

## Speciation and partitioning of cadmium and zinc in two contrasting estuaries: The role of hydrophobic organic matter

Andrew Turner,<sup>1</sup> Sophie M. Le Roux, and Geoffrey E. Millward

School of Environmental Sciences, University of Plymouth, Drake Circus, Plymouth PL4 8AA, United Kingdom

### Abstract

The hydrophobicity and particle–water interactions of cadmium (Cd) and zinc (Zn) in an “organic-poor” estuary (Plym, United Kingdom) and an “organic-rich” estuary (Beaulieu, United Kingdom) have been investigated using radiotracers. The hydrophobic fraction of dissolved Cd (retained by a reverse-phase C<sub>18</sub> column) was about 50% in the River Beaulieu and less than 10% in the River Plym, and in both cases this fraction decreased rapidly with increasing salinity, such that only a few percent was hydrophobic at salinities above 10. Hydrophobicity of Cd was unaffected by the addition of suspended sediment particles, indicating that hydrophobic and hydrophilic forms adsorb in accordance with their relative abundance or that rapid reequilibration of dissolved Cd species occurs after specific forms have undergone adsorption. In the Plym, a logarithmic, salinity-dependent reduction in the sediment–water distribution coefficient,  $K_D$ , and a high proportion of adsorbed Cd bound exchangeably indicate that particle–water interactions of Cd in environments of moderate concentrations of organic matter are governed by inorganic processes. In the Beaulieu, more uniform  $K_D$ s and a significantly lower exchangeability of adsorbed Cd indicate that organic interactions might also be important. In both estuaries, the hydrophobic fraction of dissolved Zn was between about 80% and 100% and displayed an increase with increasing salinity and a reduction in the presence of suspended sediment particles. Throughout the Beaulieu, and in the Plym above salinities of about 4,  $K_D$  also increased with increasing salinity. These observations were interpreted and modeled in terms of the preferential uptake and salting out of hydrophobic complexes of Zn and indicate that, regardless of the concentration of organic matter, the speciation and uptake of Zn in many estuaries might be strongly influenced by hydrophobic interactions.

It is becoming increasingly evident that one of the principal controls on the adsorption of transition metals to mineral surfaces is the concentration and nature of organic ligands. Davis and Leckie (1978) were among the first to study the effects of a range of different synthetic organic ligands on the adsorption of trace metals to hydrous oxides, and they demonstrated that metal adsorption was either enhanced or reduced depending on whether or not coordinating groups were involved in binding with the mineral surface. A general observation of the many studies undertaken since is that in the presence of most (but not all) organic ligands, metal adsorption is enhanced at low pH and reduced at high pH (Warren and Haack 2001).

Far less often studied are the effects of natural organic ligands on the adsorption of metals to natural, heterogeneous (and often organic-rich) suspended particles. Such studies rely on the addition of a radiotracer analogue of the metal of interest to a natural particle suspension and on controlling the concentration (or presence) of dissolved organic ligands. Accordingly, Paulson et al. (1994) demonstrated that the distribution coefficient defining adsorption of copper to marine sediment was doubled once aqueous organic matter was removed by solid-phase extraction, while we showed that the distribution coefficient defining nickel adsorption to estuarine sediment was enhanced by almost an order of magnitude once dissolved organic matter was decomposed by ultravi-

olet photolysis (Turner et al. 1998). Qualitatively, these results clearly demonstrate the effects of dissolved organic matter on trace metal removal, and are consistent with the competitive effects of organic ligands and adsorption sites for dissolved metal, and metal complex adsorption at near- or above-neutral pH. However, complete removal of refractory organic matter by any method is not possible, and the significance of these resistant organic ligands for metal binding may outweigh their relative abundance. Moreover, there is also scope for desorption of organic matter from natural particles suspended in near organic-free indigenous water.

To overcome these potential problems, we determined dissolved Hg(II) complexes in estuarine waters that were retained by reverse-phase C<sub>18</sub> “Sep-Pak”-type columns, both before and after adsorption to sediment was effected (i.e., in the absence and presence of suspended sediment particles; Turner et al. 2001). These columns consist of octadecyl carbon moieties chemically bonded to silica gel supports and are designed to separate hydrophobic organic species from hydrophilic (organic and inorganic) species in an aqueous medium. Separation of species by these columns is not based on any thermodynamic principle or simple chemical property but is believed to be relevant to heterogeneous environmental and biological partition processes (Donat et al. 1986; Groschner and Appriou 1994). The results of our study demonstrated adsorption of Hg(II) complexes of differing hydrophobicity in estuaries of widely varying geochemical characteristics, but a common salinity dependence of Hg(II) adsorption that was consistent with the partitioning behavior of a neutral solute.

In the present study, we apply this empirical approach to examine the hydrophobicity of cadmium (Cd) and zinc (Zn) complexes and the influence of these complexes on metal

<sup>1</sup> Corresponding author (aturner@plymouth.ac.uk).

### Acknowledgments

This work was funded, in part, by the CNRS (France), grant 6521. The authors wish to acknowledge the laboratory and analytical support of A. Fisher (UoP). We also thank two anonymous reviewers for their incisive and constructive comments.

Table 1. Chemical characteristics of the water and sediment samples used in the experiments.

	Salinity	pH	DOC (mg L <sup>-1</sup> )		
<i>Water samples</i>					
Plym river water	<0.3	6.74	2.0		
Plym seawater	32.8	8.11	1.5		
Beaulieu river water	<0.3	6.93	17.7		
Beaulieu seawater	33.9	8.09	1.6		
	Al (%)	Fe (%)	Mn (μg g <sup>-1</sup> )	POC <sup>a</sup> (%)	SSA <sup>b</sup> (m <sup>2</sup> g <sup>-1</sup> )
<i>Sediment samples</i>					
Plym	6.92	2.50	534	2.1	6.1
Beaulieu	3.37	3.67	280	6.9	6.9

<sup>a</sup> Particulate organic carbon concentration.

<sup>b</sup> Specific surface area by BET N<sub>2</sub> adsorption.

adsorption to sediment under simulated estuarine conditions. Although many aspects of their chemistries are similar, Cd and Zn have very different affinities for organic ligands in the aquatic environment (Tipping et al. 1998; Town and Filzella 2000), and they serve as contrasting metals for the purposes of this investigation. We use samples from two estuaries selected for their differing geochemical characteristics; namely, the Plym (southwest United Kingdom), an “organic-poor” estuary that drains granitic moorland and whose sediment comprises a significant fraction of kaolinite derived from mining activities in the middle catchment, and the Beaulieu (southern United Kingdom), an “organic-rich” estuary whose low-lying watershed is dominated by forest.

## Methods

*Sample collection and characterization*—Water samples from the Beaulieu and Plym estuaries were collected from the shore in acid-cleaned 5-liter polyethylene bottles from above the limit of saline intrusion (river end-member) and near to the estuary mouth (marine end-member) and were stored at 4°C. Samples were filtered, within 24 h of collection, through acid-cleaned 0.45-μm cellulose-acetate filters (Millipore) and were stored at 4°C in the dark in acid-cleaned 1-liter polyethylene bottles until further use. For the analysis of dissolved organic carbon (DOC), additional water samples were collected in ashed 250-ml borosilicate bottles and stored in a similar fashion. These samples were filtered through 0.7-μm GF/F Whatman filters and acidified by the addition of 300 μl of concentrated phosphoric acid before being analyzed using a Shimadzu TOC-5000 total organic carbon analyzer. Chemical characteristics of all water samples are given in Table 1.

Surficial, oxic scrapes of intertidal sediment were collected from the upper reaches of the estuaries using a plastic spatula and were stored at 4°C in acid-cleaned polyethylene bottles. Within 24 h of collection, the sediment samples were wet sieved through a 63-μm nylon mesh using indigenous river water, and the resulting sediment slurries were stored at 4°C in the dark in acid-cleaned polyethylene bottles until use in the adsorption experiments. The physical and chemical properties of the mud (<63 μm) fraction of sediment are broadly similar to those of suspended particles in shallow

estuarine and coastal environments (van Alsenoy et al. 1993), but the mud fraction affords a better representation of the time-averaged, bulk particle characteristics of the system. From a practical standpoint, particle normalization also minimizes potential effects on the experimental results that arise from variations in particle size and particle concentration.

Portions of air-dried sediment samples were used for chemical characterization (see Table 1). Thus, aluminum, iron, and manganese were determined by graphite furnace atomic absorption spectrometry following total sample digestion in hydrofluoric acid (BDH Aristar, Poole), specific surface area was determined using a BET N<sub>2</sub> gas adsorption technique, and particulate organic carbon was determined using a Shimadzu TOC-5000 total carbon analyzer following sample digestion in 0.1 mol L<sup>-1</sup> HCl (BDH Analar, Poole).

*Speciation and partitioning experiments*—General approach: Assumptions of the radiochemical approach adopted in this study are that added radiotracers behave identically to the corresponding stable metals and that the addition of a small quantity of radiotracer analogue does not significantly perturb preexistent chemical equilibria (Anderson et al. 1987). We added <sup>109</sup>Cd and <sup>65</sup>Zn to our samples to final concentrations of about 0.02 nM and 18 nM, respectively. Although background concentrations of stable Cd and Zn in our samples were not measured, the added tracer concentrations are well below dissolved Cd and Zn concentrations typical of British coastal waters (up to 0.75 nmol L<sup>-1</sup> and 35 nmol L<sup>-1</sup>, respectively; Laslett 1995) and estuaries (up to 5 nmol L<sup>-1</sup> and 300 nmol L<sup>-1</sup>, respectively; Martino et al. 2002). We also added <sup>109</sup>Cd and <sup>65</sup>Zn to filtered water samples before the addition of suspended sediment particles in order to allow the radiotracers to equilibrate with preexistent ligands and metals.

Operational definitions of metal speciation: Hydrophobicity ( $f_H$ ) is defined as the fraction of metal (or radiotracer) that is retained by a reverse-phase C<sub>18</sub> column and eluted by dilute acid according to an approach described elsewhere (Groschner and Appriou 1994). Hydrophobic forms of metals include neutral or near-neutral complexes with many humic substances and amino acids, aromatic ligands, and small

organic ligands, whereas hydrophilic species include metal ions, charged inorganic complexes, and small, charged organic complexes. Although there is potential for adsorption of some hydrophilic species by uncapped silanol groups of  $C_{18}$  columns (Donat et al. 1986), detailed studies of the columns we use have demonstrated that adsorption of metals in ligand-free water is not significant (Groschner and Appriou 1994). Nevertheless, it is important to appreciate that our definition of hydrophobicity is operational and that this characteristic may be related to, but is unlikely the same as, a lipophilic or cell-permeable fraction of metal (Phinney and Bruland 1994).

The uptake or partitioning of dissolved metal in the presence of estuarine sediment is defined in terms of the sediment–water distribution coefficient,  $K_D$  (v/w); that is, the ratio of particulate or adsorbed activity (w/w) to dissolved activity (w/v). The particulate phase encompasses metal that is physically or chemically bound to suspended sediment particles, whereas the dissolved phase encompasses inorganic and organically complexed metal species in true solution as well as metals that are physically or chemically bound to filterable colloidal particles. We used a particle concentration of  $100 \text{ mg L}^{-1}$  in our experiments, which is realistic for meso- and macrotidal estuarine environments. Preliminary experiments showed that  $K_D$  was not sensitive to particle concentration in the range of 60 to  $300 \text{ mg L}^{-1}$ , indicating that artifacts caused by adsorption of metals to colloidal particles were not significant.

Exchangeable and leachable forms of adsorbed metal are defined as the fractional activities on suspended sediment particles that are recovered sequentially by  $1 \text{ mol L}^{-1} \text{ NH}_4\text{OAc}$  and  $1 \text{ mol L}^{-1} \text{ HCl}$ , respectively, and the residual fraction of adsorbed metal is defined as the fractional activity on the particles remaining after these digestions. The exchangeable fraction refers to metal that is loosely bound to the particle surface through (mainly) ionic and electrostatic interactions, such as ion exchange and surface complexation (Ure et al. 1993). The leachable fraction refers to metal that is more tightly bound to the particle surface, through covalent interactions, for example, or that has migrated into the matrix of reactive mineral oxides and clay minerals (Martino et al. 2002). The residual fraction includes metal that has bonded to or migrated within minerals that comprise the core of the particle and metal that is associated with resistant (or acid-insoluble) particulate organic matter.

**Experimental procedure:** Filtered end-member samples were mixed in various proportions to volumes of 100 ml in 125-ml acid-cleaned polyethylene bottles in order to simulate the estuarine salinity gradient. A small quantity of carrier-free  $^{109}\text{Cd}$  and  $^{65}\text{Zn}$  (Amersham International) was pipetted into the bottles to achieve isotope activities of about  $100 \text{ Bq ml}^{-1}$ . Samples were left to equilibrate for 12 h in the dark at  $20^\circ\text{C}$  before a 20-ml aliquot was pipetted into a scintillation vial and counted on a high-performance Wallac 1480 Wizard 3  $\gamma$ -counter with NaI detection (Perkin-Elmer). Another 20-ml aliquot was passed through an acid-cleaned, methanol-conditioned reverse-phase  $C_{18}$  column (200 mg  $C_{18}$  resin, Bond Elut, Merck Eurolab) under gravity at a flow rate of about  $20 \text{ ml h}^{-1}$  and collected in a scintillation vial

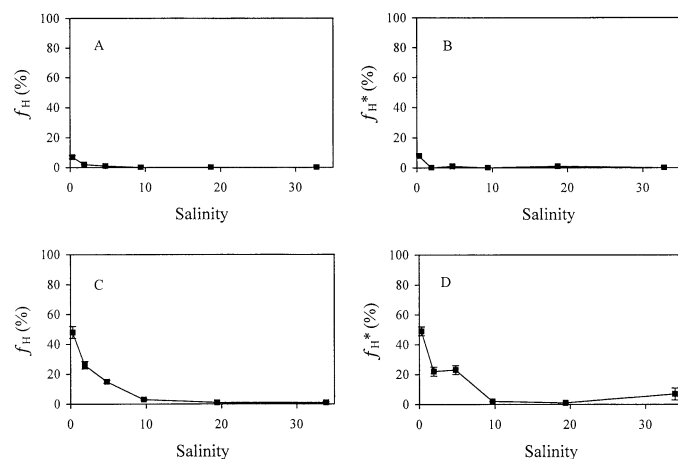


Fig. 1. The hydrophobic fraction of dissolved Cd as a function of salinity: (A) Plym Estuary in the absence of particles; (B) Plym Estuary after adsorption onto suspended sediment particles; (C) Beaulieu Estuary in the absence of particles; and (D) Beaulieu Estuary after adsorption onto suspended sediment particles. Error bars represent the standard deviation about the mean value derived from five separate experiments.

and counted as above. Columns were eluted with  $10 \text{ ml}$  of  $2 \text{ mol L}^{-1} \text{ HNO}_3$  (BDH AnalaR, Poole) to extract adsorbed and occluded hydrophobic species (Plavsic and Branica 1986; Abbasse et al. 2002), and the eluates were collected in scintillation vials and counted in a similar manner. Isotope recovery exceeded 95% in all experiments, and the difference in the activities of the original sample and the sample passing the column was, therefore, used to calculate metal hydrophobicity ( $f_H$ ).

To the remaining samples, an aliquot of sediment slurry was added to attain a particle concentration of  $100 \text{ mg L}^{-1}$ . Samples were incubated at  $20^\circ\text{C}$  in the dark and under constant agitation for 24 h before particle and water phases were separated by filtration through  $0.45\text{-}\mu\text{m}$  filters, and 20-ml filtrates were transferred to scintillation vials and counted as above. Additional aliquots of filtrates were passed through  $C_{18}$  columns and counted in order to define the hydrophobic fraction of metal remaining in the solution after adsorption had taken place ( $f_H^*$ ). Filters were then air-dried and weighed and digested sequentially in acid-cleaned 30-ml polyethylene tubes by 20 ml of  $1 \text{ mol L}^{-1} \text{ NH}_4\text{OAc}$  (BDH AnalaR, Poole) for 5 h and by 20 ml of  $1 \text{ mol L}^{-1} \text{ HCl}$  (BDH AnalaR, Poole) for 5 h. Filters and filtrates from both digestions were counted to determine the exchangeable, leachable, and residual fractions of adsorbed metal.

All experiments investigating hydrophobicity, partitioning, and solid-state speciation were undertaken in quintuplicate, and results were generally reproducible to within 5%.

## Results and discussion

**Hydrophobic fraction of dissolved metal**—The hydrophobic fraction of dissolved Cd in the Plym and Beaulieu estuaries, both before and after adsorption had taken place, is shown as a function of salinity,  $S$ , in Fig. 1. In the Plym, this fraction ranges from about 8% in freshwater to less than

Table 2. Percentage of Cd and Zn retained by reverse-phase  $C_{18}$  columns in fresh water and marine environments.

Location		DOC (mg L <sup>-1</sup> )	Cd	Zn	Reference
Plym Estuary, UK	River water	2.0	7	94	This study
	Seawater	1.5	<1	99	
Beaulieu Estuary, UK	River water	17.7	48	90	This study
	Seawater	1.6	<1	98	
Mersey Estuary, UK	River water	9.7	20	35	Turner et al. (2002)
	Seawater	1.8	<1	90	
Aber-Wrac'h Estuary, France	River water	—	25	—	L'Her Roux et al. (1998)
	Seawater	—	<5	—	
River Vienne, France		5.3–6.8	<1–10	—	Garnier et al. (1997)
Venice Lagoon, winter		—	<1–4	2–6	Martin et al. (1994)
Venice Lagoon, spring		—	<1–4	2–24	
English Channel		—	<1	72	Abbasse et al. (2002)
Western Mediterranean		—	<1	0.3–5.5	Yoon et al. (1999)
Central North Pacific		0.5–1.8	—	8	Donat et al. (1986)

1% above  $S \sim 10$ , and this fraction appears to be independent of whether or not suspended particles are present (that is,  $f_H \sim f_H^*$ ). In the Beaulieu, the hydrophobic fraction of Cd decreases from about 50% in freshwater to a few percent above  $S \sim 10$ , both in the absence and presence of suspended particles.

Quantitatively, these results are in broad agreement with results from other studies of Cd speciation employing reverse-phase  $C_{18}$  columns, as shown in Table 2, and are consistent with its relatively low affinity for natural organic matter compared with other transition metals (Tipping et al. 1998). A significantly greater fraction of hydrophobic Cd in the River Beaulieu than the River Plym implies that the concentration (and likely the nature) of dissolved organic matter dictates the hydrophobicity of Cd in natural freshwaters. More generally, data from Table 2, as plotted in Fig. 2, indicate an exponential dependency of Cd hydrophobicity on the concentration of riverine dissolved organic matter (defined analytically as DOC), indicating that the effect is related to the availability of a specific pool of hydrophobic ligands. That is, the proportion of available ligands increases exponentially with increasing DOC concentration. With re-

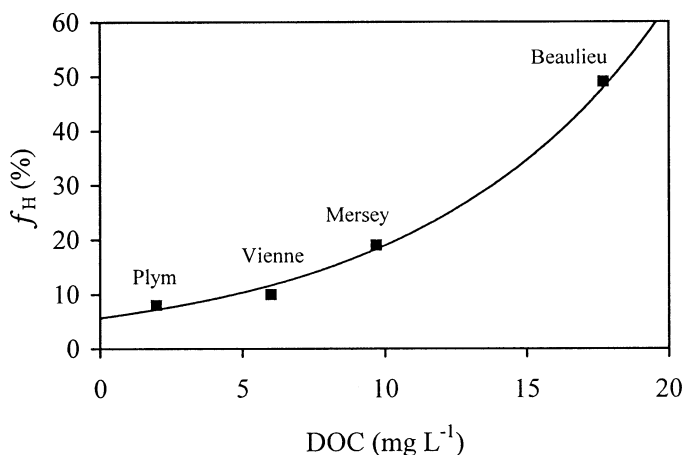


Fig. 2. The hydrophobic fraction of dissolved Cd in various rivers (see Table 2) as a function of the concentration of dissolved organic carbon (DOC).

spect to the salinity distribution of hydrophobic Cd, results are consistent with a reduction in the concentration of organic matter from river water to seawater (Moran et al. 1991; Turner et al. 1998) and with the propensity of Cd to form strong chloro-complexes in saline water (Paalman et al. 1994). That the hydrophobicity of Cd was unaffected by the presence of particles indicates either (i) hydrophobic and hydrophilic species adsorb in accordance with their relative abundance, or (ii) rapid reequilibration of dissolved Cd species occurs after specific forms have undergone adsorption.

In contrast, the hydrophobic fraction of dissolved Zn (Fig. 3) ranges from about 80% to nearly 100% and exhibits an increase with increasing salinity. The hydrophobicity of Zn is similar in the Plym and Beaulieu estuaries, indicating that the availability of hydrophobic ligands in these estuaries is not a limiting factor, but hydrophobicity is reduced in both cases by up to 10% in the presence of suspended particles and after adsorption has taken place (that is,  $f_H > f_H^*$ ). Thus,

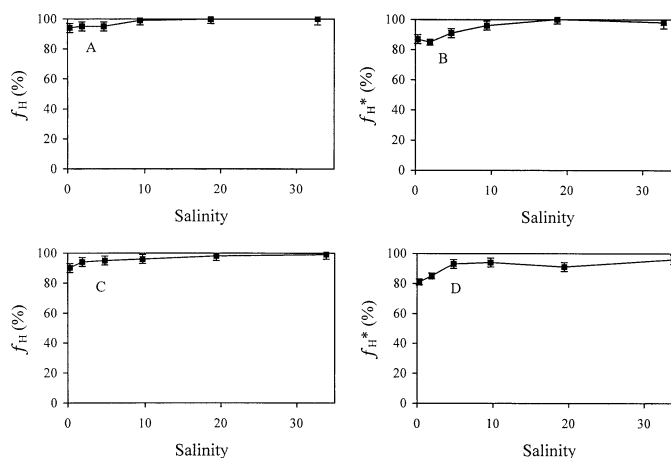


Fig. 3. The hydrophobic fraction of dissolved Zn as a function of salinity: (A) Plym Estuary in the absence of particles; (B) Plym Estuary after adsorption onto suspended sediment particles; (C) Beaulieu Estuary in the absence of particles; and (D) Beaulieu Estuary after adsorption onto suspended sediment particles. Error bars represent the standard deviation about the mean value derived from five separate experiments.

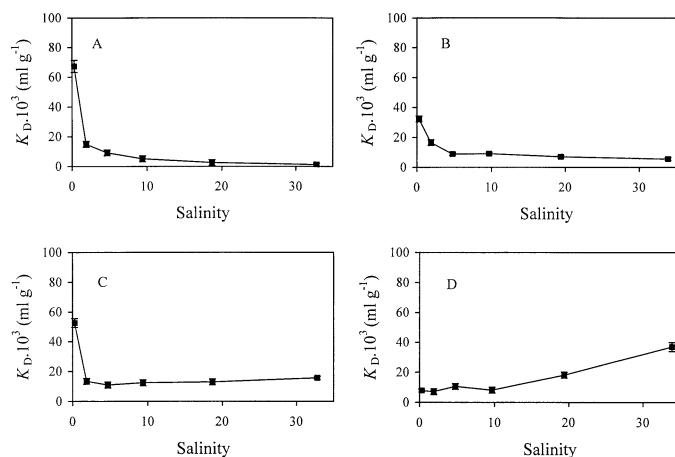


Fig. 4. Sediment–water distribution coefficients as a function of salinity: (A) Cd in the Plym Estuary; (B) Cd in the Beaulieu Estuary; (C) Zn in the Plym Estuary; and (D) Zn in the Beaulieu Estuary. Error bars represent the standard deviation about the mean value derived from five separate experiments.

unlike Cd, hydrophobic complexes of Zn are preferentially removed from the aqueous phase over hydrophilic species, and the original speciation of dissolved Zn is not reestablished.

Measurements of the hydrophobicity of Zn reported in the literature are highly variable (Table 2). In part, this may reflect the use of different makes of  $C_{18}$  column and different eluants, although the hydrophobicity of certain metals appears to be highly sensitive to the origin and age of dissolved organic matter (Donat et al. 1986). Our results for Zn are at the upper end of previous estimates but are consistent with electrochemical measurements of the organically complexed fraction of Zn in rivers, estuaries, and coastal marine environments (Donat and Bruland 1990; Baeyens et al. 1998; Muller et al. 2001).

**Metal adsorption and partitioning**—Sediment–water distribution coefficients ( $K_D$ ) for Cd and Zn in the Plym and Beaulieu estuaries are shown in Fig. 4. The magnitude of these values is in broad agreement with the magnitude of  $K_D$ s determined in previous adsorption studies employing radiotracers (Turner 1996). Cadmium displays a reduction in  $K_D$  with increasing salinity that is characteristic of this metal and that is the combined result of competition for adsorption sites with divalent seawater cations ( $Ca^{2+}$  and  $Mg^{2+}$ ) and complexation of aqueous Cd by chloride ions (Paalman et al. 1994). These effects are more pronounced at the onset of the salt gradient, where unit increases in salinity are accompanied by several-fold increases in ionic concentration, and salinity-dependent adsorption is, therefore, best defined by a power law (Turner 1996):

$$K_D = K_D^0(S + 1)^{-b} \quad (1)$$

where  $K_D^0$ , the partitioning in freshwater, and  $b$  are data-fitted constants.

Details of power regressions of Plym and Beaulieu data, shown in Table 3, indicate greater adsorption in freshwater and a greater decline in adsorption along the salt gradient in

Table 3. Results of power regression analysis of Cd partition data (Equation 1).

	$K_D^0$ ( $ml\ g^{-1}$ )	$b$	$n$	$r^2$
Plym	70600	1.14	6	0.98
Beaulieu	29800	0.50	6	0.91

the Plym Estuary. Moreover, the speciation of adsorbed Cd (Fig. 5) indicates a greater proportion of exchangeable Cd in the Plym and an increase in this fraction on Plym particles with increasing salinity, presumably because of the increasing occupation of energetically favorable and/or strong binding sites by seawater cations (Paalman et al. 1994). Differences in the extent and nature of adsorption between the two estuaries do not appear to be related to the hydrophobicity of aqueous Cd, since retention of Cd by the  $C_{18}$  columns in both estuaries was unaffected by the presence of particles (Fig. 1), nor to pH, which is similar in both cases (Table 1). It is more likely that differences in particle composition and changes thereto engendered by increasing salinity are significant. Thus, characteristics of the adsorption and solid-state speciation of Cd in the Plym Estuary resemble those of Cd binding to claylike particles (namely, nonspecific cation exchange interactions; Comans 1987; Angove et al. 1997) and are consistent with a significant fraction of kaolinite in Plym sediments. A lesser dependency of adsorption on salinity and a smaller fraction of exchangeable Cd in the Beaulieu Estuary indicate that mineral-type adsorption sites are partly blocked by the high concentrations of adsorbed organic matter (Table 1). Thus, ion exchange is less important, and bonding at the particle surface, by both hydrophilic and hydrophobic Cd species, is more covalent and considerably stronger (Arias et al. 2001).

With respect to the adsorption of Zn (Fig. 4), inorganic speciation considerations (i.e., competitive cation adsorption

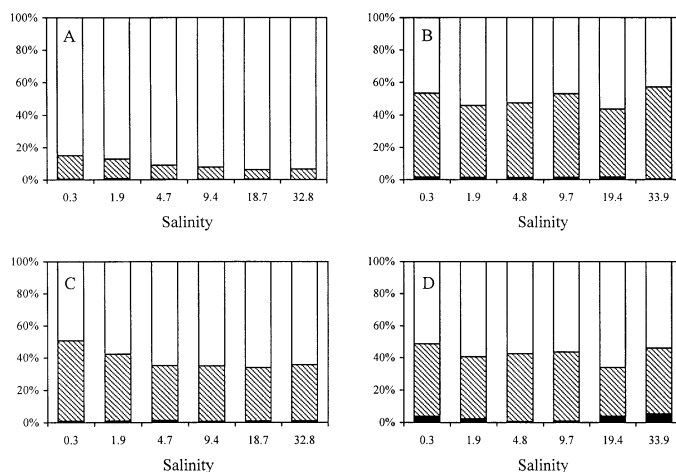


Fig. 5. The solid state speciation of adsorbed metal (A) Cd in the Plym Estuary; (B) Cd in the Beaulieu Estuary; (C) Zn in the Plym Estuary; and (D) Zn in the Beaulieu Estuary. The blank area represents exchangeable metal, the hatched area represents leachable metal, and the solid area represents residual metal. Results represent mean values derived from five separate experiments.

Table 4. Results of exponential regression analysis of Zn partition data (Equation 2).

	$K_D^0$ (ml g <sup>-1</sup> )	$\sigma_{\text{ads}}$ (L mol <sup>-1</sup> )	$n$	$r^2$
Plym	10600	0.34	4 ( $S > 4$ )	0.95
Beaulieu	6960	1.36	6	0.93

and complexation with seawater anions) dictate that  $K_D$  should decrease with increasing salinity, despite an increase in pH from river water to seawater (Millward and Moore 1982; Hegeman et al. 1992; Kraepiel et al. 1997). This effect is, however, only evident in the low salinity zone ( $S < 4$ ) of the Plym Estuary, since in the Beaulieu, and above  $S = 4$  in the Plym, an increase in the  $K_D$  with increasing salinity is observed. We have recently reported this observation for a number of transition metals in the highly contaminated Mersey Estuary (United Kingdom) and suggest that it is the result of salting out of organic metal complexes (Turner et al. 2002). A prerequisite for this effect is a strong affinity of the metal for neutral or near-neutral organic ligands, since the solubility of a neutral chemical decreases (or its propensity to adsorb increases) with increasing salinity through electrostriction (that is, the compression of water in the presence of dissolved ions). The effects of salinity on the adsorption of a neutral chemical are defined by a modified form of the Setschenow equation (Turner and Rawling 2001):

$$K_D = K_D^0 \exp(0.0352 \sigma_{\text{ads}} S) \quad (2)$$

where  $K_D^0$  is the sediment–water partitioning in freshwater and  $\sigma_{\text{ads}}$  (L mol<sup>-1</sup>) is a salting constant. Qualitatively, the aqueous speciation results for Zn are in agreement with salting out in that an increase (albeit a nonexponential one) in the fraction of hydrophobic Zn is observed with increasing salinity. The Zn partition data for the Beaulieu and Plym (above  $S \sim 4$ ) are in quantitative agreement with the salting model, and exponential fits to the data, shown in Table 4, yield salting constants of 1.36 and 0.34 L mol<sup>-1</sup>, respectively. Salting out is more significant in the Beaulieu Estuary than the Plym Estuary, partly because a greater proportion of hydrophobic complexes adsorb to Beaulieu particles. Also, since the extent of salting out depends on the size of the neutral solute, there may be a greater concentration or availability of larger ligands in the Beaulieu Estuary (Muller 1996). In general, these values are in line with our empirical estimates for other transition metals in the Mersey Estuary (about 0.7 to 2.0 L mol<sup>-1</sup>; Turner et al. 2002).

The solid-state speciation of adsorbed Zn in the Beaulieu and Plym estuaries (Fig. 5) resembles that of Cd in the Beaulieu Estuary. Thus, although ionic or surface complexation interactions of Zn species (including organic forms) might be important, the abundance and uniformity of the leachable fraction (about 40%) indicates that Zn is able to migrate into the particle matrix, and/or, given the arguments above, hydrophobic bonding of organic complexes of Zn to adsorbed organic matter is significant.

*Adsorption of hydrophobic Zn species*—Since hydrophobic species of Zn were preferentially adsorbed over hydrophilic species, the hydrophobic–hydrophilic distribution and

sediment–water partitioning were used to calculate the fraction of hydrophobic Zn that was adsorbed by sediment particles (rather than the fraction of aqueous Zn as hydrophobic Zn; Fig. 3). As an aid to the calculations and discussion, it is worthwhile considering the three competing equilibrium reactions that occur under the controlled estuarine conditions following the addition of radiolabeled Zn<sup>2+</sup> and suspended sediment particles to filtered water. First is the adsorption of hydrophilic Zn, comprising the free ion, inorganic complexes, and small, charged organic species, to suspended particles:



where S denotes an adsorption site on the particle surface. Second is the complexation of Zn by hydrophobic organic ligands, L:



where ZnL denotes a hydrophobic Zn complex. Third is the adsorption of hydrophobic Zn complexes to suspended sediment particles:



where ZnL-S (or LZn-S) denotes an adsorbed complex of Zn. The fraction of hydrophobic Zn complexes that are adsorbed,  $f_{\text{H}}^{\text{ads}}$ , is calculated as follows:

$$f_{\text{H}}^{\text{ads}} = \frac{[\text{ZnL-S}]}{[\text{ZnL}]} \quad (6a)$$

$$f_{\text{H}}^{\text{ads}} = \frac{[\text{ZnL}] - [\text{ZnL}^*]}{[\text{ZnL}]} \quad (6b)$$

where [ZnL] is the concentration of hydrophobic Zn in the absence of suspended particles, [ZnL\*] is the concentration of hydrophobic Zn remaining after sediment is added and adsorption equilibrium attained, and [ZnL-S] is the concentration of hydrophobic Zn adsorbed to sediment particles. Equation 6b can be rewritten in terms of the fraction of hydrophobic Zn before and after particle addition, as defined in Fig. 3, and the total concentration of Zn added to the reactor (or the aqueous concentration of Zn in the absence of suspended particles), [Zn]:

$$f_{\text{H}}^{\text{ads}} = \frac{f_{\text{H}}[\text{Zn}] - f_{\text{H}}^*[\text{Zn}]\{1/(1 + K_D \cdot [\text{SPM}]/10^6)\}}{f_{\text{H}}[\text{Zn}]} \quad (7a)$$

$$f_{\text{H}}^{\text{ads}} = \frac{f_{\text{H}} - f_{\text{H}}^*\{1/(1 + K_D \cdot [\text{SPM}]/10^6)\}}{f_{\text{H}}} \quad (7b)$$

where [SPM] is the suspended particle concentration and its embracing term defines the fraction of total Zn in the aqueous phase after adsorption has taken place. The fraction of hydrophilic Zn species adsorbed to suspended particles is calculated in a similar manner, but using  $(1 - f_{\text{H}})$  and  $(1 - f_{\text{H}}^*)$  instead of  $f_{\text{H}}$  and  $f_{\text{H}}^*$ , respectively.

Values of  $f_{\text{H}}^{\text{ads}}$  were calculated using the data in Figs. 3 and 4 and for an SPM concentration of 100 mg L<sup>-1</sup> and are

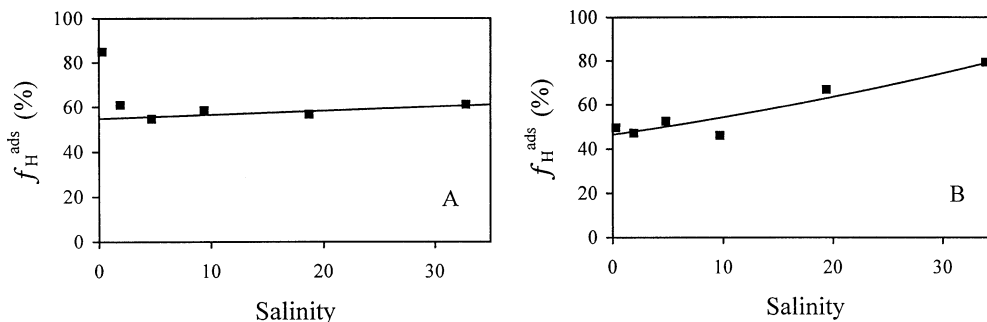


Fig. 6. The fraction of hydrophobic dissolved Zn that is adsorbed by suspended sediment particles (calculated according to Eq. 7) as a function of salinity: (A) the Plym Estuary; (B) the Beaulieu Estuary. The solid lines are best fits to the data according to Eq. 8 and whose coefficients are given in Table 5.

shown as a function of salinity in Fig. 6. These results are consistent with  $K_{DS}$  defining the partitioning of Zn in that an exponential increase in the hydrophobic fraction with increasing salinity is observed throughout the Beaulieu Estuary and in the Plym Estuary above  $S \sim 4$ . Table 5 gives results of exponential regression analysis of these data according to a relationship of the form of Eq. 2:

$$f_{\text{H}}^{\text{ads}} = (f_{\text{H}}^{\text{ads}})^0 \exp(0.0352\sigma_{\text{H}}S) \quad (8)$$

where  $(f_{\text{H}}^{\text{ads}})^0$  is the adsorbed fraction of hydrophobic Zn in freshwater and  $\sigma_{\text{H}}$  is a parameter that defines the extent of salting out of hydrophobic complexes. The magnitudes of the salting constants derived from exponential regressions of these data are smaller than those reported for the sediment-water partitioning data (Table 4). This indicates that the overall salting out process is not specific to complexes retained by the  $\text{C}_{18}$  columns, perhaps because some inorganic species were adsorbed on uncapped silanol groups and/or that the effect is not solely related to the solubility of aqueous Zn species. An additional source of salting out might be enhancement of the hydrophobicity of the particle surface through structural and charge alterations caused by particle-seawater ion interactions (Turner and Rawling 2001).

*Implications of equilibrium metal speciation*—This study has highlighted important differences in the speciation and partitioning of Cd and Zn in estuaries, as exemplified by the empirical equilibrium speciation of Cd in the Plym and Zn in the Beaulieu in Fig. 7. Here, aqueous and adsorbed species are shown as either mean values or as values derived from best-fit equations (see Eqs. 1 and 2) as a function of salinity and for a  $100 \text{ mg L}^{-1}$  particle suspension. This is an alternative approach to speciation modeling that combines hydrophilic and hydrophobic forms of aqueous metal with

particulate metal speciation. Such a speciation framework does not rely on chemical principles or constants and is not, therefore, predictive. Nevertheless, the species identified in this study are relevant to environmental and biological processes and overcome the problems and assumptions inherent in calculating organic and adsorbed species that are faced in thermodynamic modeling.

Thus, many aspects of Cd behavior in the Plym reflect general characteristics of Cd in estuaries and are consistent with its predominantly inorganic aqueous speciation (Tipping et al. 1998). These include a small percentage of hydrophobic dissolved species that is restricted to low salinities and a logarithmic reduction in the fraction of adsorbed Cd from river to sea resulting from the competing and complexing effects of seawater ions. These characteristics, coupled with the high exchangeability of adsorbed Cd, explain why desorption of Cd from suspended particles is a common observation in many estuaries of low to moderate concentrations of DOC (Kraepiel et al. 1997; Martino et al. 2002) and ensure that in seawater, where particle concentrations are typically a few milligrams per liter, more than 99% Cd occurs in hydrophilic aqueous form. In organic-rich environments, these characteristics are still evident, but aqueous Cd is more hydrophobic and potentially more bioavailable via cell or gill penetration (Phinney and Bruland 1994), and binding with suspended particles assumes a more covalent or hydrophobic nature.

In contrast, the behavior of Zn in the Beaulieu (and also in the Plym) appears to be governed, to a large extent, by its affinity for organic ligands. Accordingly, many aspects of Zn behavior are more in line with a neutral organic solute than a transition metal cation, including hydrophobic aqueous species that are partly salted out with increasing salinity. The hydrophobic and salting properties of Zn (and a number of other trace metals) have recently been reported in the Mersey Estuary (Turner et al. 2002) but do not appear to be general characteristics of trace metals in estuaries since, in many cases, dissolved organic matter and particle sorption sites appear to be in direct competition for added or pre-existent metal ions (Paulson et al. 1994; Turner et al. 1998). Clearly, the nature and concentration of organic matter are critical to the behavior of Zn and, possibly, many other transition metals in estuaries. Given the important implications

Table 5. Regression parameters defining the fraction of hydrophobic Zn undergoing adsorption to estuarine suspended particles as a function of salinity (Equation 8).

	$(f_{\text{H}}^{\text{ads}})^0$ (%)	$\sigma_{\text{H}}$ ( $\text{L mol}^{-1}$ )	$n$	$r^2$
Plym	54.8	0.088	4 ( $S > 4$ )	0.67
Beaulieu	46.4	0.446	6	0.85

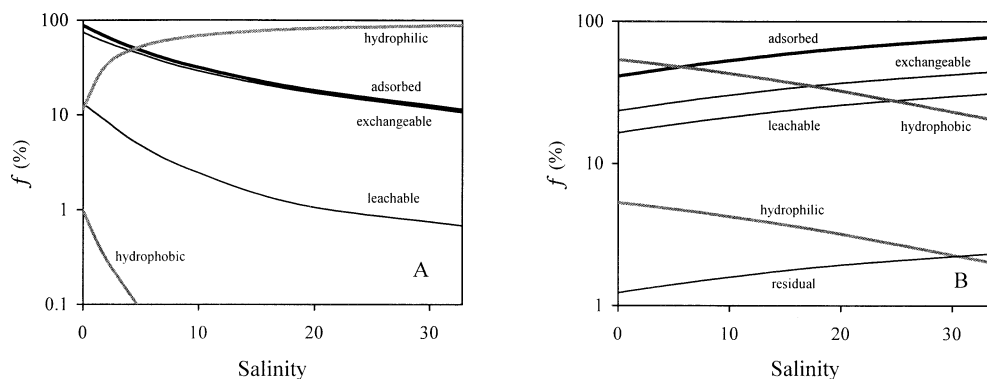


Fig. 7. The salinity-dependent speciation of (A) Cd in the Plym Estuary and (B) Zn in the Beaulieu Estuary. Fractional speciation is based on the measured forms of aqueous and adsorbed Cd and Zn (using either mean values for the estuary or best-fit salinity-dependent equations) and is calculated for a suspended sediment concentration of  $100 \text{ mg L}^{-1}$ . Note that total metal is the sum of the hydrophilic, hydrophobic, and adsorbed fractions, and that the exchangeable, leachable, and residual fractions are components of the adsorbed fraction.

for the availability, toxicity, transport, and modeling of transition metals in the aquatic environment, the effects of hydrophobic organic matter on trace metal adsorption by natural, heterogeneous suspended particles merit closer attention.

## References

- ABBASSE, G., B. OUDDANE, AND J. C. FISCHER. 2002. Determination of total and labile fraction of metals in seawater using solid phase extraction and inductively coupled plasma atomic emission spectrometry (ICP-AES). *J. Anal. Atomic Spectrom.* **17**: 1354–1358.
- ANDERSON, R. F., P. H. SANTSCHI, U. P. NYFFELER, AND S. L. SCHIFF. 1987. Validating the use of radiotracers as analogs of stable metal behaviour in enclosed aquatic ecosystem experiments. *Can. J. Aquat. Sci.* **44**: 251–259.
- ANGOVE, M. J., B. B. JOHNSON, AND J. D. WELLS. 1997. Adsorption of cadmium (II) on kaolinite. *Colloid Surf. A*. **126**: 137–147.
- ARIAS, M., B. SOTO, AND M. T. BARRAL. 2001. Interaction of cadmium with organo-mineral associations. *Agrochimica* **45**: 218–227.
- BAEYENS, W., L. GOEYENS, F. MONTENY, AND M. ELSKENS. 1998. Effect of organic complexation on the behaviour of dissolved Cd, Cu and Zn in the Scheldt estuary. *Hydrobiologia* **366**: 81–90.
- COMANS, R. N. J. 1987. Adsorption, desorption and isotopic exchange of cadmium on illite—evidence for complete reversibility. *Water Res.* **21**: 1573–1576.
- DAVIS, J. A., AND J. O. LECKIE. 1978. Effect of adsorbed complexing ligands on trace metal uptake by hydrous oxides. *Environ. Sci. Technol.* **12**: 1309–1315.
- DONAT, J. R., AND K. W. BRULAND. 1990. A comparison of two voltammetric techniques for determining zinc speciation in northeast Pacific Ocean waters. *Mar. Chem.* **28**: 301–323.
- , P. J. STATHAM, AND K. W. BRULAND. 1986. An evaluation of a C-18 solid phase extraction technique for isolating metal-organic complexes from central north Pacific Ocean waters. *Mar. Chem.* **18**: 85–99.
- GARNIER, J.-M., M. K. PHAM, P. CIFFROY, AND J.-M. MARTIN. 1997. Kinetics of trace element complexation with suspended matter and filterable ligands in freshwater. *Environ. Sci. Technol.* **31**: 1597–1606.
- GROSCHNER, M., AND P. APPRIOU. 1994. Three-column system for preconcentration and speciation determination of trace metals in natural waters. *Anal. Chim. Acta* **297**: 369–376.
- HEGEMAN, W. J. M., C. H. VAN DER WEIJDEN, AND J. J. G. ZWOLSMAN. 1992. Sorption of zinc on suspended particles along a salinity gradient: A laboratory study using illite and suspended matter from the River Rhine. *Neth. J. Sea Res.* **28**: 285–292.
- KRAEPIEL, A. M. L., J.-F. CHIFFOLEAU, J.-M. MARTIN, AND F. M. M. MOREL. 1997. Geochemistry of trace metals in the Gironde estuary. *Geochim. Cosmochim. Acta* **61**: 1421–1436.
- LASLETT, R. E. 1995. Concentrations of dissolved and suspended particulate Cd, Cu, Mn, Ni, Pb and Zn in surface waters around the coasts of England and Wales and in adjacent seas. *Estuar. Coastal Shelf Sci.* **40**: 67–85.
- L'HER ROUX, L., S. LE ROUX, AND P. APPRIOU. 1998. Behavior and speciation of metallic species Cu, Cd, Mn and Fe during estuarine mixing. *Mar. Pollut. Bull.* **36**: 56–64.
- MARTIN, J.-M., W. W. HUANG, AND Y. Y. YOON. 1994. Level and fate of trace metals in the lagoon of Venice (Italy). *Mar. Chem.* **46**: 371–386.
- MARTINO, M., A. TURNER, M. NIMMO, AND G. E. MILLWARD. 2002. Resuspension, reactivity and recycling of trace metals in the Mersey Estuary, UK. *Mar. Chem.* **77**: 171–186.
- MILLWARD, G. E., AND R. M. MOORE. 1982. The adsorption of Cu, Mn and Zn by iron oxyhydroxide in model estuarine solutions. *Water Res.* **16**: 981–985.
- MORAN, M. A., L. R. POMEROY, E. S. SHEPPARD, L. P. ATKINSON, AND R. E. HODSON. 1991. Distribution of terrestrially derived dissolved organic matter on the southeastern United States continental shelf. *Limnol. Oceanogr.* **36**: 1134–1149.
- MULLER, F. L. L. 1996. Measurement of electrokinetic and size characteristics of estuarine colloids by dynamic light scattering spectroscopy. *Anal. Chim. Acta* **331**: 1–15.
- , S. B. GULIN, AND A. KALVOY. 2001. Chemical speciation of copper and zinc in surface waters of the western Black Sea. *Mar. Chem.* **76**: 233–251.
- PAALMAN, M. A. A., C. H. VAN DER WEIJDEN, AND J. P. G. LOCH. 1994. Sorption of cadmium on suspended matter under estuarine conditions; competition and complexation with major seawater ions. *Water Air Soil Pollut.* **73**: 49–60.
- PAULSON, A. J., H. C. CURL, JR., AND J. F. GENDRON. 1994. Partitioning of Cu in estuarine waters. I. Partitioning in a poisoned system. *Mar. Chem.* **45**: 67–80.



- PHINNEY, J. T., AND K. W. BRULAND. 1994. Uptake of lipophilic organic Cu, Cd and Pb complexes in the coastal diatom *Thalassiosira weissflogii*. *Environ. Sci. Technol.* **28**: 1781–1790.
- PLAVSIC, M., AND M. BRANICA. 1986. Voltammetric investigation of copper(II) interaction with DOM isolated on Sep-Pak C<sub>18</sub> cartridges. *Ocean Sci. Eng.* **11**: 99–113.
- TIPPING, E., S. LOFTS, AND A. J. LAWLOR. 1998. Modelling the chemical speciation of trace metals in the surface waters of the Humber system. *Sci. Total Environ.* **210/211**: 63–77.
- TOWN, R. M., AND M. FILLELA. 2000. Dispelling the myths: Is the existence of L1 and L2 ligands necessary to explain metal ion speciation in natural waters? *Limnol. Oceanogr.* **45**: 1341–1357.
- TURNER, A. 1996. Trace metal partitioning in estuaries: Importance of salinity and particle concentration. *Mar. Chem.* **54**: 27–39.
- , M. MARTINO, AND S. M. LE ROUX. 2002. Trace metal distribution coefficients in the Mersey Estuary, UK: Evidence for salting out of metal complexes. *Environ. Sci. Technol.* **36**: 4578–4584.
- , G. E. MILLWARD, AND S. M. LE ROUX. 2001. Sediment-water partitioning of inorganic Hg in estuaries. *Environ. Sci. Technol.* **35**: 4648–4654.
- , M. NIMMO, AND K. A. THURESSON. 1998. Speciation and sorptive behaviour of nickel in an organic-rich estuary (Beaulieu, UK). *Mar. Chem.* **63**: 105–118.
- , AND M. C. RAWLING. 2001. The influence of salting out on the sorption of neutral organic chemicals in estuaries. *Water Res.* **35**: 4379–4389.
- URE, M., R. THOMAS, AND D. LITTLEJOHN. 1993. Ammonium acetate extracts and their analysis for the speciation of metal ions in soils and sediments. *Intern. J. Environ. Anal. Chem.* **51**: 65–84.
- VAN ALSENOY, V., P. BERNARD, AND R. VAN GRIEKEN. 1993. Elemental concentrations and heavy-metal pollution in sediments and suspended matter from the Belgian North-Sea and the Scheldt Estuary. *Sci. Total Environ.* **133**: 153–181.
- WARREN, L. A., AND E. A. HAACK. 2001. Biogeochemical controls on metal behavior in freshwater environments. *Earth Sci. Rev.* **54**: 261–320.
- YOON, Y.-Y., J.-M. MARTIN, AND M. H. COTTE. 1999. Dissolved trace metals in the western Mediterranean Sea: Total concentration and fraction isolated by C18 Sep-Pak technique. *Mar. Chem.* **66**: 129–148.

*Received: 24 November 2002*

*Accepted: 20 May 2003*

*Amended: 7 July 2003*