Bull. Environ. Contam. Toxicol. (1999) 63:720—727

Bulletin of Environmental Contamination and Toxicology

Cadmium Transfer Between Water and Sediments Studied in Laboratory Experiments and with a Computer Model

A. D. Rasmussen, O. Andersen

Department of Life Sciences and Chemistry, Roskilde University (17.2),
Post Office Box 260, 400O Roskilde, Denmark

Received: 17 May 1999/Accepted: 16 September 1999

The transfer of Cd between water and sediment is a complex process controlled by factors such as water salinity, pH and content of humic substances as well as sediment composition, redox properties and oxygenation (Luoma 1989, Davies-Colley *et al.* 1984, Lu & Chen 1977). Frequent variations in the above mentioned abiotic parameters occur in estuaries due to tidal changes and fresh water run off. Further, fresh water run off may be polluted with trace metals. A general accumulation of pollutants is believed to occur in estuarine sediments and Cd concentrations as high as 130 mg/kg dry weight sediment have been found in UK estuaries (Bryan & Langston 1992). Several parameters such as water residence time, metal concentration, salinity and bioturbation by sediment dwelling organisms could potentially influence the partitioning of metals between water and sediment (Rasmussen *et al.* 1998). For instance, in fresh water more than 70% of the total Cd is in the form of Cd^{2+}. The amount of this ionic form decreases rapidly with increasing salinity due to the formation of Cd-chloro complexes (Kester 1986, Mantoura *et al.* 1978), probably resulting in decreased adhesion of Cd to sediment particles. When salinity is increasing, the higher water concentrations of Ca^{2+} and Mg^{2+} will exchange with sediment bound Cd. Even though sediments usually contain low fractions of organic material, the affinity of this fraction for Cd is high due to the presence of functional groups such as -COOH, -OH and -SH (Stumm 1992). The affinity is believed to be independent of pH and redox processes (Davies-Coley *et al.* 1984). During oxidising conditions, Cd adheres to Fe and Mn oxides and hydroxides that are part of the inorganic fraction of the sediment. During reducing conditions, Fe and Mn bound to sulphides will exchange with Cd whereby mainly Cd monosulphides of very low solubility is formed (Di Toro *et al.* 1990). These insoluble complexes are also known as AVS (acid-volatile sulphides) (Pesch *et al.* 1995).

MATERIALS AND METHODS

Speciation of Cd was calculated using the Equilibrium Metal Speciation Model Minteqa2 (Ver. 3.11. Center for exposure assessment modelling, U.S. Environmental Protection Agency, Georgia, USA). pH was measured in water used for laboratory experiments and then fixed in the model at 7.6, 7.9 or 8.0 for calculating Cd species

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Correspondence to: A. D. Rasmussen

in freshwater, 10‰ or 20‰ salinity, respectively. The ion concentrations used are shown in Table 1. Further, the effect of pH on Cd speciation at the salinities mentioned was tested by fixing pH values of 7,8 or 9. Finally, speciation calculations were performed testing the effect of temperature (5 or 25°C), Cd amounts (0.001 or 10 mg/L) and effects of Na^+ and Cl- on Cd speciation omitting the remaining chemical species listed in Table 1.

In all laboratory experiments 2000 ml glass beakers were filled with 150 cm^3 of sediment sieved to 1 mm, either with or without ^{109}Cd, resulting in a sediment surface area of 113 cm^2. Water of 0, 10 or 20‰ salinity was carefully added where after the beakers were fitted with air tubing to aerate and stir the water. Three different water volumes were used in order to obtain ratios of 4.45, 8.85 aand 13.30 between water volume and sediment surface area. Cadmium fluxes from water to sediment were calculated by adding carrier-free ^{109}Cd (2.500 cpm/ml sea water, $CdCl_2$, specific activity 1.30 mCi/mg, DuPont, Belgium) to the water phase and measuring the activity at regular intervals in 1000 µl samples of the water phase. In order to calculate Cd fluxes from sediment to water, sediment washed in water of 0, 10 or 20‰ salinity was mixed with carrier free ^{109}Cd giving 20,000 cpm/cm^3 sediment prior to being filled in beakers as described above. This experiment was repeated using “aged” sediment where Cd and sediment had been mixed and kept with aerated overlying water for 1.5 months at salinities of 0, 10 or 20‰ before ^{109}Cd release to water was measured. ^{109}Cd activity in water and sediment samples was measured using a Pachard Cobra^{TM}II Auto-gamma counter. The kinetics of removal of Cd from the overlying water during the 24 hour period appeared to follow an exponential pattern and data were thus log-transformed where after linear regressions were performed. The slope of these regressions provided estimates of k in the following equation: $Cd = a*e^{-kt}$, where Cd is the concentration of Cd in the overlying water, a is a constant and t is time in hours. Data are presented as mean ± 1 SEM. N is stated in the figure legends. Prior to experimentation it had been tested that the slow aeration used to stirr the water results in a completely homogenous water Cd distribution in less than 1 minute and that it did not affect pH.

Table 1. Concentrations of ions used in the Minteqa2 model for calculation of fractional amounts of the Cd species. Concentrations are calculated from ASTM (1980).

Ion (mg/L)	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	
Fresh water	32.9	2.64	55.8	15.1	2.36	
10 ‰ seawater	3118	115	118	382	5476	
20 ‰ seawater	6235	229	235	765	10950	
Ion (mg/L)	F^-	Sr^{2+}	Br^-	SO_4^{2-}	CO_3^{2-}	Total
Fresh water	--	--	--	101.8	85.7	296
10 ‰ seawater	0.4	1.9	19.8	794	42	10067
20 ‰ seawater	0.8	3.89	39.5	1588	84	20130

Table 2. The percent distribution of the most common Cd species in fresh water and sea water of 10 or 20‰ salinity.

	Salinity		
Cd species	Fresh water	10 ‰	20 ‰
$CdCl^+$	0.27	59.13	51.05
$CdCl_2$	--	20.04	31.02
Cd^{2+}	60.58	13.47	6.67
$CdSO_4$	7.72	1.84	1.21
$CdCl_3^-$	--	2.00	6.72
CdOHCl	--	1.36	1.35
CdBr	--	0.15	0.13
$CdHCO_3^+$	6.67	0.29	0.23
$CdCO_3$	24.19	1.60	1.5
$Cd(SO_4)_2^{2-}$	0.08	0.12	0.13
$CdOH^+$	0.15	0.04	0.02

Table 3. Laboratory experiment. Correlations between Cd transfer rates at 0, 10 and 20‰ salinity and the fractional abundance of some Cd species at these salinities (computer model). Correlations were made at water volume to sediment surface area ratios of 4.45 and 8.85.

Cd species	Ratio = 4.45	Ratio = 8.85
Cd^{2+}	0.857	0.822
$CdSO_4$	0.854	0.809
$CdHCO_3^+$	0.837	0.764
$CdCO_3$	0.836	0.762

Table 4. The main results found in laboratory experiments and using with the computer model. "+" indicates an effect of the parameter tested. "-" indicates no effect of the parameter tested. "Nt" indicates that the parameter has not been tested. "--" indicates that testing of the parameter was not possible.

Parameter tested	Laboratory experiment	Computer modelling
Age of Cd-sediment complex	-	--
Ratio between water volume and sediment area	+	--
Water salinity	+	+
Water pH	--	+
Water temperature	Nt	-
Cd concentration	+	-

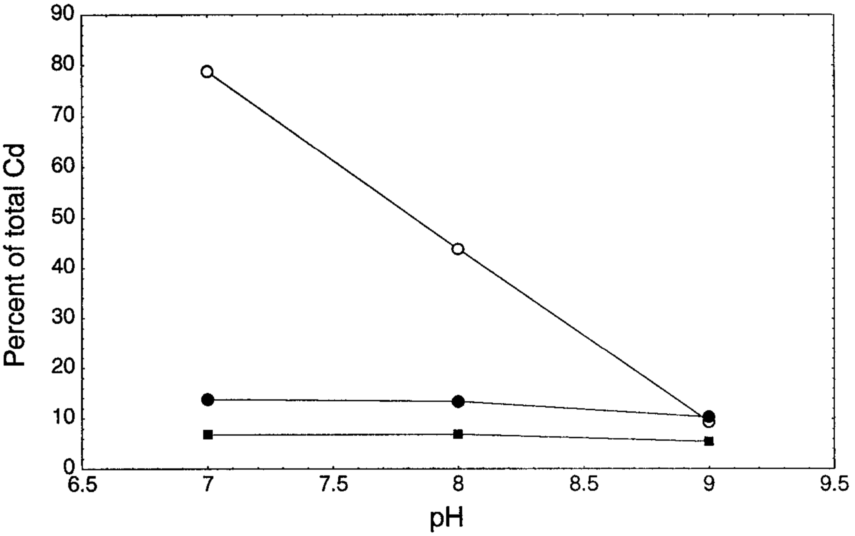

Figure 1 Fractional amounts of Cd^{2+} at 0, 10 or 20‰ salinity at pH 7, 8 or 9. Legend: ○: 0‰ salinity, ●: 10‰ salinity, ■:20‰ salinity.

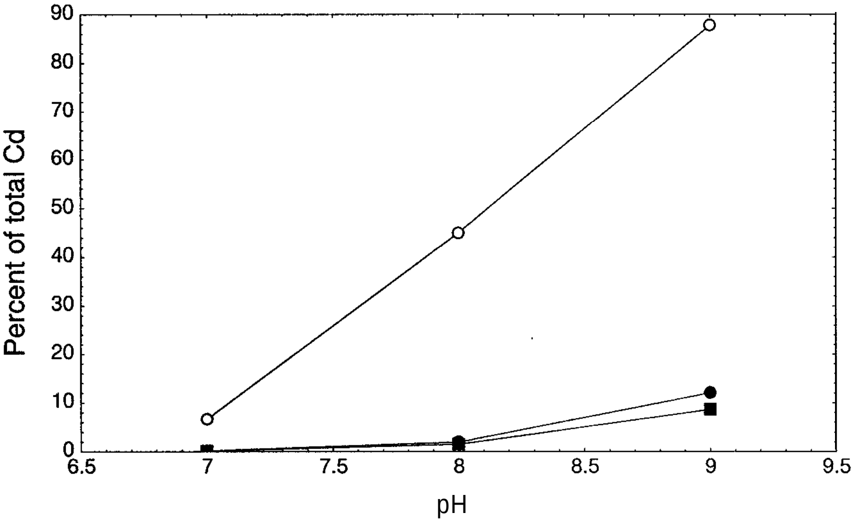

Figure 2 Fractional amounts of $CdCO_3$ at 0, 10 or 20‰ salinity pH 7, 8 or 9. Legend: ○: 0‰ salinity, ●: 10‰ salinity, ■:20‰ salinity.

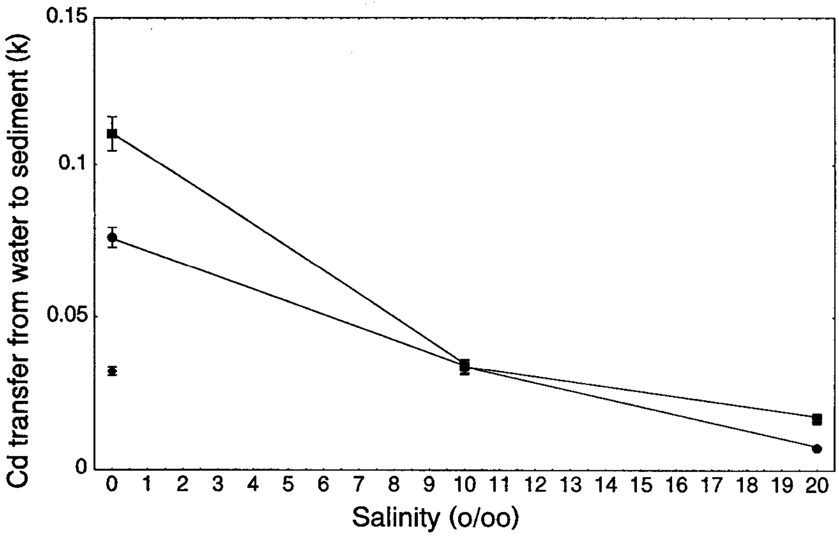

Figure 3 Cadmium transfer rates (k values) from water to sediment. ANOVA: Salinity: $p < 0.0001$, water-sediment ratio: $p < 0.0001$. N = 5 in all groups. Legends: ■: ratio = 4.45, ●: ratio = 8.85, ◆: ratio = 13.30.

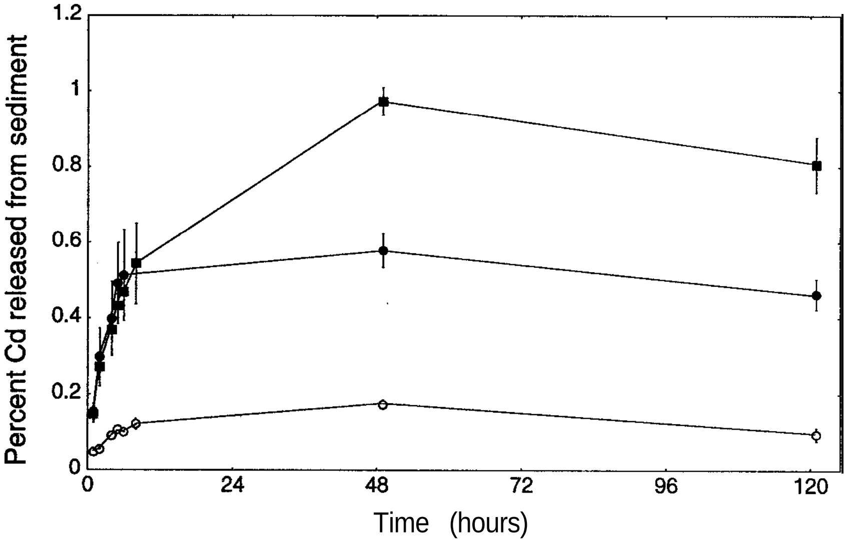

Figure 4 Effects of salinity on the release of Cd from newly contaminated sediment. Legend: ○: 0‰ salinity, ●: 10‰ salinity, ■: 20‰ salinity. N = 3 in each group.

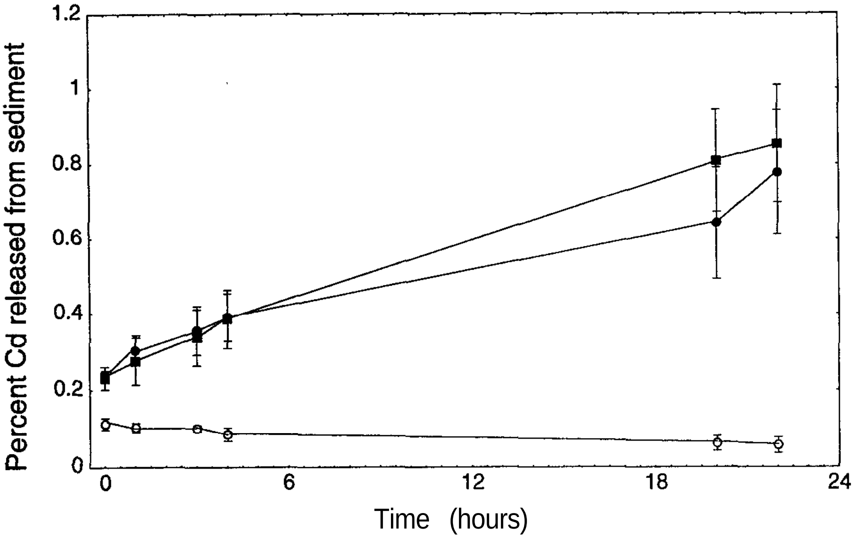

Figure 5 Effects of salinity on the release of Cd from aged contaminated sediment. Legend: O: 0‰ salinity, ●: 10‰ salinity, ■: 20‰ salinity. Note that time scale is different from figure 5. N = 3 in each group.

RESULTS AND DISCUSSION

Temperature (5 or 25°C) had no effect on Cd speciation (data not shown) as the equilibrium constants for the relevant Cd species vary only slightly over the small temperature range of 20°C used here. The Cd concentration (0.001 or 10 mg/L,) also had negligible effect on the speciation of Cd at any salinity (data not shown) due to the high concentrations of Cd-complexing inorganic solutes (carbonates in fresh water and chlorides in sea water). The change in concentrations of inorganic solutes (salinity) did, however, strongly affect the relative amounts of the various Cd species (Table 2), as previously shown (Mantoura *et al.* 1978). The main species in fresh water, Cd^{2+}, representing 61% of total Cd, decreased with increasing salinity to 7% in 20‰ seawater. This was mainly due to the formation of Cd-Cl complexes, that increased from 0.27% in fresh water to approximately 89% of total Cd in 20‰ seawater. Salinity is generally considered to be the most deciding factor for Cd speciation due to the formation of Cd-Cl-complexes while pH changes causes Cd species to vary only within a few percent of total Cd (Kester 1986). This result was confirmed by the present study as the effect of pH on Cd speciation was very pronounced in fresh water due to formation of mainly $CdCO_3$ (Figs. 1 & 2). At salinities of 10 or 20‰, Cd speciation was affected only slightly by pH. Also, modellations using only Na^+ and Cl^- instead of the chemical species listed in Table 1 gave results comparable to those listed in Table 2.

The transfer of Cd from water to sediment significantly decreased at increasing salinities (Fig. 3). It is reasonable to assume, that the concentration of the Cd^{2+} ion could account for most of the Cd adhering to sediment particles as indicated by the strong correlations observed between Cd transfer rates and the relative amounts of Cd species present (Table 3). Metal ions are believed to bind strongly to sediment particles due to the mainly anionic surfaces (Stumm 1992). The Cd transfer from water to sediment significantly decreased with increasing ratio between water volume and sediment surface area (Fig. 3). The water depth and residence time in natural system are therefor likely to affect the amount of Cd transferred from water to sediment.

The release of Cd from sediment was rapid and depended on salinity (Figs. 4 & 5). Cadmium adsorbed to sediment particles can be liberated due to ligand exchange reactions with water Cl^- ions. The Cd-Cl complexes thus formed have poor affinity for sediment particles (Davies-Colley *et al.* 1984). The release was fast reaching a maximum after approximately 48 hours and then tended to decrease during the next approximately 70 hours. Sediments are known to age and thereby Cd-sediment particle interactions are modified (Salomons & Förstner 1984). Also, the weakly alkaline pH of seawater will stabilise sediment oxides and thereby Cd adsorption (Elderfield *et al.* 1979). However, our results indicate that the release of Cd from "fresh" and "aged" contaminated sediments followed the same pattern, i.e. almost no release from sediments at 0‰ salinity, and higher but equal releases from sediments at 10 or 20‰ salinity. Fresh water Cd-contaminated sediments transferred to 32‰ salinity have been shown to release Cd for at least 35 days (Prause *et al.* 1985). In the experiments presented here Cd transfer rates were calculated on the basis of the initial few hours of an experiment and therefore do not tell anything about when and at what ratio an equilibrium will be reached.

The data indicate that temperature and Cd concentration, within their normal ranges in estuaries will not influence Cd speciation. Salinity changes, however, cause a marked change in Cd speciation and this had a strong effect on Cd transfer from water to sediment. Also, the ratio between water volume and sediment surface area (and thus water depth and residence time in the estuary) conceivably will influence estuarine Cd kinetics.

Acknowledgments This work was supported by two grants from the Danish Natural Sciences Research Council to O.A. The manuscript was greatly improved after comments by Peter E. Holm, Institute for the water environment, and Valery E. Forbes, Roskilde University.

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