

&lt;Review&gt;

## Prediction of Sediment-Bound Metal Bioavailability in Benthic Organisms: Acid Volatile Sulfide (AVS) Approaches

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**Abstract** - Benthic organisms dwell in sediment-water interface that contains significant amount of organic and inorganic contaminants. Their feeding behavior is highly related with sediment itself and pore water in the sediments, especially in case of deposit feeder (i.e. polychaete, amphipod). The acid volatile sulfide (AVS) is one of the important binding phases of sediment-bound metals in addition to organic matter and Fe and Mn oxide fractions in sediments, particularly in anoxic sediments. The AVS model is a powerful tool to predict metal bioavailability and bioaccumulation in benthic organisms considering SEM/AVS mole ratios in surficial sediments. However, several biogeochemical factors must be considered to use AVS model in the sediment-bound metal bioavailability.

**Key words** : benthic organism, metal, bioavailability, AVS

### Introduction

Anthropogenic activities have increased the flux of many trace metals to the sediments of aquatic ecosystems (Nriagu *et al.* 1983; Winterhalder 1995). In the sediment of urban estuaries, lakes and coastal areas, contaminant trace metals are found in concentrations that exceed crustal abundance (Forstner and Wittman 1981; Mudroch 1983; Nriagu 1990). Trace metal contamination can be monitored by the direct collection and analysis of water and sediment, however, such measurements are limited in determining reliable metal concentrations affecting aquatic organisms (Phillips and Rainbow 1993). Previous studies have suggested that using accumulated metal concentrations in biota should be more effective than using metals in water or sediments to monitoring metal contamination in environments (Landrum *et al.* 1992; McCarty and Mackay 1993;

Luoma 1995; Borgmann and Norwood 1997) because the bioavailability of a contaminant metal in sediment is already accounted for in the organism.

When considering the use of an organism as a biomonitor, the bioaccumulation and toxicity of sediment-bound metals are major factors. A good biomonitor should be tolerant, accumulate a particular contaminant, and be widespread and abundant (Martin and Coughtry 1982; Phillips and Rainbow 1993). Various deposit (i.e. clams) and suspension feeders (i.e. mussels) have been developed as biomonitors for contaminant metals in marine environments. In contrast, most freshwater benthic organisms with the exception of some large animals (i.e. bivalve molluscs) have been studied for metal toxicity (Borgmann and Norwood 1995; Jackson *et al.* 1995) rather than as biomonitors. Recently, however, some freshwater insects (i.e. *Chaoborus*) and amphipod species (i.e. *Gammarus fasciatus*, *Diporeia* spp.) have been developed as biomonitors for contaminant metals (i.e. Cu, Zn) (Amyot and Pinel-Alloul 1994; Plénet 1995; Croteau *et al.* 1998; Song 2000).

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The bioavailability of sediment-bound metals at the sediment-water interface is fundamentally important to interaction of metal and benthic organism and to determine biomonitor for contaminant metal because it directly affects metal accumulation and toxicity to the organism. Prediction of metal bioavailability in sediments, however, is difficult because of the presence of multiple binding sites on sediment particles (Luoma 1989; Luoma and Fisher 1997). Furthermore, benthic organisms may take-up dissolved metals and assimilate particulate metals in food (Fisher *et al.* 1996). In particular, dissolved metals in pore water are more bioavailable to most benthic organisms and thus may be easily accumulated in tissues (Rainbow and White 1989; Di Toro *et al.* 1990; Croteau *et al.* 1998). Therefore, reliable predictions of the influence of sediment-bound metals to accumulation and toxicity for benthic organisms are correspondingly difficult.

Previous field and laboratory studies have been conducted to examine the influence of different geochemical phases of metal partitioning in sediments on the bioavailability of metals to benthic organisms (Tessier *et al.* 1984; Harvey and Luoma 1985; Campbell *et al.* 1988; Decho and Luoma 1994; Song and Breslin 1998). Various binding phases have been proposed to predict metal bioavailability in contaminated sediment. In oxic sediment, iron and manganese oxides are considered as predominant binding phases of metals (Davies-Colley *et al.* 1985; Luoma 1989; Tessier *et al.* 1993). The dominant binding phase for metals in anoxic sediment appears to be sulfide associated with iron (i.e. FeS) (DiToro *et al.* 1990). In both oxic and anoxic sediments, organic carbon often represents an important secondary binding phase (Decho and Luoma 1994; Gagnon and Fisher 1997).

For the bioavailability of metals in various binding phases of sediments, extractable metals by the gut digestive fluids or the digestive tract are considered as bioavailable metals due to the aggressive biochemical reactions in digestive systems (Mayer *et al.* 1996; Chen and Mayer 1999). Similarly, metals extracted by weak chemicals may be considered as bioavailable to benthic organisms because weak chemicals also simulate digestive gut fluids in organisms (Tessier *et al.* 1984; Campbell *et al.* 1988; Luoma 1989).

Recently, it has been proposed that the concentration of acid volatile sulfide (AVS) in anoxic and suboxic freshwater and marine sediments can be utilized to predict the bioavailability of pore-water and sediment-bound metals (i.e. Cd, Cu, Ni, Pb, Zn), and therefore, to predict the accumulation and toxicity of metals to benthic organisms (Di Toro *et al.* 1990; Ankley *et al.* 1991; Ankley 1996).

In this study, AVS chemistry in sediment-water interface and the role of AVS to predict bioavailability of sediment-bound metal to benthic organism including some different interpretations of previous study results for the AVS model are described based on previous literatures and my study results.

### AVS Chemistry in Sediment-Water Interface

Specifically, AVS was defined as the sulfide liberated from wet sediment by treatment with 1 N HCl (Di Toro *et al.* 1990). The AVS model is primarily based on equilibrium partitioning, which enables metals to competitively displace the iron from its association with sulfide, thereby forming an insoluble metal-sulfide complex.

The AVS-metal pools affecting metal bioavailability and bioaccumulation in benthic organisms look similar in the thin upper layer of marine and freshwater sediments because AVS-metal relationships are primarily limited in the surficial layer (i.e. ~2 cm) in both sediments. However, the AVS-metal pools affecting benthic organisms may be different between freshwater and marine sediments in deeper layers because AVS formation and metal geochemical cycling are linked between the sediment-water interface and deeper layers.

The distribution of AVS in sediment may primarily be controlled by the flux of  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{S}$  related with sulfate reduction and the production of redox-sensitive metals (i.e. Fe, Mn) in sediment. Settled organic matter (i.e. dead animal, humic acid, detritus) from the water column to the sediment undergoes early diagenesis in surficial sediments (Berner 1980). Due to organic matter decomposition, dissolved oxygen is rapidly depleted in surficial sediment converting oxic sediment to suboxic and/or anoxic sediments. After consuming available oxygen in other electron acceptors (i.e. nitrate, iron

oxide, manganese oxide) in the surficial sediment, sulfate reduction is followed by the production of H<sub>2</sub>S in pore water. The produced hydrogen sulfide is used for forming metal sulfide (i.e. FeS, MnS, CdS, CuS, ZnS) defined as AVS (extracted by 1 N HCl).

Sediment depth profiles of other electron acceptors are important to determine the production of metal sulfides and they vary due to differences in the amount of supplied organic matter concentrations between freshwater and marine sediments. In estuarine and coastal sediments, sulfate reduction is dominant due to high organic matter concentrations. Therefore, it is often impossible to determine reasonable Fe<sup>2+</sup> and Mn<sup>2+</sup> profiles due to the immediate formation of metal sulfides (i.e. FeS, FeS<sub>2</sub>, MnS) (Davison 1985). In deep-sea sediment, however, depth profiles of all electron acceptors including sulfate and methane are observed due to low organic matter concentrations (Froelich *et al.* 1979). Freshwater sediment contains much less sulfide than marine sediment but it contains higher organic matter contents than deep-sea sediment (Davison 1985). Therefore, sulfate reduction is limited by low sulfide concentrations and methane fermentation may be dominant in freshwater sediment.

The stability of metal sulfides is affected by various factors including redox potential, concentrations of sulfide and other dissolved metals (i.e. Fe, Mn, Cu, Cd, Ni) in pore water. Particularly, Fe and Mn distributions are the most important factors because concentrations of both metals are much greater than other metal (i.e. Zn, Cu, Cd, Ni) concentrations in sediments and compete with metals to form metal sulfides. The distribution of Fe and Mn is depended on the vertical variation of redox potential in the sediment. Prior to sulfate reduction, Fe and Mn oxides are reduced to free ions. The free Fe and Mn are mainly distributed in the redox-boundary, complex with sulfides diffused from the below the redox-boundary to the upper pore water and produce FeS and MnS which are major pools of AVS in sediments. These reactions may be less in freshwater sediment than in marine sediment because sulfate reduction is not a dominant process for organic matter decomposition in freshwater sediment. The Fe and Mn in sulfide complexes are easily substituted by other divalent metals (i.e. Zn, Cu, Cd, Ni) in equilibrium with the aqueous

phase and produce ZnS, CuS, CdS and NiS that also are involved in AVS (Di Toro *et al.* 1990). The stability of a certain metal-sulfide (i.e. ZnS) is then affected by other divalent metals (i.e. Cu, Cd and Pb) because sulfide forms of these metals have lower solubility products than the certain metal-sulfide (Di Toro *et al.* 1990).

Formation of pyrite (FeS<sub>2</sub>) is a primary factor for sulfide scavenging from surficial sediment. The pyrite is produced from the further reaction between FeS and S<sub>2</sub><sup>0</sup> mediated by bacteria in anoxic sediments. The pyrite is a more resistant mineral phase than FeS and is not soluble in the acid (i.e. 1 N HCl) extraction used to measure AVS. Without exposures to oxic conditions (i.e. air, oxygenated water), pyrite is not easily dissolved (Stumm and Morgan 1981). The pyrite production may be higher in marine sediment than in freshwater sediment because sulfate concentrations are fundamentally higher in marine sediment than in freshwater sediment, although iron is abundant in both sediments.

The geochemical cycling of metals (i.e. Zn) related with sulfide (i.e. AVS) may also be different between freshwater and marine sediments due to the differences of physiochemical properties in freshwater and seawater including metal species, sulfides and carbonate concentrations and water circulation. For example, the most abundant dissolved Zn species in seawater are Zn<sup>2+</sup>, ZnOH<sup>+</sup> and ZnCl<sup>+</sup> (Bruland 1989). The mean free dissolved Zn concentrations are not significantly different between freshwater and marine waters (Summerhayes and Thorpe 1996). The ZnOH<sup>+</sup> and ZnCl<sup>+</sup> may be higher in seawater than in freshwater due to a higher pH and a higher chloride concentration in seawater than in freshwater, although they may be less reactive with sulfide than the dominant free Zn (Zn<sup>2+</sup>). Carbonate (CO<sub>3</sub><sup>2-</sup>) concentrations may also be an important factor affecting Zn cycling because carbonate scavenges Zn as ZnCO<sub>3</sub> (s). Due to the higher concentration of carbonate in marine water than in freshwater, scavenging of Zn by ZnCO<sub>3</sub> (s) may be more significant in marine sediment than in freshwater sediment (Summerhayes and Thorpe 1996). Dissolved Zn in deeper water may be redistributed due to water circulation. In estuarine and coastal areas (i.e. coastal upwelling), water movement is more active than in lakes. In lakes, water circulation may be largely dependant on seasonal

circulation caused by the change of water density and/or ground water input. Therefore, geochemical cycling of Zn related with AVS is more active and complicate in marine sediment than in freshwater sediment.

### Role of AVS to Sediment-Bound Metal Bioavailability

According to the AVS model, as long as the molar ratio of simultaneously extracted metal (SEM) to AVS is  $< 1$  (or  $SEM-AVS < 0$ ), the number of sulfide binding sites in sediment will exceed the amount of metal present in the system, and all metal should be bound. If this is the case, bioavailable metals in pore-water should be low and toxicity to benthic organisms should not be observed. Conversely, when the quantity of SEM exceeds that of AVS on a molar basis ( $SEM/AVS > 1$  or  $SEM-AVS > 0$ ), all sulfide binding sites should be occupied, resulting in excess metal in the pore-water. Therefore, free metal is bioavailable and bioaccumulation and toxicity to benthic organisms may be observed.

In general, when  $SEM/AVS$  ratios  $> 1$  high dissolved metal concentrations in pore-water are observed, and metal (i.e. Cd, Cu, Ni, Pb, Zn) bioavailability and its corresponding accumulation and toxicity to most benthic organisms are reasonably well predicted using the AVS model (Carlson *et al.* 1991; Di Toro *et al.* 1991; Casas *et al.* 1994; Hare *et al.* 1994; Pesch *et al.* 1995; Berry *et al.* 1996; DeWitt *et al.* 1996; Hansen *et al.* 1996; Liber *et al.* 1996; Sibley *et al.* 1996). However, some deviations occur in the prediction of metal bioavailability using the AVS model at  $SEM/AVS$  ratios  $< 1$  (Carlson *et al.* 1991; Ingersoll *et al.* 1994; Pesch *et al.* 1995; Besser *et al.* 1995; Wang *et al.* 1999; Griscom *et al.* 2000). For the reasons of the occurrence of metal accumulation in benthic organisms with  $SEM/AVS$  ratios  $< 1$ , several possible explanations have been suggested.

Pesch *et al.* (1995) assumed that metal-contaminated sediment could have been associated with the mucus layer on the surface of the polychaete (i.e. *Neanthes arenaceodentata*) at  $SEM/AVS$  ratios  $< 1$ . However, this type of phenomenon may vary for different organisms and has not been fully examined. Carlson *et al.* (1991)

suggested that sediment in the gut of undepurated organisms might have contributed to metal body burden. However, metal accumulation in a benthic organism (i.e. *Chironomus tentans*) was also observed with  $SEM/AVS$  ratios  $< 1$  after depuration of gut contents (Besser *et al.* 1995). Ingersoll *et al.* (1994) suggest that although the AVS model may be useful for predicting concentrations of dissolved metals in pore water, the dissolved metals may underestimate the bioavailable fraction of metals in the sediment.

Metal accumulation in benthic organisms at  $SEM/AVS$  ratios  $< 1$  may also be affected by the contribution of coexistence-metals in the sediment, particularly when the solubility product of the coexistence metal-sulfide is less than that of a certain metal sulfide. For example, if other metals (i.e.  $\Sigma SEM-Cd, Cu, Pb$ ) already occupied AVS, then Zn cannot complex with AVS and be bioavailable even at  $SEM-Zn/AVS$  ratios  $< 1$ . These results may not be simply explained by the AVS model. Therefore, when a certain metal concentration is not dominant compared to other coexistent-metal concentrations (i.e. in uncontaminated environments), observation of a certain metal accumulation at  $SEM$ -a certain metal/ $AVS$  ratios  $< 1$  may include an error induced by the difference of individual metal sulfide stoichiometry (personal communication with Dr. Robert Aller in SUNY at Stony Brook).

For metal accumulation at  $SEM/AVS$  ratio  $< 1$ , Ankley (1996) suggests that metal uptake may occur through ingestion and digestion of contaminated particulate matter in the sediment. Similarly, in radiolabeled sediment feeding experiments, investigators observed that metals associated with AVS-rich sediment are assimilated in organisms (i.e. clam, mussel, polychaete), which means that metals associated with sulfides and anoxic sediment are bioavailable (Griscom *et al.* 2000; Lee *et al.* 2000). It is likely that metals associated with AVS can undergo considerable changes in chemical conditions within the guts of organisms. However, Chen and Mayer (1999) conducted a comparison of biomimetic and AVS approaches for the assessment of sediment-bound Cu to various deposit feeders and suggested that  $SEM-Cu$  over estimates the bioavailability of sediment-bound Cu.

Based on my study results which were examined the

influence of AVS on Zn bioavailability and bioaccumulation in *Diporeia* spp. at SEM-Zn/AVS ratios  $< 1$  and  $> 1$  in 28 day sediment microcosm experiments, pore water-Zn ( $< 0.1 \mu\text{mol L}^{-1}$ ) and  $\text{MgCl}_2$ -Zn ( $< 0.01 \mu\text{mol g}^{-1}$ ) concentrations were not detected due to the partitioning of Zn in these fractions into AVS (Song, 2000). However, significant concentrations ( $> 0.27 \mu\text{mol g}^{-1}$ ) of NaOAc-Zn were detected and correlated with *Diporeia* tissue Zn concentrations at SEM-Zn/AVS ratios  $< 1$  in the study. These results suggest that sediment ingestion was the primary Zn uptake pathway for *Diporeia* at SEM-Zn/AVS ratios  $< 1$  and NaOAc-Zn was the sediment phase most closely correlating with *Diporeia* Zn accumulation. Meanwhile, pore water-Zn,  $\text{MgCl}_2$ -Zn and NaOAc-Zn concentrations increased and all of these sediment phases were significantly correlated with *Diporeia* tissue Zn concentrations at SEM-Zn/AVS ratios  $> 1$  in the study. In addition, a kinetic model approach designed to separate possible Zn uptake pathways suggested that pore water was the primary (61 ~ 73%) *Diporeia* Zn uptake pathway, however, sediment ingestion (NaOAc extractable Zn) also significantly contributed (27 ~ 39%) to *Diporeia* Zn accumulation at SEM-Zn/AVS ratios  $> 1$  (Song 2000). In both cases (SEM-Zn/AVS ratios  $< 1$  and  $> 1$ ), SEM-Zn concentrations did not show any relation with *Diporeia* tissue-Zn concentration implying that SEM-Zn was not the major phase contributing to Zn accumulation in *Diporeia*.

For the bioavailability of metals related with AVS in natural environments, various geochemical processes may affect changes of AVS resulting in change of metal bioavailability. That is, the formation and stability of sulfides in sediments are affected by many biotic and abiotic factors, including sulfate concentrations, loading of labile organic matter, redox conditions, and temperature (Herlihy and Mills 1985). For example, concentrations of AVS in surficial sediments have been shown to vary seasonally (Herlihy and Mill 1985; Leonard *et al.* 1993; Liber *et al.* 1994), presumably due to changes in rates of formation versus oxidation of AVS.

Oxidation of surficial sediments can also occur as a result of the bioturbation of benthic organisms (Aller 1978; Lawrence *et al.* 1982; Matisoff *et al.* 1985; Peterson *et al.* 1996). These results imply that the change of AVS in sediments may also affect changes in the bio-

availability of sediment-bound metals; including metals associated with other binding fractions (i.e. easily extractable, organic matter) in sediments (Calamono *et al.* 1990; Ankley *et al.* 1993; Slotton and Reuter 1995).

## Conclusion

AVS model is useful tool to predict sediment-bound metal bioavailability in benthic organism due to significant influence of AVS on biogeochemistry in sediment-water interface either field or laboratory microcosm. However, there are several biogeochemical factors that have to consider applying AVS model to examine sediment-bound metal bioavailability. The biological factors that affect on AVS model include kinds of organisms (i.e. kinds of deposit feeders, selectivity of organic matters, ability of accumulation rather than regulation of metals), digestion system of the selected organism (i.e. gut pH and redox condition). The geological factors are kinds of used sediments (i.e. freshwater or marine sediments), oxidation state of the sediments (i.e. bioturbation, air bubbling), concentration of organic matter and grain size. Meanwhile, redox condition of sediments, pH of pore water and concentration of AVS and other trace metals must be considered as chemical factors in the AVS model.

Although AVS model contains complicate factors, it is powerful to predict bioavailability and bioaccumulation of sediment-bound metals in benthic organisms. Especially, when SEM/AVS ratios  $< 1$ , most metals in pore water are adsorbed into AVS in sediments resulting in less bioavailable sediment-bound metals to benthic organism. However, metals in easily extractable phases (i.e. NaOAc-fraction) in sediments is still available to benthic organism at SEM/AVS ratios  $< 1$  according to study results of Song (2000). It means that AVS is one of the important geochemical phases as other metal-binding phases (i.e. organic matter, Fe and Mn oxide and several chemically extractable fractions) which are in competitive relationship each other for metal adsorption. To examine bioavailability and bioaccumulation of sediment-bound metals in benthic organisms, therefore, AVS and corresponding biotic and abiotic factors in addition to other possible binding phases in sediment-

water interface must be considered.

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