

Hydrophobicity and reactivity of trace metals in the low-salinity zone of a turbid estuary

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Abstract

We chemically fractionated water samples from the low-salinity zone of a turbid estuary (Tamar, UK) using C18 columns to examine the controls on the complexation, hydrophobicity, and reactivity of dissolved trace metals (Co, Cu, Mn, and Pb). The hydrophobic (C18-retained) fraction of metal was related to the solubility of metal in the amphiphilic solvent, *n*-octanol, and in acid-base titrations and for all metals this fraction exhibited a peak centered around pH 7–8 in both freshwater and brackish water. In freshwater, hydrophobicity decreased in the order Pb > Cu > Mn > Co, and in brackish water, hydrophobicity was either reduced (Cu and Pb) or enhanced (Co and Mn) compared to freshwater, but in all cases peaks were more distinct. Salinity distributions of dissolved trace metals in the estuary indicated significant removal of Co, Cu, and Mn, and a source of Pb that was coincident with the onset of the turbidity maximum, and all distributions could be accounted for empirically by end-member water mixing and sediment resuspension. Salinity distributions of the hydrophobic fraction of metal were not consistent with any variation in water composition (including pH), but revealed that this fraction was preferentially removed from (Co, Cu, and Mn) or added to (Pb) the aqueous phase in the vicinity of the turbidity maximum. Removal implies that hydrophobic species are more reactive than hydrophilic species, and that either re-equilibration between these fractions is not attained within the hydrodynamic timescales of the upper estuary, or new equilibria are established by the buffering effects of additional anions and ligands in the water column. Addition of hydrophobic species of Pb coincided with minimum total and hydrophobic concentrations of Co, Cu, and Mn, and could, therefore, be explained in terms of reduced competition for nonspecific hydrophobic ligands from these and other (e.g., Al) metals in this region of the estuary.

It is well established that estuaries modify the concentrations and fluxes of riverine chemicals that reach the oceans (Berner and Rao 1994; Shiller and Mao 2000). Such modification results from a variety of chemical and biological reactions that are promoted in environments where the bulk composition of water is subject to rapid and significant change (Turner and Millward 2002). From an environmental and biological standpoint, however, and in particular with respect to trace metals, of at least equal importance to changes in absolute concentration or flux are changes in chemical speciation (Campbell 1995).

Electrochemical analyses indicate that, for many trace metals, organic complexes dominate speciation in estuaries (Zhang et al. 1990; Martino et al. 2004), whereas size fractionation studies indicate different proportions of colloidal forms, many of which are also organic, for different metals (Dai et al. 1995; Choe et al. 2003). With the exception of colloidal aggregation, however, there is little field evidence of changes in trace metal speciation or fractionation effected by or associated with chemical reactivity in estuaries and, in particular, in the low-salinity, high-turbidity zone where reactivity is generally most pronounced (Morris 1986). This is perhaps surprising given that laboratory studies have dem-

onstrated that the kinetics and mechanisms of sorption reactions are sensitive to metal speciation (Düker et al. 1995; Martino et al. 2003). Such a discrepancy may, partly, be attributed to the inability of many analytical schemes to discriminate forms of trace metals that have different reaction pathways, and in particular those that are involved in or independent of particle–water interactions. In other words, detection of the bulk organic fraction of dissolved metal may not be sufficiently specific for the purposes of defining metal reactivity in estuaries.

Recently, we distinguished hydrophobic and hydrophilic species of radiolabeled trace metals, added to filtered estuarine samples, using C18 columns (Turner et al. 2001, 2004). Experimental results revealed that, after the addition of estuarine particles, the more hydrophobic forms, or in some cases the more hydrophilic forms, were preferentially removed from solution. Although the chemical fractions of trace metals that we distinguished are only operational, since hydrophobicity itself is a relative measure, the results afforded a valuable insight into the likely biogeochemical pathways of each form, including the nature of their interactions with suspended particles. Such observations therefore have important implications regarding our understanding of the biogeochemical availability, cycling, and fate of riverine trace metals across the freshwater–seawater interface.

In the present study, we extend this approach to determine the distributions and controls on the hydrophobic–hydrophilic fractionation of dissolved trace metals in the River Tamar and the low-salinity zone of its estuary. A combination of field measurements and laboratory experiments in-

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volving natural samples is used to examine the factors regulating the reactivity of metals at the freshwater–brackish water interface. The catchment of the Tamar (southwest England) comprises open moorland and agricultural land. Riverine organic matter is derived mainly from erosion of soil and degradation of vegetation, whereas elevated concentrations of trace metals in the water column and sediments are the legacy of extensive sulfidic ore workings that took place throughout the watershed up until the end of the 19th century (Lindsay and Bell 1997). The low-salinity zone of the macrotidal Tamar estuary is characterized by a pronounced turbidity maximum, whose precise magnitude and location is dependent on river flow and tidal state (Grabemann et al. 1997), affording an ideal natural reactor for the study of trace metal fractionation and its relationship with particle–water interactions.

Methods

Sampling and sample characterization—The main sampling campaign for this study was undertaken in March 2003. Thus, the river end-member was sampled from the shore from just above the tidal limit, and the estuary was sampled likewise and on the same occasion along a single 12-km transect encompassing the turbidity maximum during an ebb tide. For reference, these samples are named in alphabetical sequence (A to G) with increasing distance seaward. For additional experimental work that is also reported, we undertook repeat samplings of the river end-member as required (February, May, and July 2003).

At each site, conductivity, salinity, pH, and temperature were measured using calibrated Hanna or YSI electrodes. Water samples for the experiments and metal analyses were collected in acid-cleaned 2-liter high-density polyethylene bottles. Additional 250-ml samples for the analysis of dissolved organic carbon (DOC) were collected in ashed Pyrex bottles. Bottles were rinsed twice with water before being filled and stored cool ($<10^{\circ}\text{C}$). All samples were filtered in the laboratory within 4 h of collection through 47-mm-diameter filters by vacuum filtration. Samples for the experiments (A, C, and G) and metal analyses were filtered through preweighed 0.45- μm pore size cellulose acetate filters (Millipore) using an acid-cleaned polysulfone filtration unit (Nalgene), and were stored at 4°C and in the dark in clean polyethylene bottles until further use (within 48 h). Aliquots of filtrates used for experimental study were also analyzed for Ca and Mg by inductively coupled plasma (ICP) optical emission spectrometry using a Perkin Elmer Optima 3000, and for alkalinity and chlorinity by titration with sulfuric acid and silver nitrate, respectively. Millipore filters were dried in a laminar flow hood, reweighed, and stored in a vacuum desiccator until analyzed (within 2 months), and the dry weight of solids and corresponding filtrate volumes were used to calculate the concentration of suspended particulate matter (SPM). Samples for DOC analysis were filtered through 0.7- μm pore size glass fiber filters (GF/F, Whatman) using an ashed Pyrex filtration unit, and aliquots of filtrate were stored in borosilicate vials at 4°C after being acidified with 100 μl of 5 mol L^{-1} HCl. The concentration of DOC

in the acidified sample aliquots was determined using a Shimadzu TOC-5000 total organic carbon analyzer calibrated with potassium phthalate standards.

Metal fractionation—In this study we used “Sep-Pak”-type C18 columns to distinguish hydrophilic and hydrophobic metal fractions in the filtered samples. In practice, hydrophobic forms of metal are normally preconcentrated on a C18 column from a relatively large sample volume (~ 1 liter), and this fraction is then eluted with a small volume (typically a few milliliters) of a polar solvent such as methanol (Mackey 1985; Xu et al. 2002). Thus, preconcentration improves detection, whereas elution minimizes potential interferences arising from metal adsorption to or trapping within the silica matrix. Since we aimed to investigate the effects of a range of environmental variables on hydrophobic metal associations in turbid fresh and brackish water samples, a practical difficulty of this approach would have been the requirement for filtering and processing a large number of high-volume samples. Accordingly, we determined the fraction of dissolved metal that is retained on the columns by difference between the metal concentrations in the original samples and in small aliquots of the samples that had passed through the columns, as outlined below. Our definition of hydrophobic is, therefore, operational, and refers to metal species that are retained by C18 but that are not necessarily available for elution by a polar solvent.

We activated and conditioned silica-bonded reverse-phase C18 columns (sorbent weight = 200 mg; Bond Elut) by successively passing through 10 ml of methanol (HPLC-grade, Aldrich), 10 ml of 0.3 mol L^{-1} HNO_3 (Aristar, BDH), 10 ml of methanol, and 20 ml of Millipore Milli-Q water. An aliquot of filtered sample was passed through a column under gravity at room temperature ($18\text{--}22^{\circ}\text{C}$) and at a flow rate of about 20 ml h^{-1} , and collected in an acid-cleaned, screw-topped 50-ml polyethylene centrifuge tube (Fisher Scientific). We used 10 ml for most samples, but 5 to 45 ml in an experiment in which we investigated the effects of sample volume on metal retention. A separate 10-ml aliquot of filtered sample was transferred directly into a centrifuge tube, and the difference in metal concentration between the two aliquots was used to calculate the concentration and fraction of hydrophobic metal in the original sample. This procedure was undertaken in triplicate for unamended samples, and individually for samples whose pH had been adjusted or to which ionic metal had been added (see following).

Adjustment of pH—The effects of pH on metal fractionation were examined in two filtered water samples collected from the axial transect of the upper estuary. Namely, a freshwater sample from the landward reaches of the turbidity maximum (sample C), and a brackish water sample from the saline end-member of the turbidity maximum (sample G). A series of 100-ml aliquots of sample was prepared in covered, acid-cleaned 150-ml polyethylene beakers. The pH of each aliquot was adjusted by dropwise addition of either 0.1 mol L^{-1} HNO_3 or 0.1 mol L^{-1} NaOH (Aristar, BDH) to create a pH range from about 3 to 9. The sample aliquots were allowed to equilibrate for 16 h before the final pH was re-

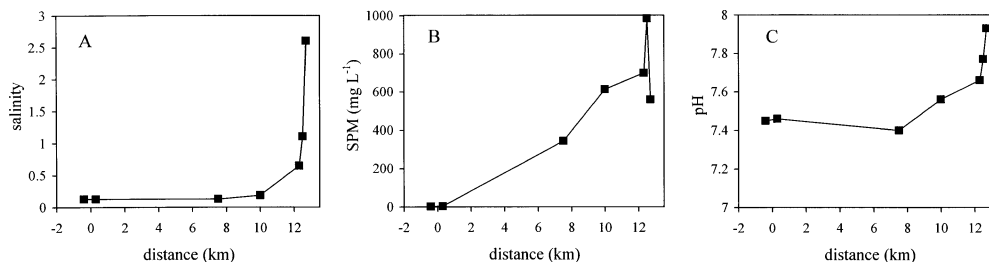


Fig. 1. Distributions of (A) salinity, (B) suspended particulate matter, and (C) pH in the Tamar estuary, sampled during March 2003, as a function of axial distance from the tidal limit.

corded and 10-ml aliquots were passed through the C18 columns.

Metal titrations—We also added selected ionic metals (Cu, Pb, and Al) to aliquots of a filtered river water sample to investigate potential competition among metals for ligands forming hydrophobic complexes. Individual metal solutions were prepared by diluting ICP-grade standards in Milli-Q water in 100-ml polyethylene volumetric flasks. Appropriate volumes of diluted standard were added to individual 10-ml sample aliquots in clean centrifuge tubes to give final metal concentrations (in $\mu\text{g L}^{-1}$) ranging from about 20–35 (Cu), 5–20 (Pb), and 80–120 (Al). Addition of metal did not alter the pH of the samples, which were then left to equilibrate at room temperature for 16 h before being passed through the C18 columns.

Octanol extraction—For selected river water samples collected on a number of occasions, we undertook an independent assessment of trace metal hydrophobicity by determining the extent of metal extraction in *n*-octanol according to the technique described in Turner and Mawji (2004). Briefly, six 5-ml aliquots of sample were pipetted into 50-ml polyethylene centrifuge tubes that had been cleaned successively in detergent, acid, and water, and to three aliquots 5 ml of *n*-octanol (HPLC-grade, Aldrich) were added and the contents shaken on a horizontal shaker at 300 rpm for 16 h at room temperature. The octanol and water phases were then separated by centrifugation for 1 h at 3000 g, and 4 ml of the remaining aqueous phase were pipetted into a clean centrifuge tube, taking care not to sample the octanol or disturb the octanol–water interface. The octanol-soluble concentration of metal was determined from the difference between the mean metal concentrations in the three unprocessed aliquots and in the three extracted aliquots. Concentration differences were typically smaller than those derived from the column approach, and we only report octanol extraction where the concentration difference was statistically significant ($p < 0.05$) according to a two-tailed paired *t*-test.

Particle digestion—The total extractable concentrations of particulate metals were determined following digestion of a single Millipore filter from each sample in HNO_3 . Thus, 5 ml of concentrated HNO_3 (AnalaR, BDH) were added to each filter in a 25-ml borosilicate beaker, and the contents were heated to about 80°C for 4 h on a hot plate, taking care not to completely evaporate the acid. The cooled contents

were transferred to a 25-ml borosilicate volumetric flask and made up to the mark using 2 mol L^{-1} HNO_3 . The accuracy of the method was evaluated by digesting, in triplicate, a certified reference sediment (MESS-3; National Research Council for Canada), and three unused filters were digested individually as procedural blanks.

Trace metal analysis—Once original or processed filtered sample aliquots were transferred to the centrifuge tubes they were either analyzed for trace metals within 24 h, or acidified with 50 μl of 5 mol L^{-1} HNO_3 and analyzed within a few days. Metal concentrations in sample aliquots and nitric digests of particles were determined by inductively coupled plasma–mass spectrometry (ICP-MS) using a Plasmaquad PQ2 Turbo (Thermo Elemental). The instrument was calibrated using acidified standards, and indium-115 was added to all samples and standards for internal standardization. We determined a range of trace metals in all samples, but here we focus on those that were least affected by contamination or interferences from the C18 columns, and that displayed contrasting behaviors (namely, the weakly binding metals, Co and Mn, and the strongly binding metals, Cu and Pb). Limits of detection, defined as three times the standard deviation of measured concentrations in Milli-Q water, varied for each set of analyses as the composition of Milli-Q water and the performance of the ICP-MS appeared to exhibit some variation. In general, however, detection limits (in $\mu\text{g L}^{-1}$) were on the order of 0.3 for Cu and 0.03 for Co, Mn, and Pb.

The measured concentrations of the selected metals in a certified reference river water (SLRS-2; National Research Council of Canada) were within about 10% of certified values. Analysis of the HNO_3 digests of the certified reference sediment revealed that measured metal concentrations were up to 20% lower than the corresponding certified concentrations, presumably because some metal-bearing silicate minerals are resistant to acid decomposition.

Results and discussion

Sampling conditions and sample characteristics—Our sampling campaign of the upper Tamar estuary (samples A through G) embraced a pronounced turbidity maximum, and indicated that freshwater extended to the landward limit of this feature (Fig. 1). Estuarine water was slightly basic, and pH increased conservatively with respect to salinity by about half a unit from freshwater to brackish water. Mean daily

Table 1. Physicochemical characteristics and dissolved trace metal concentrations of the River Tamar (sample A), and the freshwater and brackish water end-members of the turbidity maximum of the Tamar estuary (samples C and G, respectively). Trace metal concentrations are given as the mean and standard deviation of three determinations.

	Sample A	Sample C	Sample G
Conductivity* ($\mu\text{S cm}^{-1}$)	29.7	30.0	4900
Salinity*	0.13	0.13	2.61
pH*	7.45	7.40	7.93
Temperature* ($^{\circ}\text{C}$)	11.2	11.6	11.9
DOC† (mg L^{-1})	3.42	2.85	2.78
SPM‡ (mg L^{-1})	3.0	344	560
Chlorinity (mg L^{-1})	40	40	1500
Alkalinity as CaCO_3 (mg L^{-1})	40	40	70
Ca (mg L^{-1})	17.6	17.8	46.3
Mg (mg L^{-1})	6.4	6.4	91.3
Al ($\mu\text{g L}^{-1}$)	30.5 ± 3.21	17.9 ± 1.14	21.0 ± 0.82
Co ($\mu\text{g L}^{-1}$)	8.32 ± 0.66	3.26 ± 0.14	6.68 ± 0.37
Cu ($\mu\text{g L}^{-1}$)	14.1 ± 1.0	7.1 ± 0.8	14.5 ± 0.8
Mn ($\mu\text{g L}^{-1}$)	29.9 ± 1.5	2.0 ± 0.1	21.2 ± 0.8
Pb ($\mu\text{g L}^{-1}$)	0.08 ± 0.00	0.28 ± 0.04	0.25 ± 0.04

* Measured in situ.

† DOC, dissolved organic carbon; ‡ SPM, suspended particulate matter.

freshwater flows for the 5 d prior to sampling were between 6.7 and $7.7 \text{ m}^3 \text{ s}^{-1}$, compared with a yearly average value of $18 \text{ m}^3 \text{ s}^{-1}$. From these flows, and the empirical algorithm given by Uncles et al. (1983), we estimate flushing times of between 1 and 2 d for the estuarine section sampled, and less than 1 d for the turbidity maximum zone contained therein.

Physicochemical characteristics and dissolved trace metal concentrations of the samples used for experimental study (namely, the river end-member, and the freshwater and brackish water end-members of the turbidity maximum) are given in Table 1. Multiple samplings of the river end-member revealed that its composition was relatively constant during periods of limited to moderate rainfall, but that trace metal concentrations either increased (Cu, Mn, and Pb) or decreased (Co) following periods of protracted precipitation. Potential sources that are metal-specific and sensitive to hydrological conditions include contaminated riverine sediment, and spoil heaps and adit effluents of abandoned metal mines.

Evaluation of fractionation scheme—For the purposes of this study, we define trace metal hydrophobicity, or the fraction (or percentage) of hydrophobic metal, f_{H} , as the degree of dissolved metal association with hydrophobic organic matter. Thus, hydrophobic complexes may result from metal–ligand complexation, and hydrophobic assemblages, such as colloids or clathrate-type structures, may arise through other physical or chemical interactions. (Note that the two types of associations are not distinguished in future discussion and the terms complex and complexation are all-embracing.) Our operational definition of trace metal hydrophobicity is based on the net retention of metal by a C18 column (Garnier et al. 1997; Turner et al. 2004):

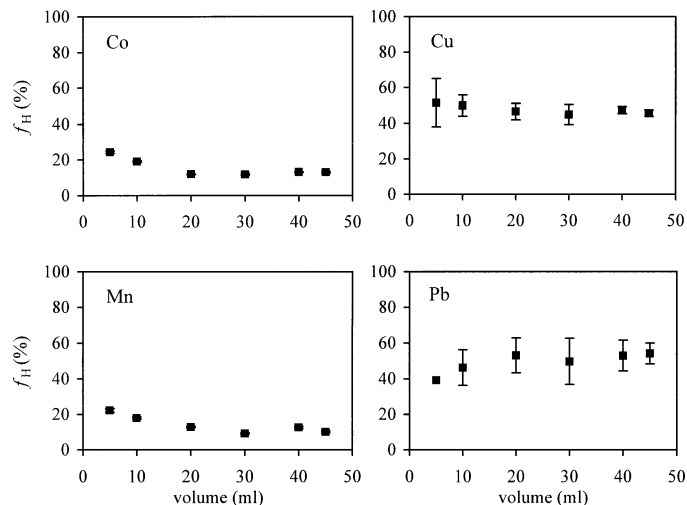


Fig. 2. The fraction of hydrophobic (C18-retained) dissolved trace metal, f_{H} , in Tamar river water (sample A) as a function of sample volume processed. Error bars were calculated from the product of the relative standard deviation of $[\text{Me}_{\text{H}^*}]$, and the value of f_{H} derived from the mean values of $[\text{Me}]$ and $[\text{Me}_{\text{H}^*}]$ ($n = 3$).

$$f_{\text{H}} = 1 - ([\text{Me}_{\text{H}^*}]/[\text{Me}]) \quad (1)$$

where $[\text{Me}]$ and $[\text{Me}_{\text{H}^*}]$ are the respective dissolved metal concentrations in the sample before and after processing through the column.

The fractions of dissolved metals in Tamar river water (sample A) that were retained by the C18 columns are shown as a function of sample volume processed in Fig. 2. The order of retention appears to reflect the relative affinities of the metals for humic substances in freshwaters (Ross and Sherrell 1999; Liu and Gonzalez 2000). Retention of Cu and Pb was independent of sample volume processed, indicating that hydrophobic sites on the columns do not become saturated within the sample volume tested, and that organic matter adsorbing to the columns does not provide additional sites for the retention of metal. Retention of Co and Mn exhibited a reduction between 5 and 20 ml, suggesting that some charged species may adsorb to uncapped sites on the silica matrix but that these sites become rapidly occupied with increasing volume of sample processed.

In river water sampled on a number of occasions, we compared metal retention by C18 columns with metal extraction in *n*-octanol, an amphiphilic, lipidlike solvent. Fractional octanol extraction, f_{o} , was calculated as follows:

$$f_{\text{o}} = 1 - ([\text{Me}_{\text{o}^*}]/[\text{Me}]) \quad (2)$$

where $[\text{Me}]$ and $[\text{Me}_{\text{o}^*}]$ are the respective dissolved metal concentrations in the sample before and after octanol extraction. Octanol extraction of Cu was detected in all samples analyzed (Fig. 3), and there is a direct correlation between f_{o} and f_{H} , although column retention is about 30% greater than solvent extraction. Octanol extraction of Co, Mn, and Pb was detected in a single sample of river water collected after a period of extended local rainfall, and there is qualitative agreement between the hydrophobicities of these metals as determined by both approaches. Thus, the fraction of metal that is retained by C18 in the present study

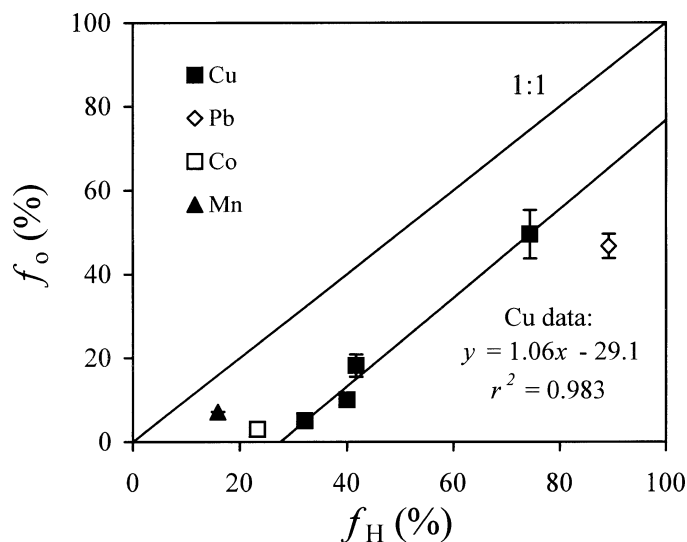


Fig. 3. The fraction of octanol-soluble dissolved trace metal versus the fraction of C18-retained dissolved trace metal in Tamar river water sampled on several occasions. Error bars for f_o were calculated from the product of the relative standard deviation of $[Me_o]$, and the value of f_o derived from the mean values of $[Me]$ and $[Me_o]$ ($n = 3$). Equivalent error bars for f_H are not shown for clarity.

is related to, but is generally greater than, the fraction of metal that is soluble in a solvent representative of amphiphilic biological surfaces. In other words, at least with respect to the metals and environment under study, bonded C18 moieties appear to be less hydrophobic than *n*-octanol.

pH dependence of f_H —To gain an insight into the nature of the trace metal species that are retained by C18, we determined the pH dependence of f_H for Co, Cu, Mn, and Pb in the freshwater and brackish water end-members of the estuarine turbidity maximum (samples C and G, respectively) by acid-base titration, and the results are shown in Figs. 4 and 5. In freshwater, the pH dependence of f_H is similar for all metals, although the magnitude and phasing of f_H are different in each case. Thus, f_H generally increases with increasing pH to around pH 8, an effect that is consistent with metal occupation of acidic (e.g., phenolic and carboxylic) sites on a heterogeneous series of natural ligands (Christl et al. 2001). Thereafter, a small reduction in f_H is evident, suggesting that available ligands at higher pH are more hydrophilic, or that complexes with inorganic anions (e.g., OH^- , CO_3^{2-}) assume greater importance.

In brackish water, all metals exhibit more distinct maxima in f_H of differing breadth and magnitude, but centered around neutral conditions. Accordingly, for Cu and Pb, and compared with freshwater, f_H is reduced throughout the pH range studied. For strongly binding metals, such a reduction is more likely the result of the electrostatic effect of seawater ions on natural organic substances rather than the competitive effects of divalent seawater cations for organic binding sites (Pinheiro et al. 1999; Lu and Allen 2002). That the reduction in f_H in the presence of seawater ions is greatest under basic conditions implies that the electrostatic effect is

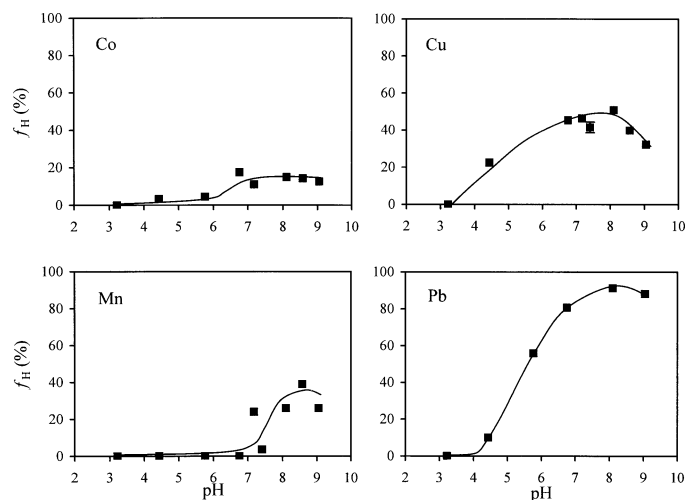


Fig. 4. The fraction of hydrophobic (C18-retained) dissolved trace metal, f_H , as a function of pH in freshwater taken from the upper reaches of the turbidity maximum of the Tamar estuary (sample C; Table 1). The solid lines are best “eye-fits” to the data.

more significant, or more selective toward the hydrophobic component of organic ligands, at higher pH.

Displacement from natural organic ligands by seawater cations is predicted to be greater for the weakly binding metals, Co and Mn (Hamilton-Taylor et al. 2002). However, for Co the maximum in f_H is greater in brackish water than in freshwater, and for Mn it is shifted toward lower pH in brackish water. Significantly, under circumneutral conditions and for both metals, f_H is enhanced in brackish water compared with freshwater. It is possible that, because of their size and conformation, complexes of these metals are *salted out* as water attains a more ordered structure in the presence of dissolved ions, an effect that appears to be significant for complexes of a number of metals in other estuaries (Turner et al. 2001, 2004).

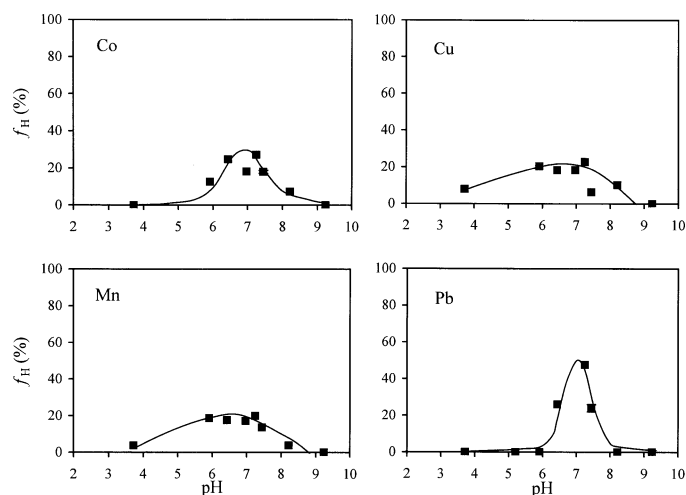


Fig. 5. The fraction of hydrophobic (C18-retained) dissolved trace metal, f_H , as a function of pH in the brackish water end-member of the turbidity maximum of the Tamar estuary (sample G; Table 1). The solid lines are best “eye-fits” to the data.

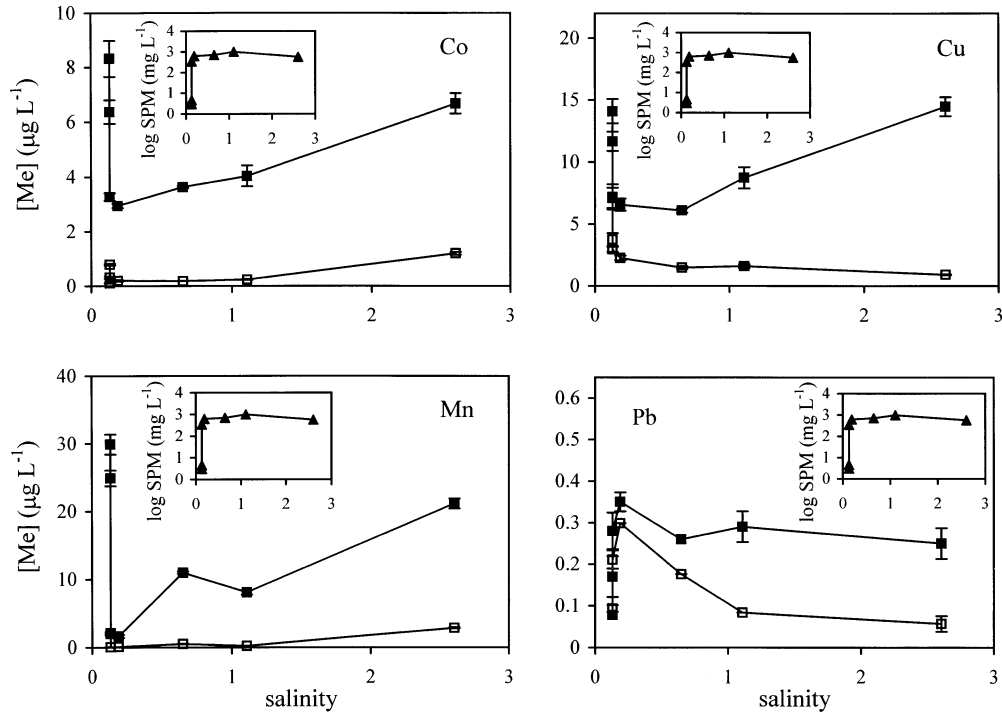


Fig. 6. Salinity distributions of total and hydrophobic dissolved trace metal concentrations (as filled and open squares, respectively) in the upper Tamar estuary (samples A through G). Error bars represent the standard deviation about the mean of three determinations (total metal), or the product of the relative standard deviation of $[Me_{H^+}]$ and the mean value of $([Me] - [Me_{H^+}])$ derived from three separate experimental determinations (C18-retained metal). Note, in many cases error bars were smaller than the size of the symbol. The salinity distributions of suspended particulate matter (SPM) concentration are shown inset.

Trace metal distributions and reactivity in the upper estuary—The upper reaches of the Tamar estuary afford an ideal natural reactor to examine the combined effects of pH, salinity, and concentration of SPM on dissolved trace metal fractionation and reactivity. Concentrations of dissolved Co,

Cu, Mn, and Pb are shown as a function of salinity in Fig. 6, and corresponding distributions of the hydrophobic fraction of metal are shown in Fig. 7. Assuming that the composition of river water is not subject to significant change during the flushing time of the upper estuary (estimated as 1–2 d), deviations from linearity in metal-salinity distributions may be attributed to either chemical reactivity or the presence of additional, external or internal, sources of metal. Thus, dissolved Cu and Mn exhibit significant removal that is approximately coincident with the onset of the turbidity maximum (see insets to Fig. 6), in agreement with previous investigations of these metals in the upper reaches of the Tamar estuary (Ackroyd et al. 1986). Our results also indicate that Co (along with Al, As, Cd, Ni, and Zn; results not shown) behaves likewise. In contrast, however, there is an internal source of dissolved Pb that is coincident with the removal of other metals.

The main driver for the removal of Co, Cu, and Mn, and the addition of Pb in this region of the estuary appears to be related to the abrupt change in concentration of SPM at the freshwater–brackish water interface. Variations in SPM concentration, coupled with the mixing of end-members, were able to reproduce the distributions of all dissolved metals studied according to the following empirical equation:

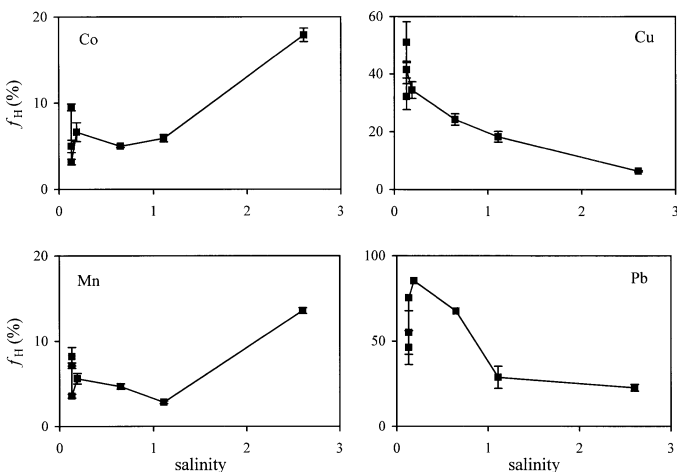


Fig. 7. Salinity distributions of the hydrophobic fraction of dissolved trace metals, f_H , in the upper Tamar estuary (samples A through G). Error bars were calculated from the product of the relative standard deviation of $[Me_{H^+}]$, and the value of f_H derived from the mean values of $[Me]$ and $[Me_{H^+}]$ ($n = 3$).

$$[Me] = \alpha S \pm \beta/[SPM] + \gamma \quad (3)$$

where $[Me]$ represents the salinity-dependent dissolved met-

Table 2. Results of multiple regression analyses of salinity-dependent dissolved metal distributions ($n = 7$) in the upper Tamar estuary (Eq. 3). Values in bold indicate that estimates are statistically significant ($p < 0.05$).

Metal	α	β (mg L ⁻¹)	γ ($\mu\text{g L}^{-1}$)	r^2
Co	1.46	16.2	2.71	0.991
Cu	3.21	24.9	5.56	0.944
Mn	7.28	86.8	2.01	0.948
Pb	-0.024	-0.670	0.310	0.916

al concentration, S is salinity, and α , β , and γ are data-fitted constants whose estimates, derived from multiple regression analyses of each data set, are given in Table 2.

The general success of this model, indicated by the regression results and the agreement between observed and calculated metal concentrations shown in Fig. 8, suggests that metal reactivity is controlled by adsorption onto or desorption from suspended particles. A requirement for such a mechanism is a shift in the sorptive capacity or composition of the suspended particles with increasing particle concentration. Particulate trace metal concentrations on a w/w basis are shown as a function of [SPM] in Fig. 9. With regard to Co, Cu, and Mn, inverse relations suggest that particles re-suspended in the turbidity maximum zone are depleted of metal compared with ambient (permanently) suspended particles, and that the thermodynamic tendency for the sorptive removal of these metals from the dissolved phase therefore exists. Conversely, the distribution of particulate Pb indicates that re-suspended particles are, in the main, enriched compared with ambient particles. By the same reasoning, there exists a thermodynamic tendency for desorption of this metal, provided that particulate associations are sufficiently labile. The preferential, long-term accumulation of Pb in (re-suspendable) estuarine bed sediments may be attributed to the significance of abandoned lead mines (compared with other metal mines) flanking the banks of the Tamar below the tidal limit (Hamilton-Jenkin 1974). Desorption of Pb has recently been observed in the turbidity maximum of the Mersey estuary, UK, in which a variety of industrial discharges has resulted in significant accumulation of Pb in the bed sediments (Martino et al. 2002).

Trace metal hydrophobicity in the upper estuary—The salinity distributions of C18-retained dissolved trace metals are given in terms of both the fraction of hydrophobic metal, f_H (Fig. 7), and its absolute concentration, $[\text{Me}_H]$ (Fig. 6). In agreement with the experimental results obtained under circumneutral conditions (Figs. 4 and 5), metals exhibit either a net decrease (Cu and Pb) or net increase (Co and Mn) in f_H with increasing salinity. In all cases, however, salinity distributions of f_H are nonlinear. This suggests that interactions between seawater ions and hydrophobic ligands are nonconservative with respect to salinity, or that hydrophobic metal is selectively removed from or added to the local water column. The significance of the latter mechanism(s) is supported by two further observations. First, variations in f_H are significant in the freshwater reaches of the estuary where water composition (and presumably metal speciation) is rel-

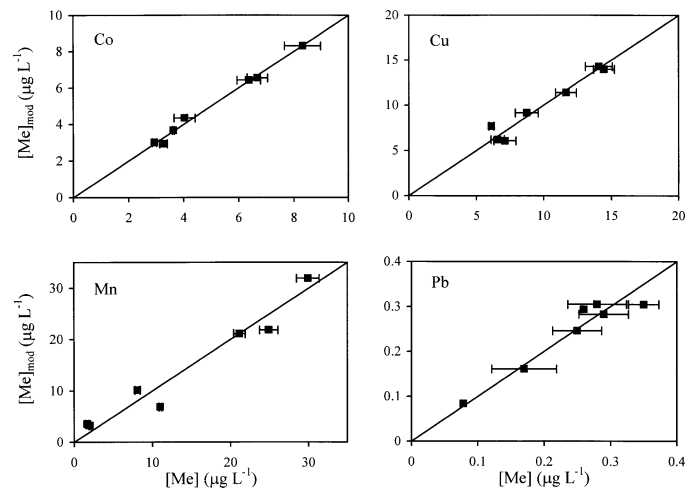


Fig. 8. Modeled, $[\text{Me}]_{\text{mod}}$, versus measured, $[\text{Me}]$, concentrations of dissolved trace metals in the upper estuary of the Tamar (samples A through G). Modeled concentrations were derived from the coefficients given in Table 2 and application of Eq. 3, and measured concentrations are given as the mean and standard deviation of three determinations of each sample. Solid lines represent unit slope.

atively invariant, but SPM concentrations vary considerably (Fig. 1). Second, distributions of f_H across the entire region were reproduced reasonably well by a model of the form of Eq. 3 (see Table 3):

$$[f_H] = \alpha_H S \pm \beta_H / [\text{SPM}] + \gamma_H \quad (4)$$

where α_H , β_H , and γ_H are data-fitted constants. With respect to Co, Cu, and Mn, therefore, distributions imply that hydrophobic complexes are preferentially removed by suspended particles over hydrophilic forms throughout the turbidity maximum zone, although the effect appears to be partly offset by the existence of a secondary source of hydrophobic metal below a salinity of 1. The detection of such reactivity also requires that the original or equilibrium hy-

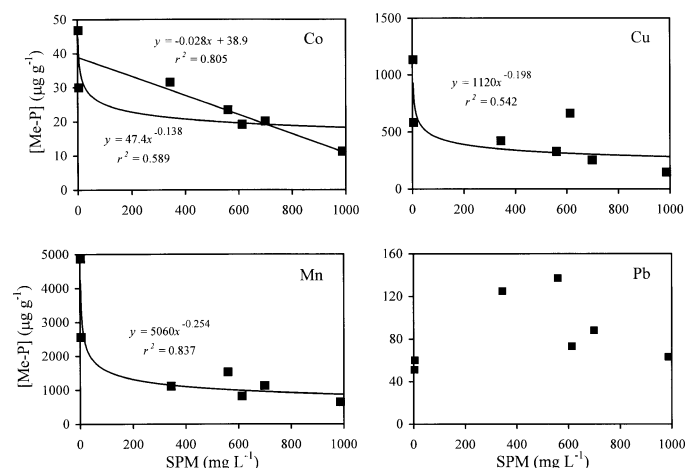


Fig. 9. Concentrations of particulate (HNO_3 -digestible) trace metals, $[\text{Me-P}]$, as a function of suspended particulate matter (SPM) concentration in the upper Tamar estuary (samples A through G). Solid lines represent best-fit power (or linear; Co only) regressions.

Table 3. Results of multiple regression analyses of salinity-dependent distributions of f_H ($n = 7$) in the upper Tamar estuary (Eq. 4). Values in bold indicate that estimates are statistically significant ($p < 0.05$).

Metal	α_H	β_H (mg L ⁻¹)	γ_H (%)	r^2
Co	5.46	15.8	2.46	0.845
Cu	-12.1	33.5	35.6	0.844
Mn	3.48	14.7	2.89	0.667
Pb	-24.6	-90.7	79.1	0.778

drophobic–hydrophilic fractionation of these metals is not re-established in the local water column. This suggests that either (1) there is insufficient time within the turbidity maximum for re-equilibration of aqueous species between the hydrophobic and hydrophilic fractions, or (2) new equilibria are established relatively rapidly by the buffering effects of a multitude of hydrophilic anions, counterions, and ligands in the water column. Consistent with the former kinetic effect, exchange reactions of metals with many types of organic ligands in natural waters are generally slower than sorption reactions (Millward et al. 1992; Xue et al. 2001). In other words, in the turbidity maximum of the Tamar estuary, it is possible that particle–water interactions of trace metals are closer to equilibrium than exchange reactions involving metals and hydrophobic organic ligands. However, it must be appreciated that the length of time involved in storage and manipulation of filtered samples (up to 48 h) exceeded the flushing time of the turbidity maximum (estimated as <1 d). More feasible, therefore, is that there is relatively rapid attainment of (or progress toward) new equilibria involving nonhydrophobic species, and that either the availability of hydrophobic ligands is limited, or, to some degree, these ligands are specific to the metals studied.

In contrast, there is a distinctive peak in hydrophobic Pb in the turbidity maximum zone of the estuary that is coincident with the secondary source of Co, Cu, and Mn noted above. Although there is a thermodynamic drive for desorption of Pb from resuspended estuarine particles, it is unlikely that the more hydrophobic species are preferentially desorbed. More plausible explanations for this peak require either a source of component-complexing ligands that is specific to (or more important for) Pb, or competition for available, and presumably less specific, ambient ligands from other trace metals. With regard to the former, it is possible that tidal disturbance of bed sediment during the formation of the turbidity maximum is accompanied by the injection of Pb-specific hydrophobic ligands, and that these ligands are able to outcompete sorption sites on resuspended particles for dissolved Pb. Undefined, metal-specific ligands appear to exist in natural waters (Qian et al. 1998), and pore waters are known to be an important source of complexing ligands for trace metals in shallow coastal waters (Skrabal et al. 1997), although such a source was not detected from distributions of the bulk DOC in the Tamar. Alternatively, the peak in f_H could be related to the competitive effects of certain trace metals for ligands that form hydrophobic complexes. Thus, because the implicated source of dissolved Pb is approximately coincident with the removal of other dissolved trace

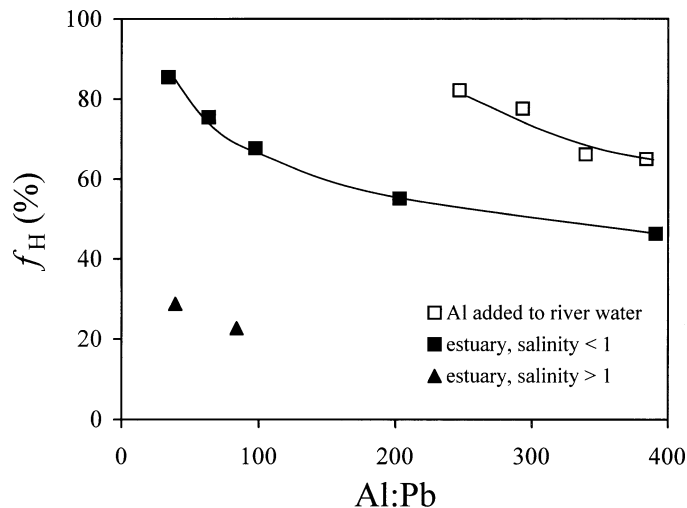


Fig. 10. Hydrophobic fraction of dissolved Pb, f_H , as a function of dissolved Al:Pb concentration ratio (on a mass basis) in the river and upper estuary of the Tamar. The solid lines are best “eye-fits” to the data.

metals, there exists an order of magnitude increase in the concentration of Pb relative to other metals in the upper estuary. Despite the removal of some (metal-specific) ligands via the sorption of hydrophobic complexes onto suspended particles, we predict a greater availability of less-specific hydrophobic ligands, or a greater tendency for Pb to complex with these ligands, in this region of the estuary.

The competitive effects among the trace metals studied was investigated in an independent set of experiments in which we added individual ionic metals to a sample of Tamar river water collected on a separate occasion before determining f_H . We also included Al in these experiments as the presence of trivalent metals is known to affect the speciation and binding of other trace metals (Pinheiro et al. 2000; Tang and Johannesson 2003). Note, however, that Al was precluded from more general study since it was prone to interferences from the C18 columns. Within the environmentally realistic concentrations used and the timescale of the experimental incubations (16 h), it was found that Al was most able to displace hydrophobic ligands from the divalent metals, and in particular Pb, in agreement with the results of independent complexation experiments using humic substances (Pinheiro et al. 2000). Our results are shown in Fig. 10 in terms of the hydrophobic fraction of Pb as a function of the Al:Pb concentration ratio on a mass basis. Also shown are the data from the axial sampling of the Tamar estuary, discriminated according to where samples were taken from. Thus, the magnitude of the reduction in f_H for Pb observed in the river and upper reaches of the turbidity maximum, where the competitive effects of seawater cations were least important, is similar to the reduction engendered by experiment in river water, although the phasing of the effect is different in each case.

To summarize, the hydrophobic fraction of dissolved trace metal that we have targeted by C18 retention is either preferentially removed from (Co, Cu, and Mn) or added to (Pb) the low-salinity zone of the Tamar estuarine water column.

That removal of the former is detectable suggests that ligands binding with these metals are, to some extent, metal-specific or limited in supply. The peak in hydrophobic Pb may be explained in terms of either a source of Pb-specific ligands, or reduced competition for less-specific ligands from other trace metals in this region of the estuary.

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