（AVS）   '

Assessing the toxicity of Cr and Cd in the Ell-Ren river sediments by using acid volatile sulfide and interstitial water

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Tubifex sp.
SEM / AVS   4.5(Cr)
3.0(Cd)   *Tubifex* sp.
（AVS）   IWTU (interstitial
(SEM)   SEM / AVS   water toxic unit)   1.5

SEM – AVS

Tubifex sp.

AVS

AVS   SEM

AVS   SEM

SEM / AVS

AVS   SEM

SEM / AVS   AVS   SEM

（SEM – AVS）   AVS   SEM

Tubifex sp.

ABTRACT

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) contained in sediment and interstitial water for *Tubifex* sp., the predominant benthic macro-invertebrate, in sediments of the Ell-Ren river by using AVS and interstitial water.

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 4.5 for SEM_{Cr} / AVS or 3 for SEM_{Cd}/ AVS. Furthermore, the critical points of lethal toxicity for Cr and Cd (contained in in interstitial water) to *Tubifex* sp. were all about at the value of 1.5 IWTU (interstitial water toxic unit).

Keywords: Acid volatile sulfide; Benthic macroinvertebrate; Heavy metal; Sediment; 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 insoluable 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 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 (Cr and Cd) to the benthic macroinvertebrate (*Tubifex* sp.).

METHODS

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^2 and total length of 65 km.

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 confluent sites of the San-Yeh-Kong river into the Ell-Ren river (sites 4 and 5).

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 $H_2S_{(aq)}$. Then, $H_2S_{(aq)}$ 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 Cr concentration in filtrate was denoted by SEM_{Cr}. The acute toxicity tests of heavy metals for *Tubifex* sp. were performed by using sediments spiked with Cr or Cd. The procedures of toxicity tests followed the methods of Di Toro *et al.* (1993). Interstitial water toxic units (IWTU) is defined as the values of metal concentrations in interstitial water divided by the 10-d LC_{50} in water-only tests.

RESULTS AND DISCUSSION

Spatial distribution of AVS

Concentrations of AVS in sediments of the Ell-Ren river system varied remarkably among different sites (Fig. 1). AVS concentrations in sediments ranged from near zero (among layers of sites 2, 3, 6,and 7) to greater than 40 µmol/g (among layers of site 5). Figure 1 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 confluent 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: confluent sites of the San-Yeh-Kong river into the Ell-Ren river ＞ the estuarine sites ＞ the upstream sites.

Spatial distribution of SEM

Figure 2 shows that the concentrations of SEM in sediments ranged from near zero to greater than 80 µmol/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. 3. 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 (SEM -

AVS). Figure 4 shows that most of (SEM - AVS) values calculated at sites 4 and 5 are negative; whereas most of (SEM - AVS) values calculated at other sites are positive. This result is consistent with the findings of SEM/AVS. From Figs 3 and 4, 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 Cr or Cd for *Tubifex* sp. were performed by using spiked sediments. Figure 5 shows that the mortality of *Tubifex* sp. is related to the molar ratio of SEM to AVS. For sediments with SEM_{Cr} / AVS > 4.5, the mortality of *Tubifex* sp. increased dramatically; whereas sediments with SEM_{Cd} / 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 (SEM / AVS) < 4.5 for Cr and (SEM / AVS) < 3 for Cd, which relate to the inhibition of the excess AVS on the activity of Cu or Pb at different sampling sites. In addition, for sediments with SEM_{Cr} / AVS > 4.5, the mortality of *Tubifex* sp. was greater than 80%; whereas sediments with SEM_{Cd} / AVS > 9, the mortality of *Tubifex* sp. was greater than 80%. Furthermore, the acute toxicity tests of Cr or Cd in the interstitial water for *Tubifex* sp. were also performed. Figure 6 shows that the mortality of *Tubifex* sp. is related to the values of IWTU. The critical points of

lethal toxicity for Cr and Cd to *Tubifex* sp. were all about at the value of 1.5 IWTU.

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 Ell-Ren river system, and the toxicity of heavy metals (Cr and Cd) 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 Ell-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 4.5 for SEM_{Cr} / AVS or 3 for SEM_{Cd} / AVS. Furthermore, the critical points of lethal toxicity for Cr and Cd (contained in in interstitial water) to *Tubifex* sp. were all about at the value of 1.5

IWTU.

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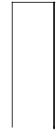Fig. 1. Spatial distribution of AVS in sediments of the Ell-Ren river system.

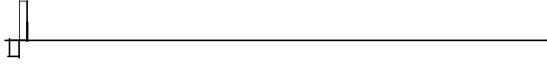**Fig. 2. Spatial distribution of SEM in sediments of the Ell-Ren river system.**

Fig. 3. Spatial distribution of the differences between SEM and AVS.

Fig. 4. Spatial distribution of the molar ratios of SEM to AVS.

Fig. 5. Percentage mortality of the *Tubifex* sp. as a function of molar ratio of SEM to AVS.

Fig. 6. Percentage mortality of the *Tubifex* sp. as a function of IWTU.