

## 二仁溪底泥中酸可揮發性硫(AVS)之分佈

### DISTRIBUTION OF ACID VOLATILE SULFIDE IN THE ELL-REN RIVER SEDIMENTS

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#### ABSTRACT

The aim of this study is to find the spatial distribution of sediment toxicity indicators, acid volatile sulfide (AVS), simultaneously extracted metal (SEM), (SEM / AVS) and (SEM - AVS), contained in the Ell-Ren river sediments, and to assess the toxicity of heavy metals (Cu and Pb) for *Tubifex* sp., the predominant benthic macroinvertebrate in the Ell-Ren river. Results show that the concentrations of both AVS and SEM do not correlate with the sediment depth. Low molar ratios of SEM to AVS (ranged from near zero to 1.9) are found at sites enriched with SEM and AVS; whereas high molar ratios of SEM to AVS (up to 128) are found at other sites with low concentrations of SEM and AVS. The molar differences between SEM and AVS (SEM - AVS) are negative at sites enriched with SEM and AVS (i.e., heavily heavy-metal polluted and anoxic); whereas low (positive) values of (SEM - AVS) are found in more clean and oxic sites. These results indicate that the remobility and bioavailability of heavy metals contained in sediments of the Ell-Ren river system are low. In the toxicity tests, the mortality of *Tubifex* sp. increased with the increasing molar ratio of SEM to AVS. In addition, the critical point of lethal toxicity to *Tubifex* sp. was found largely at the values of 2 for  $SEM_{Cu}/AVS$  or 3 for  $SEM_{Pb}/AVS$ .

#### KEYWORDS

Acid volatile sulfide; benthic macroinvertebrate; heavy metals; sediments; simultaneously extracted metal; toxicity

#### INTRODUCTION

The bioavailability of heavy metals in sediments is influenced by the extent and binding forms that heavy metals associated with the sediments. The most efficient fixation of heavy metals in sediments take place by associating with sulfides. Acid volatile sulfides (AVS), pyrite ( $FeS_2$ ), and organic sulfur (e.g. carbon-bound sulfur and sulfate esters) are recognized as sulfide phases in sediments. Sulfur compounds are produced by

means of the bacterial reduction of sulfates, which are utilized as the electron receptors in the reactions of organic matters oxidized by bacteria. Recent studies have shown that a key partitioning phase controlling the activity of some divalent cationic metals in sediments is acid volatile sulfide (Di Toro *et al.*, 1990; Howard and Evans, 1993; Berry *et al.*, 1996; Van den Berg *et al.*, 1998). Acid volatile sulfides are comprised mainly of amorphous iron monosulfides (FeS) that are the most easily liberated among sulfides phases. Acid volatile sulfides in anoxic sediments are the pools of reactive, solid-phase sulfides of iron, which can react with divalent metals, such as Cd, Cu, Pb, Ni, and Zn, to form very insoluble precipitates. This process comprises of two reactions. The first reaction proceeds with the dissociation of amorphous FeS, which is a large reservoir of sulfide in anoxic sediments. The second reaction is that of divalent metal ions with sulfide to form insoluble precipitates. Simultaneously extracted metal (SEM), the amount of metals liberated during AVS extraction, and acid volatile sulfides had been ever proposed as the tools for predicting sediment toxicity (Di Toro *et al.*, 1990; Ankley *et al.*, 1991; Di Toro *et al.*, 1992; Berry *et al.*, 1996; DeWitt *et al.*, 1996). When the molar ratio of SEM to AVS is smaller than one, there is no acute toxicity for aquatic organism; while the ratio of the molar concentrations of SEM to AVS exceeds one, there is potentially acute toxicity for aquatic organism. In addition, the molar difference between SEM and AVS was also used to a basis to predict likely metal bioavailability (Ankley *et al.*, 1996).

To assess the potential availability of heavy metals contained in sediments, the spatial and temporal distribution of AVS and SEM had ever been studied in a subtropical mangrove forest (Mackey and Mackay, 1996), an anoxic mesotrophic lake sediments (Howard and Evans, 1993), and marine and freshwater sediments (Besser *et al.*, 1996; Van den Hoop *et al.*, 1997; Van den Berg *et al.*, 1998).

The aim of this study is to demonstrate the distribution of sediment toxicity indicators, acid volatile sulfide, simultaneously extracted metal, (SEM / AVS) and (SEM - AVS) in sediments of the Ell-Ren river, and to assess the availability of these indicators for predicting the toxicity of heavy metals (Cu and Pb) to the benthic macroinvertebrate (*Tubifex* sp.).

## METHODS

### Study area

The Ell-Ren river and its main tributary, the San-Yeh-Kong river, locate in the southern Taiwan. They have been heavily polluted with heavy metals in last two decades incoming by industrial and agricultural wastewater, especially waste metal recycling wastewater. The Ell-Ren river system has catchment area of about 350 km<sup>2</sup> and total length of 65 km.

### Sampling and samples preparation

The sediment corer (Wildco, USA) used consisted of a hollow stainless-steel core barrel (5.3 cm in inner diameter, 50 cm in height), a polycarbonate core tube, a core catcher, a core cutter (for the better penetration of the sediment), and a core valve (allowing water to pass freely). The sediment corer was used to collect

sediments from different depth of the Ell-Ren river system in summer of 1998. Seven sampling sites were established at the upstream (sites 1 and 2) and the estuary (sites 6 and 7) of the Ell-Ren river, the midstream of the San-Yeh-Kong river (site 3) and inflow site of the San-Yeh-Kong river into the Ell-Ren river (sites 4 and 5). Immediately following that, the sediment-contained polycarbonate core tube was removed from the barrel and kept at the upright position to avoid upward and downward mixing. The core tube was sealed with plastic caps before placing in a cooler. In our laboratory, each sediment core was extruded from the core tube and then separated by PVC blades into several depth layers (a 2-cm layer for the upper-part of the sediment core (0 - 10 cm), a 5-cm layer for the middle-part (10 - 30cm), and a 10-cm layer for the lower-part).

### **Chemical analyses and Toxicity tests**

To determine the concentrations of both AVS and SEM, a procedure initiated by Allen *et al.* (1993) was used. Acid volatile sulfides was analyzed by using 6 M cold acid (HCl) to solve solid phase sulfide to  $\text{H}_2\text{S}_{(\text{aq})}$ . Then,  $\text{H}_2\text{S}_{(\text{aq})}$  was purged with oxygen-free nitrogen gas, and thereby be trapped. The amount of sulfide was determined spectrophotometrically by its reaction with *N, N*-dimethyl-*p*-phenylenediamine contained in the mixed diamine reagent (MDR) to form methylene blue. Simultaneously extracted metal was measured by detecting the filtrate of residual cold acid with AAS (GBCAA 908, Australia). It is noted that the total amounts of measured heavy metals, including Cu, Zn, Pb, Ni, Cr, Co, and Cd, were denoted by SEM; whereas the measured Cu concentration in filtrate was denoted by  $\text{SEM}_{\text{Cu}}$ . The acute toxicity tests of heavy metals for *Tubifex* sp. were performed by using sediments spiked with Cu or Pb. The procedures of toxicity tests followed the methods of Di Toro *et al.* (1993).

## **RESULTS AND DISCUSSION**

### **Spatial distribution of AVS**

Concentrations of AVS in sediments of the Ell-Ren river system varied remarkably among different sites (Fig. 2). AVS concentrations in sediments ranged from near zero (among layers of sites 2, 3, 6, and 7) to greater than 40  $\mu\text{mol/g}$  (among layers of site 5). Figure 2 also shows that concentrations of AVS differed within sites (especially sites 2, 3, 6, and 7), between different layers of sediment core. The differences between different layers are not consistent among all sites, which might be resulted from the spatial heterogeneity of sediments and the discharging uncertainty of pollution sources. High concentrations of AVS were found at sites 4 and 5, which located at the inflow sites of the San-Yeh-Kong river into the Ell-Ren river; whereas low concentrations of AVS were found at other sites (especially sites 6 and 7), which locate at the estuary. The upper layers of sites 4 and 5 had high AVS concentrations, indicating these layers situate at anoxic environment. The order of AVS concentrations at different sampling sites is as follows: inflow sites of the San-Yeh-Kong river into the Ell-Ren river > the estuarine sites > the upstream sites.

### **Spatial distribution of SEM**

Figure 3 shows that the concentrations of SEM in sediments ranged from near zero to greater than 80  $\mu\text{mol/g}$  (among layers of site 5). SEM concentrations at the upper layers of sites 4 and 5 were much higher than those of other sites, which indicates the upper layers of sites 4 and 5 had been heavily polluted with heavy metals. Obviously, the spatial distribution of SEM among different sites and depth were not consistent, which were similar to the findings of AVS in this article. Moreover, the order of SEM concentration at different sampling sites were also the same as that of AVS.

### **Spatial distribution of the molar ratio of SEM to AVS**

The molar ratios of SEM to AVS distributed among different sites and depth are shown in Fig. 4. Low molar ratios of SEM to AVS (ranged from near zero to 1.9) are found at sites 4 and 5, which had been enriched with SEM and AVS; whereas high molar ratios (up to 128) of SEM to AVS are found at other sites (especially site 3), which were more clean and oxic (i.e., sediments with low concentrations of both SEM and AVS) than sites 4 and 5. This result indicates that heavy metals may not show toxic effects at highly heavy-metal polluted sediments due to the excess AVS; whereas higher metal activity may be found at more clean and oxic sediments.

### **Spatial distribution of the molar difference between SEM and AVS**

The another relationships between SEM and AVS can be expressed as the molar difference between SEM and AVS ( $\text{SEM} - \text{AVS}$ ). Figure 5 shows that most of ( $\text{SEM} - \text{AVS}$ ) values calculated at sites 4 and 5 are negative; whereas most of ( $\text{SEM} - \text{AVS}$ ) values calculated at other sites are positive. This result is consistent with the findings of SEM/AVS. From Figs 4 and 5, it can be concluded that the remobility and bioavailability of heavy metals contained in sediments of the Ell-Ren river system are low.

### **Acute toxicity**

The acute toxicity tests of Cu or Pb for *Tubifex* sp. were performed by using spiked sediments. Figure 6 shows that the mortality of *Tubifex* sp. is related to the molar ratio of SEM to AVS. For sediments with  $\text{SEM}_{\text{Cu}} / \text{AVS} > 2$ , the mortality of *Tubifex* sp. increased dramatically; whereas sediments with  $\text{SEM}_{\text{Pb}} / \text{AVS} > 3$ , the mortality of *Tubifex* sp. increased remarkably. This findings is largely consistent with the results of Di Toro et al. (1992). No mortality in excess of 50% was observed for sediments with  $(\text{SEM} / \text{AVS}) < 2$  for Cu and  $(\text{SEM} / \text{AVS}) < 3$  for Pb, which relate to the inhibition of the excess AVS on the activity of Cu or Pb. In addition, for sediments with  $\text{SEM}_{\text{Cu}} / \text{AVS} > 3$ , the mortality of *Tubifex* sp. was greater than 80%; whereas sediments with  $\text{SEM}_{\text{Pb}} / \text{AVS} > 8$ , the mortality of *Tubifex* sp. was greater than 80%.

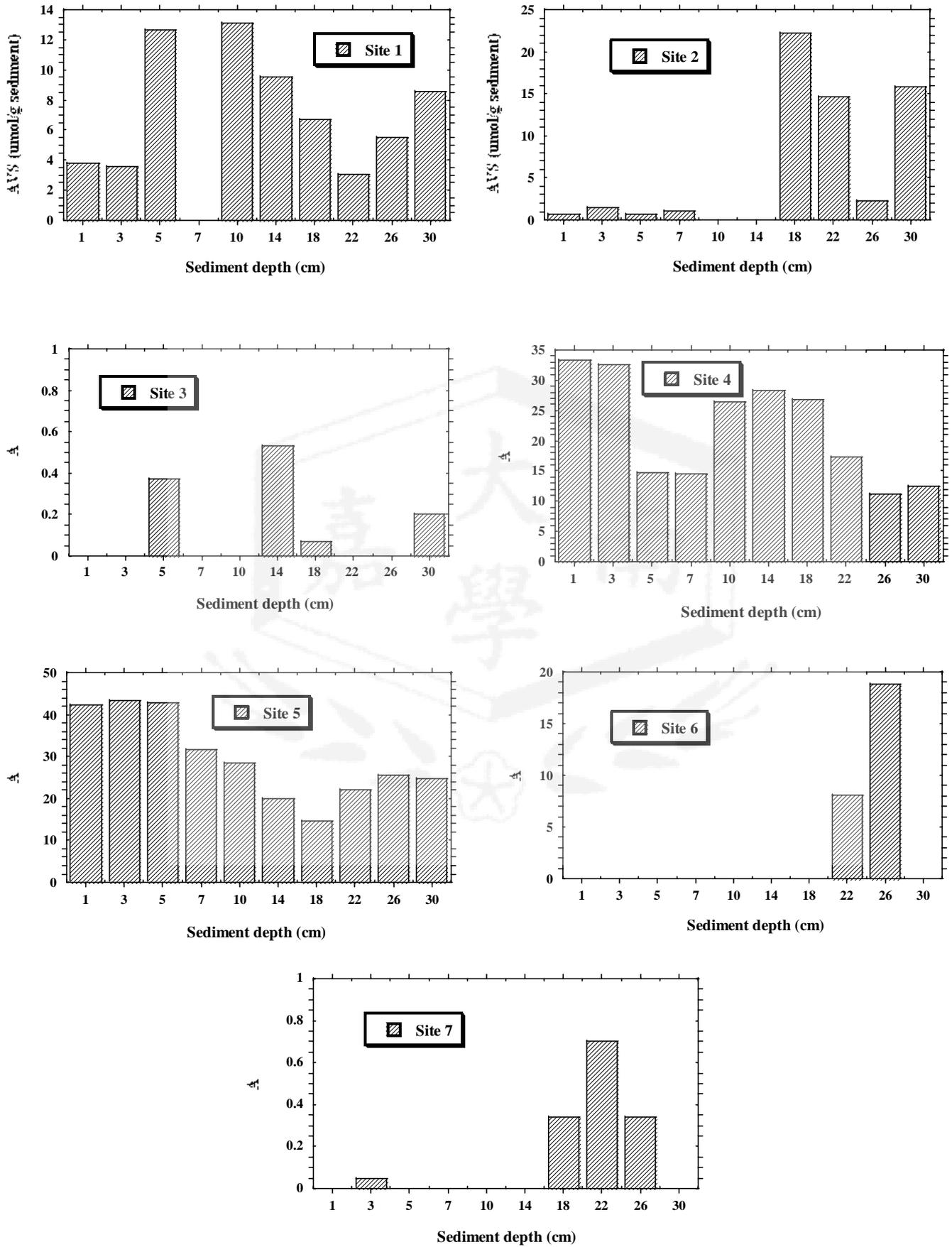


Fig. 2 Spatial distribution of AVS concentrations at different sampling sites.

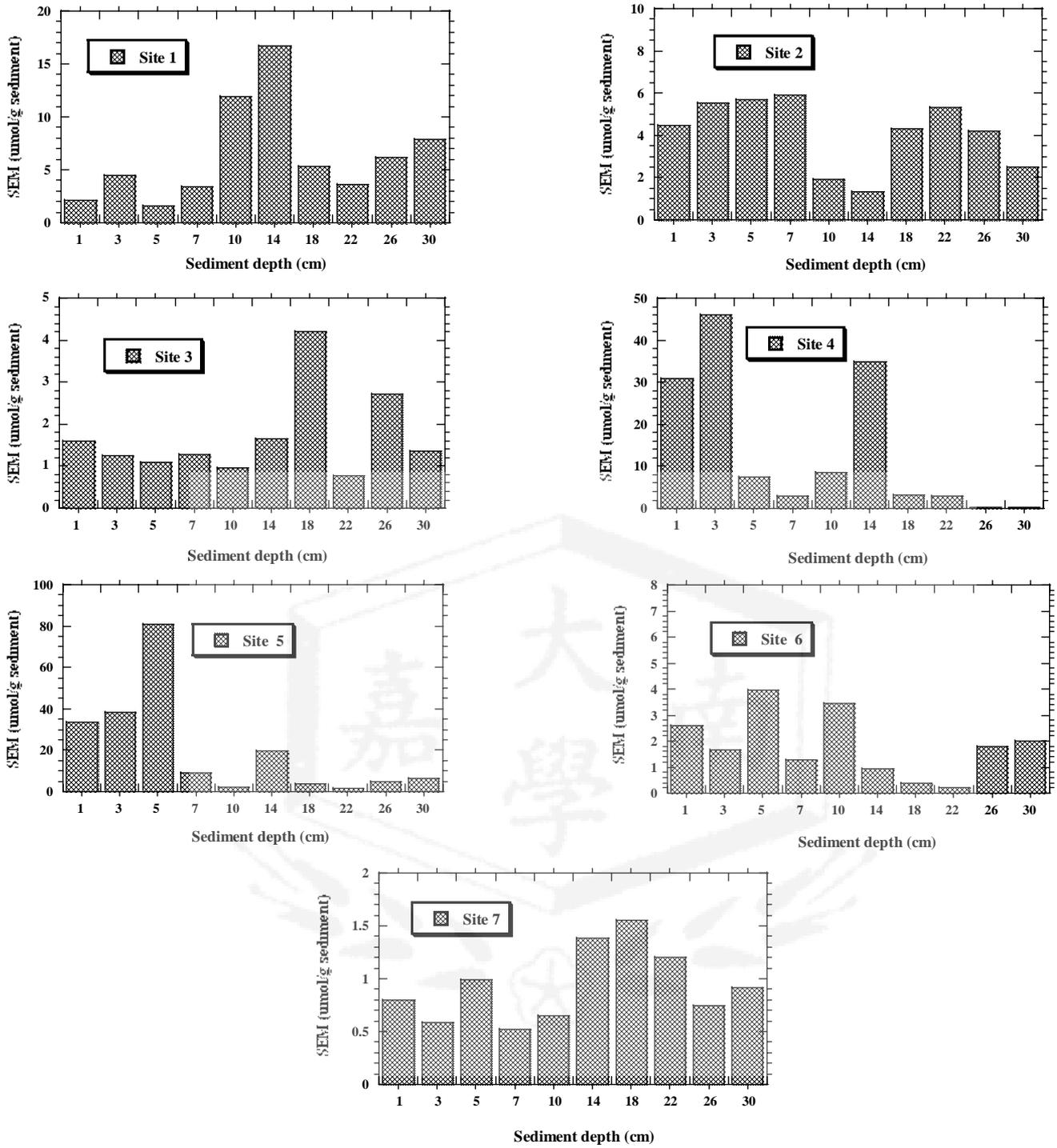


Fig. 3 Spatial distribution of SEM concentrations at different sampling sites.

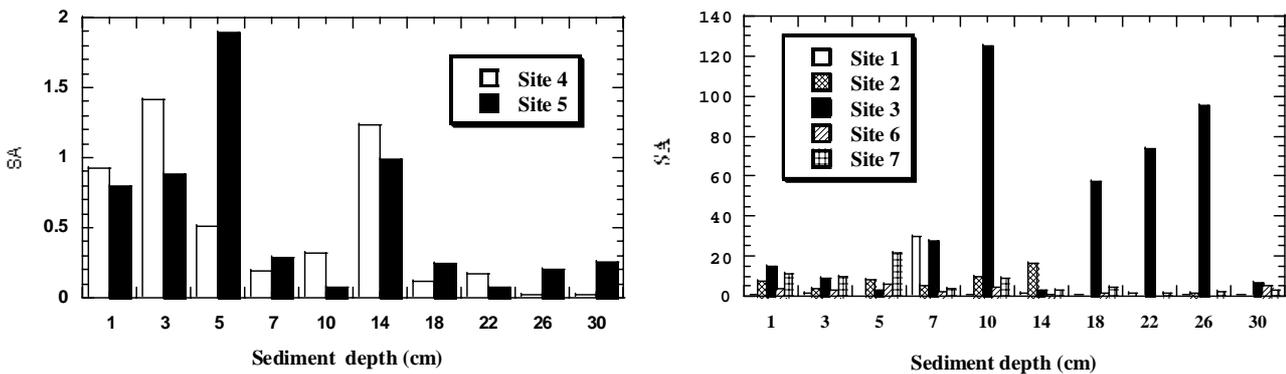


Fig. 4. Spatial distribution of the molar ratio of SEM to AVS at different sampling sites.

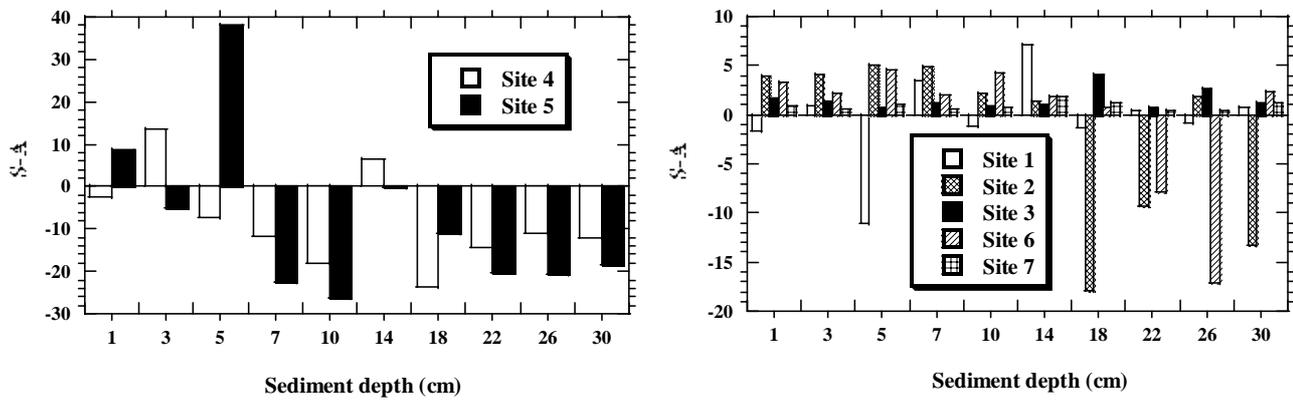


Fig. 5. Spatial distribution of molar difference between SEM and AVS at different sampling sites.

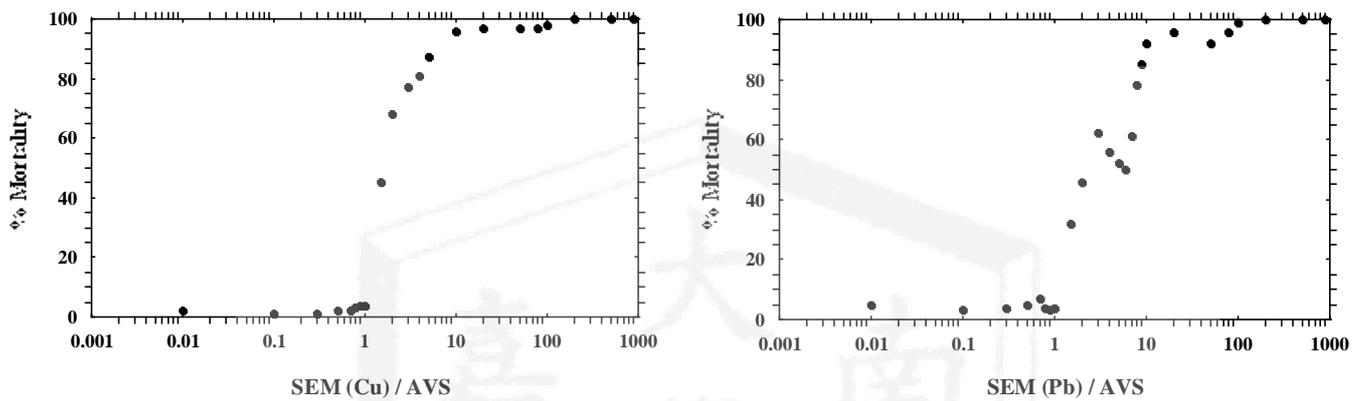


Fig. 6. Percentage mortality of the *Tubifex* sp. as a function of molar ratio of SEM to AVS.

## CONCLUSIONS

The spatial distribution of sediment toxicity indicators, acid volatile sulfide (AVS), simultaneously extracted metal (SEM), (SEM / AVS) and (SEM - AVS), contained in sediments of the Eil-Ren river system, and the toxicity of heavy metals (Cu and Pb) for *Tubifex* sp., are observed in this article. Results indicate that the concentrations of both AVS and SEM do not correlate with sediment depth. Low molar ratios of SEM to AVS (ranged from near zero to 1.9) are found at sites enriched with SEM and AVS; whereas high molar ratios of SEM to AVS (up to 128) are found at other sites, which contained low concentrations of SEM and AVS. Moreover, the molar difference of SEM with AVS (SEM - AVS) are negative in some sampling sites, which contained high concentrations of SEM and AVS (i.e., heavily heavy-metal polluted and anoxic); whereas low (positive) values of (SEM - AVS) are found in more clean and oxic sites. These results reveal that the bioavailability of heavy metals contained in sediments of the Eil-Ren river system is low. In the toxicity tests, the mortality of *Tubifex* sp. increased with the increasing molar ratio of SEM to AVS. In addition, the critical point of lethal toxicity to *Tubifex* sp. was found largely at the values of 2 for  $SEM_{Cu}/AVS$  or 3 for  $SEM_{Pb}/AVS$ .

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