Heavy Metal Exchange Processes in Sediment–Water Systems

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ABSTRACT / Experimental data for sorption of Hg, Cd, Cu, and Pb by sand, silt, and organic-rich sediments from the Ottawa River, Canada show significant conformity to Langmuir's equation. Values of the bonding energy constant and the sorption maximum correlate directly with organic content and mean grain size (ϕ). Desorption experiments indicate that the heavy metals form stable complexes in nitrilotriacetate (NTA) and NaCl Solutions, with the following desorption ratios: Hg, 1:1 (Cl^-:NTA); Pb, 1:10; Cd, 1:2. Serial and batch desorption studies under various conditions show that the cation-exchange order in the sediments is Hg > Pb > Cu > Cd. For a given heavy metal the partition coefficient between sediment and solution is not greatly changed by the presence of another cation, provided the latter has the same order of concentration. If, the concentration of one cation exceeds another by more than 10, however, significant desorption of the less concentrated ion takes place on a mass action basis.

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Introduction

Nonpolluted natural waters are normally characterized by a steady state with regard to their content of biomass and heavy metals. The delicate balance between producers and decomposers of biomass may be disturbed by excessive addition of nutrients or toxic substances, including heavy metals, commonly from human-made sources. Some of the metals are known to undergo biotransformation to toxic organic forms, which may be passed along the food chain to human (Nelson and others 1971, D'Itri 1972).

The states in which heavy metals occur in natural waters can be characterized into three major physicochemical forms:

1. Labile (or ion exchangeable)
2. Bound or complexed to microsolutes of organic and/or inorganic origin in the size range of ≤ 2 nm
3. Associated with macrosolutes and colloidal and particulate matter

The understanding and quantification of exchange processes occurring at the sediment–water interface is important in formulating a model for the speciation and transport of heavy metals. The sediment is a complex mixture, with four main components: silica, clays, organic matter, and oxides of iron and manganese. The term "silica," as used here, includes minerals other than clays and ferromanganese oxides; in most cases they are silicates, commonly silica in the form of quartz. The association of heavy metals with sediments can range from weak van der Waals forces to strong covalent bonding, coprecipitation with ferromanganese oxides, and incorporation within crystal lattices (Jonasson 1970, Gibbs 1973). The release of sorbed heavy metals into the bulk water is dependent on partition coefficients, which in turn are related to sediment characteristics, the type of heavy metal, and other environmental parameters. Desorption may be a slow process, posing a long-term problem even after the sources of pollution are eliminated.

The study reported here is part of the Ottawa River Project, a joint University of Ottawa–National Research Council of Canada investigation into the distribution and transport of mercury in a fluvial ecosystem. It is based on bed sediment samples from a 4.8-km section of the Ottawa River (Fig. 1), which has been studied intensively by Project personnel (Hart 1972, Miller 1974, 1976). The sediments are characteristically well-sorted sands in midchannel and silty sands at channel margins (Rust and Waslenchuk 1976). Logging on the river causes high but extremely variable organic content, which is generally more concentrated in the finer sediment. Mercury pollution has come mainly from pulp and paper mills, including one located in the north channel of the study area (Fig. 1). Mercury-bearing effluent from these sources was largely controlled in 1971 and mercury levels in the bed sediment have declined significantly since (Rust and Waslenchuk 1976).

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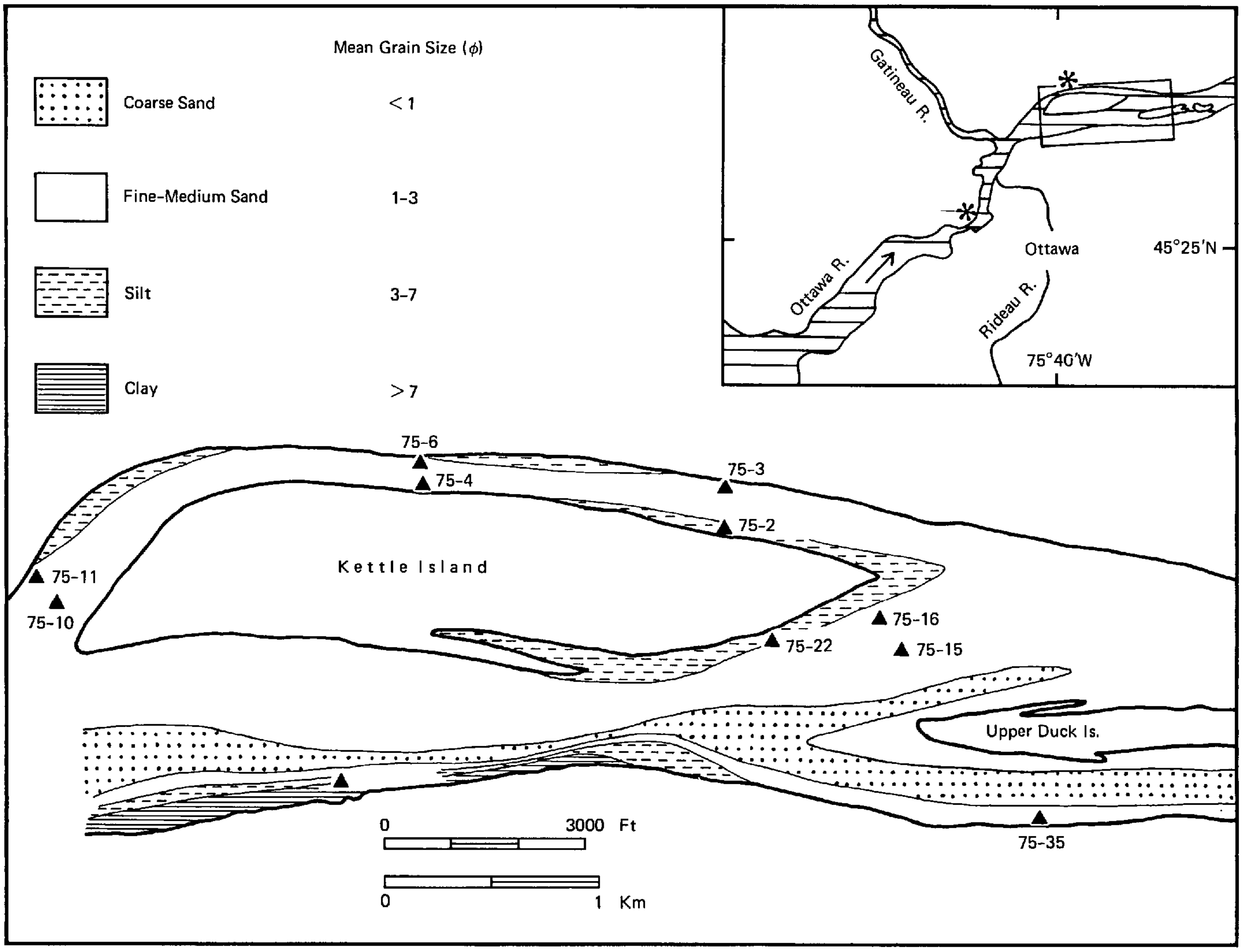

Figure 1. Map of study area showing sample locations and grain size distribution of bed sediment after Rust and Waslenchuk (1976). Asterisks on insert map indicate locations of pulp/paper mills.

In an earlier paper (Ramamoorthy and Rust 1976), we reported a preliminary study of the mercury sorption and desorption characteristics of some bed sediment samples from the 4.8-km study section. This work has now been extended as follows:

1. The number and variety of samples have been increased.
2. We have studied the influence on desorption of the pollutants nitrilotriacetate (NTA) and sodium chloride. Nitrilotriacetate is a surfactant used in detergents and is known to form strong complexes with heavy metal ions (Sillen and Martell 1971), whereas NaCl is used extensively in the Ottawa area for deicing highways. Knowledge of the effects of NaCl is also important when comparisons between freshwater and marine ecosystems are attempted.
3. Cadmium, Cu, and Pb were included in the study to investigate cation-exchange processes and interelement displacement in sediments under conditions comparable to those of natural systems. These metals were chosen because of their widespread industrial use and their common occurrence with minor mercury in sulfide ores (Jonasson and Boyle 1972). Major pollution sources of these metals and their toxicities have been described by Fishbein (1972) and Cheremisinoff and Habib (1972).

Experimental Procedure

General methodology

Measurements of the free (ionic) forms of heavy metals using metalion-specific electrodes, and the accuracy and limitations of the technique were outlined by Ramamoorthy and Kushner (1975a,b). A Jarrell-Ash 810 Atomic Absorption Spectrophotometer was used for analyzing total heavy metal content, including free and complexed forms. Metal nitrates have been used throughout, because the nitrate ion is a very weak complexing agent and the nitrates are completely ionized under the experimental conditions used in this study. Glassware was cleaned with NOChromix-H_2SO_4 acid and rinsed with large quantities of distilled water. Ramamoorthy and Kushner (1975a) and Bothner and Carpenter (1970) have shown that sorption of Hg^{2+} and the other heavy metals tested on glass surfaces is negligible during the experimental period. All metal binding experiments were repeated at least once for each metal ion; measurements were reproducible to ±2%. Grain-size parameters were determined by sieve and pipet analysis and organic content by ashing the sediment samples at 400°C for 24 hr.

Sorption studies

The sorption experiments were carried out as follows: 100 ml of aqueous solution of $M(NO_3)_2$ was thermostated and millivolt readings were recorded on tape. About 1 g of untreated sediment was accurately weighed and added to the solution, and the solution was stirred; millivolt readings were monitored automatically at regular time intervals. The experiments were performed for initial concentrations of 0.25, 0.5, 1,0, 2.0, 5.0, 10.0, and 20.0 ppm of heavy metal ion. Equilibration was indicated by constancy in millivolt readings. The concentration at equilibrium was read from the calibration plots and the difference between $[M]_{\text{equil}}$ and $[M]_{\text{initial}}$ was taken to be the amount sorbed by sediment. Values of amount of metal ion sorbed and the equilibrium metal ion concentration at seven initial metal ion concentrations of 0.25, 0.5, 1.0, 2.0, 5.0, 10.0, and 20.0 ppm were used to construct the sorption isotherm for each metal and each sediment sample in order to compute the sorption parameters. Sorption studies of all four metal ions Hg, Pb, Cd, and Cu were not carried out for all sediments. Sorption of Hg was studied on all samples of sediment except 75.4. Sorption of all four metals were carried out on one sample, 75-6, a sediment well mixed with wood chips and relatively high in organic content. Three representative sediment samples, 75-15, coarse sand; 75-22, fine sand, and 75-35, clay, were used in the sorption of Cu, Cd, and Hg. The rest were used to study the sorption of either one or two metal ions.

Desorption studies

Heavy metal desorption experiments were conducted on four different sediment samples, with varying grain size and organic content. The sediment was left overnight to saturate with a 2-ppm heavy metal solution and was then analyzed for sorbed metal by atomic absorption spectroscopy and ion-specific electrode, after it had been washed several times with distilled water to remove nonsorbed ions. Heavy metal sorption was found to be about 99% of the initial metal concentration and was found comparable to the amount sorbed in the sorption experiments.

The samples were leached for 4 days in a shaker, in the presence of (1) 100 ml of 10^{-4} M NaCl solution and (2) 100 ml of 5×10^{-5} M NTA solution. The phases were then separated, the sediment was washed with distilled water, and the heavy metal content was determined by atomic absorption (AA) after acid extraction. The supernatent solution, which was in equilibrium with the sediment, was also assayed for heavy metal content by AA. Two other types of desorption experiments were conducted.

Batch experiments. The sediment was loaded with a cadmium solution overnight, washed to remove nonsorbed Cd, dried slowly at room temperature, and divided into five fractions. Two fractions were assayed for Cd and the other three were treated individually with solutions of Cu, Pb, and Hg. The sediment and supernatent fluid were separated and analyzed for metal_1 and metal_2; the molar ratio and the order of cation exchange were then calculated.

Serial experiments. These studies were similar to the batch experiments except that the same sample was treated with all four metal ions in sequence. A sand (sample 75-22) was used, although the heavy metal sorption was relatively low, because separation of sediment and solution was relatively easy and complete. Three types of serial experiments were performed:

a. The sample was loaded with Cd (as in the batch experiments above) and was then equilibrated with Cu solution for 4 days. After this, the sediment and water phases were separated and analyzed for Cd and Cu, following the standard washing procedure. The experiment was continued with Pb and then with Hg (i.e., in order of increasing binding strength).
b. The sediment was loaded with Cd and ion exchanged in reverse sequence: Hg, then Pb, and then Cu.
c. The sediment was loaded with the strongest binding ion, Hg, and ion exchanged in sequence of increasing binding strength: Cd, then Cu, and then Pb.

Results

Sorption studies

The sorption data for all sediment samples were fitted to the linear form of the Langmiur equation:

$$C/x/m = (1/kb) + (C/b)$$

where C is the equilibrium concentration of the sorbate (the metal ion), x/m is the amount of sorbate per unit mass of sorbent, k is a constant related to the bonding energy of the sediment for heavy metals, and b is the sorption maximum. Seven sets of $C/x/m$ and C data corresponding to initial metal ion concentrations of 0.25, 0.5, 1.0, 2.0, 5.0, 10.0, and 20.0 ppm of metal ion were fitted to the linear form of Langmiur's equation in each case. For each sample b and k were determined using the least squares method to compute the most probable slope and intercept of each curve. For the sake of brevity, only b and k values are given in Table 1 but not $C/x/m$ and C data for all the various initial concentrations of each metal ion. The correlation coefficients between b and k (Table 1) indicate that the sorption data show significant conformity to Langmuir's equation. Relatively high values of b indicate that the Ottawa River sediments studied have a substantial capacity to sorb heavy metal ions. Values of k are also high, suggesting a strong bonding between sediments and heavy metal ions. Regression analysis shows that b and k correlate directly with organic content and with ϕ mean grain size (Table 2).

Desorption studies

Table 3 is derived from published data (Sillen and Martell 1971, Hahne and Kroontje, 1973); Table 3a gives the proportions of various heavy metals bound in natural waters at neutral pH

Table 1 Heavy Metal Sorption by Ottawa River Sediments

	Sediment properties				Experimental data			
	Original	Organic	Grain size (ϕ)*					
Sample number	Hg (ppb)	matter (%)	Mean	Std. Dev.	M^{2+}	*b*	*k*	Correlation† coefficient
75-15	1	0.6	1.18	0.58	Cd	1.90	2.50	0.991
					Hg	2.38	4.30	0.994
					Cu	1.85	—	0.976
75-35	6	3.2	7.09	1.18	Cd	19.49	2.42	0.952
					Hg	11.19	9.12	0.942
					Cu	21.88	14.28	0.998
75-11	31	5.2	3.00	0.98	Cd	3.29	0.26	0.998
					Hg	23.70	4.06	0.985
75-6	250	35.7	2.63	0.69	Cd	3.48	2.46	0.997
					Hg	10.76	16.02	0.984
					Cu	11.00	2.42	0.975
					Pb	30.86	1.08	0.897
75-16	4	0.6	1.32	0.48	Hg	2.61	2.67	0.989
					Cu	2.13	0.70	0.985
75-22	4	2.4	1.89	0.35	Cd	1.18	1.38	0.986
					Hg	3.35	1.78	0.907
					Cu	1.99	0.41	0.883
75-45	26	1.3	6.55	1.81	Cd	9.37	8.08	0.993
					Hg	47.62	3.89	0.514
75-10	7	1.2	2.14	0.50	Hg	8.42	10.61	0.996
75-4	33	9.9	2.44	0.93	Cd	4.17	0.23	0.934
75-3	15	94.5	2.01	0.67	Hg	19.34	5.17	0.992
75-2	5	0.6	2.61	0.33	Hg	2.70	6.40	0.983

*ϕ, − $\log_2$ mm.

†These highly significant correlation coefficients derived from seven data pairs of *C/x/m* versus *C* confirm the fitting of sorption data to the linear form of Langmuir's equation and computation of *b* and *k*.

and salinity 10^{-4} *M* NaCl. It shows that Hg^{2+} is completely bound to chloride at this concentration and is the only one of the four metals studied that does this.

Our results are consistent with heavy metal binding as highly stable complexes in chloride and NTA leaches. As expected from Table 3, it was found that almost 100% of the Hg was desorbed from sediment within 6 hr in both NaCl and NTA solutions. Table 4 shows that the approximate desorption ratios of heavy metal ions from a given sediment by chloride versus NTA are as follows: Hg, 1:1 (Cl^-:NTA); Pb, 1:10; Cd, 1:2. With the exception of cadmium, these results are consistent with previous data (Table 3b). Chloride solution desorbed about 50% Cd from the sediments (except for sample 75-11, for which desorption was less), whereas the action of NTA solution followed the expected stability order of metal–NTA complexes. Our results suggest that the cadmium–sediment binding constant must be less than $10^{1.8}$ (≡ cadmium–chloride binding).

Metal solubilization from various sediments by NTA has been studied earlier. Banat and others (1974) have shown that Cu, Cd, and Pb are solubilized to a large extent even with relatively low NTA concentrations; the amounts solubilized are positively correlated with both time of shaking and NTA concentrations and this is true for Pb at NTA $\leq$ 10 ppm. Gregor (1972) observed similar effects, with Pb being mobilized 12 times higher than the normal concentrations. Zitko and Carson (1972) reported measurable release of heavy metals, including Hg and Cd, from sediments by low concentrations of NTA. Our results are in good agreement with earlier studies showing that heavy metal–NTA complexing accounts for the mobilization of metals from sedi-

Table 2 Correlation Coefficients Relating Langmuir Isotherm Parameters, Percent Organic Matter and Grain Size of Sediments*

Factors correlated	Sorption maxima (*b*)	Bonding energy constant (*k*)
Organic matter (%)	0.996	0.810
Mean grain size (ϕ)	0.780	0.820

*In some cases, up to two widely scattered points were excluded.

Table 3a

M^{2+}	Fraction of total M^{2+} bound in:	
(10^{-4} *M*)	[OH]:10^{-7} *M*	[Cl$^-$]:10^{-4} *M*
Hg	1.0	1.0
Pb	0.85	0
Cd	0	0
Cu	0	0

Table 3b (Data from Sillen and Martell 1971)

Metal ion	Log stability constants	
M^{2+}	Cl$^-$ complexes	NTA complexes
Hg	15.15	14.60
Pb	1.73	11.47
Cd	1.80	10.00
Cu	2.05	13.05

ments. Importantly, the NTA complexes of soft acids (Ahrland, 1966), such as Hg, Cd, Pb, and Cu, are persistent in the aquatic systems because of their slow or absent biodegradability (Thom, 1971). The applications, toxicology, and bioenvironmental impact of NTA have been reviewed recently (Mottola, 1974).

The order of cation exchange from sediment was found to be Hg > Pb > Cu > Cd under a variety of exchange conditions (Table 5). From the analytical data of heavy metal concentration in water and sediment phases, the partition coefficients or stability constants (*K*) of the heavy metal ions were calculated:

$$K = [M^{2+}] \text{ in sediment phase}/[M^{2+}] \text{ in aqueous phase}$$

The relative consistency of *K* values (Table 6) confirms the fact that the partitioning of heavy metal ions between the sediment and the overlying water is not greatly perturbed by the presence of other heavy metal ions, at least when their concentrations are about the same order of magnitude. The results also suggest that sediments can act as heavy metal ion exchangers on a mass action basis, that is, when the concentration ratios differ by more than an order of magnitude. The latter circumstance could be an important mechanism for the release of heavy metal ions to the overlying water column in natural enviornments.

Discussion

The sorption studies indicate that Ottawa River sediments can act as efficient sinks for heavy metals, despite the fact that well-sorted sand is the dominant sediment type in the study area (Fig. 1). One reason for this is that commercial use of the river for logging adds a loading of organic material that is significantly greater than the natural amount. The ability to sorb heavy metal ions is increased by the presence of organic particles and by finer mineral grains. Both are more abundant close to the river banks, especially in embayments.

Unless strong leaching agents (for example, NaCl and NTA) are present in sufficient concentration (about 10^{-4} *M*), the mobility of heavy metal ions is low and they persist on sediments for a considerable period of time. Relative to freshwater environments, marine ecosystems should be subject to greater desorption of heavy metals into the aqueous phase because of chloride complexing and a reduced degree of bonding to sediment particles. This may explain why Loring (1975) has found a lack of association between mercury and iron in sediments of the Gulf of St. Lawrence, whereas this association is strong in Ottawa River sediments (Rust and Waslenchuck 1976). However, because of the generally low energy of marine depositional environments, it is possible that chloride-complexed heavy metals can remain in interstitial water and escape but slowly into the overlying water column. In the fluvial environment the transport of bed sediment as bedload and in suspension introduces a much greater degree of physical interaction of water and sediment. The energetic physical environment of river as opposed to marine sediments there-

Table 4a Mercury Desorption from Ottawa River Sediments*

Sample number	[Hg^{2+}]$_{\text{initial}}$ (ppm)	Leachate	Location of Hg^{2+}	[Hg^{2+}] (ppm)	Percent of [Hg^{2+}]$_{\text{initial}}$ desorbed
75-16	4.1	Chloride	Sediment	1.2	—
		Chloride	Supernat.	2.9	71
		NTA	Sediment	1.5	—
		NTA	Supernat.	3.7	90
75-22	11	Chloride	Sediment	2.4	—
		Chloride	Supernat.	8.6	78
		NTA	Sediment	2.6	—
		NTA	Supernat.	8.4	76

*Concentrations of leachates were the same for all desorption experiments. [Chloride] = 10^{-4} *M*; [NTA] = 5×10^{-5} *M*.

Table 4b Lead Desorption from Ottawa River Sediments*

Sample number	[Pb^{2+}]$_{\text{initial}}$ (ppm)	Leachate	Location of Pb^{2+}	[Pb^{2+}] (ppm)	Percent of [Pb^{2+}]$_{\text{initial}}$ desorbed
75-16	100	Chloride	Sediment	92.5	—
		Chloride	Supernat.	7.5	7.5
		NTA	Sediment	30	—
		NTA	Supernat.	70	70
75-22	104.4	Chloride	Sediment	96.5	—
		Chloride	Supernat.	7.9	7.6
		NTA	Sediment	21	—
		NTA	Supernat.	83	80
75-10	92.5	Chloride	Sediment	72.7	—
		Chloride	Supernat.	19.8	21
		NTA	Sediment	26.5	—
		NTA	Supernat.	66	71
75-11	68	Chloride	Sediment	58	—
		Chloride	Supernat.	10	15
		NTA	Sediment	33	—
		NTA	Supernat.	35	51

*Concentrations of leachates as in Table 4a.

Table 4c Cadmium Desorption from Ottawa River Sediments

Sample number	[Cd^{2+}]$_{\text{initial}}$ (ppm)	Leachate	Location of Cd^{2+}	[Cd^{2+}] (ppm)	Percent of [Cd^{2+}]$_{\text{initial}}$ desorbed
75-16	68	Chloride	Sediment	33	—
		Chloride	Supernat.	34	50
		NTA	Sediment	7	—
		NTA	Supernat.	62	91
75-22	53	Chloride	Sediment	28	—
		Chloride	Supernat.	25	47
		NTA	Sediment	3.3	—
		NTA	Supernat.	49	92
75-10	60	Chloride	Sediment	26	—
		Chloride	Supernat.	34	57
		NTA	Sediment	7	—
		NTA	Supernat.	52	87
75-11	72	Chloride	Sediment	62	—
		Chloride	Supernat.	9.9	14
		NTA	Sediment	N.D.	—
		NTA	Supernat.	71	98

fore tends to favor desorption in fluvial systems, partly counteracting the effects of high salinity in the sea.

The results of desorption experiments with several heavy metal ions present show the importance of ionic interactions. For example, additional Hg is desorbed in the presence of an order of magnitude excess of other heavy metals. This is a likely situation where metallic pollution comes from sulfide ores in natural exposures or from mine waste: Hg is in trace amounts relative to Pb, Zn, Cu, etc. (Sears 1971). In addition to the toxicity of the major heavy metals, therefore, Hg is more available for biologic uptake from the water under these conditions.

Conclusions

1. Data on sorption of Hg, Cd, Cu, and Pb by Ottawa River bed sediments can be fitted to the linear form of Langmuir's equation.
2. High values of the bonding energy constant and the sorption maximum show that the sediments have a substantial capacity to sorb heavy metal ions. These parameters correlate directly with organic content and mean grain size (ϕ).
3. High rates of desorption of Hg, Cu, Cd, and Pb result from leaching samples with NaCl and nitrilotriacetate solutions. The two leachates give rise to approximately equal desorption of mercury.
4. Desorption of mercury is increased by the presence of another heavy metal ion (Cd, Pb, Cu) in a greater than order of magnitude concentration.
5. The mobility and persistence of heavy metal ions is in part dependent on the extent of their sorption onto sediments and their redistribution is a function of desorption processes at the sediment–water interface. Both are controlled by the nature of heavy metal bonding, sediment type, and water chemistry.

Table 5a Batch Displacement of Cadmium from Ottawa River Sediment Sample 75-22: Cadmium Content = 67 μg/g Sediment

Displacing metal ion	[Cd] displaced (ppm)	[Displacing metal] in solution (ppm)	[Displacing metal]$_{\text{initial}}$ (ppm)
Cu	50 (74%)	840	975
Pb	50	590	1000
Hg	52 (77%)	310	500

Serial Displacement of Cadmium from Ottawa River Sediment Sample 75-22: Cadmium Content = 67 μg/g Sediment

Displacing metal	[Cd] displaced (ppm)	[M^{2+}]$_{\text{equil}}$ in solution (ppm)	[M^{2+}]$_{\text{initial}}$ (ppm)	[Cu]$_{\text{displaced}}$ (ppm)	[Pb]$_{\text{displaced}}$ (ppm)
Cu	52 (77%)	850	975	—	—
Pb	0	700	1000	59 (47%)	—
Hg	0	360	500	27 (41%)	238 (79%)

Table 5b Serial Displacement of Cadmium from Ottawa River Sediment Sample 75-22: Cadmium Content = 67 μg/g Sediment

Displacing metal	[Cd]$_{\text{displaced}}$ (ppm)	[M^{2+}]$_{\text{equil}}$ in solution (ppm)	[M^{2+}]$_{\text{initial}}$ (ppm)	[Hg]$_{\text{displaced}}$ (ppm)	[Pb]$_{\text{displaced}}$ (ppm)
Hg	56 (83%)	320	500	—	—
Pb	0	790	1000	36 (20%)	—
Cu	0	910	975	11. (7.7%)	90 (43%)

Serial Displacement of Mercury from Ottawa River Sediment Sample 75-22: Mercury Content = 25.7 μg/g Sediment

Displacing metal	[Hg]$_{\text{displaced}}$ (ppm)	[M^{2+}]$_{\text{equil}}$ in solution (ppm)	[M^{2+}]$_{\text{initial}}$ (ppm)	[Cd]$_{\text{displaced}}$ (ppm)	[Cu]$_{\text{displaced}}$ (ppm)
Cd	3.1 (12%)	805	900	0	0
Cu	1.2 (5.3%)	845	975	82 (86%)	0
Pb	1 (4.6%)	670	1000	2 (15%)	60 (46%)

Table 6 Partition Coefficients of Heavy Metal Ions for Ottawa River Sample 75-22 from Heavy Metal Ion-Exchange Experiments

Metal ion	Serial displ.* Regular	Serial displ.* Reverse	Batch displ.*	Serial displ.†
Cu	0.15	0.07	0.13	0.15
Pb	0.43	0.27	0.55	0.49
Hg	0.39	0.56	0.38	0.43
Cd				0.12

*displ. = displacement. Refers to sediments loaded with cadmium initially and ion exchanged with other heavy metal ions. Batch, regular, and reverse serial displacements are as described under Experimental Procedure in the text.

†Refers to sediments loaded with mercury initially and ion exchanged with other heavy metal ions as described under Experimental Procedure in the text.

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