\Sigma_{SEM}^{Zn}$, and $\Sigma_{SEM}^{Ni}$, respectively. For example, $\Sigma_{SEM}^{Cd}$ used for [SEM − AVS] evaluation include the molar concentrations of Ag, Cu, Pb, and Cd. $\Sigma_{SEM}^{total}$ will be defined as sum of all the metals considered in this study (Cu, Pb, Cd, Zn, and Ni).

Results

AVS and SEM. Concentrations of AVS varied as expected due to manipulation and surface oxidation. Following the 18-d incubation with the oxidized water column, surface [AVS] (0–0.5 cm) decreased by 65–95%, while [AVS] at depth remained near the initial concentrations (Table 1, Figure 1). Surficial [AVS] varied with treatment from 0.2 to 8.8 \( \mu \)mol/g [AVS] in the deep sediment varied with treatment from 0.6 to 31.5 \( \mu \)mol/g (Table 1). In the variable SEM series (same nominal [AVS]), measured [AVS] varied from 0.3 to 2.1 \( \mu \)mol/g in the surface and 4.5–7.5 \( \mu \)mol/g at depth. One cause of this variability was that [AVS] were positively correlated with concentrations of extractable metals (\( p < 0.001 \)) (Figure 2A).

Concentrations of SEM also varied as expected. Concentrations of Cd, Ni, and Zn − SEM differed among the control and M1−M4, as designed, but were similar among the four AVS series treatments (S1− S4) and the No-animal treatment (Table 1). [SEM] for all three metals also changed little over depth or during the 18-d incubation period, except that Zn and Cd in the surface sediment of S4 were ~50% higher than in the S1– S3 sediments. The contribution of spiked metals to the $\Sigma_{SEM}^{total}$ increased in the order of Cd (0.6–0.8%) < Ni (25–30%) < Zn (~70%). Cu and Pb (not spiked) contributed 25% and 12% of $\Sigma_{SEM}^{total}$ for the Control and M1, respectively, but were <4% of $\Sigma_{SEM}^{total}$ in other treatments.

The extractabilities (SEM/total metal) of Cd, Ni, and Zn in the sediment were 88 ± 9, 91 ± 12, and 89 ± 6% (mean ± SD), respectively. No significant relationship was found between the extractability of Cd, Ni, and Zn and [AVS]. However, the proportion of extractable Cu had a negative relationship with [AVS] in the sediments (Figure 2B). The extractable Cu ranged from 0.15 to 0.35 \( \mu \)mol/g, while total Cu was nearly constant (0.75 \( \mu \)mol/g for all treatments. The extractability of Cu was higher in surface than in deep sediment for a given [AVS].

The depth variations of [SEM − AVS] for Cd, Ni, and Zn after the 18-d incubation are shown in Figure 3. A strong vertical gradient in [SEM − AVS] was observed for all metals with a maximum at the surface as a result of declining [AVS] toward the surface. [SEM$^{Cd}$ − AVS] and [SEM$^{Zn}$ − AVS] were > 0 in the surface sediments of all treatments as a result of oxidation of AVS by the overlying water. However, at depths > 0.5 cm, these values were near the initial nominal values. The [SEM$^{Cd}$] for all treatments was only small fraction of [AVS]. Therefore, [SEM$^{Cd}$] − AVS] were < 0 in most treatments; only a few samples had positive values at the surface.

Porewater Metals. Porewater Cd, Ni, and Zn concentrations increased with the decreasing [AVS] in the variable AVS series or with increasing [SEM] in the variable SEM series (Figure 3). The highest PW Cd was always observed in the surface (0–0.5 cm), but PW Ni and Zn distributions were more complex (Figure 3). Porewater Cd concentrations were relatively constant at depths > 0.5 cm and were inversely related to [AVS]. Porewater Ni and Zn concentrations in S3 and S4 had surface maxima, reflecting sharp vertical profiles...
of [SEM – AVS] in these treatments. Those profiles having higher PW Ni and Zn in the deep sediments displayed either little vertical variation or a minimum in the surface. Among the treatments, the variability of PW Ni and Zn was less in the surface sediment than in the deep sediments (Figure 3).

Porewater Cd and Ni concentrations in the No-animal treatment were comparable to the respective treatment with animals (M2), consistent with little difference in [SEM – AVS] between these two treatments, but PW Zn was higher in No-animal treatment than in M2 (Figure 3).

When PW metal concentrations from all treatments and depths were compared with [SEM] or [SEM – AVS], they were best related to [SEM – AVS] (Figure 4). Values from all treatments followed a single relationship (Figure 4). Porewater Cd concentrations were not significantly correlated to extractable Cd concentrations (Figure 4). Porewater Ni and Zn were related to extractable metal concentrations, but the relationship was driven by the treatments that varied spiked metal concentrations and was confounded by covariance with [SEM – AVS]. Porewater Cd started to increase when [SEM, cd – AVS] values approached zero. Porewater Ni and Zn were under or near detection limits when [SEM – AVS] < 0, but high concentrations were observed when the difference was > 0 (Figure 4).

**Discussion**

The manipulation of AVS in the present study has several advantages. Oxidation is physical/chemical rather than a biogeochemical process and thus can be more readily controlled than reduction. Discrete [AVS] can be achieved quantitatively, by mixing oxic and anoxic sediments. The treatment sediments are all of otherwise similar character (e.g., particle size, TOC, total metal). A wide range of AVS to SEM relationships can be obtained. Finally, this approach allows use of moderate metal concentrations to achieve the desired [SEM – AVS].

A couple of previous studies (11, 33) have manipulated AVS in experimental sediments. The approaches included bubbling the overlying water with air (33) or using sediments from different origins (11). Bubbling oxidizes a limited amount of AVS only in surface sediments. Using sediments of different origins complicates interpretation due to differences in sediment characteristics including TOC and particle size, which could affect metal partitioning and bioavailability. Otherwise, most previous studies varied [SEM – AVS] by spiking metals into sediments of a single [AVS]. In those cases, relatively high metal concentrations are necessary to achieve the desired range of SEM/AVS (14, 34). More importantly, [SEM] co-varies with [SEM – AVS], possibly confounding determination of causation.

The redox gradient in the present experiments was typical of many natural sediments (20, 31). A vertical gradient of AVS in the present study is several advantages. Oxidation is physical/chemical rather than a biogeochemical process and thus can be more readily controlled than reduction. Discrete [AVS] can be achieved quantitatively, by mixing oxic and anoxic sediments. The treatment sediments are all of otherwise similar character (e.g., particle size, TOC, total metal). A wide range of AVS to SEM relationships can be obtained. Finally, this approach allows use of moderate metal concentrations to achieve the desired [SEM – AVS].

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"Surface sediments" (35, 37–39). The geochemical characteristics of "surface sediments" will be dependent upon how deep the surface sediment is defined or sampled. For example, the depth-weighted (AVS) in our S4 treatment increased from 8.8 μmol/g for 0–0.5 cm to 24 μmol/g for 0–3 cm. [SEM] in AVS was 2.2 μmol/g in the 0–0.5 cm but would be −15 μmol/g if "surface sediment" was integrated across the 0–3 cm. PW Cd was 1 μmol/L in 0–0.5 cm, but would be 0.17 μmol/L if integrated from 0 to 3 cm. The surface oxidized layer has long been recognized as an important component of the benthic environment for various benthic organisms (7, 16, 40), but a standardized way of defining "surface sediments" is needed. The more anoxic sediment included in the definition, the more likely it will underestimate the [SEM] at the (often oxidized) environmental interface most relevant to most infauna.

The general relationships between PW metal concentrations and [SEM] observed in this study are consistent with other laboratory and field studies (4, 14, 35, 41). But detailed profiles in PW seemed to be controlled by a combination of [SEM] and diffusion of metals to overlying water. The treatments displaying maxima in PW metals at the surface (e.g., all the PW Cd had [SEM] ≥ 0 in the surface sediments and deep sediments with [SEM] < 0. Consistent with this, Gobell et al. (42) observed maximum PW Cd concentrations in the oxygenated surface sediments from the Laurentian Trough, Gulf of St. Lawrence. However, some sediment treatments in the present study displayed surface maxima in [SEM] but not in pore water. These had a large excess SEM (SEM) > 0) and high PW metal concentrations at all depths. The large concentration gradient between porewater and overlying water in the latter sediments could have enhanced the diffusion of metals from the porewater in the surface sediments to overlying water as observed in field (21, 39) studies. Additionally, animal activity seemed to be responsible for lower PW Zn in the M2 treatment compared to respective sediments without animals. Aller (16), Santschi et al. (17), and Di Toro et al. (43) have suggested that bioturbation and irrigation alters the geochemical properties of sediments. The complexity of PW profiles and their dependence on factors other than depth-averaged AVS are important reasons that surface sediments on the scale of 1 cm should be carefully considered in studies of metal fate and bioavailability.

Although PW metals generally followed [SEM], large variations of PW metal concentrations were found over a small range of excess SEM when [SEM] > 0 (Figure 4). To further understand the behavior of PW metals as related to [SEM], we calculated apparent distribution coefficients (Kdpw), as defined by

\[
K_{dpw} (L/kg) = \frac{SEM (mg/kg)}{PW metal (mg/L)}
\]  

Among studies from the literature (Figure 5), Kdpw is negatively related to [SEM]. For example, most Kdpw values for Cd and Zn ranged from 10^−3 to 10^−5 when [SEM] > 0. The relationship emphasizes the strong affinity of Cd, Ni, and Zn to sulfides over other ligands. However, Kdpw also varied by 2 or 3 orders of magnitude for a given value of [SEM]. This variation could result from differences in experimental conditions, some of the most important of which are equilibration time, metal concentration, and sediment characteristics (e.g., particle size, chemical/mineral composition, TOC content) (17, 44–46). Kdpw from field sediments (12, 20, 47) were generally higher than from most experimental sediments (Figure 5). Equilibration time may be an important factor in this difference, because metals are equilibrated with sediments over long periods in nature. Carlson et al. (48) and Sibley et al. (38) reported that laboratory incubation of metal contaminated sediments resulted in decreased PW Cd and Zn concentration with time (Figure 5). Metal concentrations could also explain some differences in Kdpw between laboratory and field. Kdpw values continuously decreased with increasing metal concentration when [SEM] > 0 in our experiments. If metal binding sites and strength are dependent on metal concentrations in sediments, then high metal additions in short-term laboratory studies could exaggerate the PW metal partitioning beyond those found in the natural conditions.

Metals and sulfides interact in a complicated fashion. For example, the increase of AVS at higher spiked metal concentrations, both in surface and deep sediments, suggested that the spiked metals retarded the oxidation of AVS.
treatments was probably easily oxidizable Fe sulfides, whereas the AVS in higher SEM sediments could have been Ni and Zn sulfides, which have lower oxidation rates than Fe sulfides (11, 21). The inverse relationship between Cu—SEM extractability and AVS levels was also found in previous studies with natural and laboratory spiked sediments (22, 50–52).

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Supporting Information Available

Chemical analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(9) Morse, J. W.; Miller, F. J.; Cornwell, J. C.; Richardson, D. Earth-Science Rev. 1987, 24, 1–42.