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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 sediments spiked 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] in the surface sediments decreased by 65−95% due to oxidation during incubation; initial [AVS] was maintained at 0.5−7.5 cm depth. PW metal concentrations were correlated with [SEM − AVS] among all data. But PW metal concentrations were variable, causing the distribution coefficient, Kd_{pw} (the ratio of [SEM] to PW metal concentrations) to vary by 2−3 orders of magnitude at a given [SEM − AVS]. One reason for the variability was that vertical profiles in PW metal concentrations appeared to be influenced by diffusion as well as [SEM − AVS]. The presence of animals appeared to enhance the diffusion of at least Zn. The generalization that PW metal concentrations are controlled by [SEM − AVS] is subject to some important qualifications if vertical gradients are complicated, metal concentrations vary, or equilibration times differ.

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 benthic 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*). Multiple physical, chemical, and biological processes could 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

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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)

	AVS (μmol/g)						SEM (μmol/g)											
	t = 0 d		t = 18 d				t = 0 d			t = 18 d								
										Cd			Ni				Zn	
treatment			surface[a]		deep[b]		Cd	Ni	Zn	surface		deep	surface		deep		surface	deep
control	5.0	(0.1)[c]	0.4	(0.4)	4.5	(0.3)	0.002	0.2	0.8	0.002	(0.000)	0.001 (0.001)	0.2	(0.0)	0.2	(0.0)	0.8 (0.0)	0.8 (0.0)
M1	5.8	(0.4)	0.3	(0.1)	4.7	(0.1)	0.017	0.6	1.8	0.018	(0.002)	0.019 (0.000)	0.5	(0.0)	0.6	(0.1)	1.7 (0.1)	1.9 (0.1)
M2	6.2	(0.9)	1.3	(0.2)	5.7	(0.4)	0.050	2.7	6.7	0.059	(0.002)	0.060 (0.002)	2.6	(0.2)	2.9	(0.1)	7.0 (0.4)	7.4 (0.3)
M3	7.1	*d*	2.0	*d*	6.0	*d*	0.086	4.0	10.6	0.087	*d*	0.086 *d*	4.1	*d*	4.0	*d*	10.4 *d*	10.3 *d*
M4	7.2	(0.1)	2.1	(0.1)	7.1	(0.6)	0.180	6.0	15.3	0.185	(0.018)	0.190 (0.018)	6.3	(0.1)	6.0	(0.2)	15.1 (0.7)	15.1 (1.0)
S1	0.6	(0.2)	0.2	(0.2)	0.6	(0.1)	0.058	2.8	7.0	0.060	(0.005)	0.052 (0.007)	3.0	(0.2)	2.6	(0.2)	7.6 (0.2)	6.5 (0.7)
S2	6.2	(0.9)	1.3	(0.4)	5.7	(0.4)	0.050	2.7	6.7	0.059	(0.002)	0.060 (0.002)	2.6	(0.2)	2.9	(0.1)	7.0 (0.4)	7.4 (0.3)
S3	14.9	*d*	4.1	*d*	13.3	*d*	0.056	2.8	7.2	0.066	*d*	0.060 *d*	2.9	*d*	3.0	*d*	8.1 *d*	7.6 *d*
S4	35.4	(1.0)	8.8	(0.7)	31.5	(1.1)	0.058	2.6	7.2	0.089	(0.012)	0.056 (0.036)	3.4	(0.5)	2.5	(1.5)	10.5 (1.6)	6.8 (3.8)
No-anm[e]	6.5	(0.0)	1.0	(0.6)	5.4	(0.5)	0.050	2.6	6.5	0.050	(0.002)	0.053 (0.002)	2.6	(0.1)	2.7	(0.1)	6.8 (0.1)	6.7 (0.1)

[a] Values from 0 to 0.5 cm section. [b] Depth-averaged from 0.5 to 7.5 cm sections. [c] Values in parentheses are concentration differences between two replicates. [d] Represents no replicate. [e] Represents the treatment without animals.

[SEM] constant (see below). Sediment with S2-level AVS but without spiked metals was used as a control treatment. Following appropriate sediment manipulation, 5 different species of test animals (10 *Macoma balthica,* 10 *Potamocorbula amurensis,* 14 *Neanthes arenaceodentata,* 20 *Heteromastus filiformis, and* 20 *Spiophanes missionensis*) were added to each experimental sediment for the bioaccumulation study (see ref *22* for details). Densities of test animals were comparable to those found in natural sediments (*23*−*27*). A treatment without animals (No-animal) was also included to test the effect of animal activity on metal partitioning. The No-animal treatment employed M2 sediments. All treatments had two replicates except for M3 and S3 treatments, which had only one replicate.

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 N_2 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] 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 ϕ, and the percentages of sand, silt and clay were 1, 74, and 25%, respectively.

The metal stock solutions for spiking experimental sediments were made by dissolving appropriate amounts of reagent grade $CdCl_2$, $NiCl_2 \cdot 6H_2O$, and $ZnSO_4 \cdot 7H_2O$ in deoxygenated water at a salinity of 25. The sediments for the M1−M4 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 N_2 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.

Sediment Sampling and Analysis. All the sediment samples were handled in a glovebag filled with N_2 gas. The experimental containers and glassware used for chemical analysis and sample storage were acid washed and then soaked in deaerated Milli-Q water for 1 wk. Sediment samples for SEM and AVS analyses were collected at the end of 18-d incubation with test animals. Three replicate cores were taken from each container using 140-mL syringe cores (5-cm diameter). The cores were immediately transferred into a glovebag under N_2 atmosphere and sectioned to 5 depth intervals (0−0.5, 0.5−1.5, 1.5−3, 3−4.5, and 4.5−7.5 cm, from surface to bottom). 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

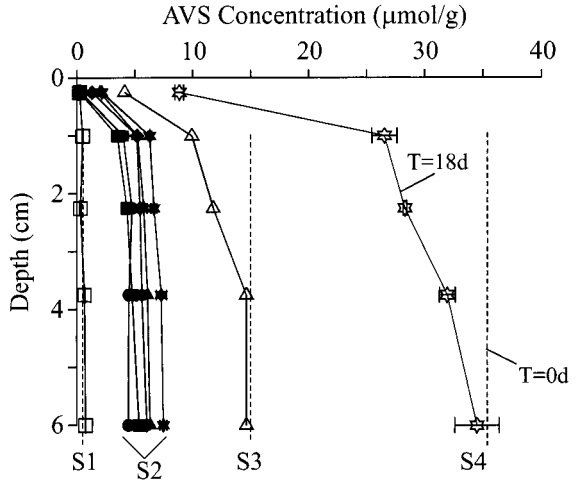

FIGURE 1. Vertical profiles of [AVS] (μmol/g) following 18 d incubation in the variable AVS series [S1 (□), S2 (◆), S3 (△), S4 treatment (✡)] and variable SEM series [control (●), M1 (■), M2 (◆), M3 (▲), M4 treatment (✱)]. The dashed lines represent initial [AVS] (μmol/g) at the beginning of incubation in S1, S3, and S4. The error bar represents the concentration difference between two replicates. S2 and M2 is an identical treatment.

with ultrapure hydrochloric acid (Ultrex) to a final pH of 1−2 and stored at room temperature until analysis.

AVS analyses were conducted within 2 weeks after sampling as recommended by Lasorsa and Casas (*30*). The [AVS] and [SEM] were determined by the cold-acid (1 N HCl) purge and trap technique described by Boothman and Helmstetter (*31*). The [SEM] and porewater metals were determined by ICAP-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 ΣSEM_{Cd}, ΣSEM_{Zn}, and ΣSEM_{Ni}, respectively. For example, ΣSEM_{Cd} used for [SEM − AVS] evaluation include the sum of the molar concentrations of Ag, Cu, Pb, and Cd. ΣSEM_{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 μmol/g; [AVS] in the deep sediment varied with treatment from 0.6 to 31.5 μmol/g (Table 1). In the variable SEM series (same nominal [AVS]), measured [AVS] varied from 0.3 to 2.1 μmol/g in the surface and 4.5−7.5 μmol/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 ΣSEM_{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 ΣSEM_{total} for the Control and M1, respectively, but were < 4% of ΣSEM_{total} in other treatments.

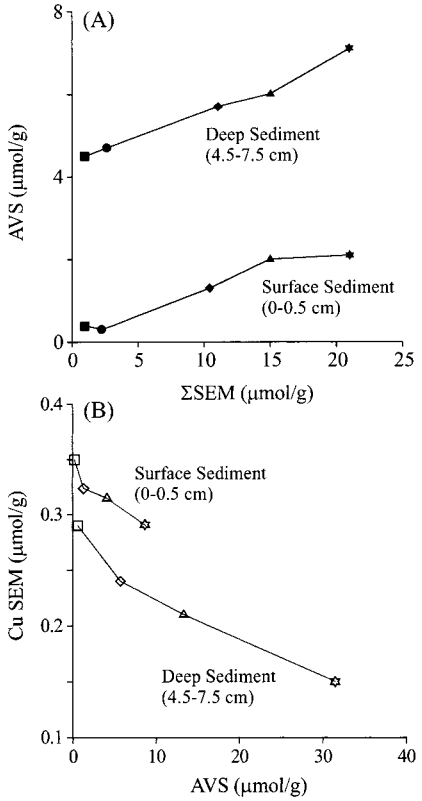

FIGURE 2. (A) Relationship of [AVS] (μmol/g) to the sum of the extractable metals (ΣSEM) in the surface and deep sediment from control (●) and variable SEM series [M1 (■), M2 (◆), M3 (▲), M4 treatment (✱)]. (B) Relationship of AVS (μmol/g) to Cu SEM (μmol/g) in the surface and deep sediment from variable AVS series [S1 (□), S2 (◆), S3 (△), S4 treatment (✡)].

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 μmol/g, while total Cu was nearly constant (0.75 μmol/g) for all treatments. The extractability of Cu was higher in surface than in deep sediment for a given [AVS].

The depth variations of [ΣSEM − AVS] for Cd, Ni, and Zn after the 18-d incubation are shown in Figure 3. A strong vertical gradient in [ΣSEM − AVS] was observed for all metals with a maximum at the surface as a result of declining [AVS] toward the surface. [ΣSEM_{Ni} − AVS] and [ΣSEM_{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 ΣSEM_{Cd} for all treatments was only small fraction of [AVS]. Therefore, [ΣSEM_{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

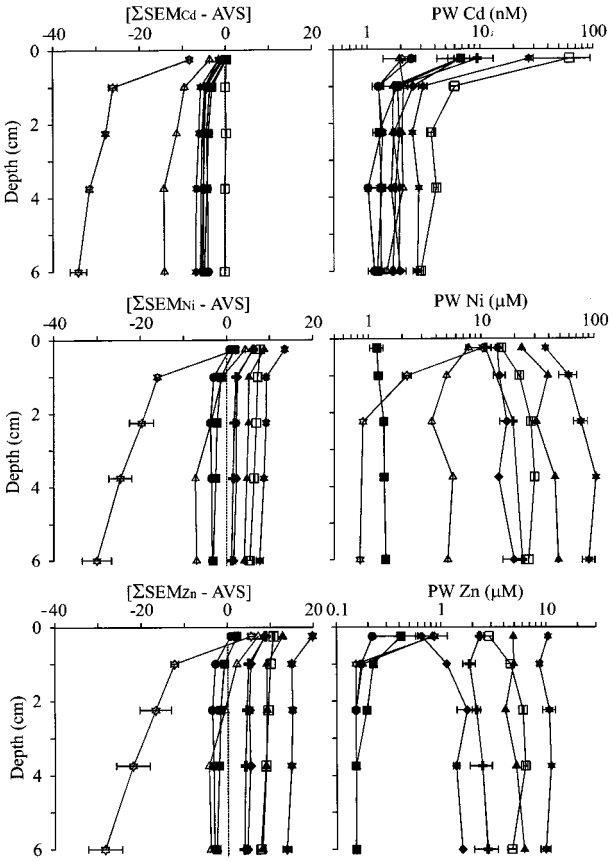

FIGURE 3. Vertical profiles of [ΣSEM − AVS] (μmol/g) and PW Cd (nM), Ni (μM), and Zn (μM) in the variable AVS series [S1 (□), S2 (◆), S3 (△), S4 treatment (✡)], variable SEM series [control (●), M1 (■), M2 (◆), M3 (▲), M4 treatment (✱)], and No-animal treatment (+). The error bar and dotted vertical lines represent concentration difference between two replicate treatments and [SEM − AVS] = 0, respectively.

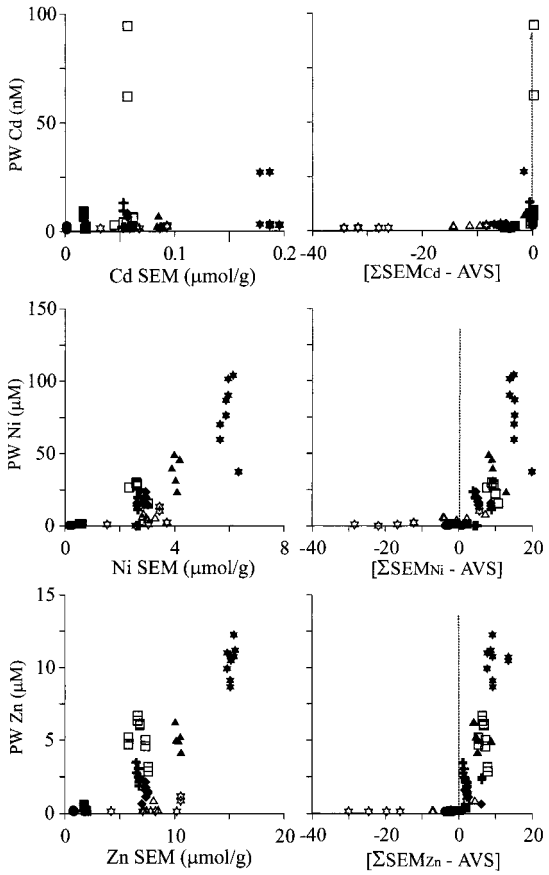

FIGURE 4. Porewater Cd (nM), Ni (μM), and Zn concentration (μM) as a function of SEM, and [ΣSEM − AVS] (μmol/g) for the variable AVS series [S1 (□), S2 (◆), S3 (△), S4 treatment (✡)] or variable SEM series [control (●), M1 (■), M2 (◆), M3 (▲), M4 treatment (✱)] and No-animal treatment (+). The dotted vertical lines represent [SEM − AVS] = 0.

of [ΣSEM − 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 [ΣSEM − 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 [ΣSEM − AVS], they were best related to [ΣSEM − 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 [ΣSEM − AVS]. Porewater Cd started to increase when [ΣSEM_{Cd} − AVS] values approached zero. Porewater Ni and Zn were under or near detection limits when [ΣSEM − 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 difference 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 necessary 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 was also found in some other laboratory studies (*34*−*36*), but few studies adopted fine-scale sampling of porewater at multiple depths (e.g., ref *20*). The AVS minima in the surface sediments were most likely due to oxidation by the overlying water. The vertical AVS gradient caused [SEM − AVS] and PW metal concentrations to change with depth. The changes were most pronounced from 0 to 0.5 cm. In natural and experimental sediments, AVS is typically determined from

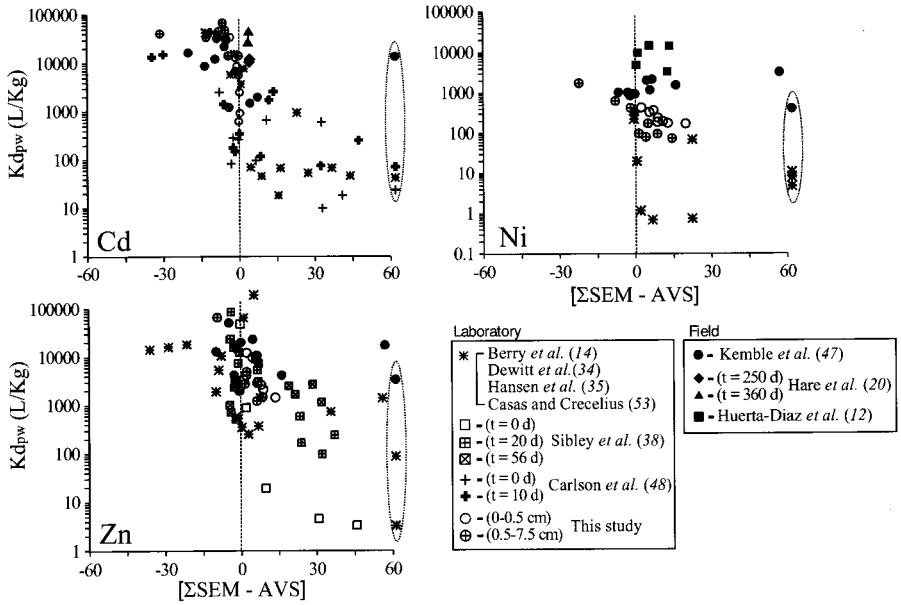

FIGURE 5. Apparent partition coefficient (Kd_{pw}) (L/Kg) between metals in porewater and sediments (SEM) as a function of [ΣSEM − AVS] (μmol/g) calculated from this study and literatures. The dashed vertical lines represent [ΣSEM − AVS] = 0. The data in enclosed in dotted line had [ΣSEM − AVS] > 60. The *t* = *x* d represents that metals were equilibrated with sediments for *x* days.

"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. [ΣSEM_{Zn} - 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 Zn 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 − AVS] at the (often oxidized) environmental interface most relevant to most infauna.

The general relationships between PW metal concentrations and [ΣSEM − AVS] 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 [ΣSEM − AVS] and diffusion of metals to overlying water. The treatments displaying maxima in PW metals at the surface (e.g., all the PW Cd) had [ΣSEM − AVS] ≥ 0 in the surface sediments and deep sediments with [ΣSEM − AVS] < 0. Consistent with this, Gobeil 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 − AVS] but not in pore water. These had a large excess SEM ([ΣSEM − AVS] ≫ 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 ≤ 1 cm should be carefully considered in studies of metal fate and bioavailability.

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

$$Kd_{pw}\ (L/kg) = \frac{SEM\ (mg/kg)}{PW\ metal\ (mg/L)} \qquad (1)$$

Among studies from the literature (Figure 5), Kd_{pw} is negatively related to [ΣSEM − AVS]. For example, most Kd_{pw}s for Cd and Zn ranged from 10^3−10^5 when [ΣSEM − AVS] < 0. The range was from 10^1−10^3 when [ΣSEM − AVS] > 0. The relationship emphasizes the strong affinity of Cd, Ni, and Zn to sulfides over other ligands. However, Kd_{PW} also varied by 2 or 3 orders of magnitude for a given value of [ΣSEM − AVS]. 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*). Kd_{pw}s 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 Kd_{pw} between laboratory and field. Kd_{pw} values continuously decreased with increasing metal concentration when [ΣSEM − AVS] > 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

(see also refs *34*−*36*, *49*). Most of the AVS in low SEM treatments was probably easily oxidizable Fe sulfides, whereas the AVS in higher SEM sediments could have been Ni and Zn sulfides, which have slower 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.

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