ORIGINAL ARTICLE

Modeling on adsorption–desorption of trace metals to suspended particle matter in the Changjiang Estuary

Y. Y. Zhang · E. R. Zhang · J. Zhang

Abstract The uptake and release of trace metals (Cu, Ni, Zn, Cd, and Co) in estuaries are studied using river and sea end-member waters and suspended particulate matter (SPM) collected from the Changjiang Estuary, China. The kinetics of adsorption and desorption were studied in terms of environmental factors (pH, SPM loading, and salinity) and metal concentrations. The uptake of the metals studied onto SPM occurred mostly within 10 h and reached an asymptotic value within 40 h in the Changjiang Estuary. As low pH river water flows into the high pH seawater and the water become more alkaline as it approaches to the seaside of estuary, metals adsorb more on SPM in higher pH water, thus, particulate phase transport of metal become increasingly important in the seaward side of the estuary. The percentage of adsorption recovery and the distribution coefficients for trace metals remained to be relatively invariable and a significant reduction only occurred in very high concentrations of metals (>0.1 mg L^{-1}). The general effect of salinity on metal behavior was to decrease the degree of adsorption of Cu, Zn, Cd, Co, and Ni onto SPM but to increase their adsorption equilibrium pH. The adsorption–desorption kinetics of trace metals were further investigated using Kurbatov adsorption model. The model appears to be most useful for the metals showing the conservative behavior during mixing of river and seawater in the estuary. Our work demonstrates that dissolved concentration of trace metals in estuary can be modeled based on the metal concentration in SPM, pH and salinity using a Kurbatov adsorption model assuming the natural SPM as a simple surfaced molecule.

Introduction

Suspended particulate matter (SPM) in rivers and estuaries is considered to exert a major influence on the behavior and bioavailability of solutes, especially metals (Stumm 1992; Eisma 1993; Ferrira et al. 1997). Researchers have established that SPM is a significant transport agent for trace metal contaminants in stream environments (e.g. estuary) (Characklis and Wiesner 1997; Neal et al. 1997; Webster et al. 2000). As a result, there is growing interest in the nature of the binding interactions between SPM and trace metal contaminants. Many studies have demonstrated the importance of sorption by SPM in affecting the dissolved concentrations, bioavailability, and residence times of trace metals in waters (Hamilton-Taylor et al. 1997; Grantza et al. 2003; Hatje et al. 2003). Moreover, the practical applications of metal adsorption behavior in wastewater treatment plants and remediation operations in situ are of paramount importance. A fundamental understanding of sorption processes is therefore a requirement for understanding environmental fate, transport modeling, and managerial decisions.

Model simulations have been recently used to study the behaviors of trace metals in estuaries (Muller et al. 1994; Sung 1995; Turner 1996). And numerous trace-metal

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adsorption studies have been performed on well-characterized solid surfaces, predominantly metal oxides (e.g. ferric oxide) (Misak et al. 1996; Trivedi and Axe 2001), the applicability of these results to the kinetics of metal partitioning in natural environments remains unclear. Natural SPM present in estuaries and coastal environment consists of a variety of components, ranging from clays, sand and metal oxides to organic detritus. These compound particles are expected to have a wide range of surface chemical properties and trace-metal adsorption characteristics (Hatje et al. 2003). Conclusions drawn from experiments based on environmental conditions are not only of necessity more empirical, but also more directly applicable.

In the study, we report the results from laboratory batch experiments on the adsorption and desorption kinetics of Cu, Zn, Cd, Co, and Ni as a function of particle loading and salinity, using suspended particles from Xuliujing in Changjiang Estuary. The current investigation aimed to obtain a better understanding of trace metal sorption by natural particles and hence to improve our knowledge of the behavior of trace metal in estuaries.

The Changjiang River is the fourth largest aquatic system, after the Amazon, Zaire, and Orinoco, draining into the world ocean. The Changjiang Estuary is one of the largest estuaries in China. It discharges 928.2×10^9 m^3 $year^{-1}$ of water into the East China Sea (Milliman et al. 1985; Zhang et al. 1999), and has an average suspended sediment level of 544 mg L^{-1}. Within the maximum turbidity zone, the concentrations of SPM can soar to 1.3×10^3 mg L^{-1}. The maximum turbidity zone coincides with 5–25‰ of salinity where it is a plume front (Xie and Li 1990). The pH ranges from 7.7 to 8.3 (Zhang and Zhang 2003) and the salinity are 0–33 in winter and 0–34 in summer in the Changjiang Estuary (Wang KS et al. 1990; Wang ZF et al. 1990).

Sample collection and methods

Sampling and sample characterization

Samples used for the experiments were collected from the Changjiang Estuary, in July 2001. Xuliujing (i.e. riverine end-member) (Fig. 1) and marine end-member water samples were collected from the sea surface in 25-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 a mixture of intermediate salinity obtained by mixing end-member waters are presented in Table 1.

After sedimentation, the supernatant was siphoned off. The concentrated sediment slurry was then collected into 5-L, acid-cleaned, polyethylene bottles and stored at 4°C in
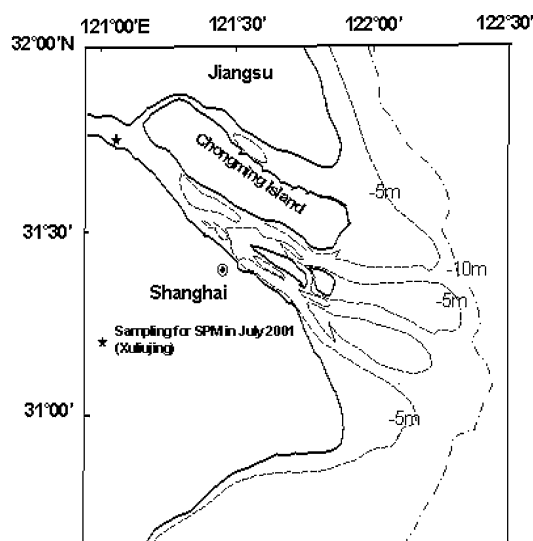

Fig. 1 Sampling sites of experiment in the Changjiang Estuary

darkness. For batch sorption and kinetics experiments, aliquots of this sediment slurry were used to obtain target SPM loadings.

Aliquots of sediment slurry were freeze-dried for additional analysis. Particulate organic carbon (POC) concentrations and mineralogy were determined, by metric combustion using an Element analyzer and by X-ray diffraction, respectively. Trace metals were also analyzed by ICP-AES (Plasma 2000, Perkin Elmer) after being digested with HF-HNO3-HClO4 in closed Teflon systems (Table 2).

Metal solution preparation

In most experiments, multiple metal spikes Cu, Co, Zn, Ni, and Cd were added together. Stock solutions of metals were prepared for concentrated solutions (1,000 mg L^{-1}) with a 3% HNO$_3$ solution. Working metal solutions were obtained by further dilution in 3% HNO$_3$ or by centrifuging and filtering the Xuliujing solution.

Kinetic equilibrium experiments

Adsorption kinetic experiments were performed with a SPM mass loading of 224 mg L^{-1} at 25.0 ± 0.1°C, under ambient light. The SPM was well-mixed or homogenized in 100-mL centrifuge tubes using mechanical shaking with end-member water for overnight. Spikes of high concentrations of Cu, Zn, Co, Cd, and Ni were added to each tube to yield high concentration samples (i.e. 1.5 mg L^{-1}) similar to the SPM concentration. After allowing the metals to be contacted with SPM for 0 to 70 h, 50-mL aliquots were sub-sampled into centrifugal tubes and centrifuged at 3,000 rev./min to separate the liquid and solution phases. The upper water for the heavy metal analysis was acidified

Table 1 Characteristics of suspended particles matter and natural solutions employed in simulating experiments

Water	Salinity	pH		SPM (mg L^{-1})							
Fresh water	0	8.06		374							
High salinity	33.4	8.21		38							
Sediment	POC (%)	Granularity of SPM (μm)		Main composition of SPM (%)							
				Na	Mg	Al	Si	K	Ca	Ti	Fe
Xuliujing	1.3	6.76		0.36	1.34	7.47	20.20	2.20	2.70	0.30	4.01

Table 2 Concentration of five trace metals for SPM in the Changjiang River (mg kg^{-1})

Time of survey	Cu	Zn	Cd	Co	Ni	Reference
1980–06	68	100	–	24	84	Li et al. (1984)
1981–08	71	115	–	25	72	Li et al. (1984)
1980–06 to 11	45.6	123	0.33	19.5	–	Qu et al. (1984)
1980–1984	48	182	0.33	–	–	Qu and Yan (1990)
1984–09 to 10	62.3	–	0.32	–	124	Zhang et al. (1990)
1986–01	46.9	–	0.60	–	52	Zhang and Ying (1996)
1986–06 to 07	40.0	–	0.73	–	50	Zhang and Ying (1996)
1987–10	50.3	94.3	0.28	25.9	52	Zhang and Ying (1996)
1988–09 to 10	60.7	92.7	0.44	32.4	64	Zhang et al. (1999)
2001–07	56.4	87.3	0.45	29	77	This study
2001–11	62.3	94.1	0.37	24	65	This study
2002–05	59.1	92.3	0.48	28	71	This study
Average	56	109	0.43	26	71	
Standard deviation	±9.6	±29.7	±0.14	±3.8	±21.7	

Table 3 pH, SPM, and metal concentrations in suspensions for desorption and adsorption experiments

	Equilibrium pH	SPM (mg/L)	Mental concentration in series I (mg L^{-1})					Mental concentration inseries II (mg L^{-1})				
			Cu	Zn	Cd	Co	Ni	Cu	Zn	Cd	Co	Ni
Adsorption	8.07 ± 0.17	442 ± 13	1.57	1.46	1.50	1.42	1.64	3.24	3.18	3.27	3.08	3.11
Desorption	8.07 ± 0.2	442 ± 13	1.62	1.71	1.47	1.50	1.70	3.40	3.22	3.19	2.99	3.28

with HNO$_3$ to pH < 2, and sediment obtained after centrifuging was added to 5-mL HNO$_3$ (4 M) to rinse the adsorbed metal ions. We then used ICP-AES to analyze the amounts of dissolved and adsorbed metal concentrations.

Batch sorption experiments

Batches of water samples with various SPM concentrations, from 86 ± 2 to 1,033 ± 30 mg L^{-1} (typical SPM concentrations in the Changjiang Estuary) were prepared. The samples were shaken thoroughly to achieve the homogeneity as much as possible, and then 100-mL aliquots of the sample were transferred to the polyethylene bottles. The metal solution was added to these bottles to increase the resulting metal concentrations to 1.12–8.23 mg L^{-1}. A high concentration was deliberately made

in order to eliminate the contamination effects, which might arise from handling of samples. The pH of the water sample was adjusted with HCl (0.05 M) and NaOH (0.05 M) solution to 5.0–9.0 to simulate the in situ condition in estuary.

These sample bottles were capped and sealed in plastic bags. They underwent constant stirring at 25 ± 1°C, in the temperature-controlled agitator (Model: HZ-9211K) until the predetermined time. A total of 50-mL aliquots of the sample were transferred into centrifugal tubes and centrifuged at 3,000 rev./min for fifteen minutes to separate the liquid and solid phase metals. The dissolved and adsorbed metals contents were analyzed subsequently as described in the kinetic equilibrium experimental section.

The effect of salinity on the sorption behavior of metals were carried out using East China seawater, Xuliujing

water, and their mixtures (S = 3.3, 9.9, 23.1). An aliquot of the sediment slurry was then added to each reactor, such that the resulting SPM concentrations (SPM = 300 ± 9 mg L^{-1}) were typical of those encountered in Changjiang Estuary.

Desorption experiments were carried out by placing the particles in 50 mL water parcels in the centrifuge tubes. Particles resulted from the previous sorption experiments were utilized for the desorption experiments. Particles were allowed to contact with water for 40 h by mechanically shaking the tubes, and then the tubes were centrifuge to separate the liquid and solid phases. The metal concentrations in liquid phases were determined subsequently. The desorbed trace metals, i.e. present in the dissolved phase, were determined (Table 3).

Sample analysis

Particles size was measured by COUNTER-LS (Model: LS 100Q).

Adsorbed metals were determined by ICP-AES (Model: Plasma 2000, Perkin Elmer) after being rinsed SPM using 4 M HNO$_3$ for 3 h (Wu et al. 1997), and metals in the solution separated from the SPM were also determined directly by ICP-AES (Model: Plasma 2000, Perkin Elmer). Each experiment was carried out in triplicate. The standard deviation of metal concentrations from the independent triplicate experiments were usually within 5% of the mean.

Plastic bottles, burettes, and centrifugal tubes and laboratory wares for sample collection and analysis were washed with hot detergent and rinsed with distilled water. And then, they were immersed in HNO$_3$ (1:4) for at least 1–2 weeks and underwent a 1-day soak in Milli-Q water followed by rinsing in Milli-Q water and drying in a laminar-flow clean hood prior to their use.

Results

Kinetic equilibrium time

The adsorption characteristics of metals studied with SPM concentration of 224 mg L^{-1} and pH of 8.06 were followed with time. The duration of metal to reach its asymptotic value of adsorbed density (mg Metal g^{-1} of SPM) was found to be less than 5 h for Cu, 20 h for Zn, Co, and Ni, 40 h for Cd (Fig. 2). Therefore, the duration of the subsequent kinetic experiments were maintained over 40 h in order to ensure for all the five metals studied to be reach their equilibrium with respect to SPM.

Generally, in this batch experiments, the recovery of the metals was less than 100% in the system. Wilson et al. (2001) demonstrated that the sorption of the metals onto
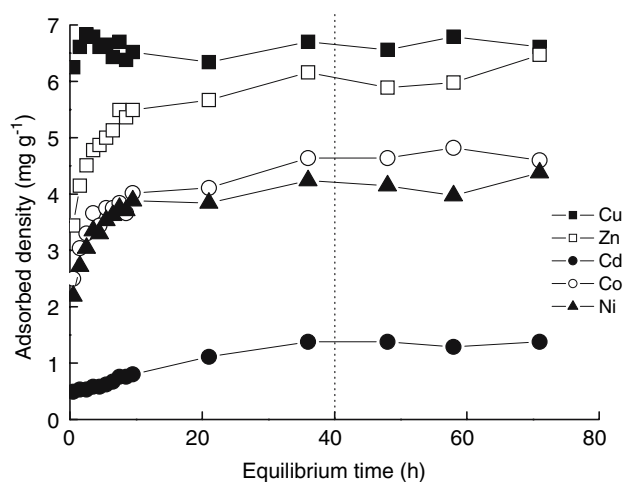

Fig. 2 Adsorption kinetic curves of five metals (Cu, Zn, Cd, Co and Ni) on to SPM (pH = 8.05, SPM = 224 mg L^{-1}, T_m = 1.5 mg L^{-1}). *Vertical bars* represent standard error of the mean (n = 3)

the container wall should be recognized, even if the container made of hydrophobic materials. Hence, the percentage adsorption in this study can be defined as

$$E(\%) = \frac{[M]_{\text{Ads}}}{[M]_{\text{Ads}} + [M]_{\text{Dis}}} \times 100\% \qquad (1)$$

where E (%) is the percentage of adsorption, $[M]_{\text{Ads}}$ is the concentration of adsorbed metals, and $[M]_{\text{Dis}}$ is the concentration of dissolved metals at sorption equilibrium.

Adsorption kinetics

The adsorption–desorption behavior of the metals onto SPM was investigated in terms of pH, SPM, salinity, and metal concentrations and experimental results are presented in Figs. 3, 4, 5, 6, 7, 8. Adsorption edges for metal adsorption on to SPM in different conditions illustrated the sigmoid character. Among the environmental variables, pH for the samples from the Changjiang Estuary exerted a significant effect on the solid–liquid partition of the trace metals (Fig. 3). The percentage adsorption (%) of the five metals in the experiments increased significantly as pH increased and at a given pH, it decreased as the concentration of SPM increases.

The percentage adsorption of trace metals in the Changjiang Estuary decreased with increasing concentrations of trace metals in solution (Fig. 8). The adsorption of the trace metals onto SPM followed the order Cu > Zn > Co > Ni > Cd. The amount of metal adsorbed was inversely related to metal loadings for all studied metals. The proportion of adsorption, however, varied among metals. A decrease in adsorption with an increase in metal concentration was obviously observed for Co and Ni. At pH of

Fig. 3 Adsorption edges for Cu, Zn, Cd, Co, Ni (T_{Cu}: 0.94 ± 0.06 mg L^{-1}, T_{Zn}: 0.93 ± 0.043 mg L^{-1}, T_{Cd}: 0.98 ± 0.03 mg L^{-1}, T_{Co}: 0.90 ± 0.08 mg L^{-1}, T_{Ni}: 0.97 ± 0.04 mg L^{-1}) onto SPM in freshwater. The range of pH between *dotted lines* in the graph is the range of pH in Changjiang Estuary. *Vertical bars* represent standard error of the mean ($n = 3$)
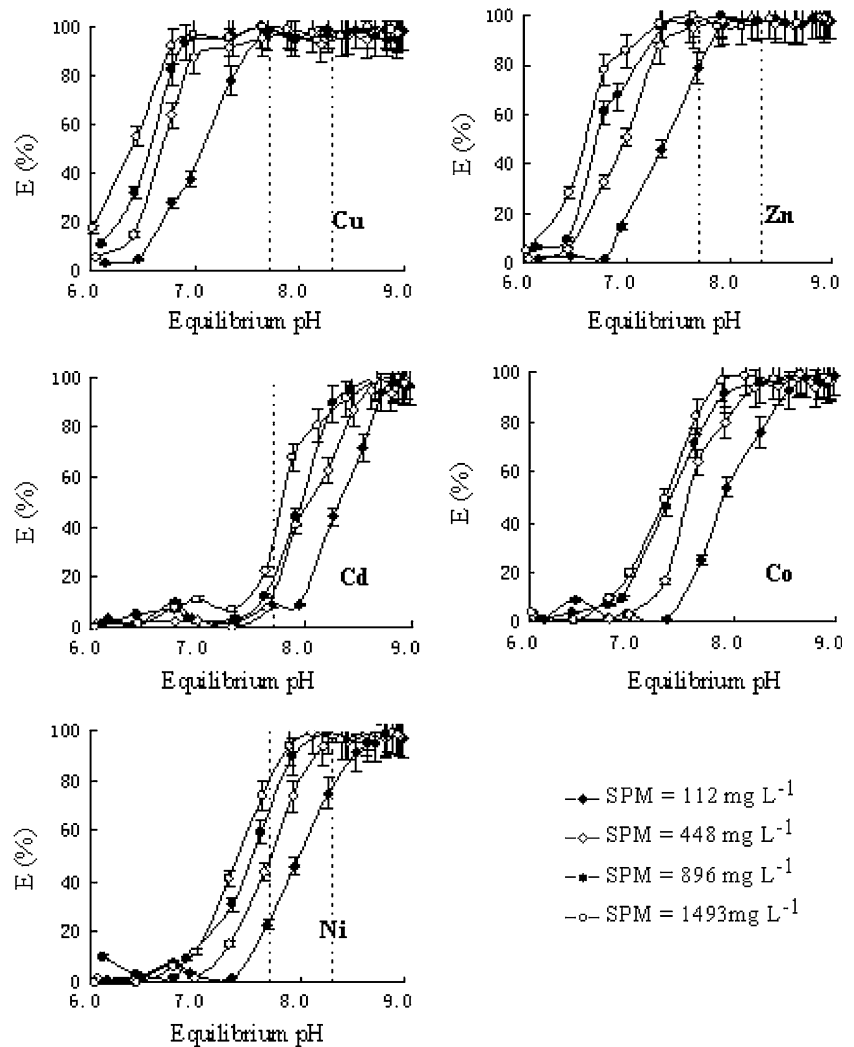
7.6–8.3 (typical values in the Changjiang Estuary), the percentage of adsorption for Co and Ni decreased from 90 to 40%, while Cd decreased from 80 to 40% with initial concentrations of 1–8 mg L^{-1}.

Adsorption of Cu, Zn, Co, Ni, and Cd onto suspended particles (Fig. 4) was considerably reduced as salinity increase. In the experiment, the value of the equilibrium pH increased as salinity increased.

Desorption kinetics

The desorption behavior of metals adsorbed onto SPM in seawater was investigated with respect to the salinity change (Fig. 5). Percent desorption and percent residual adsorption (the percent of dissolved metals after sorption in the system) metal-specific and a function of salinity. Percent desorption and percent residual adsorption could be defined as

$$\% \text{ Desorption} = \frac{[M]_{\text{Des}}}{[M]_{\text{Ads}}} \times 100\% \qquad (2)$$

and

$$\% \text{ Residual adsorption} = \frac{[M]_{\text{Dis}}}{[M]_{\text{Ads}} + [M]_{\text{Dis}}} \times 100\% \qquad (3)$$

For these metals, desorption was higher in seawater than in fresh water. A sharp increase in percent desorption with an increase in salinity was obviously observed in low salinity ($S < 10$) water. However, changes of percent desorption varied little in high salinity ($S > 10$) water. The amount of metal released increased with an increase in metal concentration was previously observed for Cu, Zn, and Cd in high salinity water. We also found that percent residual adsorption was higher than the percent desorption.

Fig. 4 Adsorption edges for Cu, Zn, Cd, Co and Ni ($T_{Cu} = 1.47$ mg L^{-1}, $T_{Zn} = 1.48$ mg L^{-1}, $T_{Cd} = 1.51$ mg L^{-1}, $T_{Co} = 1.42$ mg L^{-1}, $T_{Ni} = 1.53$ mg L^{-1}) on to suspended particulate matter (SPM = 300 ± 9 mg L^{-1}) in salinity water and freshwater. *Vertical bars* represent standard error of the mean ($n = 3$)
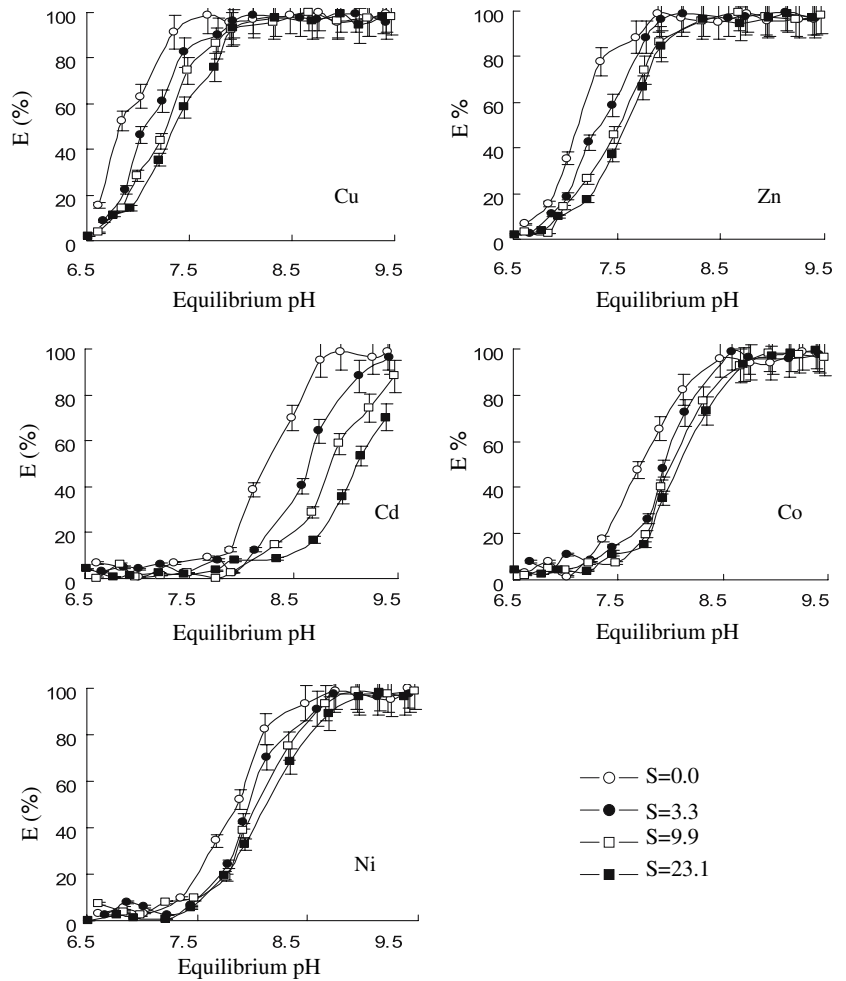
Adsorption model of trace metals

The Kurbatov adsorption model (Kurbatov et al. 1951) was utilized assuming a reversible exchange of the active group of SPM with metal ions in the aqueous solution to simulate the absorption/desorption behavior of trace metals in relation to environmental factors. The derivation of the model is given in the Appendix. This relationship among adsorption percentage and environmental variables can be obtained from,

$$E(\%) = \frac{10^{\left\{x\cdot\left[pH_{eq}-pH_{1/2}\right]\right\}}}{1 + 10^{\left\{x\cdot\left[pH_{eq}-pH_{1/2}\right]\right\}}} \times 100\% \tag{4}$$

$$
\begin{aligned}
x &= X_{SPM}\cdot\log(SPM) + X_S\cdot\log(S+1)\\
&\quad + X_{T_{Me}}\cdot\log(T_{Me}) + X\\
pH_{1/2} &= P_{SPM}\cdot\log(SPM) + P_S\cdot\log(S+1)\\
&\quad + P_{T_{Me}}\cdot\log(T_{Me}) + P
\end{aligned}
\tag{5}
$$

where experiential parameters X_{SPM}, X_S, and $X_{T_{Me}}$ are slopes of data x differing against $\log(SPM)$, $\log(S+1)$, and

$\log(T_{Me})$ respectively. In Fig. 11, P_{SPM}, P_S, and $P_{T_{Me}}$ represent slopes of $pH_{1/2}$ (i.e. pH of 50% uptake) changed with $\log(SPM)$, $\log(S+1)$, and $\log(T_{Me})$.

Discussion

Effect of pH

The observed metal uptake behavior onto SPM with respect to pH variation of water is qualitatively similar to that of particles whose surface characteristics is more simpler than estuarine SPM, such as metal oxides (Dzombak and Morel 1990), therefore the interaction of dissolved metals with deprotonated sites on the surfaces of the SPM may be described in similar fashion. Adsorption increases sharply within a narrow range of pH from 6 to 7 for Cu, 6 to 8 for Zn and Zn, and 7.6 to 8.0 for Cd, 7 to 8 for Ni and relatively invariant with pH changes for the rest of pH range of 6 to 9 in our mixing experiment. A sharp gradient was observed within less than 2 pH unit (i.e. $\Delta pH = 1$–2) (Fig. 3). Since the pH in the Changjiang Estuary is 7.7–8.3,

Fig. 5 The percentage of Cu, Zn, Cd, Co, and Ni adsorbed and desorbed in solution (pH = 8.0 ± 0.1) as a function of salinity for SPM loading of 442 ± 13 mg L^{-1}. Concentrations of trace metals were T_{Cu} = 1.57 mg L^{-1}, T_{Zn} = 1.46 mg L^{-1}, T_{Cd} = 1.50 mg L^{-1}, T_{Co} = 1.42 mg L^{-1}, T_{Ni} = 1.64 mg L^{-1} and T_{Cu} = 3.24 mg L^{-1}, T_{Zn} = 3.18 mg L^{-1}, T_{Cd} = 3.27 mg L^{-1}, T_{Co} = 3.08 mg L^{-1}, T_{Ni} = 3.11 mg L^{-1} in series I and II, respectively. *Vertical bars* represent standard error of the mean (n = 3)
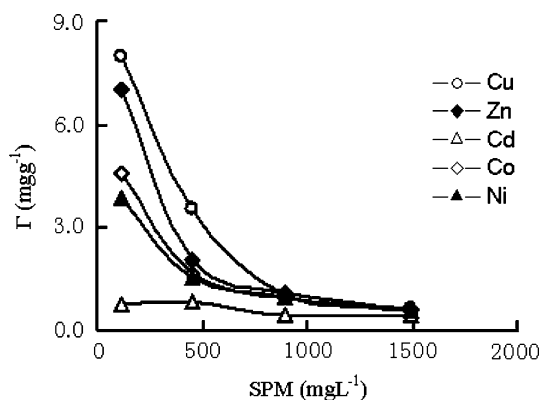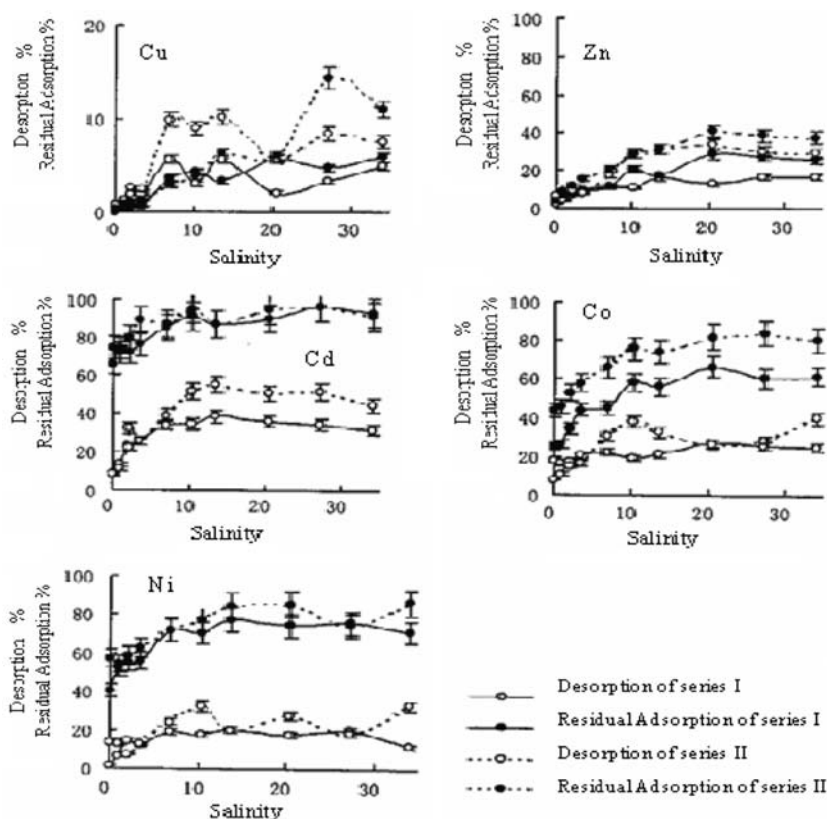

Fig. 6 Adsorption densities in solution (S = 0.0; pH = 8.0 ± 0.1) as a function of SPM loadings

Cd, Co, and Ni adsorption are likely to significant relative to that of Cu in Changjiang Estuary.

Cu and Cd are adsorbed considerably in the low pH range. The Cu adsorption is almost complete at pH 5.0–7.0 and Cd adsorption is almost complete at pH 7.0–8.5 as occurred on Fe oxides particles (Chen 1986). The adsorption of Cu and Cd reached its asymptotic value up to 7.8 and 9.0, respectively, at pH 6.0–8.0 and Cd adsorption is almost complete at pH 7.5–9.0 (Table 4). The organic components of the SPM surface may contribute to the extended adsorption in the higher end of pH,

since SPM from the Changjiang Estuary is heterogenic in composition, and is made up of inorganic particles and organic detritus (Li et al. 2001). It has been suggested that surface species are responsible for promoting sorption (Hatje et al. 2003).

Distribution coefficient K_d and adsorption density

Our batch experiments showed that the increase in SPM concentration also increases the percent adsorption of the metals onto SPM (Fig. 3), whereas adsorption density Γ (i.e. mass of adsorbate per unit SPM) decreases with an increase in SPM loading in a given solution (Fig. 6).

The use of distribution coefficients (K_d) is a useful parameter for describing solid–solution interactions. The K_d is calculated as below:

$$K_d = \frac{10^6 \cdot [M]_{Ads}}{[SPM] \cdot [M]_{Res}} = \frac{10^3 \cdot C_p}{C_w} \tag{6}$$

where $[M]_{Ads}$ and $[M]_{Res}$ are the concentrations of adsorbed metal and dissolved metals at equilibrium of sorption (mg L^{-1}), [SPM] is the concentration of SPM (mg L^{-1}), C_p is the concentration of particle trace metals (mg g^{-1}), and C_w is the dissolved metals in solution (mg L^{-1}). K_d is a conditional constant that is easily implemented within a modeling framework (Hatje et al. 2003).

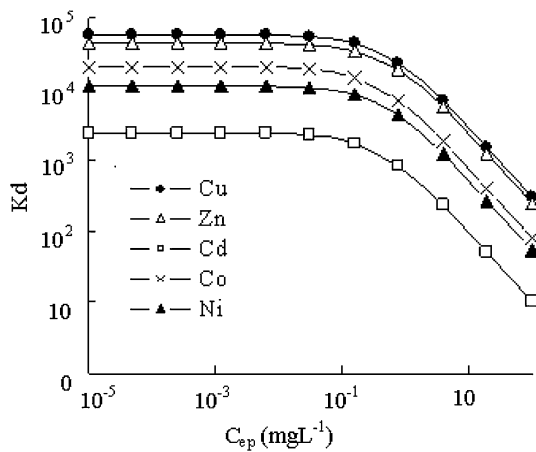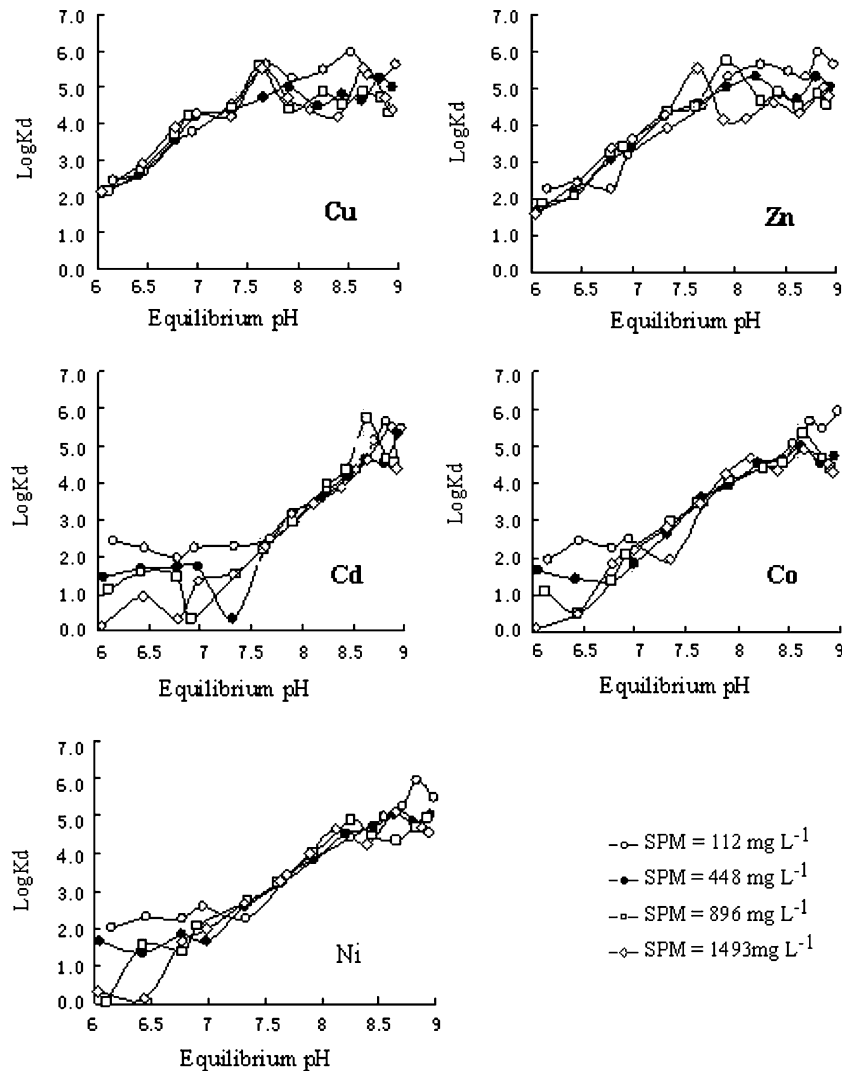**Fig. 7** Distribution coefficient (log K_d) as a function of pH

Fig. 8 Distribution coefficient as a function of dissolved metal

Table 4 Sudden increase adsorption of the five metals on to SPM at pH range

Metal	Xuliujing	
	ΔpH	ΔE
Cu	6.0–8.0	>90
Zn	6.0–8.0	>80
Cd	7.5–9.0	10–80
Co	7.0–8.5	20–100
Ni	7.0–8.5	20–100

ΔpH is the region of pH corresponding to the percentage adsorption of heavy metals jump from 10 to 90%; ΔE is the region of the percentage adsorption corresponding to the change of pH

Variations in K_d with pH for each of the elements in different SPM loadings in our experiment were shown in Fig. 7. Although K_d has been suggested to be dependent on

SPM concentration, i.e., it decreases with higher concentrations of SPM (Benoit et al. 1994; Wen et al. 1999). This phenomenon did not occur in our adsorption experiments. K_d is dependant on pH, but independent of SPM loading. This is in agreement with the findings of Mouchel and

Martin ([1990]). The origin of the particle concentration effect is the subject of controversy, but it may be related to the existence of colloidal forms of metals (Honeyman and Santschi, [1989]). Colloids are included with the filtrate fraction when 0.45 μm pore-sized filter is used to separate the dissolved and particulate fractions. If the concentrations of colloids increase in proportion to the quantity of SPM, then a decrease in the apparent partition coefficient with increasing SPM is expected.

Adsorption density (Γ) can be expressed by Langmuir equation:

$$\Gamma = \Gamma_0 \frac{kC_{eq}}{1 + kC_{eq}} \qquad (7)$$

where Γ_0 is the maximum of Γ, C_{eq} stands for the equilibrium concentration of metal in solution, and k is the equilibrium constant of adsorption.

Combining Eqs. (6) and (7), K_d can be rewritten as

$$K_d = \frac{10^3 \cdot \Gamma}{C_{ep}} = \frac{10^3 \cdot k \cdot \Gamma_0}{1 + kC_{ep}} \qquad (8)$$

The sensitivity of K_d with the variation of dissolved metal concentrations were computed according to Eq. (8) in Fig. 8. K_d values were observed to be invariable in the lower C_{eq} (<0.1 mg L^{-1}), however they decreases in higher C_{eq}. The concentration of metals in the Changjiang Estuary is far below 0.1 mg L^{-1}, thus the variation in trace metal concentration and SPM concentration barely influences the K_d, if the pH and salinity (ionic strength) in the estuary are constant.

K_d values in the large would rivers are relatively invariable (Table 5) further shows that concentrations of trace metals are controlled by SPM concentration.

Irreversibility of adsorption–desorption

It is well known that the concept of kinetic reversibility/ irreversibility is different from the thermodynamic revers-

ibility concept. A thermodynamically reversible process is characterized by an infinitesimal resulting rate and infinitesimal deviation of the system from equilibrium. In experiments on the adsorption of metals, it seems rather impossible to meet these requirements; the adsorption of metals at solid or liquid interfaces is in many cases kinetically irreversible. The extent of adsorption is smaller in seawater compared to freshwater (Fig. 4). This difference is probably due to competition of major seawater ions (particularly Ca^{2+} and Mg^{2+}) with metals for active sites on the particles. In the Changjiang Estuary, desorption of trace metals from SPM in seawater increases with higher salinity, and desorption occurs mainly in low salinity ($S < 10$) water. However, the percentage of residual adsorption is dramatically higher than that of desorption, especially in high salinity water (Fig. 5). The distribution of trace metals between solid and liquid phase is irreversible in the Changjiang Estuary. Sorption hysteresis (It is a history-dependent character of the adsorbate accommodation in random nanoporous structures may result from a rugged free energy landscape with many local minima separated by free energy barriers.) may be existing in the system, and the release of trace metals from the seawater particles is limited. The amount of metal released is related to metal concentration, which implies that when SPM with higher amounts metals enters the estuary, it can release more metals into the high salinity water. The irreversibility of adsorption–desorption demonstrates that the distribution of heavy metals between solid–liquid in the Changjiang Estuary is not only controlled by thermodynamics but also controlled by actual factors in dynamics. Several processes can be proposed to explain the irreversible migration of metals into the solid lattice (the incorporation of metals into the mineral lattice would be out of scope of the current manuscript or expand substantially in order to stand alone): sorption on high energy binding sites, formation of stable associations with organic compounds, intraparticle diffusion, oxidation, precipitation, and ageing of oxides which then become more refractory (e.g. Payne et al. [1994]; Trivedi and Axe [2000]).

Table 5 Distribution coefficients (log K_d) for trace metals in some large world river

River	Cu	Zn	Cd	Co	Ni	Reference
Changjiang	4.33–4.49		5.09–5.23			Huang and Zhang (1994)
Huanghe	4.04–4.40	5.02–5.98	4.90–5.99	5.53–6.29	4.76–5.16	Zhang et al. (1990)
Minjiang	4.52		5.16			Lin et al. (1989)
Jiulongjiang	4.69	5.66	5.20	6.64	5.99	Li et al. (1988)
Mississippi	4.15–4.27		4.60–4.98		4.35–4.69	Trefry et al. (1986)
St. Lawrene	4.53	4.60	4.09	4.95	4.43	Yeats and Bewers (1982)
Nile	5.15–5.25					Abdel-Moati (1990)

Application of the model

The concentration of trace metals in SPM in the Changjiang Estuary has been relatively invariable for the last 2 decades (Table 2). The average metal concentrations were used as the model concentration of particle trace metals in our model. When the concentration of particle trace metals is very low, K_d values will obtained constantly (It could be calculated by Eq. (8), in "Distribution coefficient Kd and adsorption density" section). The typical range of concentration of SPM in the Changjiang Estuary is 100–1,000 mg L^{-1} and the concentration of the five trace metals is very low. The effect of the concentration of trace metals can be ignored in the model.

The concentration of trace metals in the Changjiang Estuary can be considered as

$$C_w = C_{dil} + C_{s-l} \qquad (9)$$

which becomes

$$C_w = C_{riv} + \frac{S \cdot (C_{sea} - C_{riv})}{S_0} \qquad (10)$$

where C_w is the concentration of trace metals in the Changjiang Estuary (µg L^{-1}), C_{dil} is the concentration of trace metals calculated according to the theoretical dilution line (µg L^{-1}) (Liss and Pointon 1973), C_{s-l} is the concentration of trace metals adsorbed onto SPM (µg L^{-1}), C_{riv} is the concentration of trace metals in the river end-member (µg L^{-1}), C_{sea} is the concentration of dissolved trace metals in the sea (µg L^{-1}), S is the salinity of waters, and S_0 is the salinity gradient of East China seawater.

Studies of particle trace metal formation show that the exchangeable form occupies 1.6–24% of the particle form and the sum of the exchangeable form and the oxyhydrogen form occupy 4.3–57% of the particle form (Zhang et al. 1990). Hence, we suppose that 25% of particles can effectively participate in the solid–liquid interphase action (The oxyhydrogen forms could be exchanged by metal ions, 25% is the largest occupy percent of the exchangeable and the mean of occupy percent of the sum of the exchangeable and oxyhydrogen forms, so we suppose that 25% should be useful for model prediction.). Therefore, the concentration of trace metal controlled by adsorption–desorption can be written as

$$C_{s-l} = 0.25 \times 10^{-3} \times [\text{SPM}] \cdot C_P \cdot (1 - E) \qquad (11)$$

$$x = X_{SPM} \cdot \log(\text{SPM}) + X_S \cdot \log(S+1) + X$$
$$\text{pH}_{1/2} = P_{SPM} \cdot \log(\text{SPM}) + P_S \cdot \log(S+1) + P \qquad (12)$$

$$E(\%) = \frac{10^{\{x \cdot [\text{pH} - \text{pH}_{1/2}]\}}}{1 + 10^{\{x \cdot [\text{pH} - \text{pH}_{1/2}]\}}} \times 100\% \qquad (13)$$

According to Eq. (11), input variables of SPM, Salinity, and pH (Table 6) are only required to simulate concentration of dissolved trace metals in estuary, if the source of metals can be assumed to be the river only. These variables were measured during a 2001 cruise in the Changjiang Estuary (Zhang and Zhang 2003).

Table 6 The parameters of SPM, salinity and pH input to model

S	SPM (mg L^{-1})	pH	S	SPM (mg L^{-1})	pH	S	SPM (mg L^{-1})	pH	S	SPM (mg L^{-1})	pH	S	SPM (mg L^{-1})	pH	S	SPM (mg L^{-1})	pH
0.03	176	7.90	0.05	135	7.73	0.05	145	8.13	0.05	128	7.82	0.14	159	8.15	9.21	96	7.91
0.03	2017	7.72	0.05	121	8.15	0.05	122	8.18	0.05	198	7.93	0.15	1019	8.15	9.86	484	8.09
0.04	374	8.17	0.05	124	8.19	0.05	81	8.19	0.05	121	8.18	0.15	173	8.19	11.94	73	7.76
0.04	99	8.18	0.05	163	8.16	0.05	137	8.18	0.05	136	8.21	0.20	214	8.22	13.21	33	8.04
0.04	308	7.87	0.05	131	8.13	0.05	112	8.12	0.05	199	8.08	0.21	645	7.89	13.73	269	8.03
0.04	143	8.19	0.05	183	8.16	0.05	258	8.14	0.06	349	8.17	0.21	352	8.13	14.29	22	8.04
0.04	259	8.18	0.05	311	8.13	0.05	161	8.09	0.07	429	8.14	0.21	250	7.80	15.73	66	7.85
0.04	73	8.00	0.05	344	8.19	0.05	117	8.19	0.07	69	8.14	0.25	166	8.19	15.80	848	7.96
0.05	285	8.10	0.05	245	8.17	0.05	113	8.18	0.11	56	8.08	0.32	181	8.14	15.87	120	7.77
0.05	68	8.20	0.05	63	8.22	0.05	198	7.89	0.11	174	8.16	0.40	425	7.90	16.35	2125	8.02
0.05	149	8.19	0.05	52	8.13	0.05	183	8.17	0.11	184	8.19	0.49	335	8.16	17.19	89	8.02
0.05	232	8.19	0.05	131	8.20	0.05	94	8.15	0.12	496	8.20	0.54	921	7.83	18.17	1098	7.90
0.05	96	8.18	0.05	166	7.87	0.05	65	8.17	0.12	31	8.12	1.01	223	8.29	18.30	401	8.02
0.05	81	8.14	0.05	70	8.16	0.05	59	8.13	0.13	328	8.16	2.40	628	8.11	20.91	199	7.84
0.05	388	8.19	0.05	145	8.15	0.05	129	8.11	0.13	319	8.01	3.35	312	7.83	24.17	634	7.80
0.05	256	8.19	0.05	119	8.19	0.05	329	7.93	0.14	295	8.14	4.53	705	8.10	29.34	207	7.85

Fig. 9 Concentration of dissolved trace metals in the Changjiang Estuary. The data in the figure are from the literature (Edmond et al. 1985; Chen 1986; Wang KS et al. 1990; Wang ZF et al. 1990; Elbaz-Poulichet et al. 1987 and Elbaz-Poulichet et al. 1990)
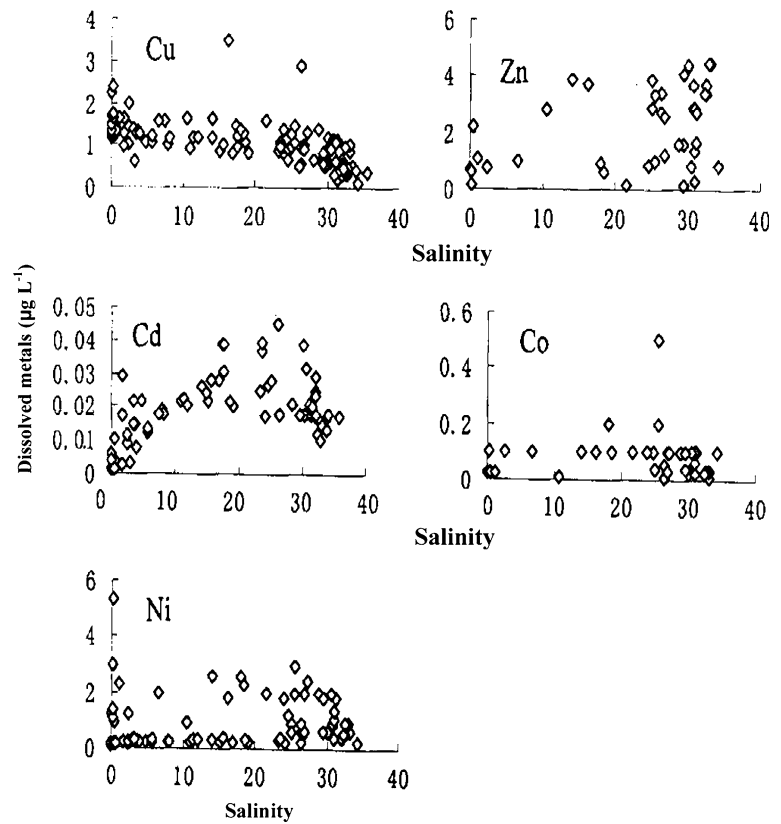
The concentrations of the dissolved metals are in Fig. 9. Figure 10 shows the comparison between simulation and reference in situ concentrations (Edmond et al. 1985; Chen 1986; Elbaz-Poulichet et al. 1987; Wang et al. 1990a, b; Elbaz-Poulichet et al. 1990).

We found that the simulation results are in good agreement with the observed data, Cu and Ni in some extent. However, Zn, Co, and Cd are not. The good agreement between model and in situ concentration of Cu appears to be due to the conservative nature of Cu in estuary (Fig. 9). The results from the simulation and reference are similar, which indicates that the concentration of dissolved Cu is controlled by the effect of adsorption–desorption onto SPM in the fresh-saline water mixing process. In the observed data, when the salinity values exceed 30, the concentration of dissolved Cu decreases, presumably because of biological uptake as a micronutrient (Stumm and Morgan 1996), or through combining with organic material (Tang et al. 2002).

The simulation result shows concentration of dissolved Zn is as the linear function of salinity. When the salinity is <20, the two results between the simulation and the observed are in accord, that is, sorption is the main factor controlling the dissolved Zn in the Changjiang Estuary. When the salinity exceeds 20, there exists a deviation between the two results. It may be caused by biological

uptake or another complex process (e.g. oxidation–reduction action) (Zwolsman and van Eck 1999).

Model simulation results are higher than observed data. This may be because we supposed 25% of particles can effectively participate in the solid–liquid interphase action, and the 25% is high for Cd. Dissolved Cd is mainly in the result of rock weathering and the percentage of active Cd is very low (Nriagu and Pacyna 1988). However, the simulation results demonstrate that Cd is released from SPM in a salinity range of 0–30. It is probably only exchangeable Cd that is released due to complexation with chloride (Hatje et al. 2003), which means that although the inorganic Cd speciation in seawater is dominated by chlorocomplexes, Cl^- is only partly responsible for desorption of Cd. The much higher concentration of Ca^{2+} and Mg^{2+} in seawater compared 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 (Hatje et al. 2003; Paalman et al. 1999).

We also found that in the simulation Co and Ni were released to the dissolved phase. Ni is remobilized in the lower salinity ($S < 5$) water, which is consistent with simulation experiments (Edmond et al. 1985; Chen 1986).

The estimated similarities and differences between simulation results and observed results is expected based on the influence of SPM, salinity, and pH on the dissolved

Fig. 10 The comparison between simulation results and reference results. According to the data, the range of salinity (0–30) was divided into six sections: 0–1, 1–2, 2–4, 9–14, 15–20 and 24–29. The average and standard deviation of simulation and reference results could be calculated in each section, respectively. Using the calculated average and mean value of salinity the figure was conducted. *Vertical bars* represent standard error of the calculated average and mean value
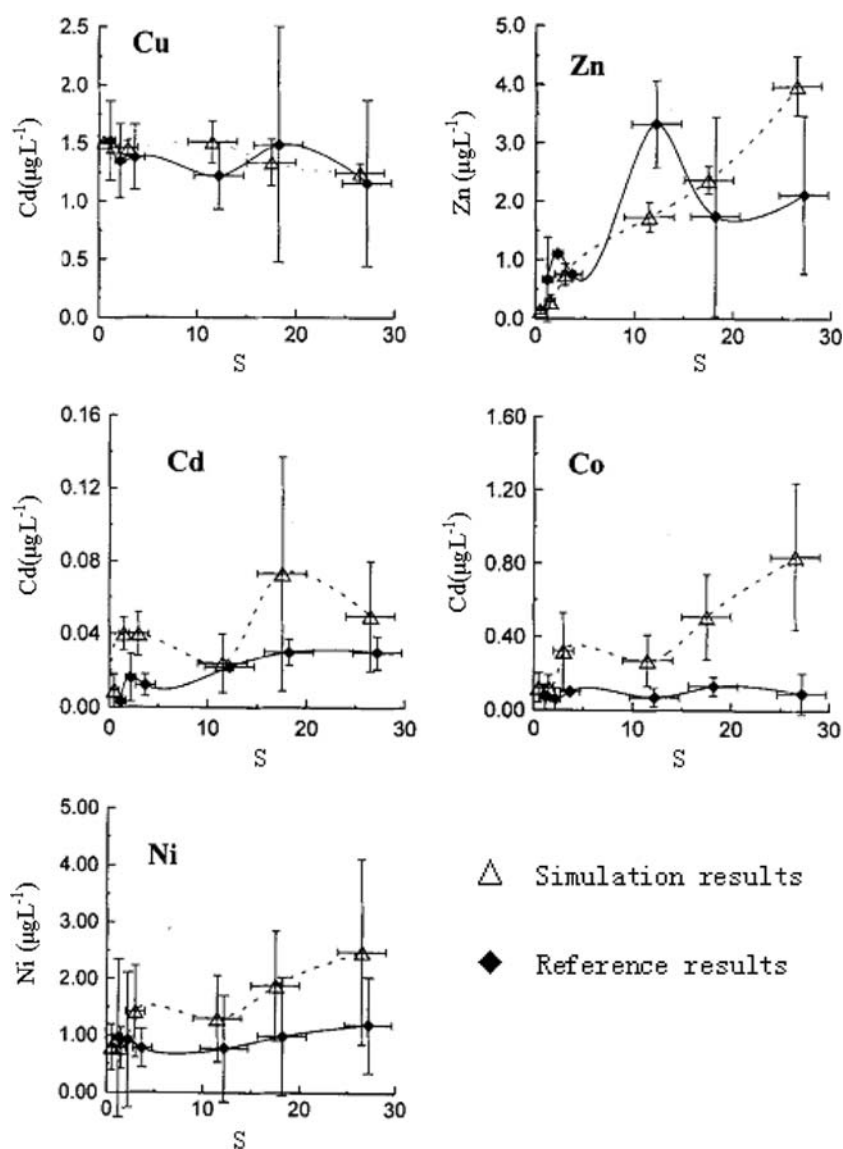
trace metals; the simulation model is a good representation of the Changjiang Estuary, especially in the high turbidity area where salinity <20.

Conclusion

The implications of kinetics of adsorption–desorption processes are most obvious under strong gradients in pH, salinity, and SPM concentrations such as those observed in estuarine mixing zones. The application of adsorption–desorption kinetic studies using batch experiments has given us valuable insight into the nature in the Changjiang Estuary.

The results showed that adsorption edges for metal adsorption to SPM under different conditions illustrate the sigmoid curve characteristic of transition metals. Changes in pH for the samples from the Changjiang Estuary have a significant effect on the solid–liquid partition of trace metals Cu, Zn, Cd, Co, and Ni. The adsorption percentage of the five metals in the experiments was increased with pH—specifically increasing the pH of the water samples induced partitioning of metals to solid phases. The percentage of the adsorption and partitioning coefficients for trace metals in the Changjiang Estuary deceased significantly with higher concentrations of elements.

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, we would expect that most of the studied trace metals (i.e. Cu, Co, Cd, Ni, and Zn) would be trapped in the estuarine environment as the metals are mostly associated with the

particulate phase in estuaries. The model developed here is in accordance with the observed distribution patterns of stable elements in the Changjiang Estuary.

Appendix

The data interpretation can be approached using the Kurbatov adsorption model (Kurbatov et al. 1951), which was initially applied to the adsorption of metals by hydrate-oxide, but later used in the adsorption of trace metals to suspended particles from natural waters (Lead et al. 1999; Wilson et al. 2001). Adsorption of metals by suspended particles could be assumed to be an exchange of the active group with metal ions (e.g. Grantza et al. 2003). Suspended particulate materials are heterogenic in composition but there exist some active groups (i.e., –OH, –COOH and –NH$_2$) on the surface of the mineral and giant organic molecules (humus) in water. These can exchange with metal ions on the surface of SPM (Wilson et al. 2001), that is,

$$\equiv S-OH_x + M \overset{K}{\leftrightarrow} \equiv S-OM + x \cdot H \qquad (14)$$
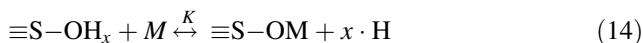
where $\equiv S-OH$ is the surface active potential of SPM in the Changjiang Estuary, M is the metal added to the simulation system, $\equiv S-OM$ is the metal adsorbed by SPM, and H is the hydrogen ion. In Eq. (2), x and K are adsorption parameters with x being the exchange coefficient and K the apparent adsorption equilibrium constant.

In Eq. (14), K could be expressed by

$$K = \frac{[\equiv S-OM] \cdot [H]^x}{[\equiv S-OH_x] \cdot [M]} \qquad (15)$$

where $[\equiv S-OM]$ is the adsorbed metal concentration (mg L^{-1}), [H] is the hydrogen ion concentration (mol L^{-1}), $[M]$ is the dissolved metal concentration (mg L^{-1}), i.e., the metal concentration at adsorption equilibrium, and $[\equiv S-OH_x]$ is the amount of surface active potential in equilibrium. The Eq. (15) can also be re-arranged as

$$\log \frac{[SOM]}{[M][SOH_x]} = x \cdot pH + \log K \qquad (16)$$

When the metal concentration is very low against particle concentration, Eq. (16) can be simplified as

$$[\equiv S-OH_x] \approx [\equiv S-OH_x]_0 = k \cdot SPM \qquad (17)$$

hence, $[\equiv S-OH_x]$ can be replaced by $(k \cdot SPM)$, and Eq. (16) becomes

$$\begin{aligned} \log \frac{[\equiv S-OM]}{[M]} &= x \cdot pH_{eq} + \log K + \log[\equiv S-OH_x] \\ &= x \cdot pH + \log K + \log \{k \cdot SPM\} \end{aligned} \qquad (18)$$

The data of the adsorption for the five metals by SPM from the sampling site can be predicted by Eq. (18), and the adsorption parameters (e.g. x and K) can be evaluated by the slope and interception of the lines and list in Table 7.

For a given SPM level, salinity, and metal concentration, Eq. (18) can be re-organized:

$$\log \frac{[\equiv S-OM]}{[M]} = x \cdot pH + \log K' \qquad (19)$$

The ratio of solid–liquid partitioning of trace metals is defined as

$$D = \frac{[\equiv S-OM]}{[M]} \qquad (20)$$

The percentage of adsorption can be also calculated by

$$E(\%) = \frac{D}{1+D} \times 100\% \qquad (21)$$

In Eq. (19), $\log \frac{[\equiv S-OM]}{[M]}$ is plotted against the pH at equilibrium in the same SPM, salinity, and metal concentration systems, respectively. The slope (x) and the interception $(\log K')$ of the plots can be obtained and the percentage adsorption E (%) can be plotted against the pH at equilibrium (Fig. 11).

The Eq. (18) can be reorganized using the ratio of solid–liquid partitioning D.

Table 7 Linear fitting results of the five metals adsorption on to SPM

| | Xuliujing ($S = 0$) | | | | |
	Cu	Zn	Cd	Co	Ni
X	2.08	1.88	2.43	1.92	2.06
log K	−16.6	−15.7	−22.2	−17.2	−18.4
γ^2	0.95	0.94	0.98	0.96	0.97
n	16	20	19	18	20

x: slope of the Eq. (18), log K: intersect of the Eq. (18), γ^2: correlation coefficient of the fitted line, n: the number of fitted data
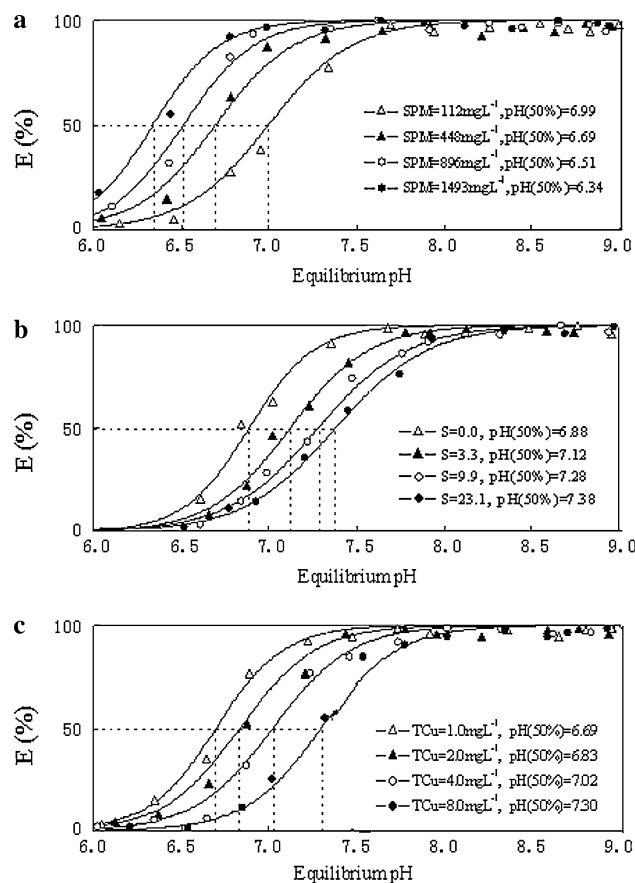
Fig. 11 Relationships between pH1/2 and SPM, salinity, and T_m (metal concentration). **a** $S = 0.0$, $T_{Cu} = 1.0$ mg L^{-1}, **b** SPM $= 300$ mg L^{-1}, $T_{Cu} = 1.5$ mg L^{-1}, **c** $S = 0.0$, SPM $= 448$ mg L^{-1}

$$pH_{eq} = -\frac{1}{x} \cdot \log \left\{ \frac{K \cdot [\equiv S-OH_x]}{D} \right\} \qquad (22)$$

When the percentage adsorption [E (%)] is equal to 50%, the pH (i.e. pH of 50% uptake) can be calculated by Eq. (22):

$$pH_{1/2} = -\frac{1}{x} \cdot \log \left\{ K \cdot [\equiv S-OH_x] \right\} \qquad (23)$$

Namely,

$$\log D = x \cdot \left(pH_{eq} - pH_{1/2} \right) \qquad (24)$$

$$E(\%) = \frac{10^{\left\{ x \cdot [pH_{eq}-pH_{1/2}] \right\}}}{1 + 10^{\left\{ x \cdot [pH_{eq}-pH_{1/2}] \right\}}} \times 100\% \qquad (25)$$

In Fig. 11, pH$_{1/2}$ increases with higher levels of SPM and salinity and the availability of dissolved metals.

The linear relationship of x and pH$_{1/2}$ against SPM, salinity, and metal concentrations are further examined in Fig. 12. In Fig. 12, the expression of SPM, salinity (S),

and metal concentrations (T) for a given system x and pH$_{1/2}$ of Cu adsorbed by SPM from Xuliujing can be written as

$$x = X_{SPM} \cdot \log(SPM) + X_S \cdot \log(S + 1)$$
$$\qquad + X_{T_{Cu}} \cdot \log(T_{Cu}) + X$$
$$pH_{1/2} = P_{SPM} \cdot \log(SPM) + P_S \cdot \log(S + 1) \qquad (26)$$
$$\qquad + P_{T_{Cu}} \cdot \log(T_{Cu}) + P$$

where experiential parameters X_{SPM}, X_S, and $X_{T_{Cu}}$ are slopes of data x compared against $\log(SPM)$, $\log(S + 1)$, and $\log(T_{Cu})$ respectively (Table 8). P_{SPM}, P_S, and $P_{T_{Cu}}$ represent slopes of pH$_{1/2}$ as affected by $\log(SPM)$, $\log(S + 1)$, and $\log(T_{Cu})$.

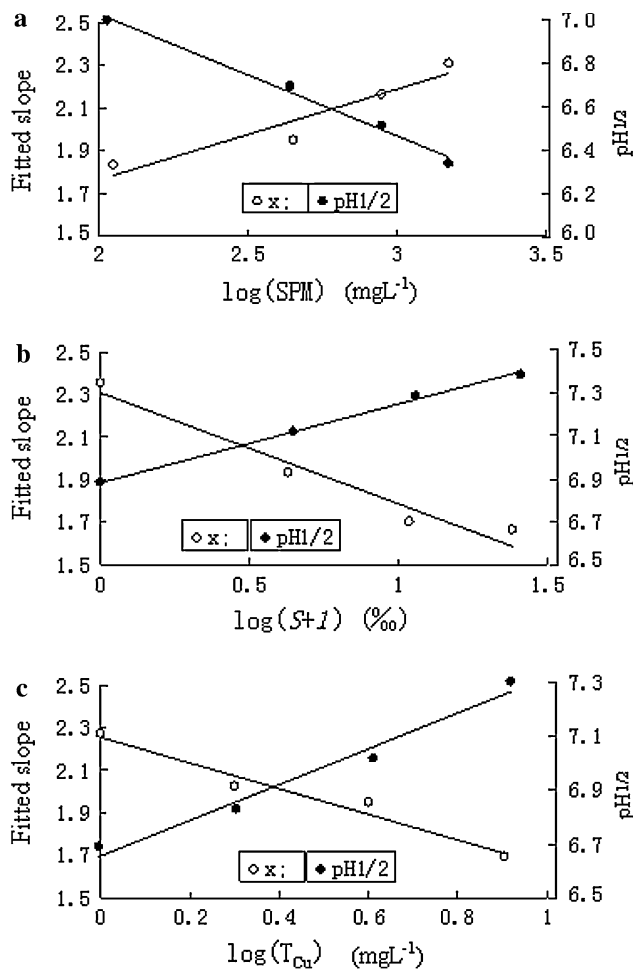Equation (27) is employed to calculate X and P:

Fig. 12 Relationships between the fitted slope, pH$_{1/2}$, and SPM, salinity, and T_m (metal concentration). **a** $S = 0.0$, $T_{Cu} = 1.0$ mg L^{-1}, **b** SPM $= 300$ mg L^{-1}, $T_{Cu} = 1.5$ mg L^{-1}, **c** $S = 0.0$, SPM $= 448$ mg L^{-1}

Table 8 The simulation parameters for five metals adsorption onto suspended sediments in the Changjiang Estuary

SPM	Metal	Parameters							
		X_{SPM}	X_S	X_{T_m}	P_{SPM}	P_S	P_{T_m}	X	P
Xuliujing	Cu	0.42	–0.52	–0.60	–0.57	0.37	0.53	1.15	8.19
	Zn	0.53	–0.48	–0.56	–0.60	0.30	0.55	0.87	8.52
	Cd	0.19	–0.86	–0.62	–0.44	0.61	0.71	2.15	9.23
	Co	0.35	–0.33	–0.62	–0.55	0.25	0.52	1.47	9.05
	Ni	0.36	–0.17	–0.78	–0.59	0.23	0.57	1.29	9.23

$$X = x - [X_{SPM} \cdot \log(SPM) + X_S \cdot \log(S+1) + X_{T_{Cu}} \cdot \log(T_{Cu})]$$
$$P = pH_{1/2} - [P_{SPM} \cdot \log(SPM) + P_S \cdot \log(S+1) + P_{T_{Cu}} \cdot \log(T_{Cu})] \quad (27)$$

All the parameters (i.e. x, $pH_{1/2}$, X_{SPM}, X_S, $X_{T_{Cu}}$, P_{SPM}, P_S, and $P_{T_{Cu}}$) of experiment can be calculated from Figs. 11 and 12. When these experiential parameters are substituted into Eq. (27), X and P can be calculated and listed in Tables 7 and 8. The average of X and P are considered as the parameters of Eq. (27).

The other metals can also be calculated as Cu is, and the experiential parameters of other metals can also be calculated according to the above equations. The values are listed in Table 8. A good fit is achieved when we input the parameters of SPM, Salinity, pH, and concentration of the metals from the batch experiments to the model. The correlation coefficients of the fitted curve γ^2 are from 0.95 to 0.99.

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