Kinetics of trace element uptake and release by particles in estuarine waters: effects of pH, salinity, and particle loading

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Abstract

The uptake and release of ^{109}Cd, ^{51}Cr, ^{60}Co, ^{59}Fe, ^{54}Mn, and ^{65}Zn were studied using end-member waters and particles from Port Jackson estuary, Australia. The kinetics of adsorption and desorption were studied as a function of suspended particulate matter (SPM) loading and salinity. Batch experiments showed that the position and slope of the pH edges are dependent on the metal and on the salinity of the water (except for Mn). The general effect of salinity was to move the adsorption edge to higher pH values, with the greatest change being found for Cd. Most of the metals showed relatively simple kinetics with an increase in uptake as a function of time and suspended particle concentrations. The time dependence of Cd uptake was more complex, with an initial adsorption phase being followed by strong mobilization from the suspended sediments, explained by chlorocomplexation and competition with seawater major cations. The reversibility of the sorption decreased in the order Co>Mn>Zn>Cd>Fe>Cr. The percentage of adsorbed metal released in desorption experiments was greater in seawater than freshwater for Cd, Zn, and Co. These results are important in understanding the cycling of pollutants in response to pH, salinity, and particle concentrations in estuarine environments. In addition, they give valuable insight into the important mechanisms controlling the partitioning of heavy metals in the Port Jackson estuary.
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Keywords: Kinetics; Adsorption; Desorption; Trace elements; Port Jackson estuary

1. Introduction

Adsorption onto suspended particulate matter (SPM) and bottom sediments is an important process controlling dissolved metal concentrations, bioavailability, and toxicity to biota, and both the fate and transport of trace metals (Jannasch et al., 1988; Comber et al., 1996). Moreover, the practical applications of adsorption in wastewater treatment and remediation operations are of paramount importance. A fundamental understanding of sorption processes is therefore a requirement for environmental fate, transport modelling, and managerial decisions.

Previous adsorption studies can generally be clustered into two groups. On one hand, studies have focussed on naturally occurring solids and solutions in order to closely simulate environmental conditions (e.g. Nyffeler et al., 1984; Garnier et al., 1997; Ouddane et al., 1999; Ciffroy et al., 2001). Natural solids present in estuaries and rivers comprise a diverse array of components, ranging from clays to metal oxides to organic detritus. A mixture of such materials would be expected to have a wide range of surface chemical properties and trace-metal adsorption characteristics. The modelling of such experimental results is very complex. Alternatively, numerous trace-metal adsorption studies have been performed on well-characterized solid surfaces, predominantly metal oxides (Misak et al., 1996; Trivedi and Axe, 2001), but these may have little relevance to the kinetics of metal sorption in natural environments. Conclusions from the experiments approaching environmental conditions are not only of necessity more empirical, but also more directly applicable.

In the current study, we report the results from laboratory investigations of the adsorption and desorption kinetics of ^{109}Cd, ^{51}Cr, ^{60}Co, ^{59}Fe, ^{54}Mn, and ^{65}Zn, as a function of particle loading and salinity, using water and particles from Port Jackson estuary. Advantages of using radioisotopes to

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simulate the behaviour of their stable counterparts include: freedom from contamination; easily attainable mass balance; possibility of working at ultratrace levels; the noninteracting nature of isotopes at trace levels; ability to study many elements simultaneously; and the ability to study mechanisms, reversibility, and kinetics of environmental reactions (Amdurer et al., 1982; McCubbin and Leonard, 1995). This latter attribute is enhanced by the fact that the laboratory environment allows the systematic variation of key experimental variables (e.g. pH, ionic strength) under controlled conditions.

This study was undertaken in the Port Jackson estuary, as it is one of the Australia's most contaminated estuaries, yet systematic and comprehensive data on trace-metal partitioning (Hatje et al., 2003) and kinetics are still very limited. The current investigation aimed to enhance the understanding of the reactivity of trace metals and attempted to define environmental conditions that favour adsorption and desorption of trace metals in both freshwater and seawater. Moreover, this study also aimed to provide suitable data for the improvement and calibration of models describing trace-metal kinetics in estuarine waters. Understanding the reactivity of trace metals is essential to predict the fate and transport of these elements in the environment and to optimize remediation efforts.

The Port Jackson estuary, also known as Sydney Harbour, is approximately 30 km long and drains a heavily populated and partially industrialised area of approximately 500 km^2. The estuary is well mixed and almost entirely saline under low-flow conditions as a result of limited freshwater inputs and tidal turbulence. A long history of contamination inputs has resulted in high levels of trace metals in the estuary (e.g. Irvine and Birch, 1998; Hatje et al., 2001a, 2003).

2. Experimental section

2.1. Sampling and sample characterization

Samples used for the experiments were collected from the Port Jackson estuary, southeast Australia, in April 2001. Fluvial (Upper Parramatta River) and marine end-member water samples were collected from the shore in 10-l, acid-cleaned, polyethylene bottles. Water samples were filtered through acid-cleaned 0.45-µm Millipore filters and stored at 4 °C in darkness. Characteristics of end-member water samples, and of a mixture of intermediate salinity, obtained by mixing end-member waters, are presented in Table 1.

Oxic surface estuarine sediments were collected manually from an intertidal mud flat using a plastic spatula and sieved through a 63-µm pore size, acid washed, nylon mesh using ambient water. The concentrated sediment slurry was stored at 4 °C in darkness. For batch sorption and kinetics experiments, aliquots of this sediment slurry were used to obtain target SPM loadings.

Table 1
Characteristics of the end-member water samples and sediments

Water	Salinity	pH	Temperature (°C)	SPM (mg l^{-1})
Freshwater	0.12	7.34	17.0	110
Intermediate salinity[a]	5.6	7.83	nd	nd
High salinity	31.6	8.18	19.6	2.5

Sediment	SSA (m^2 g^{-1})	POC (%)	Mineralogy	
Upper estuary	20.8	4.3	kaolinite, quartz, sergeevite	

[a] Mixture of fresh and marine end members; nd = not determined.

Aliquots of sediment slurry were also dried at 60 °C and grounded using a pestle and mortar for additional analyses. Specific surface area (SSA), particulate organic carbon (POC) concentrations, and mineralogy were determined, respectively, by BET nitrogen adsorption, combustiometrically using a CNS analyzer, and by X-ray diffraction (Table 1). Trace metals (Table 2) were also analysed by ICP-MS after a 0.05 M hydroxylamine hydrochloride in 25% acetic acid (v/v) leach (Tessier et al., 1979).

2.2. Batch sorption experiments

Adsorption edges were performed with a mass loading of 0.5 g l^{-1} and two ionic strengths (i.e. freshwater and seawater; Table 1), at 22 ± 1 °C, under ambient light. The sediment slurry was equilibrated overnight, under mechanical shaking, with unspiked end-member waters in 30-ml centrifuge tubes at the desired pH (2 to 9). Spikes of high specific activity of ^{109}Cd, ^{51}Cr, ^{59}Fe (Amersham International), ^{60}Co, ^{54}Mn, and ^{65}Zn (Australian Radioisotopes) were added to each experiment to yield high activity in samples (i.e. 250–1000 Bq ml^{-1}), so that counting times and errors were minimized, while radioisotope plus carrier concentrations were lower than end-member water concentrations. Following 48 h of incubation, with constant shaking, 15-ml aliquots were filtered through a 0.45-µm pore size, 25-mm diameter Millipore syringe-driven filter units, and filtrates were γ-counted.

2.3. Kinetic experiments

An adaptation of the constant suspension method of Duursma and Bosch (1970) was used to study sorption kinetics. Adsorption experiments were carried out for seawater, freshwater, and a mixture (salinity 5.6) in covered 1-l glass reactors. Reactors were soaked in experimental waters for at least 24 h before use. Spikes of the radiotracer mixture, the same as for the batch sorption experiments, were equilibrated for 72 h with constant stirring, at 22 ± 1 °C, under natural light. An aliquot of the sediment slurry was then added to each reactor, such that the resulting SPM concentrations (0.03 to 0.5 g l^{-1}) were typical of those encountered in estuaries. After contact times ranging from 0.25 to 168 h,

Table 2
Metal concentrations determined in sediment samples using an extraction with 0.05 M hydroxylamine hydrochloride in 25% acetic acid

Sediment	Cd (mg kg^{-1})	Cr (mg kg^{-1})	Co (mg kg^{-1})	Zn (mg kg^{-1})	Fe (mg g^{-1})	Mn (mg kg^{-1})
Upper estuary	0.66	29.1	4.68	379	5.71	63.2

15-ml aliquots were subsampled and filtered through 0.45-μm pore size, 25-mm diameter Millipore syringe-driven filter units. Filters and filtrates were γ-counted. The change in pH during experiments, after equilibration time, was less than 0.005 unit h^{-1}.

Particles originating from sorption experiments were also used for desorption experiments. After contact times of 0.5 and 168 h, 100-ml aliquots were sampled from each reactor and filtered onto 0.45-μm pore size, 47-mm diameter Millipore filters. The particle-bearing filters obtained were then resuspended in 100-ml filtered water. After 3 h contact time, the water was once again filtered. The desorbed radio-isotopes, i.e. present in the dissolved phase, were γ-counted.

2.4. Sample counting

Gamma-energies were counted using a high-performance Ortec HPGe p-type detector coupled to an Ortec 92X Spectrum Master™. Each sample was counted for 2 h, yielding a maximum of 3% standard deviation from counting statistics. The counts from filtrate and filters were corrected for radioactivity decay, and the same container geometry was used for standards and samples.

Mass balance calculations for control experiments ($n = 5$), in the absence of particles, showed that a maximum of 14% of total activity of ^{109}Cd, ^{60}Co, ^{51}Cr, ^{54}Mn, and ^{65}Zn was lost to reactor walls and filter units combined. Recovery of Fe, as will be discussed below, was low (10–40%) in seawater control experiments and over 95% for freshwater experiments. The mass balance for experiments in the presence of SPM ranged from 73% to 118% and averaged $97 \pm 7\%$. Reproducibility of replicate kinetic experiments was better than $\pm 5\%$.

3. Results and discussion

3.1. pH dependence

Adsorption edges for metal adsorption to SPM (Fig. 1) illustrate the sigmoid curve characteristic of transition metals. The observed metal uptake behaviour is qualitatively similar to results for simpler surfaces, such as metal oxides (e.g. Dzombak and Morel, 1990), and can be interpreted in terms of interaction of dissolved metals with deprotonated sites on the surfaces of the SPM. Sudden increase in adsorption occurred over a narrow range of 1 to 2 pH units. Cobalt and Mn presented a very steep slope compared to less 'particle reactive' elements such as Cd. The variation in slope reflects differences in metal-binding intensities, site densities, and reaction stoichiometries. For most elements, the position of the sorption edge was dependent on salinity. A shift to more alkaline pHs was observed for adsorption edges of trace metals in seawater, except for Mn, and the effect of the increased ionic strength was more important for Cd and Zn than for the other elements. The shift in the adsorption edges suggests that metal ions retain their waters of hydration upon sorption to amorphous oxide coatings, possibly forming outer sphere surface complexes, as suggested by Lutzenkirchen (1997). Misak et al. (1996) demonstrated that the decrease in the activity coefficient with increase in ionic strength could explain the adsorption edges shift. In other sorption studies, the shift in pH edges has been attributed to a competitive ion exchange mechanism (Kraepiel et al., 1999). The nature of the background electrolyte may also play an important role on metal adsorption edges; stronger electrolytes, such as NaCl, affect the degree of metal complexation more than less reactive anions, resulting in pronounced ionic strength effects (Criscenti and Sverjensky, 1999).

As observed by Charlet and Manceau (1992) in studies performed on Fe oxides, Cr was adsorbed in the low pH range. The Cr adsorption was almost complete (i.e. more than 93%) at pH 4 in freshwater and pH 5 in seawater, and beyond, the curves reached a plateau (Fig. 1). Chromium and Fe displayed similar behaviour and presented pH$_{50}$ (i.e. pH of 50% uptake) of ~ 3.5 and ~ 4, respectively, in freshwater. At pH higher than 5, however, a promotive ionic strength effect was observed, with an increase of Fe and Cr uptake in seawater compared to freshwater. It has been suggested that doubly charged surface species are responsible for promoting sorption at high ionic strength; when surface coverage is decreased, the electrostatic repulsion decreases and the promotive ionic effect disappears (Lutzenkirchen, 1997). Hence, it can be concluded that the occurrence of promotive ionic strength effects may depend on the experimental conditions chosen.

It is well known that organic matter has a significant effect on the kinetics of Fe adsorption, with organic complexes accounting for the vast majority of dissolved Fe that remains in solution (Nolting et al., 1998). The amount and source of organic ligands (i.e. various structure and functional properties) lead to different Fe oxidation characteristics (Rose and Waite, 2002). Therefore, the different pH dependence observed for Fe in seawater, compared to freshwater, is possibly largely associated with the rates of complexation of Fe and the rate of oxygenation of the Fe (II)-organic complexes. The similarity of pH edges and adsorption kinetics, as will be discussed below, of Cr and Fe suggested that mechanisms controlling their removal
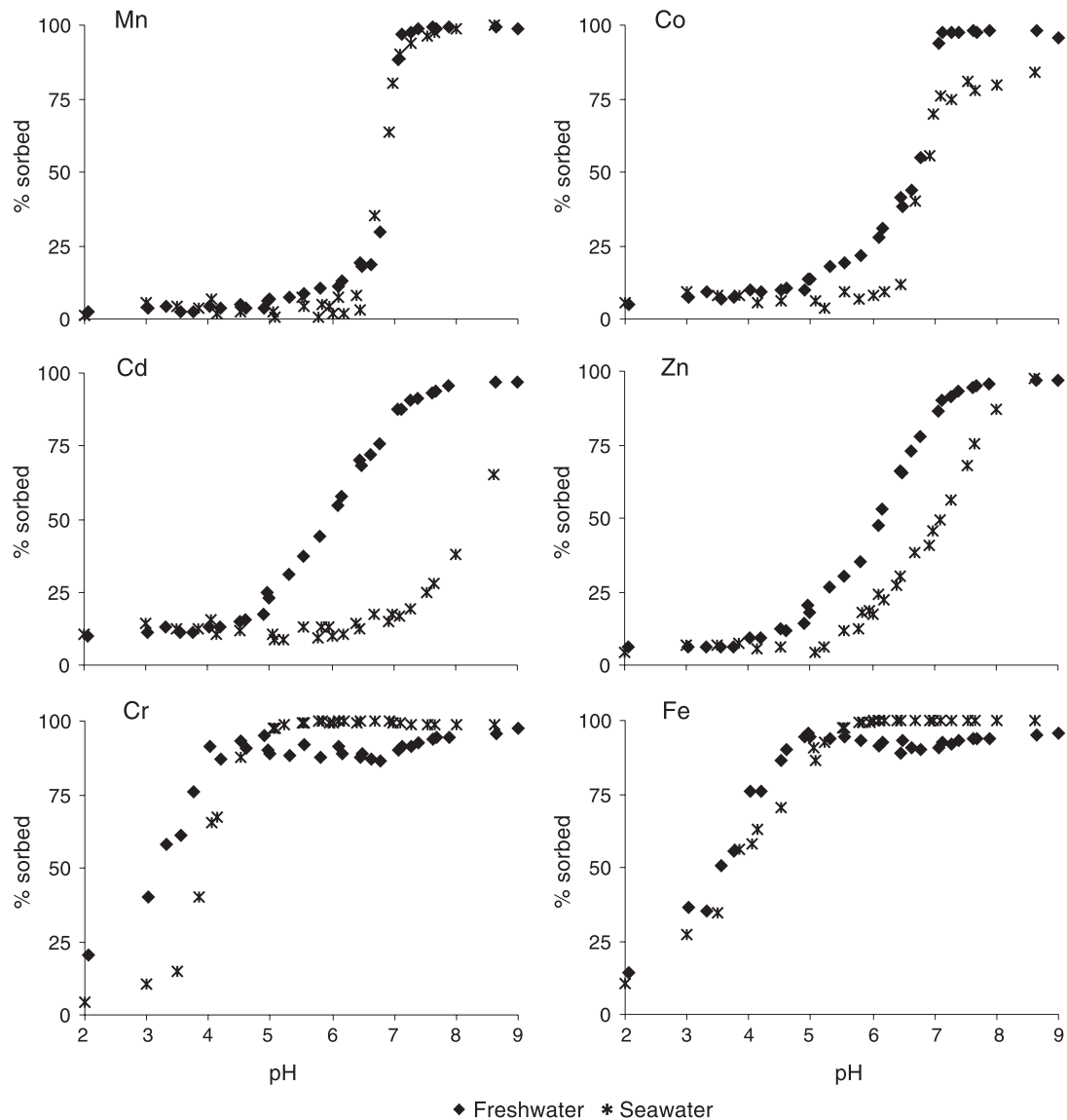
Fig. 1. Adsorption edges for [109]Cd, ^{60}Co, ^{51}Cr, ^{59}Fe, [54]Mn, and [65]Zn onto suspended particulate matter in seawater (salinity 31.6) and freshwater.

from solution are closely related, i.e. Fe oxidation, precipitation, and coprecipitation of Cr. This hypothesis, however, needs further investigation.

The adsorption behaviour of the studied metals, in marine and freshwater, varied according to slight changes in pH conditions. These results have important implications on the comportment of trace metals in estuaries, where physicochemical variables (i.e. salinity, pH, and SPM) may vary greatly even in a short period of time and space.

The common increase in pH with increasing salinity, observed in Port Jackson estuary (Hatje et al., 2001a), will favour the sorption of trace metals onto SPM, according to our results. This suggests an increase association of trace metals to particles towards the estuary mouth, which favours the retention of metals in the estuary, since net transport in the coastal zone is directed landward. The adsorption behaviours of the radioisotopes presented here are in agree-

ment with previous field studies with stable trace-metal counterparts in Port Jackson estuary (Hatje et al., 2001a, 2003).

3.2. Adsorption kinetics

The fraction of radiotracers present in solution as a function of time is presented in Fig. 2. All considered elements presented two-step kinetics, with a short period of relatively fast surface sorption followed by a longer period of redistribution to more strongly bound forms within the sediment. The relative importance of each process varied greatly between elements.

Cadmium, Cr, and Zn showed fast kinetics, with limited slow sorption, whereas Co, Fe, and Mn displayed a more progressive sorption. These differences in behaviour can be seen by comparing the final adsorption percentage (i.e. at
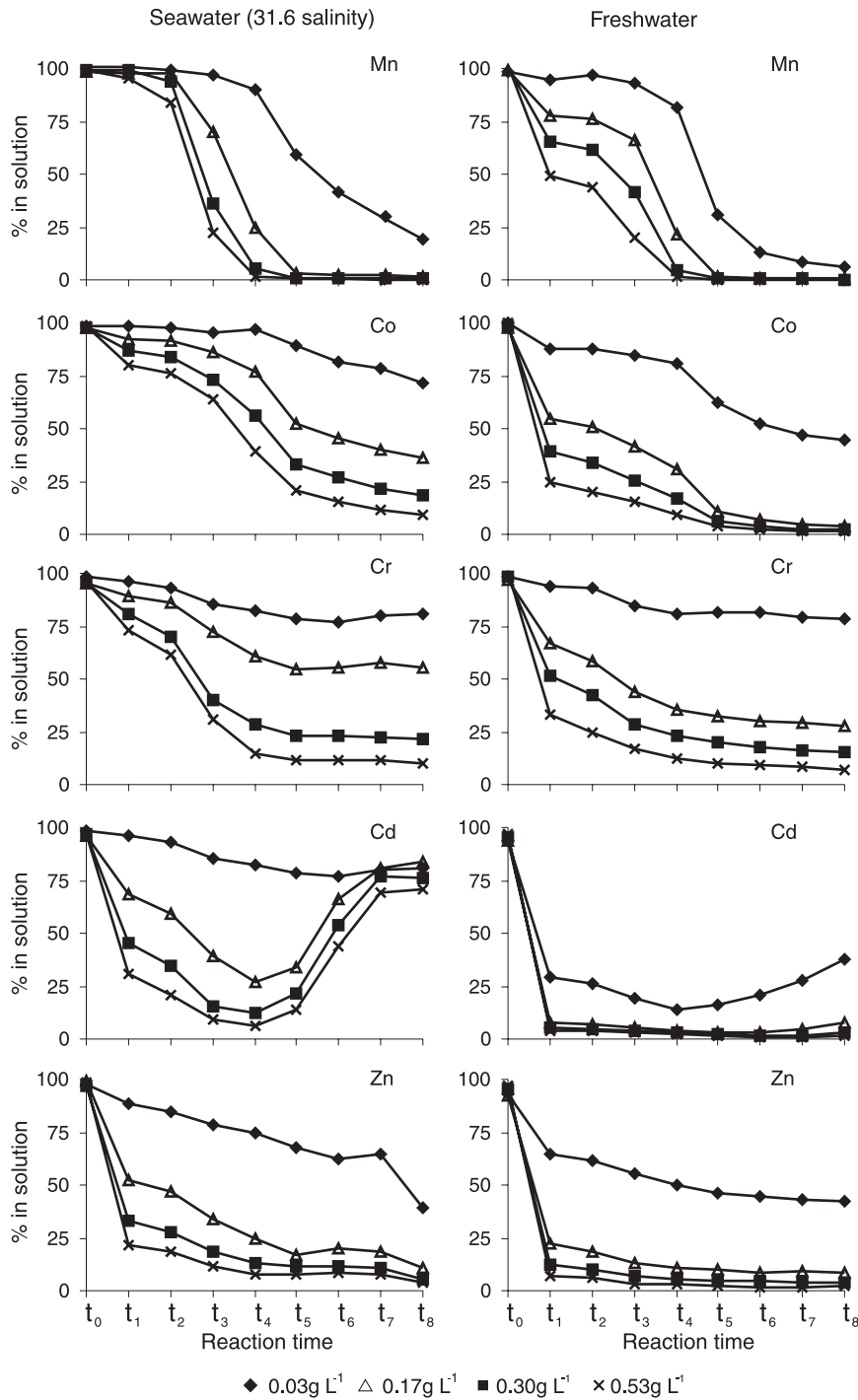
Fig. 2. The percentage of ^{109}Cd, ^{60}Co, ^{51}Cr, ^{59}Fe, ^{54}Mn, and ^{65}Zn in solution as a function of time for seawater (salinity 5.6) and freshwater. Reaction times are: $t_0 = 0$ h; $t_1 = 0.25$ h; $t_2 = 0.5$ h; $t_3 = 2$ h; $t_4 = 6$ h; $t_5 = 24$ h; $t_6 = 48$ h; $t_7 = 96$ h; and $t_8 = 168$ h.

168 h) with the value at 0.5 h (Fig. 2). Cobalt and Mn exhibited slow sorption kinetics, with a maximum of 25% and 15%, respectively, uptake of dissolved phase in the first 0.5 h in seawater. In freshwater, the initial uptake was up to 80% for Co and 55% for Mn. The oxidation of Mn and the formation of Mn oxide coatings, at least in part, control the relatively slow increase of Mn and Co uptake compared to

the other elements. Autocatalytic effects of preexisting Mn oxide coatings (Stumm and Morgan, 1981) enhance oxidation of Mn. Therefore, the higher the particle loading, the higher the autocatalysis sites per unit volume of the system, hence higher uptake. Slow kinetics have also been explained as a result of the "colloidal pumping", i.e. the use of colloids as an intermediary in particle removal (Honeyman

and Santschi, 1989; Stordal et al., 1996; Wen et al., 1997). This process has been invoked to explain the slow kinetics of trace metal uptake from seawater and freshwater (Nyffeler et al., 1984; Stordal et al., 1996).

Iron kinetics (not shown) were similar to that presented by Co and Mn in freshwater. The behaviour of Fe in seawater, however, will not be discussed here because a large amount of Fe (10–40%) was lost during the experiments. The loss of dissolved Fe can possibly be explained by adsorption on wall surfaces, oxidation of Fe by O_2 followed by precipitation, thermodynamically favoured when added to seawater, and limited amount of ligands in seawater.

Chromium, Cd, and Zn show rapid sorption kinetics with up to 97% removal in the first 0.5 h. After the fast initial process, the sorption of Cr and Zn proceeded at a slower pace, reaching a plateau, i.e. equilibrium, after 24 h. A discernible equilibrium was not attained for Zn in high salinity water, nor for Cd, regardless of salinity, as will be discussed below.

The fast processes are generally attributed to the formation of surface complexes. The slow processes can be attributed to diffusion into micropores (Paalman et al., 1994), to slow kinetics of ancillary reactions which perturb the equilibrium of the sorption reaction (Morel, 1983), or in the case of surface precipitation, they can also be attributed to lattice penetration and recrystallization (Davis et al., 1987; Payne et al., 1994; Trivedi and Axe, 2000).

In seawater, both the rate and extent of adsorption are reduced compared to freshwater. This difference is probably due to competition of major seawater ions (particularly Ca and Mg) with metals for active sites on the particles, and also chlorocomplexation, at least for Cd and Zn.

Cadmium displayed more complex kinetics than the other elements. The fast initial sorption (Fig. 2), during the first 6 h, was followed by a strong mobilization of Cd during the remainder of the experiment, and no apparent equilibrium was attained after 168 h. The results also showed that the increase in salinity and particle concentrations enhanced the Cd mobilization (Fig. 2). Cadmium mobilization was also observed in freshwater for the low particulates load (0.03 g l^{-1}). However, it was smaller than in both high and intermediate salinity waters. The very low salinity (Table 1), and possibly the presence of low concentrations of Ca^{2+} and Mg^{2+} in freshwater, may explain the desorption observed in freshwater. There were, however, no alterations in the experimental conditions, i.e. SPM loading, pH, and/or temperature, at the reaction time of 6 h, to explain the mobilization of Cd. Moreover, none of the other elements presented such mobilization. Thus, this mobilization does not appear to be an experimental artifact.

Model calculations have shown that an increase in salinity causes a decrease in the adsorption of Cd in particles, and that the dissolved inorganic Cd speciation in seawater, even at low salinity, is dominated by highly stable and soluble chlorocomplexes (Comans and van Dijk, 1988; Paalman et al., 1994; Lores and Pennock, 1998). However, it is probably only exchangeable Cd that will be released due to complexation with chloride. This means that although the inorganic Cd speciation in seawater is dominated by chlorocomplexes, Cl^- itself is only partly responsible for desorption of Cd. Competition with major cations, such as Ca^{2+} and Mg^{2+}, and trace metals for active sites could also promote desorption of Cd, as has been previously reported (e.g. Paalman et al., 1994). The much higher concentration of Ca^{2+} and Mg^{2+} in seawater in comparison to Cd^{2+}, and the possibility that these cations will form higher energetic bonds on the particles, may lead to enhanced mobilization of Cd into solution. It is not clear, however, whether Cd is released from particulate matter due to complexation with chloride or due to competitive effects with divalent cations such as Ca^{2+} and Mg^{2+}, or to both.

In general, the experimental results show that an enhancement in SPM concentrations, and hence total particle surface area, promoted an increase in the removal of all the studied metals. This implies that a surface process controls the overall removal from the aqueous phase rather than a precipitation mechanism. Particle concentration has been identified as a surrogate parameter for surface site concentration (Honeyman and Santschi, 1988), and also a master variable controlling scavenging of trace metals. Moran et al. (1996) have further shown that the concentration of colloids (i.e. microparticles and macromolecules in the size range of 1 nm to 1 μm) is proportional to particle concentrations. It would be expected that the amount of colloids in freshwater would be larger than in seawater (Table 1) at the beginning of the experiment, even after 0.45-μm pore filtration, because of the procedure artifact. Ideally, therefore, three-phase partitioning should be considered. The aggregation of colloids, present in the 'dissolved' phase, with larger filterable particles during the experiment would possibly promote the removal of those particles by filtration, when separating the filtrate at each sampling time. This is consistent with the more substantial effect of SPM on concentrations of trace metals in freshwater than in seawater, in both short (0.5 h) and long (168 h) contact times. The uptake, independent of the salinity of the water, not only enhanced substantially with increasing SPM loadings, but was also faster at the initial stages.

3.3. Desorption kinetics

It is important to know whether trace metals interact reversibly with suspended particles because the extent of the reversibility controls the amount of metal that is released to solution during desorption and hence indicates the amount of metal readily available for biogeochemical processes. It is noteworthy that, compared to adsorption experiments, release experiments are scarcer.
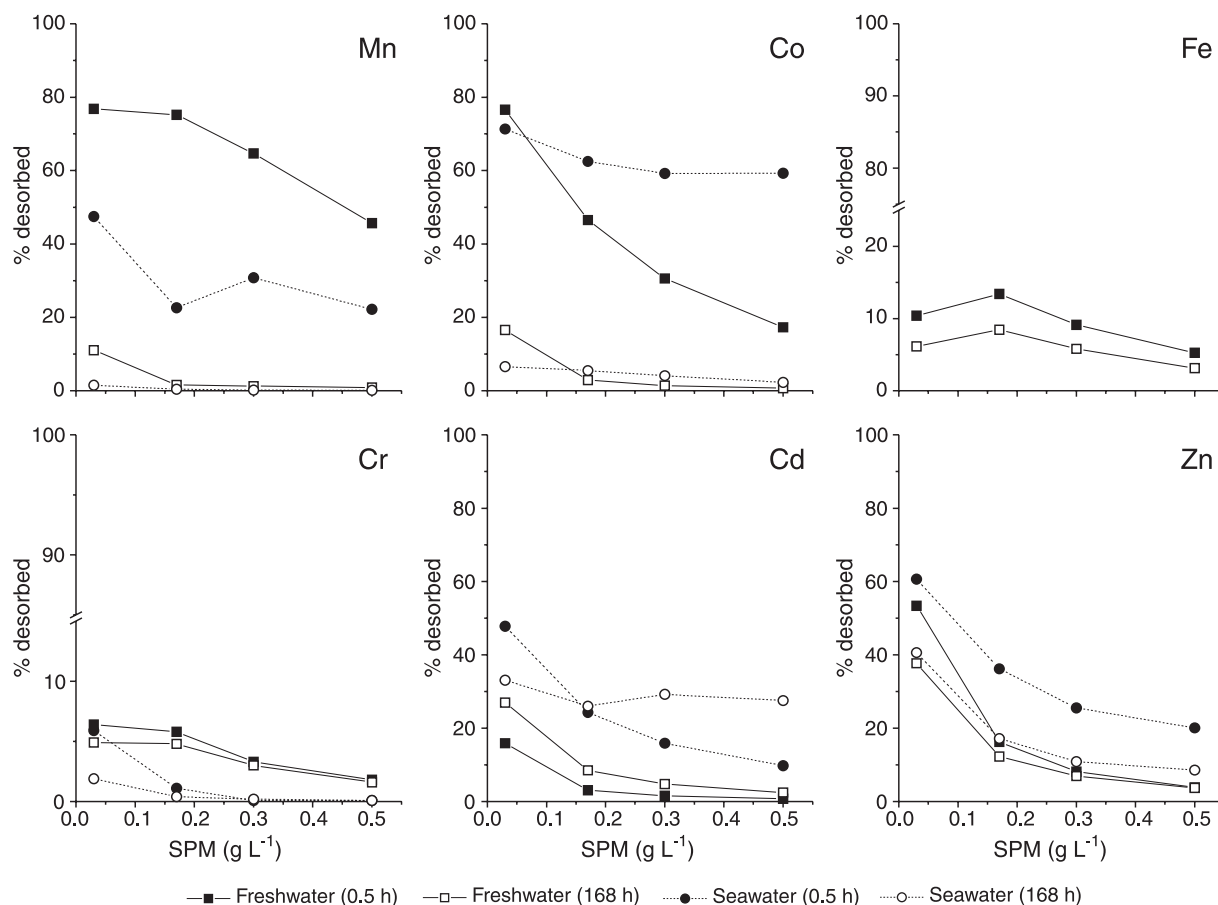
Fig. 3. The percentage of [109]Cd, ^{60}Co, ^{51}Cr, ^{59}Fe, [54]Mn, and [65]Zn desorbed in seawater (salinity 31.6) and freshwater as a function of SPM loadings. Contact time for adsorption was 0.5 and 168 h, and contact time for desorption was 3 h.

Fig. 3 shows the fraction of adsorbed trace metals that was released to the dissolved phase after 3 h of desorption. Desorption was metal-specific and was a function of SPM concentration, salinity, and adsorption contact time. The amount of metal released was inversely related to SPM loadings for all studied metals. The proportion of release, however, varied among metals. A decrease in desorption with an increase in particle concentration was previously observed for Zn (Li et al., 1984a). The decrease in the fraction released at higher particle loadings can be explained on the basis that the proportion of adsorbed metal bound by strongly binding sites will be greater when the ratio of total sorption sites to sorbing metal concentrations is higher. The greater reversibility of sorption, observed at low SPM loadings, is due to a greater fraction of metal being adsorbed to weakly binding sites.

A prolonged adsorption contact time (168 h) for Co and Mn resulted in a substantial decrease of the release of these metals from SPM, when compared to a short contact adsorption time. The high release observed for short adsorption time (i.e. 0.5 h) is attributable to desorption of the weakly bound metals from particulate surfaces. On the other hand, small desorption observed for long contact times (i.e.

168 h) indicated the importance of a slow transfer of these metals to strongly bound or nonexchangeable sites. For Mn, desorption was higher in freshwater than seawater, whereas the opposite trend was observed for Co.

The adsorption of Cr and Fe was quite irreversible, releasing a maximum of 15% of the adsorbed metals. Several processes can be proposed to explain the irreversible migration of metals into the solid lattice: sorption on high energy binding sites, formation of stable associations with organic compounds, intraparticle surface diffusion, oxidation, precipitation, and ageing of oxides which then become more refractory (e.g. Payne et al., 1994; Trivedi and Axe, 2000). Moreover, the observed irreversibility might be due to the slow desorption kinetics and, in addition, to the relatively short observation time.

As would be predicted from the adsorption experiments, desorption of Cd and Zn was greater in seawater than in freshwater. This result can be attributed to the formation of highly soluble and stable chlorocomplexes and competition with Ca^{2+} and Mg^{2+}, as described in the previous section. The increased desorption of Cd with time indicated that the process was slower than adsorption. Moreover, in the time scale of this study, Cd partitioning was not com-

pletely reversible. The lack of complete reversibility observed for Cd could be a result of the short desorption time used in the present study, compared to the work by Paalman et al. (1994) and Stranding et al. (2002). On the other hand, the amount of nondesorbable Zn increased with time, suggesting that the adsorbed Zn becomes more strongly bound to SPM, and this association strengthened over time, the same that was observed for Co and Mn.

3.4. Trace-metal partitioning, K_d

The use of partition coefficients (K_d) is a common approach for describing solid/solution interactions. The K_d was calculated as follows:

$$K_d = \frac{Me_P/m}{Me_D/V}$$

where Me_P and Me_D are the blank corrected trace metals activities on the filter and in solution, respectively; V is the volume of solution (l); and m is the mass of sediment (g) (Li et al., 1984b). Partitioning coefficients prove to be more sensitive than the fraction of metal in solution and/or adsorbed, as they better represent metal partitioning at the extremes of the range of fractional uptake, i.e. adsorption <10% or >90% (Jannasch et al., 1988). Note that K_d is not a true equilibrium coefficient, but is an empirical term, which depends on factors such as pH, temperature, solution composition, and concentration of colloids in the 'dissolved' phase, metal speciation, and heterogeneity in particle surfaces. Thus, K_d is a conditional constant that is easily implemented within a modelling framework.

Fig. 4 shows the evolution of K_d with time for each element in all studied SPM loadings. It has been suggested that at thermodynamic equilibrium, K_d should be constant and independent of particle concentration; only the rate of approach to equilibrium should be affected by SPM (Honeyman and Santschi, 1988; Wen et al., 1999). In general, this phenomenon occurred in the adsorption experiments, with limited dependence of K_d on SPM concentrations being observed. The K_d's for the range of concentration studied (i.e. 0.03 to 0.5 g l^{-1}) reached similar values after 168 h (Fig. 4). This is in agreement with the findings of Turner (1996). However, slightly lower K_d values were obtained for the experiments with the lowest mass loading (Fig. 4). This effect has been previously discussed by McKinley and Jenne (1991). As they observed, the decreased unit adsorption at lower solids concentration can be explained by the lower concentration of high energy sites. This explains both the lower K_d values obtained in these experiments as well as the greater reversibility of adsorption (discussed above). Although the sorption K_d has been reported to be independent of SPM loadings in many studies, this should only occur when the ratio of sorbing metal to suspended SPM levels is low. Under these conditions, the adsorbed concentration will be proportional to the dissolved concentration.

Nevertheless, it is interesting to note that Cd in seawater presented an inverse dependency between desorption K_d vs. SPM concentrations (i.e. particle concentration effect (PCE); O'Connor and Connolly, 1980). Correlations between the Cd desorption log K_d and log SPM are robust above $P \leq 0.05$ ($r = 0.953$), and the slope is negative (-0.36) and lower than values reported previously (Benoit et al., 1994; Benoit and Rozan, 1999). The desorption log K_d of Co in seawater and those for Cr and Fe in freshwater also decrease between 0.03 and 0.17 g l^{-1} of SPM. The origin of the PCE is the subject of much controversy, but it may be related to the existence of colloidal forms of metals (Honeyman and Santschi, 1989). Colloids are lumped with the filtrate fraction when 0.45 μm is used to separate the dissolved and particulate fractions. If the concentrations of colloids increase in proportion to the quantity of suspended macroparticles, then a decrease in the apparent partition coefficient with increasing SPM is expected. There were no differences in experimental protocols between adsorption and desorption experiments that could explain the PCE observed for these elements in the desorption studies. Definite explanations of the differences between desorption and adsorption log K_d for Cd would require additional research.

It has been previously assumed that equilibrium in adsorption/desorption processes is achieved rapidly. From Figs. 2 and 4, it can be seen that rapid sorption processes occurring in the first hour did indeed constitute an important proportion of the overall sorption. However, slower uptake processes continued for the remainder of the experiment. In fact, Zn and Cr were the only elements that reached a quasi steady state after 24 h. The length of the experiment, i.e. 168 h, however, was not enough for Mn, Co, Fe, and Cd to reach 'equilibrium'. These results suggest that dissolved and particulate Mn, Co, Fe, and Cd concentrations could show continued fluctuations for as long as a week following inputs of dissolved metals to Port Jackson estuary. In addition, if inputs occur in time scales less than a week, dissolved and particulate Mn, Co, Fe, and Cd concentrations may never reach equilibrium values. This means that sample collection after disturbances, such as tidal or wind resuspension, may detect metal concentrations that are quite different than equilibrium concentrations and that are likely to change if sampled again in later time. Depending on the magnitude and type of disturbance to the system, kinetic controls on sorption reactions may be critically relevant to interpretations of 'snap-shot' surveys monitoring dissolved metal concentrations and K_d values (Gee and Bruland, 2002). This also emphasizes the need to consider a kinetic approach to sorption/desorption modelling.

It appears that if there are no changes in the pH, composition, and concentrations of SPM, the adsorption in an estuary will be always smaller compared to the freshwater end member due to the increase in chlorinity and competition of Ca^{2+} and Mg^{2+} with trace metals. K_d's for all elements decrease from freshwater to low salinity water
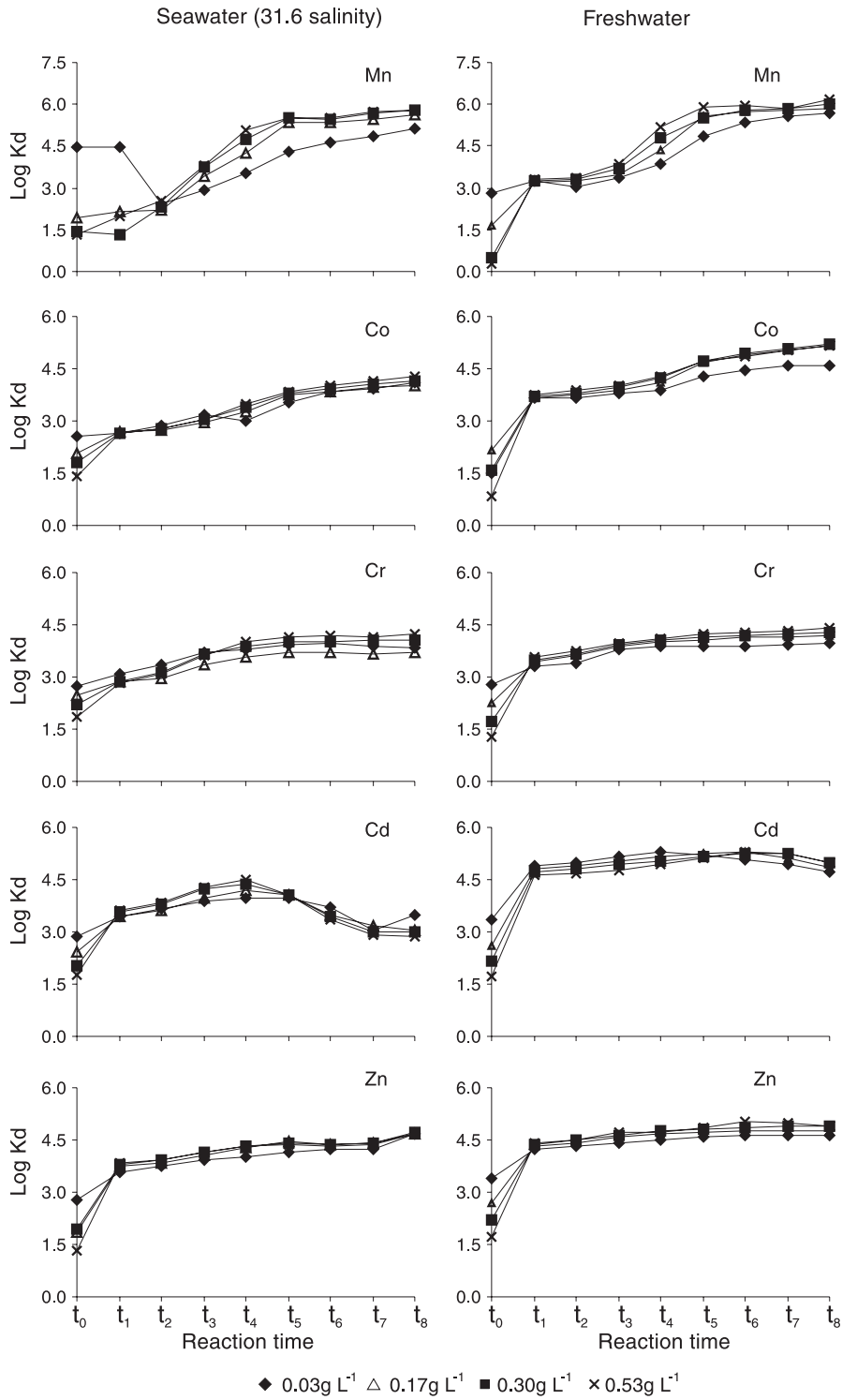
Fig. 4. Distribution coefficient (log K_d) as a function of adsorption contact time. Reaction times are $t_0 = 0$ h; $t_1 = 0.25$ h; $t_2 = 0.5$ h; $t_3 = 2$ h; $t_4 = 6$ h; $t_5 = 24$ h; $t_6 = 48$ h; $t_7 = 96$ h; and $t_8 = 168$ h.

(as exemplified for K_d at 168 h in Fig. 5), and the decrease was especially drastic for Cd. From low to high salinity (i.e. 5.6 to 31.6; Table 1), only Cd and Co K_d's continued to decrease. The magnitude of K_d in seawater is in the order Mn>Zn>Co>Cr>Cd, which is consistent with results from

other seawater partitioning experiments (Li et al., 1984a,b; Nyffeler et al., 1984). Compared with stable elements K_d values (Hatje et al., 2003), K_d's were comparable for Mn and Zn, there is, however, no available data for the other elements. As a result of the changes in kinetics, especially
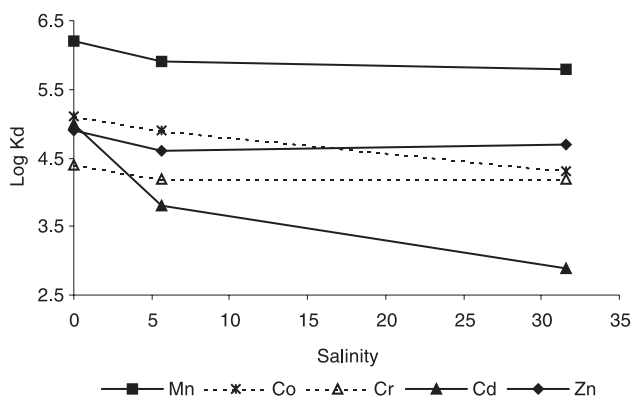
Fig. 5. Distribution coefficient (log K_d) after 168 h of contact time as a function of the salinity for SPM loading of 0.5 g l^{-1}.

due to salinity, K_d's for freshwater followed the order of Mn>Co>Zn>Cd>Cr. The restricted availability of field-derived K_d values for Port Jackson freshwater end members does not allow a comparison of the latter with the results of these experiments. However, it is expected, based on the kinetic results, that K_d's derived from field data will not represent short-term biogeochemical behaviour and will therefore be unsuitable for modelling such processes. Moreover, given the large small-scale temporal variability in metal concentrations in the freshwater end members of Port Jackson (Hatje et al., 2001b), the K_d approach might be unsatisfactory for describing solid-solution distributions in freshwaters. As previously suggested (Millward and Glegg, 1997), this concept is more useful in the estuarine and coastal waters where variations in water composition are more predictable.

4. Conclusion

The implications of kinetics of sorption/desorption processes are most obvious under strong gradients in salinity and SPM concentrations and rapidly changing environmental conditions, such as that observed in estuarine mixing zones, and/or during resuspension of bottom sediments. The application of sorption/desorption radiochemical techniques has given a valuable insight into the nature and time scale of processes occurring in Port Jackson estuary, which will assist the conceptual development of trace-metal fate and transport models. Furthermore, the results of this study could also assist in the prediction of the effect of remedial measures on the quality of the estuarine water and sediments.

The results showed that particle uptake of originally dissolved trace metals in estuarine waters can occur in a matter of minutes up to days. The majority (>50%) of dissolved metals had been transferred into the particulate phase after 24 h, except when the particle loading was 0.03 g l^{-1}. Two distinctively temporal processes of removal were identified: a faster reaction during the first 6 h followed by a slower uptake. The rate and extent of uptake enhanced with increasing SPM concentrations, implying that surface processes are controlling the uptake. Cadmium presented a strong mobilization after the initial 6 h. Chlorocomplexation and competition with major cations have been invoked to explain the mobilization observed. The overall effect of salinity was to move the adsorption edges to higher pHs (except for Mn). In the case of Cd, the effect of salinity was more important than the effect of pH.

Three major trends were revealed in desorption experiments: (1) Fe and Cr were quite irreversible, in both fresh and marine waters, in all studied particle loadings and contact times; (2) Co and Mn presented an inverse relationship between contact time and the percentage of metal desorbed, showing that these metals are associated with particulate sites involving strong interactions; and (3) Zn and Cd presented intermediate reversibility, and desorption was higher in seawater than in freshwater, implying the importance of chlorocomplexation controlling their behaviour.

All the processes discussed here play a major role in the retention of trace metals in particles and ultimately in estuaries. Based on the sorption K_d values presented here, it would be expected that most of the studied trace metals (i.e. Mn, Co, Cr, and Zn) would be trapped in the estuarine environment once the metals are mostly associated with the particulate phase in seawater and the net transport of sediments in the coastal zone is directed landward. This hypothesis is in accordance with the observed distribution patterns of stable elements in Port Jackson estuary (Hatje et al., 2003). The future use of models, based on the results presented here, will allow a better estimate of this retention.

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