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Assessment of Cadmium in Aquatic Sediment Using Dialysis Samplers with Ion-Exchange-Resin Collection

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ABSTRACT

Simultaneously extracted metals (SEM) and acid volatile sulfide (AVS) show the potential for toxicity on the basis of their ratio. Accordingly, we spiked cadmium in a range for which Cd/AVS ratios were from 0.2 to 10 in the sediment with its weight about 8 kg in each batch. Dialysis samplers with a cation ion-exchange resin (Dowex 50W-X4) collection were used in a laboratory for the determination of free cadmium concentrations in pore water of the collected sediment. When equilibrium was reached among cadmium in pore water, sediment, and ion-exchange resin, cadmium exchanged onto resin phase was regenerated with 1 *N* hydrochloric acid (OPTIMA grade) and determined using an atomic absorption spectrophotometer (Zeeman 5000) with a graphite furnace accessory. Cadmium determined using the dialysis sampler is considered as free cadmium which is related to the metal bioavailability toward aquatic biota. The developed methodology provides a new technique for assessment of free metal in aquatic sediment systems.

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INTRODUCTION

Cadmium, like copper, zinc, nickel, and lead, is commonly found in aquatic sediments. However, its concentration varies appreciably from one sediment to another (1). Cadmium in pore water exists in free and complexed forms associated with a variety of inorganic and organic ligands. Free cadmium is a portion of the dissolved metals, which is a more appropriate indicator of toxicity than total metals (2–4). Free cadmium in relation to its bioavailability for aquatic organisms was discussed by Sunda et al. (5), Swartz et al. (6), DiToro et al. (7), and Allen et al. (8). The toxicity of complexed and adsorbed portion of cadmium is reduced while free cadmium is highly bioavailable. Bioaccumulation of cadmium in aquatic biota will finally affect human health via a food chain route (9–11).

An increased amount of metal pollution due to anthropogenic and natural processes has caused major concern about metal toxic effects on the ecological web. It has now become necessary to monitor the concentration of these metals in overlying and sediment pore waters for environmental quality evaluation. In this study we focus on cadmium because of its toxic nature. The effects of other metals naturally present in the sediments on cadmium determination are small, if any. This is because the affinity of the resin governs the exchangeable metals. The analytical scheme for cadmium speciation has been applied to such natural systems as fresh water and seawater (12, 13). However, in-situ measurement of cadmium in pore water has proven difficulty without perturbation of natural conditions (14). We have investigated a new method for the determination of the concentration of free cadmium ions in pore water using a dialysis sampler with cation ion-exchange resin collection. The method is based on the equilibrium of cadmium ion among the pore water, ion-exchange resin, and sediment phases. After such an equilibration was reached, the ion-exchange resin was recovered. Cadmium which had exchanged onto resin beads was eluted using a hydrochloric acid solution. The amount of cadmium recovered from the ion-exchange resin was proportional to the concentration of free metal. Within a sampler, the ion-exchange resin was evenly spread on a membrane and covered with another piece of membrane, then tightly captured together in a Plexiglass frame. The membrane served solely to prevent sediment from mixing with the ion-exchange beads. This method contrasts with the techniques previously used by others in which a thin layer of gel was utilized instead of an ion-exchange resin (15, 16).

The ion-exchange method for metal speciation was reviewed by Neubecker and Allen (17). The principal methods we employed were those used widely by Crosser and Allen (18), Cantwell et al. (19), Zhang and Florence (20), and Werner (21). In the aquatic sediment, cadmium ion is in partition between aqueous phase pore water and sediment solid phase. The equilibrium relationships can be expressed using Eqs. (1) and (2):

$$CdL_i \Leftrightarrow Cd + L_i \tag{1}$$

$$\equiv SCd \Leftrightarrow Cd + \equiv S \tag{2}$$

where CdL_i represents the cadmium complexes with the different types of ligands, L_i, in pore water, and $\equiv SCd$ represents the adsorbed cadmium on the sediment particle surface. L_i is the inorganic and organic ligands naturally present in pore water. For simplicity in discussion, all charges are ignored for metal ions, ligands, and sediment particles. Once the dialysis sampler containing an ion-exchange resin is introduced into a sediment system, the labile cadmium will also establish equilibrium with the resin phase:

$$Cd + 2RNa \Leftrightarrow R_2Cd + 2Na \tag{3}$$

where R represents the functional groups attached on resin matrix and the ion-exchange resin is in sodium form. According to Eq. (3), the cadmium and resin-exchange process will cause Eq. (1) and (2) to shift toward dissociation reactions in order to supply the required amount of cadmium governed by resin-exchange capacity. The exchange of the cadmium complexes should be far less than that for divalent cadmium ion due to the Donnan co-ion exclusion effect (22). The conventional Dowex-type of ion-exchange resin is suitable to accomplish this as opposed to Chelex 100 resin in which the iminodiacetate functional group provides strong affinity to decompose metal complexes (23). As a result, chemical equilibrium is perturbed with a diverse effect if a Chelex-type resin is used. Because of that, we used Dowex 50W-X4 with its moderate affinity toward cadmium ion. The grain size for the selected ion-exchange resin is 100–200 mesh, and the sulfonic functional groups attached to the polystyrene and divinylbenzene are responsible for the uptake of free cadmium in the pore water. The quantity of cadmium exchanged onto the resin can be considered as labile metal, and such a process should not alter the concentration of cadmium in the aqueous phase appreciably since the pore water constantly reequilibrates with sediment that acts as an infinite pool of metals (24).

MATERIALS AND METHODS

Our dialysis sampler consisted of clear acrylic plastic (Plexiglass) with stainless steel screws shown in Fig. 1. The use of stainless steel screws give more strength than nylon ones and did not cause metal contamination. The membrane was HT-Tuffryn Gelman with a 0.45-μm pore size. The selection of TH-Tuffryn Gelman was made among three types of membrane materials

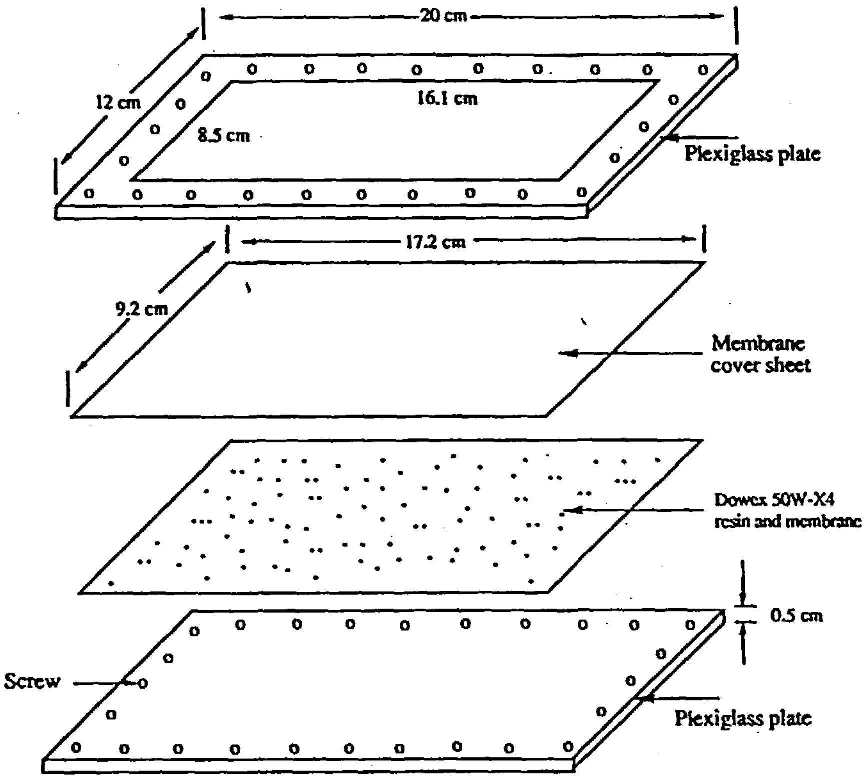

FIG. 1 A schematic diagram shows a dialysis sampler with ion-exchange-resin (Dowex 50W-X4) collection. The "sandwiched" layer of membrane is to isolate resin from sediment particles while diffusion of ions is permitted.

(polycarbonate, cellulose nitrate and acetate, and polysulfone) after testing for degradation due to sediment bacteria and for permeability and contaminate leaching due to nitric acid extraction (25). The membranes served to isolate resin beads from the sediment while providing channels for the ion-exchange process to take place. Cadmium ion adsorption or desorption with plastics, stainless steel, and membrane was assumed negligible. Therefore, the uptake of cadmium by the resin would be sole ion-exchange reaction in such a system.

The ion-exchange resin was first washed using dilute hydrochloric acid solution, then sodium hydroxide base solution, then deionized water. This series of washing steps was repeated a second time. Deionized water washing was stopped when the effluent pH from the ion-exchange column was neutral. Then the ion-exchange resin was adjusted for ionic strength by passing a solution containing calcium, magnesium, and sodium in an amount similar to the background concentrations in the pore water. The conditioned resin was stored in a laminar flow hood and air dried for use. The plastic sampler frames were soaked in distilled water for 2 days before the ion-exchange resin was packed for use. This was to prevent possible sediment oxidation caused by the presence of oxygen trapped in the sampler material.

In this paper we report a use of the dialysis sampler to determine the free cadmium concentration the sediment collected from the Lums Pond located in Newark, Delaware. Desnoyers (26) previously utilized this method to study other sediments. The collected sediment was divided into 10 batches. The weight of each batch of sediment was close to 8 kg. The average dry sediment weight versus wet sediment weight was 43.13%. Acid volatile sulfide (AVS) was determined to be 18.54 μmol/g dry weight. Cadmium nitrate salt, $Cd(NO_3)_2 \cdot 4H_2O$, was spiked to nine batches based on the Cd/AVS ratio. One batch was not spiked in order to serve as a control. The Cd/AVS ratios are shown in Table 1. It is worth pointing out that the free metal concentration changes in different sediments because of changes in the ion-exchange capacity of the sediment and the natural organic matter concentration in pore water.

Immediately after cadmium was spiked, each batch was stirred thoroughly to ensure complete mixing; then all the batches were covered with lids and left to settle for 2 weeks. After 2 weeks, sediment from the top of each batch was taken for analysis of AVS and simultaneously extracted cadmium metal (SEM-Cd) using methods outlined in Allen et al. (8). Meanwhile, the centrifuge method was empolyed to obtain pore water from sediment, which was used for cadmium determination in the pore water. As soon as this step was finished, a sampler containing about 1 g Dowex 50W-X4 ion-exchange resin from Bio-Rad, Hercules, CA, was placed horizontally into the sediment.

The dialysis samplers were placed horizontally rather than vertically in each batch of the sediment. Leveled samplers tend to avoid differences in oxidation status within the sediment profile. The time needed to reach ion-exchange equilibrium was about 1 week according to earlier kinetics experiments (24). This was also within the time frame to reach an equilibrium state as reported by Carignan (27). Two weeks were actually allowed for the

TABLE 1
Cd/AVS Ratios and Amount of Cadmium Spiked

Batch number	1	2	3	4	5	6	7	8	9	10
Cd/AVS ratio	0.0	0.2	0.4	0.6	0.8	1.0	1.5	2.5	5.0	10
Wet weight, kg	8.4	8.0	8.4	7.5	7.3	8.4	7.0	7.7	7.5	8.0
Cd spiked, g	0.0	1.43	3.02	4.04	5.22	7.55	9.49	17.3	33.7	71.4

samplers to reach equilibrium after they were put into the sediment. After the 2 weeks the samplers were taken from individual batches and the ion-exchange resin was transferred to a small-screened column for regeneration. 1 *N* hydrochloric acid (OPTIMA grade) solution was used for replacement of any Cd on the resin phase, and the collected eluant solution was analyzed by flame AAS (atomic absorption spectroscopy, Zeeman 5000) for cadmium concentrations. In addition, the eluant solution for the Cd/AVS ratio of 0.2 was analyzed by a graphite furnace AAS to achieve a lower Cd detection limit. After the samplers were removed, the top layer of sediment in each batch was removed by scraping and the bottom portion of sediment was collected for AVS and SEM-Cd analyses.

All the sample bottles were acid-washed and rinsed three times using deionized water and dried in a laminar flow hood. They were then saved in large plastic bags before use. Cadmium standards were made fresh daily from a 10 mg/L stock solution. We prepared 5, 10, and 15 μg/L of cadmium standards for furnace analysis and 2, 4, and 6 mg/L of cadmium standards for flame analysis. All measurements were duplicated.

RESULTS AND DISCUSSION

AVS determinations were performed before and after ion exchanger samplers were inserted into the 10 batch samples. Figure 2 is a plot of AVS

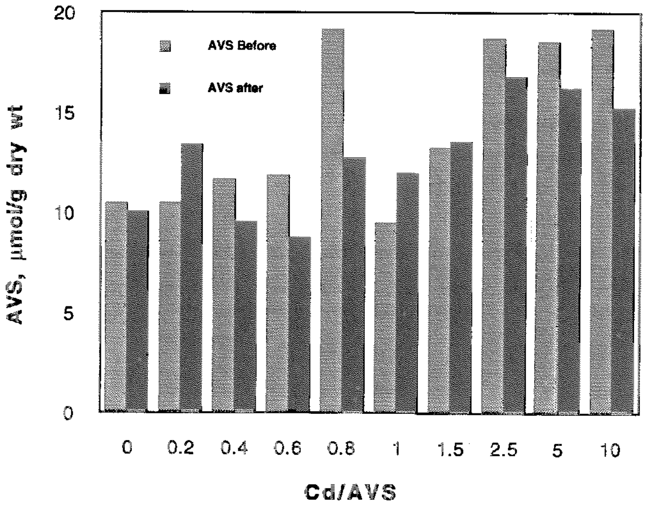

FIG. 2 AVS measurements before samplers were introduced and after samplers were removed from sediment.

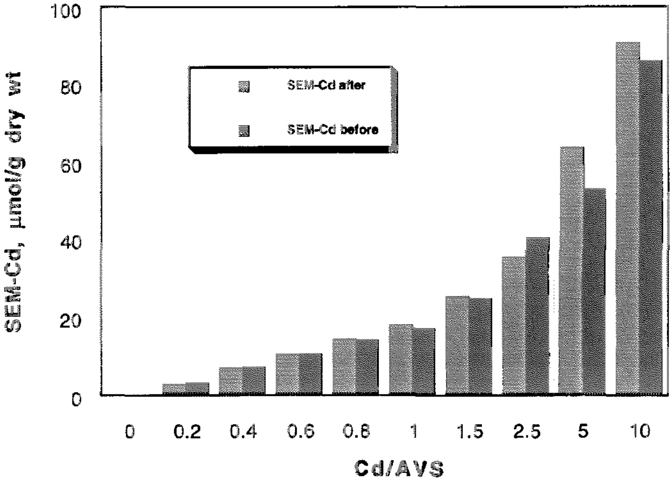

FIG. 3 SEM-Cd was measured at the beginning and end of sampler equilibration.

values at different Cd/AVS ratios. Although the collected sediment was mixed well in a large container before being subdivided into 10 small batches, heterogeneity does exist in terms of AVS changes. Ideally, AVS should have remained constant if the sediment were indeed homogeneous. The general trend is that AVS decreased after samplers were introduced. Sulfide in the sediment may be partially lost due to oxidation.

Figure 3 is a plot of SEM-Cd against Cd/AVS ratios. As the amount of spiked cadmium was increased, the SEM-Cd values correspondingly increased. The increase in SEM-Cd values after inserting the dialysis samplers results either from slow phase transformation among sediment, ion exchanger, and pore water, or from diffusion limitation. As shown in Figure 4, reduction of pore water cadmium concentration after samplers were placed also gives evidence of slow reactions. Because the resin itself has a fixed ion-exchange capacity of 5.2 meq/dry gram, its uptake of cadmium is small compared with the amount of cadmium sorbed on the sediment phase. This can also be observed from mass balance calculations.

Pore water cadmium concentrations were determined after centrifugation. Figure 4 shows pore water cadmium plotted against Cd/AVS ratios. The pore water Cd concentration at a Cd/AVS ratio of 0.2 was less than 1 µg/L. The spiked cadmium at that ratio was mostly adsorbed into the sediment phase. Therefore, the cadmium partitioning to the sediment phase is very strong. As the amount of spiked cadmium was increased, pore water Cd increased

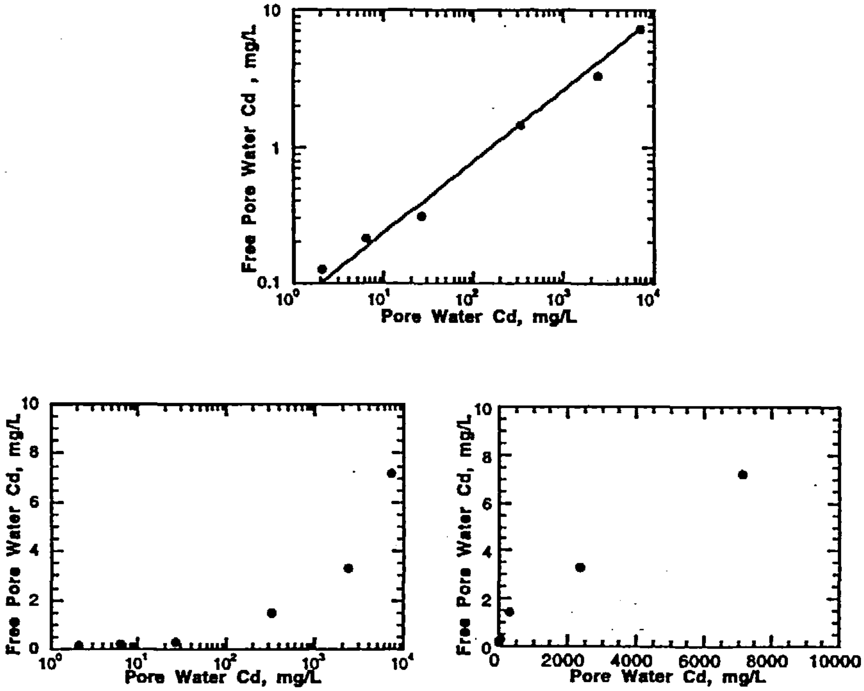

FIG. 5 Free cadmium concentrations, calculated based on the cadmium partition coefficient, and plotted against total analytically determined cadmium concentration in pore water.

Figure 6 shows resin phase cadmium versus pore water cadmium concentration at equilibrium. Based on the results of earlier studies, free cadmium in pore water was adsorbed by ion-exchange resin. The cadmium equilibrium among the pore water, ion exchange, and sediment is important because all the exchangeable cadmium onto resin can be considered as free metal, and biological response is proportional to the free cadmium portion (3, 5, 28–30). Thus, cadmium concentration from ion-exchange resin could serve as an indication of sediment toxicity. This method can provide a new way for evaluation of environmental quality.

CONCLUSIONS

The developed methodology is useful in the determination of free metal concentrations in sediment pore waters. The free portion of metal is reflected by adsorption onto ion-exchange resins fixed in a dialysis sampler. It provides

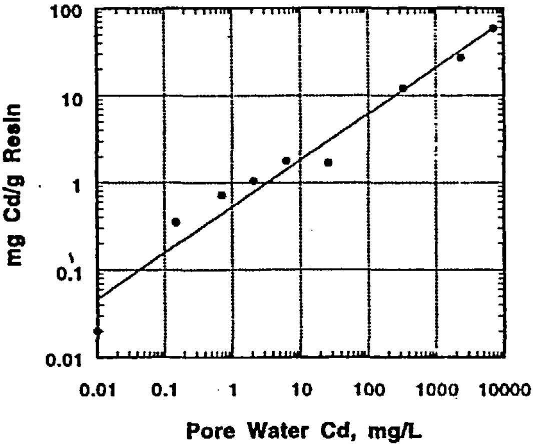

FIG. 6 Cadmium adsorbed on the ion-exchange resin (i.e., the portion of free cadmium exchangeable with resin functional groups) as a function of cadmium in pore water.

a new technique for assessment of sediment toxicity. In addition, SEM-Cd increased greatly as spiked Cd was increased, indicating more binding sites were available to respond to the increased metal loading. Those additional binding phases were organic matter and metal oxides which act as sinks.

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