Bull. Environm. Contam. Toxicol. 27, 798–805 (1981)

Marine Sediment and Interstitial Water: Effects on Bioavailability of Cadmium to Gills of the Clam *Protothaca staminea*

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Cadmium is an important contaminant entering the marine environment from both global atmospheric deposition and point source effluents in nearshore coastal areas (Nriagu 1980).

Sediments serve as an important sink for removal of dissolved Cd from the water column (Lyons & Fitzgerald 1980; Santschi et al. 1980). Since bioaccumulation and toxicity of Cd are believed to be related to the soluble Cd^{+2} ion concentration rather than the total Cd (Sunda et al. 1978; Engel & Fowler 1979), sediment sorption of soluble Cd may have important implications regarding the bioavailability and subsequent toxicity of Cd to benthic organisms. Information on the kinetics of Cd partitioning in marine sediments has been limited to artificial sediment mixtures (Oakley et al. 1981). Also, the interstitial water of natural marine sediments is typically high in dissolved organic substances (Linderbaum 1973). These may complex with Cd and could reduce its bioavailability to benthic organisms.

The gills of marine bivalves serve as the major route for bioaccumulation of dissolved trace metals. This fact has lead to the use of excised bivalve gills as a convenient assay for measuring bioavailability of metals from seawater (Crecelius et al. 1981; Carpene & George 1981; Roesijadi 1980; and Engel & Fowler 1979).

Our studies were undertaken to determine first, the kinetics of Cd sorption on a natural marine sediment and second, the degree to which this sorption as well as interstitial water might effect bioavailability of Cd to gills of the clam Protothaca staminea.

0007-4861/81/0027-0798 $01.60

METHODS

Sediment Sorption

Surface sediment (0-5 cm) was collected from the southern end of Sequim Bay, Washington, lyophilized and resuspended in natural seawater in a stirred 1 L reaction kettle maintained at 10°C under aerobic conditions (Eh = 450 mv) at pH 7.9-8.0. This suspension contained 100 g/L dried sediment. The sediment composition as determined by size fractionation was 1-3% sand, 60-62% silt and 36-37% clay. The organic carbon content as measured by microcombustion and IR carbon analysis was 30-32 mg/g.

Ten mL of the above sediment slurry was pipetted into a stirred reaction cell containing 200 mL of filtered seawater which was also held at 10°C. This represented an addition of dried sediment of 5.0 ± 0.4 g/L in the reaction cell. Following stabilization of pH, which was continually monitored, quantities of $CdCl_2$ containing ^{109}Cd were added to bring the total added Cd concentration to 0.2, 0.5, 1.0 or 2.0 μM/L. Ten mL aliquots of the treated slurry were then removed at selected times, between 1 min and 29 days, filtered through 0.4 μm Gelman® HT Tuffryn filters, and total Cd concentration determined by radioassay. Unfiltered aliquots were treated with concentrated HNO_3 prior to analysis. The radiological analyses were normalized to 10 g of solution.

Bioavailability

Three types of exposures were conducted: 1) control, consisting of 0.45 μm filtered seawater, 2) sediment interstitial water and 3) washed sediment.

Sediment interstitial water was extracted from Sequim Bay sediment by centrifugation at 3200 g for 10 min followed by filtration through a 0.45 μm Millipore® filter. To remove interstitial water, washed sediment was prepared by addition of 15 g wet weight of sediment to 1 L seawater (equivalent to 3.57 g dry wt/L) followed by centrifugation in three changes of filtered seawater. Littleneck clams (Protothaca staminea) were collected from the intertidal area of Sequim Bay and held in running seawater for 24-48 h, shucked and the gills dissected free. Each exposure was 100 mL of seawater or interstitial water in polyethylene beakers at 10°C and pH 7.8-7.9. To reduce bacterial growth during exposures all solutions were pasturized at 75°C for 30 min. After cooling, the radioisotope $^{109}CdCl_2$ was added at 0.37 μg Cd/L. After 17 h equilibration, 1 excised clam gill was added to each exposure beaker.

At time intervals, gills were removed, rinsed in clean seawater, blotted, dried at 60°C for 48 h, weighed and digested in 15 mL formic acid. A 0.5 mL subsample of the formic acid digestate was added to 15 mL of Aquasol® and counted in a liquid scintillation counter. Initially (after 17 h equilibration) and again at time intervals, gills were removed, samples of the water were collected and, in the case of the washed sediment exposure, filtered through 0.45 μm filters to determine radioactivity in the dissolved and particulate fractions. All radioactivity was corrected for counting efficiency and converted by specific activity to concentrations of Cd.

RESULTS AND DISCUSSION

Sediment Sorption

Sequim Bay clayey silt appears to have multiple adsorption sites for Cd. There appear to be at least four discrete adsorption sites in the sediment, each having a characteristic rate constant and adsorptive capacity for Cd (solid line, Fig. 1). At 1.0 μM initial total Cd these can be described as follows:

Adsorbent	Rate constant, hr^{-1}	Estimated Capacity, μg/g	Apparent Time to equilibrium
A_1	~157	2.8	~1 min
A_2	1.33	1.9	25 min
A_3	0.0457	1.6	6.6 h
A_4	0.51×10^{-3}	1.0	~300 h
Σ		7.3	

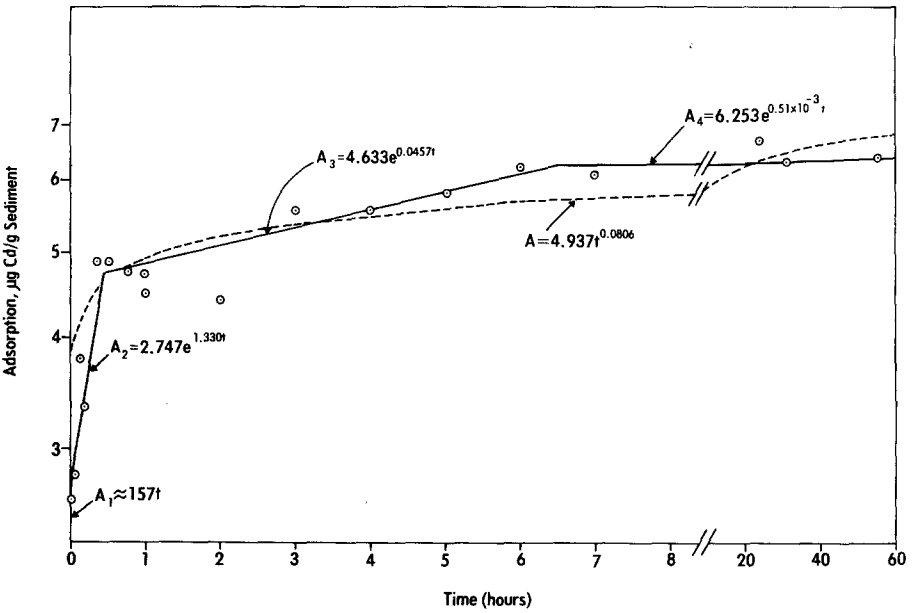

Fig. 1. Adsorption of 1 μM Cd on 5 g/ℓ Sequim Bay clayey silt. 31 °/oo salinity, 11°C and pH 8.0.

Sediment Cd adsorption can also be approximated adequately by a more generalized model which assumes that the rate of adsorption is constantly diminishing with time as equilibrium is approached (dashed line, Fig. 1) such that at 1.0 μM

$$A = 4.937t^{0.0806}$$

where A = adsorption in μg/g,

and t = time in h.

The derivative of this equation with respect to t describes the adsorption rate:

$$R = \frac{dA}{dt} = 0.398t^{-0.919}.$$

The corresponding rate equation for an initial concentration of 2.0 μM Cd (224.8 μg/L) is $R = .782t^{-0.914}$. Examining the adsorption data, it is apparent that following rapid adsorption during the first 20 to 60 min, adsorption increases slowly and linearly with time.

Cd-sediment adsorption also increases with Cd seawater concentration (Fig. 2). Combining data for the four exposure Cd concentrations yields a model of adsorption with respect to time and initial Cd concentration as follows:

$$A = 0.0438\ [Cd]^{0.9873}t^{0.085}$$

where [Cd] = initial Cd concentration in μg/L.

The adsorption rate R is $\frac{dA}{dt} = 3.72 \times 10^{-3}\ [Cd]^{0.9873}t^{-0.915}$.

The exponent for [Cd] is very nearly 1.0 indicating that the rate of adsorption is first order with respect to initial Cd concentration.

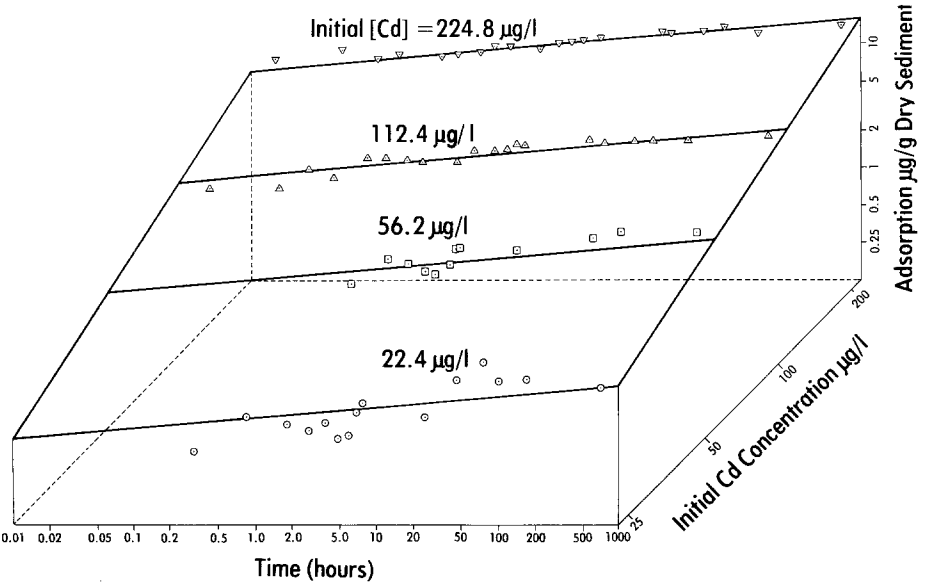

Fig. 2. Adsorption of Cd on Sequim Bay clayey silt as a function of time and initial concentration of Cd in seawater.

This model indicates that adsorption would increase indefinitely as Cd concentration increases, which is undoubtedly not the case, but it is applicable over the range at which most nearshore pollution might occur (up to at least 225 μg/L). It

also does not account for the apparently methodical variations in the data about the predicted regression lines when presented as log-log plots. These variations appear to be consistent with the multiple adsorbent model.

Bioavailability

In the absence of sediment, clam gills accumulate Cd rapidly from seawater. Accumulation was approximately linear over the 48 h exposure period (Fig. 3). The bioconcentration factor (ng/g dry wt gill ÷ ng/mL seawater) = 266x after 48 h.

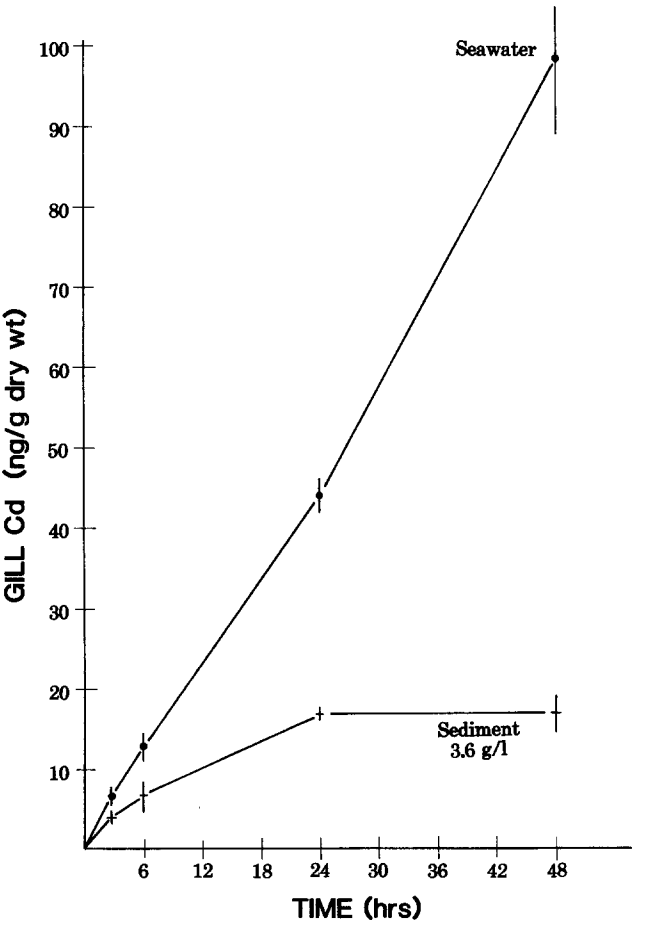

Fig. 3. Accumulation of Cd by gills of the clam Protothaca staminea exposed to seawater only or seawater plus sediment. Vertical bars = standard error, n = 3.

Substitution of extracted sediment interstitial water for filtered seawater as the exposure media had no significant effect on Cd bioaccumulation compared to the control.

The addition of small quantities of washed sediment to the exposure system, however, reduced Cd accumulation by clam gills to only 16.8 ng Cd/g dry wt in 48 h, i.e., only 17% of the control. This reduction in bioavailable Cd in the washed sediment exposure undoubtedly results from the rapid binding of the soluble (bioavailable) Cd fraction to the sediment and its removal from the water. Phelps (1979) found that accumulation of Cd by the clam Mya arenaria exposed to 10 mg/L total Cd, was reduced to only 33% of the control when 0.1 g/L of wet mud-type sediment was present in the exposure system.

Examining the distribution of the total Cd between water, gill and sediment compartments indicates that after the initial 17 h equilibration, only about 29% of the total Cd remained in the water above the sediment. Sixty-five h later (48 h after gill addition), less than 10% of the Cd remained in the soluble form (Table 1). Thus, the degree of reduction in soluble Cd after sediment addition of about 87% corresponds well with the observed reduction in gill Cd accumulation of 83% in the presence of washed sediment. According to our model for Cd-sediment association (above), after 65 hours with an initial Cd water concentration of 0.37 µg/L, the sediment should contain 23 ng Cd/g dry wt. Our measured value for sediment during the gill exposure was 12 ng total (Table 1) or 34 ng/g dry sediment.

TABLE 1. Distribution of total Cd (ng) between compartments. Gill values include baseline level of 173 ng plus accumulated Cd. 37 ng Cd added to 100 mL seawater exposure.

Treatment Compartment	Mean ng Time (hrs) 0*	48	Change-percent** Initial Final	48 hr Control Treatment
Control				
water	37.3	26.9	-27.9 (++)	NA
gill	173	180	+4.0 (+)	NA
total	210	207	-1.4 (++)	NA
Interstitial Water				
water	38.0	26.8	-29.5 (++)	-0.4 (0)
gill	173	181	+4.6 (+)	+0.6 (0)
total	211	200	-5.2 (++)	-3.4 (+)
Washed Sediment				
water	10.7	3.60	-66.4 (++)	-86.6 (++)
gill	173	174	+0.6 (0)	-3.3 (+)
sediment	19.3	12.0	-37.8 (++)	NA
total	203	190	-8.4 (++)	-8.2 (+)

* after 17 hrs incubation without gill.
** t-test, + >0.05, ++ >0.01, 0 = N.S.

This agreement between the value predicted by the model and that measured in the exposure is reasonably good considering that the Cd concentration in the gill exposure was lower than any used to construct the model.

The mass balance distribution of total Cd in the exposures shows a small (1-8%), but significant reduction in total Cd during the exposure period (Table 1). Such Cd losses have been found by others and attributed to adsorption to the walls of exposure containers (Hennig & Greenwood 1981).

Cd appeared tightly associated with the sediment. When sediment containing 32 ng Cd/g dry wt was allowed to depurate in clean seawater for 48 h it still retained 25 ng Cd/g.

On a dry weight basis, the ratio of sediment to gill in our exposure system (4.8) was quite low compared to what might be expected under field conditions. Very productive beds of P. staminea typically contain about 36 clams/m^2, i.e., equivalent to only about 5.4 g of clam gill/m^2 of sediment surface (Vanderhorst & Wilkinson 1979), or in the upper 2 cm a dry wt ratio of sediment to gill of 1,500. The increase in total Cd in the gills exposed in the presence of sediment was insignificant (Table 1). Thus, given the rapid binding of Cd to sediment found in our study and the large reservoir of sediment compared to biomass, low level additions of Cd to seawater are not likely to lead to significant bioaccumulation through the gills of suspension-feeding bivalves. Results of others also indicate that sediment-sorbed Cd is bioavailable only under certain conditions and only to some deposit-feeding species (Jenne & Luoma 1977; Neff et al. 1978; Ray et al. 1981). Even in deposit-feeding clams the reduction in bioavailability of Cd has been shown to decrease with increasing sediment-water distribution coefficients (Luoma & Jenne 1977). Bioaccumulation and toxicology experiments which disregard the strong Cd-binding capacity of sediments may greatly overestimate the importance of Cd in natural marine ecosystems.

ACKNOWLEDGEMENT

This study was supported by the U.S. Department of Energy, Office of Energy Research under Contract #DE-AC06-76RLO-1830.

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Accepted September 10, 1981