

Influence of AVS on the Partitioning of Bioavailable Zn to Various Binding Phases in Sediments

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Sediment microcosm experiments were conducted for 14 and 28 days using Zn spiked sediment to examine the changing distribution of bioavailable sediment-bound Zn at different SEM (simultaneously extracted metal)-Zn/ AVS (acid volatile sulfide) mole ratios as a function of time and amphipod density. In surficial sediments (0-1 cm), AVS concentrations significantly decreased due to bioturbation and oxidation, while SEM-Zn concentrations remained unchanged. As a result, SEM-Zn/AVS ratios in the surface sediment were greater one although the ratios were designed as less than one initially. With increasing SEM-Zn/AVS ratios in surficial sediments, concentrations of potentially bioavailable MgCl₂ extractable-Zn, NaOAc extractable-Zn and pore water-Zn significantly increased, while concentrations of SEM-Zn were not significantly varied. Results suggested that as AVS concentrations decreased, AVS bound Zn was partitioned to other sediment fractions (i.e. MgCl₂ and NaOAc extractable) and the pore water, resulting in changes in Zn bioavailability in surficial sediments. Concentrations of AVS, SEM-Zn and pore water-Zn remained unchanged in the deeper layers (>1 cm) of the sediment.

Key words: AVS, Zn, Bioavailable, SCE, Pore Water, Microcosm, Diporeia, Sediment, Metal

INTRODUCTION

Following the initial studies of Di Toro *et al.* (1990), many laboratory and field experiments have examined the influence of AVS on pore water metal concentrations, subsequent bioaccumulation, bioavailability, and toxicity of metals in marine and freshwater sediments (Ankley *et al.*, 1993; Peterson *et al.*, 1996; Lee *et al.*, 2000). Based on the AVS normalization model, all sulfide binding sites will be occupied by dissolved metals resulting in excess metal and increasing metal bioavailability in the pore water when simultaneously extracted metal (SEM)/AVS ratios are >1 (Di Toro *et al.*, 1990). Meanwhile, all dissolved metals should be bound in sulfide binding sites at SEM/AVS ratios < 1, thus they should be biologically unavailable (Di Toro *et al.*, 1990).

Even though AVS model was well studied for bioavailability, and bioaccumulation of sediment-bound metal in many microcosm experiments, the change of distribution of bioavailable sediment-bound metal by the change of metal concentrations among the AVS, easily extractable sediment fractions and pore water

was not well examined (Song, 2002).

The objectives of this study were to examine changes in Zn distribution among AVS, easily extractable sediment fractions (MgCl₂, Na-acetate) and pore water in sediment which can influence on Zn bioavailability at SEM-Zn ratios <1 and >1. Sediment microcosm experiments were conducted for 14 day and 28 days as a function of Zn concentration, exposure time, depth and *Diporeia* spp. density. *Diporeia* spp. is an appropriate invertebrate to examine behavior of sediment-bound metal by organisms because it is a dweller with a high tolerance against heavy metals in the sediment-water interface (Song, 2003).

MATERIALS AND METHODS

Sampling and handling of diporeia and sediments

Diporeia spp. and surficial sediments were collected using a PONAR grab sampler at a water depth of about 60 m in Lake Michigan in cooperation with P.F. Landrum (Great Lake Research Laboratory, NOAA). The amphipods were isolated from the surficial sediments (0-3 cm) using gentle screening with cool lake water (4-6°C). *Diporeia* were then placed in a cooler (4-6°C, dark)

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with unsieved sediments and lake water. The sediments were sieved with mesh screen (250 μm) using deoxygenated lake water in the laboratory to remove any other invertebrates and coarser material. The sieved (<250 μm) sediments were used as a substrate for *Diporeia* in microcosm experiments because *Diporeia* selectively feeds on <250 μm sized grain particles (Kraft, 1979; Song, 2003).

Preparation Zn and AVS spiked sediments

Zinc concentrations for sediment spiking were determined to achieve appropriate SEM/AVS ratios (i.e. SEM/AVS <1 and SEM/AVS >1) for the microcosm study. The lowest concentration (C0) of Zn in the sediments was defined as the concentration of Zn in the collected and sieved sediment and referred to as the unspiked control sediment. The ranges of spiked Zn concentrations (C1-C4) in the sediments were selected by considering previous literature and the adsorption rate of Zn on AVS fraction during the spiking of sediments at SEM-Zn/AVS ratios <1 and >1. Sediment Zn-spiking was conducted following previously established procedures (ASTM, 1995; Peterson *et al.*, 1996) at 4°C for 15 days. The nominal SEM-Zn/AVS ratios were prepared to be approximately 0.2 (control), 0.4, 0.8, 2 and 4 (Table 1).

Microcosm design with *diporeia* in the spiked sediments

The changes in concentrations of AVS, Zn in SEM and easily extractable fractions and pore-water was determined as a function of incubation time (0, 14 and 28 days), organism density (0, 9 and 18 amphipods per 230 cm^2) and sediment depth (0-1, 1-2 and 2-2.5 cm) (Fig. 1). Food was not supplied during the sediment incubation because *Diporeia* can survive in sediment for several months without added food (Landrum, 1989; Landrum and Faust, 1994).

Analysis of Zn in sediments and pore water

Zn concentrations in potentially bioavailable frac-

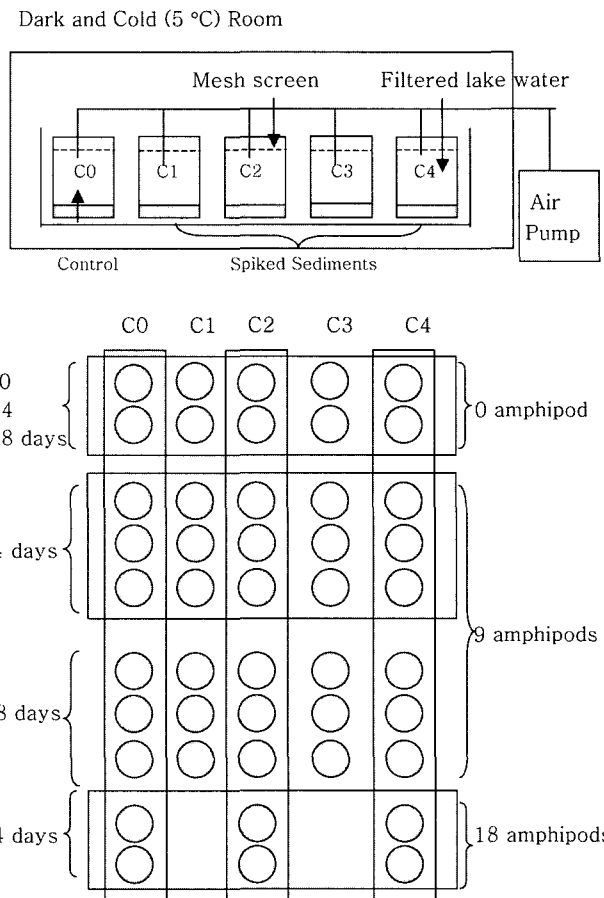


Fig. 1. Configuration of sediment microcosm experiments.

tions (MgCl_2 and Na-acetate fractions) were examined using about 4 g of wet sediment before and after each sediment microcosm experiment following a sequential chemical extraction (SCE) procedure (Tessier *et al.*, 1979).

The concentrations of AVS and SEM-Zn were measured by the diffusion-precipitation method described in Song (2000).

To analyze pore water-Zn, approximately 10 g of wet sediment was taken from each microcosm and centrifuged (30 min, 140 g). The supernatant was then filtered using a acid-rinsed syringe filter (0.45 μm) and acidified with 5 μl of ultrapure HNO_3 under a nitrogen atmosphere in a glove bag. Zinc concentrations in the sediment extracts and pore water were

Table 1. Experimental design of SEM-Zn/AVS ratios and spiking of Zn in sediments for microcosm experiments.

Conc. (No.)	C0 ^a	C1	C2	C3	C4
Nominal SEM-Zn/AVS (for 5 $\mu\text{mol/g}$ of AVS in sediment)	0.2	0.4	0.8	2	4
SEM-Zn ($\mu\text{mol/g}$ dry sed)	1.2	2	4	10	20
SEM-Zn ($\mu\text{g/g}$ dry sed)	78	131	262	654	1308
Added [Zn] ($\mu\text{g/g}$ dry sed)	-	154	308	769	1539

a: control treatment without spiking of Zn

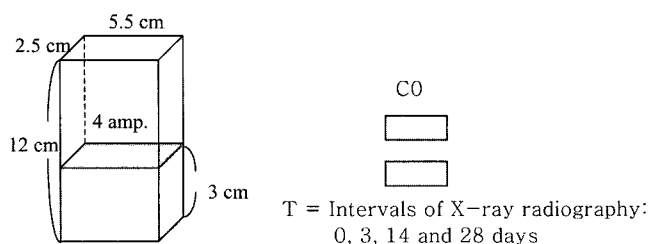


Fig. 2. Configuration of X-ray tray microcosm.

then measured by flame or graphite furnace atomic absorption spectroscopy (AAS).

Preparation of X-radiography

Bioturbation depth of *Diporeia* on the surficial sediments in C0 treatment was examined using X-radiography (Fig. 2). For this experiment, four animals were put in a X-ray tray.

Statistical analysis

Statistical analyses of the relationships between the concentrations of Zn in SEM (SEM-Zn), easily extractable fractions ($\text{MgCl}_2\text{-Zn}$ and NaOAc-Zn) and pore water (pore water-Zn) were performed by analysis of variance (ANOVA), Pearson correlation coefficients and linear regression analysis (Sokol and Rolhf, 1995).

RESULTS AND DISCUSSION

Bioturbation of sediment by *diporeia*

Based on X-ray analysis, *Diporeia* constructed small U-shape burrows up to 1 cm within 3 days (Fig. 3). *Diporeia* bioturbation depth (1 cm) coincided well with the results of previous ^{137}Cs radiolabeled sediment (Robbins *et al.*, 1979) and fluorescent particle (Lopez and Elmgren, 1989) studies. The U-shaped burrows may provide ventilation and/or the flow of nutrients and excreted materials in dissolved phases (Aller, 1978).

These findings suggest that sediments collected from the 0-1 cm depth are appropriate for examining the influence of AVS on the bioavailability of sediment-bound Zn to *Diporeia*.

AVS and Zn in various binding phases in sediments

Initially, the sediment microcosms were designed to achieve SEM-Zn/AVS ratios <1 (C0, C1 and C2) and

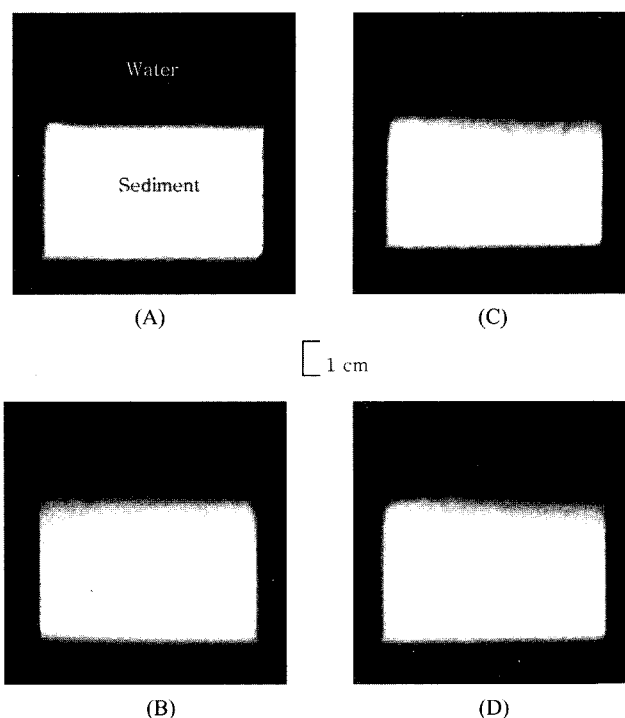


Fig. 3. X-ray figures for bioturbation of *Diporeia* at C0 treatment (A: t=0 day, B: t=3 day, C: t=14 day, D: t=28 day).

>1 (C3 and C4). AVS concentrations decreased in most sediment microcosms, with the greatest AVS decreases occurring in microcosms with low SEM-Zn (C0-C2), however, SEM-Zn concentrations remained relatively constant in the sediment microcosms during the 14 day and 28 day experiments (Fig. 4A and 4B). Therefore, SEM/AVS ratios in surficial sediments (0-1 cm) for most treatments were greater than one at the end of both 14 days and 28 days (Fig. 4C).

Experimental results in this study suggest that oxidation of AVS by the aerated overlying water and the diffusion of oxygenated water into the sediment by *Diporeia* burrowing activity (i.e. bioturbation) had important roles for AVS reduction. Consistently with our results, Lee *et al.* (2000) also observed significant (85%) decreases in AVS concentrations in control (no animal) treatments compared to AVS concentrations in initial treatments due to changing and continuous aeration of the overlying water.

AVS and SEM-Zn concentrations, and those ratios in the C0-C4 treatments at different *Diporeia* densities (2 fold) were not significantly different at 14 days (Fig. 5A-5C). Perhaps a two-fold density difference for *Diporeia* was not sufficient to cause significant differences in these parameters.

AVS concentrations were dramatically decreased in surficial sediments compare to deeper layers (1-2.5 cm),

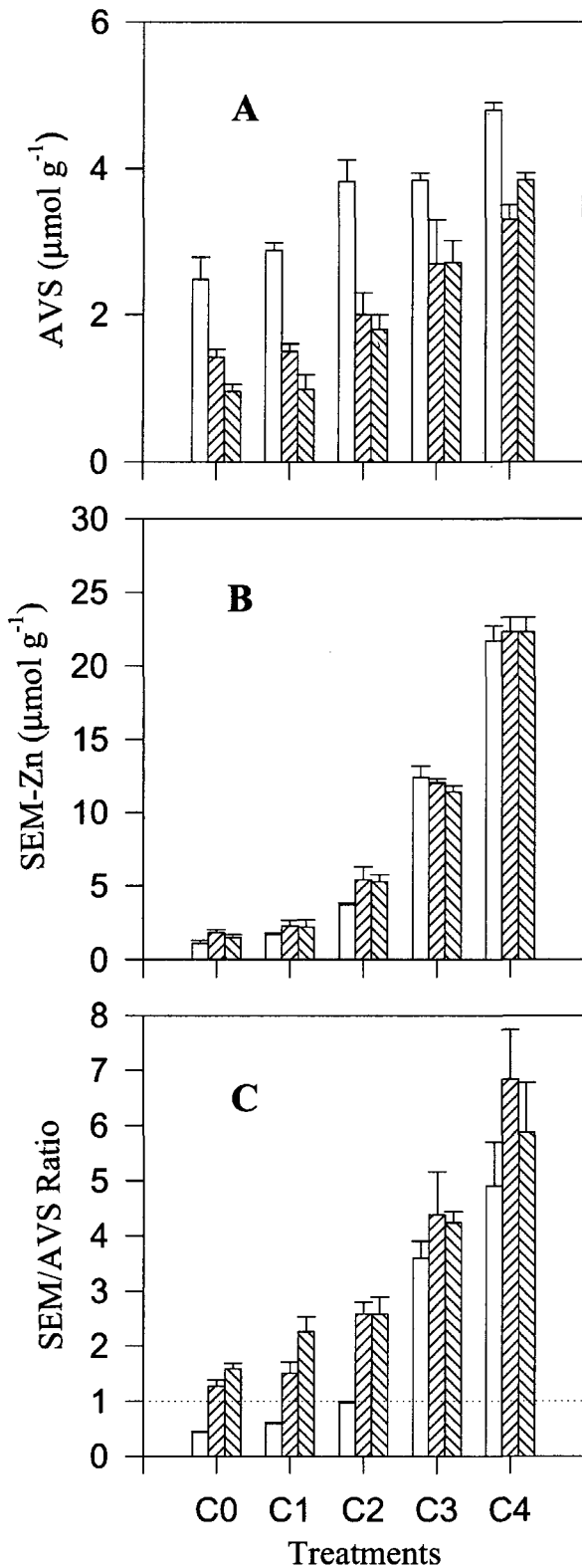


Fig. 4. AVS (A), SEM-Zn (B), and SEM-Zn/AVS ratios (C) as a function of time (\square : t=0 d, ▨ : t=14 d, ▩ : t=28 d) in microcosm surficial sediments.

however, SEM-Zn concentrations were not vertically changed as a function of time and amphipod density

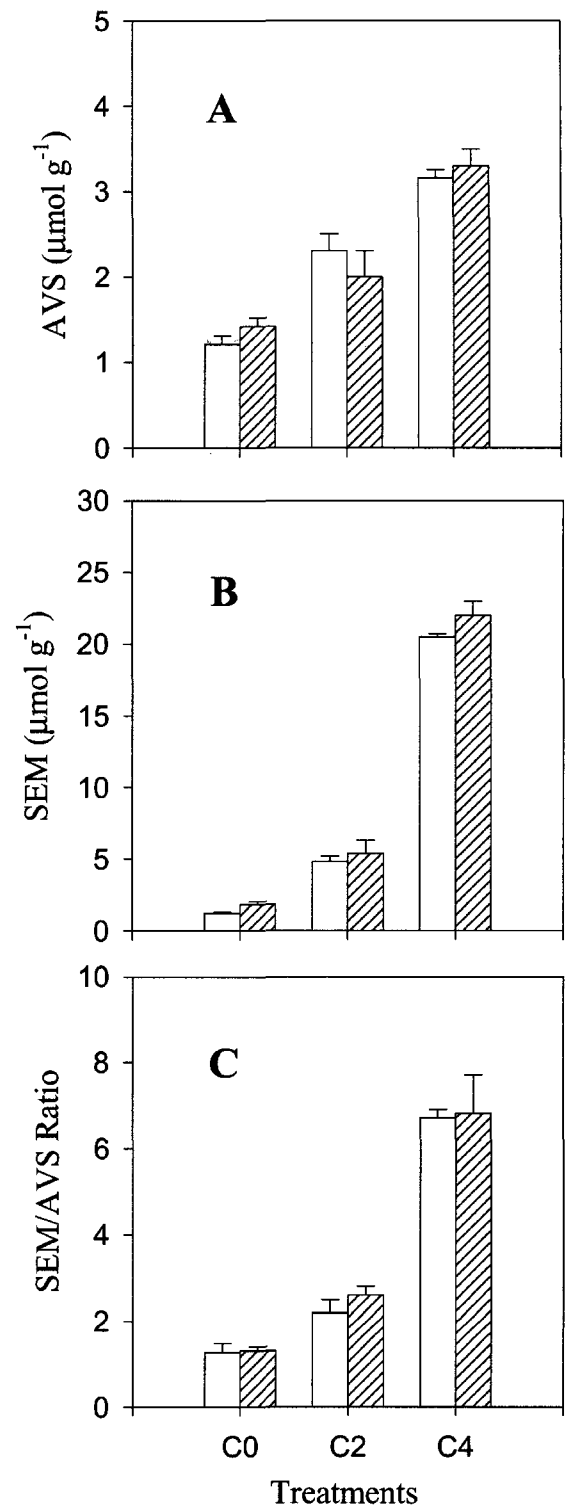


Fig. 5. AVS (A), SEM-Zn (B) and SEM-Zn/AVS ratios (C) as a function of density (\square : high density, ▨ : low density) in microcosm surficial sediments.

(Fig. 6 and 7). These results made that SEM-Zn/AVS ratios were greatest in surficial sediment compare to deeper sediment (Fig. 6 and 7). Several microcosm

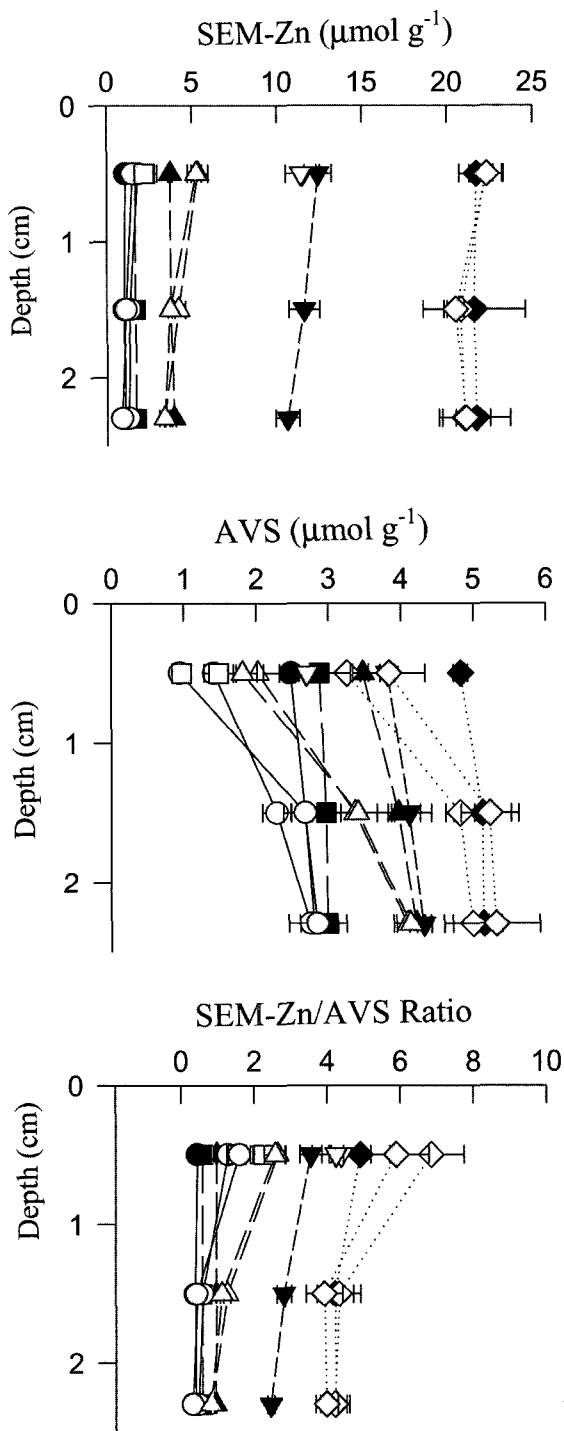


Fig. 6. Depth profile of AVS and SEM-Zn concentrations and SEM-Zn/AVS ratios as a function of time (C0: ●-t=0 d, ○-t=14 d, ○-t=28 d; C1: ■-t=0 d, □-t=14 d, □-t=28 d; C2: ▲-t=0 d, △-t=14 d, △-t=28 d; C3: ▼-t=0 d, ▽-t=14 d, ▽-t=28 d; C4: ◆-t=0 d, ◇-t=14 d, ◇-t=28 d).

studies with freshwater benthic organism (i.e. amphipods, oligochaetes, polychaetes) also showed constant AVS concentrations in deeper layers compared to surficial

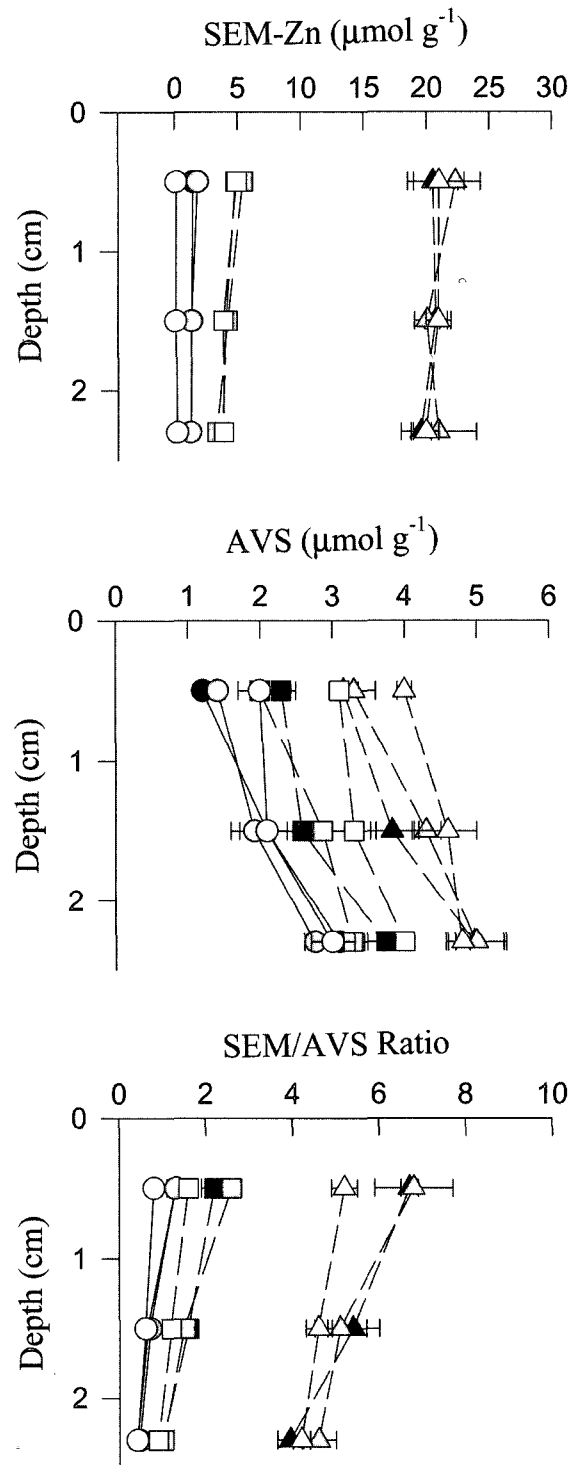


Fig. 7. Depth profile of AVS and SEM-Zn concentrations and SEM-Zn/AVS ratios as a function of density (C0: ●-high, ○-low, ○-control; C2: ■-high, □-low, □-control; C4: ▲-high, △-low, △-control).

sediments (Dewitt *et al.*, 1996; Peterson *et al.*, 1996). The depth of decreasing AVS concentrations in microcosm studies generally corresponds with the bioturbation depth of the organism investigated (Dewitt *et al.*, 1996;

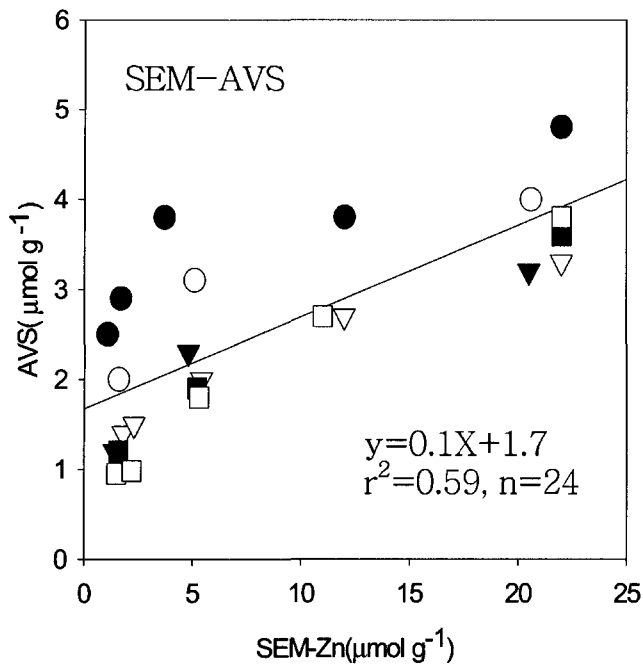


Fig. 8. Relationships between SEM-Zn and AVS in surficial sediments (0-1 cm) (●: t=0 d, amp=0; ○: t=14 d, amp=0; ▽: t=14 d, amp=9, ▼: t=14 d, amp=18; ■: t=28 d, amp=0; □: t=28 d, amp=9).

Peterson *et al.*, 1996).

Decreases in AVS concentrations in surficial sediment were greater in lower SEM-Zn treatments (C0-C2) than higher SEM-Zn treatments (C3-C4) (Fig. 4A). In addition, sediment microcosm results showed that AVS and SEM-Zn concentrations were linearly related ($r^2=0.59$, $n=24$, $P<0.05$) in surficial sediments (Fig. 8). Increasing AVS concentrations with increasing SEM-Zn concentrations implies that sulfide in sediment is stabilized by spiked Zn and Zn sulfide is thermodynamically more stable relative to iron sulfide. Peterson *et al.* (1996) also found that AVS concentrations in surficial sediments were usually greater with Zn increase in added.

Significant increases in AVS concentrations were observed in the C4 (highest SEM-Zn) treatment in the 28 day microcosms compared to the 14 day microcosms (Fig. 4A). Increases in AVS concentrations from 14 to 28 days may be due to the bacterial decomposition of organic matter (i.e. dead organisms and fecal pellets) and build up of H_2S during the additional 14 days. The change of concentrations of AVS in the sediments, therefore, is a function of oxidation of AVS by oxygen supply from water and bioturbation, the stabilization of AVS by the presence of zinc sulfide and increases in AVS concentrations by organic matter decomposition dur-

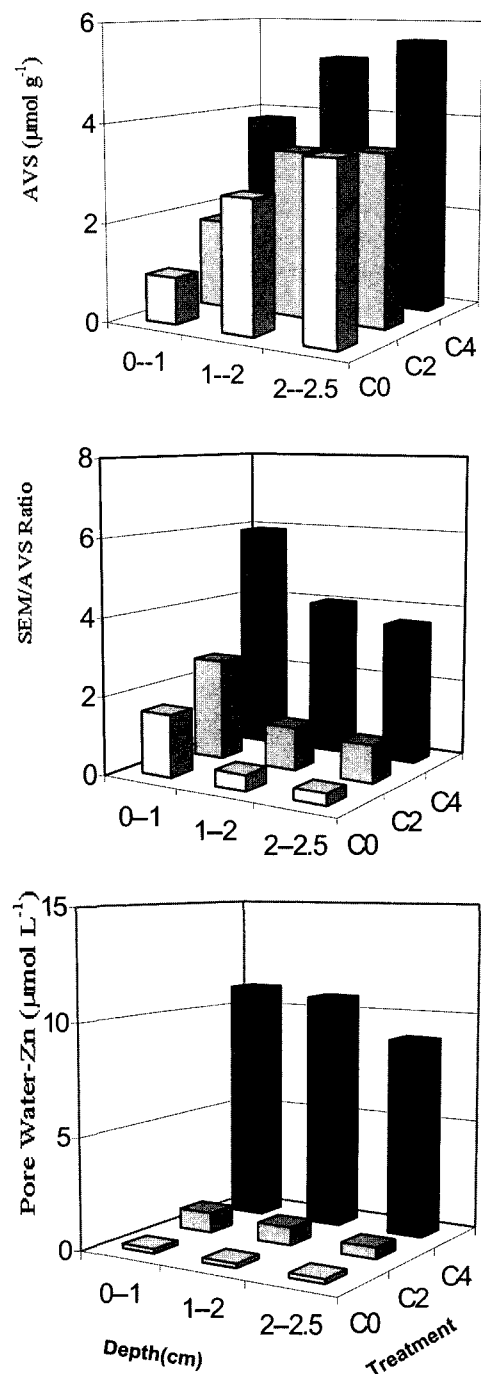


Fig. 9. Depth variation of AVS, SEM-Zn/AVS ratios and pore water-Zn concentrations in C0, C2 and C4 treatments in 28 day sediment microcosm experiments.

ing the microcosm experiments.

Decreasing pore water Zn concentrations with increasing depth generally corresponded with increasing AVS concentrations and decreasing SEM-Zn/AVS ratios as a function of time (Fig. 9). Other microcosm studies also showed decreasing SEM-Zn/AVS ratios, pore water-Zn and increasing AVS concentrations with increas-

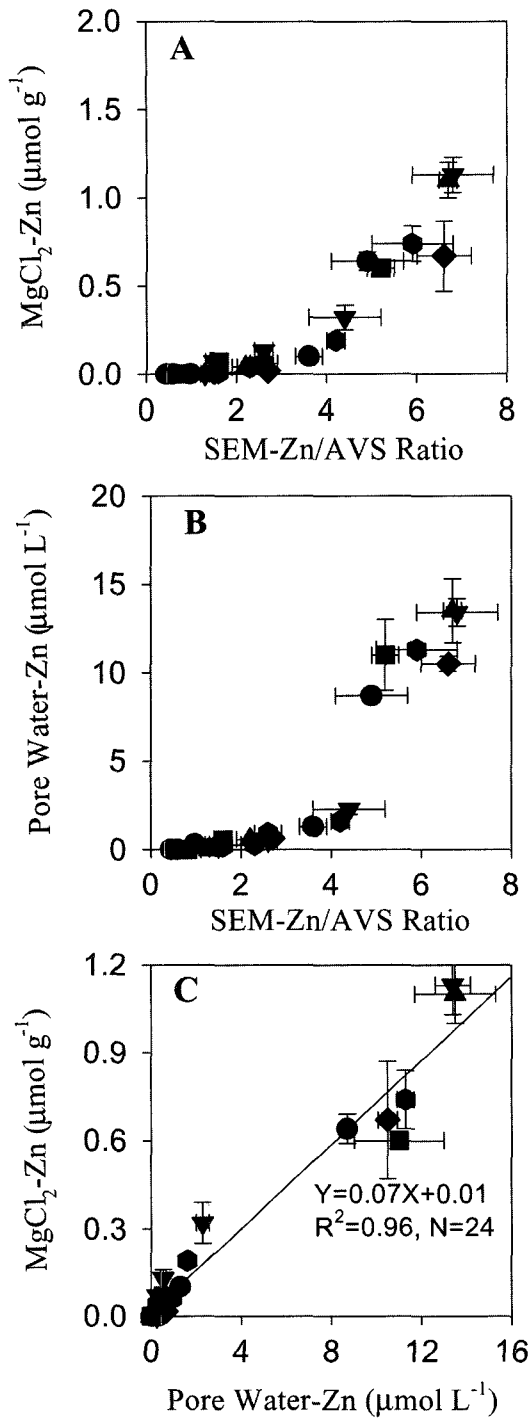


Fig. 10. Variation of MgCl₂-Zn (A) and pore water-Zn (B) concentration with SEM-Zn/AVS ratios and correlation between MgCl₂-Zn and pore water-Zn concentrations (C) (● : t=0 d, amp=0; ■: t=14 d, amp=0; ▲: t=14 d, amp=18; ▼: t=14 d, amp=9; ◆: t=28 d, amp=0, ●: t=28 d, amp=9).

ing depth (Peterson *et al.*, 1996). These results also strongly suggest that AVS is a major controlling factor for pore water-Zn distributions in anoxic sediments (Di Toro *et al.*, 1990).

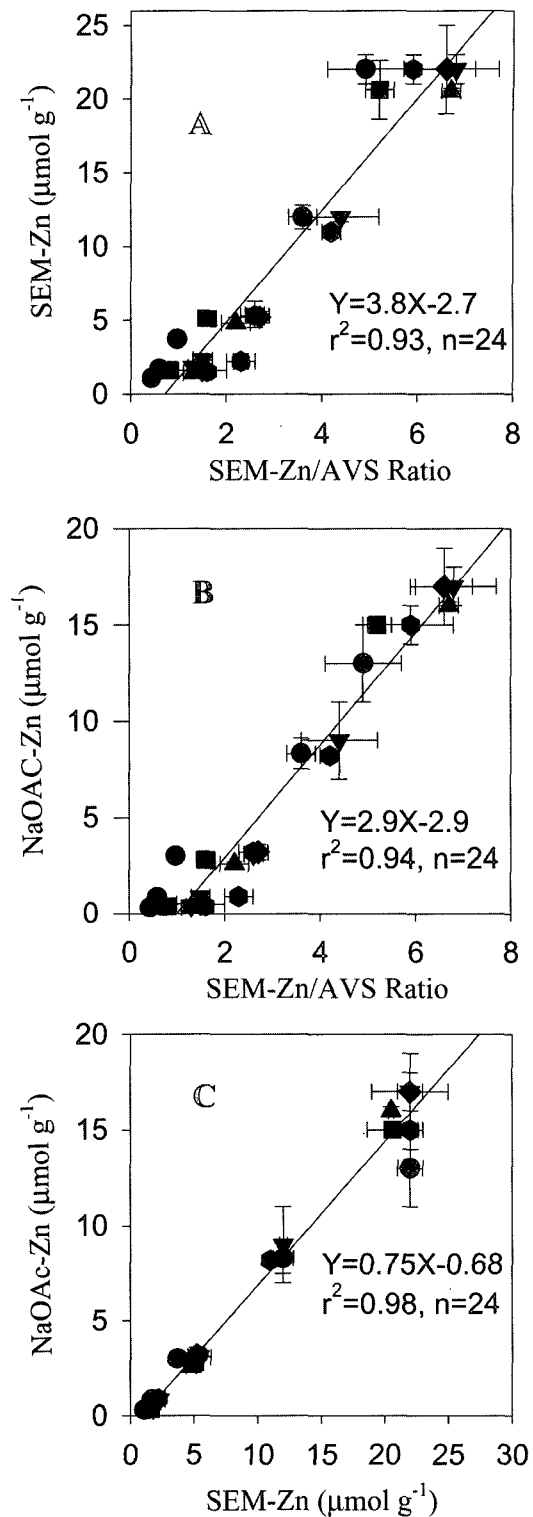


Fig. 11. Variation of SEM-Zn (A) and NaOAc-Zn (B) concentrations with SEM-Zn/AVS ratios and correlation between SEM-Zn and NaOAc-Zn concentrations (C) (●: t=0 d, amp=0; ■: t=14 d, amp=0; ▲: t=14 d, amp=18; ▼: t=14 d, amp=9; ◆: t=28 d, amp=0, ●: t=28 d, amp=9).

Changing AVS concentration, and its corresponding affect on SEM-Zn/AVS ratio, also affected the dis-

tribution of $MgCl_2$ -Zn, NaOAc-Zn and pore water-Zn in surficial sediments. NaOAc-Zn, $MgCl_2$ -Zn and pore water-Zn concentrations significantly increased with increasing SEM-Zn/AVS ratios (Fig. 10A, 10B, 11A and 11B). These results suggest that AVS is an important phase controlling factor to partitioning of Zn in sediments. In particular, pore water and the $MgCl_2$ extractable sediment fraction ($r^2=0.96$, $n=24$, $P<0.01$) and NaOAc-Zn and SEM-Zn extractable sediment fraction ($r^2=0.98$, $n=24$, $P<0.01$) were significantly correlated each other (Fig. 11C and 12C). These results may be due to the equilibrium partitioning of spiked Zn in these fractions in response to changing geochemical (i.e. SEM-Zn/AVS ratios) conditions.

SEM-Zn is defined as a simultaneously extracted Zn with AVS from sediment by 1 N HCl (Di Toro *et al.*, 1990). However, SEM-Zn does not mean that all Zn is necessarily bound by AVS, but may include Zn partitioned in either AVS or other fractions (i.e. operational $MgCl_2$ or NaOAc extractions) in sediments, which are also extractable by 1 N HCl. Therefore, although AVS concentrations decrease, SEM-Zn concentrations may not significantly change since sediment Zn is still extracted along with other fractions (i.e. $MgCl_2$ or NaOAc) as SEM-Zn. That is, binding fractions (or phases) other than AVS in sediments may play a role in controlling sediment Zn distribution. As a result, Zn partitioning in sediment can change from AVS to other binding phases (i.e. $MgCl_2$, NaOAc) or from other binding phases to AVS as geochemical conditions of sediment change.

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