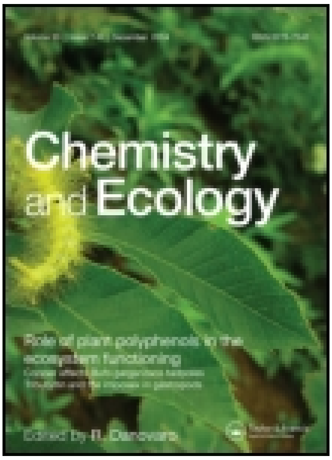

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gche20

Effects of salinity on the transformation of heavy metals in tropical estuary wetland soil

Bei Chu[ac], XiaoJiao Chen[ab], QuSheng Li[ab], YuFeng Yang[d], XiuQin Mei[ab], BaoYan He[ab], Hui Li[ab] & Ling Tan[ab]

[a] School of Environment, Jinan University, Guangzhou 510632, China

[b] Department of Education of Guangdong Province, Key Laboratory of Water/Soil Toxic Pollutants Control and Bioremediation, Guangzhou 510632, China

[c] Department of Soil, Environmental and Atmospheric Sciences, University of Missouri, Columbia, MO 65201, USA

[d] Department of Ecology, Jinan University, Guangzhou 510632, China

To cite this article: Bei Chu, XiaoJiao Chen, QuSheng Li, YuFeng Yang, XiuQin Mei, BaoYan He, Hui Li & Ling Tan (2015) Effects of salinity on the transformation of heavy metals in tropical estuary wetland soil, Chemistry and Ecology, 31:2, 186-198, DOI: 10.1080/02757540.2014.917174

To link to this article: http://dx.doi.org/10.1080/02757540.2014.917174

Chemistry and Ecology, 2015
Vol. 31, No. 2, 186–198, http://dx.doi.org/10.1080/02757540.2014.917174

Taylor & Francis
Taylor & Francis Group

Effects of salinity on the transformation of heavy metals in tropical estuary wetland soil

Bei Chu[a,c], XiaoJiao Chen[a,b], QuSheng Li[a,b]*, YuFeng Yang[d]*, XiuQin Mei[a,b], BaoYan He[a,b], Hui Li[a,b] and Ling Tan[a,b]

[a]*School of Environment, Jinan University, Guangzhou 510632, China;* [b]*Department of Education of Guangdong Province, Key Laboratory of Water/Soil Toxic Pollutants Control and Bioremediation, Guangzhou 510632, China;* [c]*Department of Soil, Environmental and Atmospheric Sciences, University of Missouri, Columbia, MO 65201, USA;* [d]*Department of Ecology, Jinan University, Guangzhou 510632, China*

(*Received 24 September 2013; final version received 18 March 2014*)

Tropical estuary wetlands are important for aquaculture and wildlife. However, many of them receive large amounts of anthropogenic heavy metals annually. Here, the transformation of spiked heavy metals, namely, Cd, Cr, Cu, Ni, Pb, and Zn, and the effects of salinity on their transformation in wetland soils after an eight-month-long incubation under moisture-saturation conditions were studied in the Pearl River estuary in China. Cd exhibited high mobility and bioavailability, with 12.2% to 25% Cd existing in the exchangeable fraction. Other heavy metals primarily existed in the reducible and oxidisable forms, and less than 2% were bound to the exchangeable fraction. Compared with the controls, contents of none of the metals associated with residual forms were significantly altered. These results imply that most exchangeable metals, except for Cd, transformed into other stable fractions through an eight-month-long ageing process, but not into the residual fraction. Thus, transformation from non-residual to residual forms was very slow in the tropical estuary wetland environment. Addition of NaCl increased the exchangeable fractions of Cd, Pb, and Zn, suggesting that increased soil salinity induced by flood tides during the dry season may enhance their mobility.

Keywords: ageing; chemical form; heavy metal; salinity effect; sequential extraction

1. Introduction

Tropical estuary wetlands are very important for aquaculture and wildlife protection. For example, as much as 6.0×10^4 ha of wetlands in the Pearl River estuary in China has been reclaimed since 1981, and many of those wetlands have been used for cultivation of aquatic crops, such as root lotus, and for aquaculture.[1] Some estuary wetlands are also habitats for many endangered aquatic animals and bird species, including national top-class protected animals such as Chinese white dolphin (*Sousa chinesis*), Chinese sturgeon (*Acipenser sinensis*), white stork (*Ciconia ciconia*), and nearly 20 other second-class protected species. Meanwhile, rapid economic growth in the Pearl River Delta region has resulted in the discharge of huge amounts of contaminants into the Pearl River. In 2010, the estuary received 2934 tons of heavy metals via direct fluvial transport by the Pearl River.[2] Sources of anthropogenic heavy metals include municipal wastewater, urban

---

*Corresponding authors. Emails: liqusheng@sina.com, tyyf@jnu.edu.cn runoff, and improperly treated industrial effluent discharge.[3] These heavy metal contaminants can harm human health, crops, and wildlife.[4,5]

Mobility and bioavailability of heavy metals have been found to depend not only on their total concentration in the environment but also on their speciation.[6] A number of environmental factors, such as pH, redox conditions, ageing, salinity, and presence of complex ligands, can affect the speciation and the fate of heavy metals in coastal estuary soils.[7,8] Generally, mobility and bioavailability of heavy metals in soils decrease with ageing of metals.[9] Ageing effects are ascribed to reactions between metal ions and the soil, which mainly include complexation, surface adsorption, exchange reactions, chelation, and precipitation of metal ions on the soil particle surface or diffusion into the mesopores and macropores of soil.[10,11] Abundant data are available on the impact of short-term (i.e., a few hours, days or weeks) and long-term (i.e., a few years or decades) ageing processes on fractionation of heavy metals spiked in soils. For example, several studies have shown that heavy metals bound to the exchangeable fraction tend to transform into other fractions within a few hours to a few weeks of incubation.[10–12] In addition, it has been reported that heavy metals in soils are predominantly bound to the residual fraction through long-term ageing processes.[13–16] However, very few studies have considered the effect of middle-term (e.g., about one year) ageing processes on transformation of heavy metals in wetland soils. Understanding such an effect is of crucial importance for risk assessment of heavy metals in estuary wetlands.

Salinity increases the mobility of heavy metals in soils.[17] For instance, high concentration of Cl^- in the soil can form stable compounds like $CdCl^+$, $CdCl_2^0$, $PbCl^+$, $PbCl_2^0$, and $PbCl_3^-$, and thereby increase Cd and Pb mobility.[18] High salinity also increases the concentrations of major cations (i.e., Na, K, Ca, and Mg) that compete with heavy metals for sorption sites of the solid phase and may result in desorption of heavy metals and promotion of their phytoavailability.[19] The Pearl River estuary wetland is significantly influenced by salinity because of tide fluctuation and seasonal variation of flow rate in the river. Saline tides can intrude landward more than fifty kilometres along the river in the dry season. However, research focusing on effects of salinity on metal fractionation in the wetland soils of this region has not been conducted to date. Therefore, the objectives of this study are (1) to examine the transformation of anthropogenic heavy metals such as Cd, Cr, Cu, Ni, Pb, and Zn at different initial concentrations in wetland soils of the Pearl River estuary after middle-term incubation, and (2) to study the effects of salinity on the fractionation of these heavy metals.

2. Materials and methods

2.1. *Soils for experiment*

Soil samples were collected from a mudflat of riparian wetland in the Pearl River estuary, southern China in the summer (wet season). The sampling area is located 40 km from Guangzhou City. Eleven sites with five replicates per site were randomly sampled to represent the wetland. The soil was saturated all the time and intermittently flooded by the saline tide in the dry season. The sampling depth was 0 cm to 20 cm from the surface. Before sampling, the soil redox potential (Eh) was determined at 10 cm depth by inserting polished platinum electrodes to the desired depth and allowing them to equilibrate for 15 min before measuring the voltage against a calomel electrode with a pH/mV-meter. Immediately after sampling, soil moisture was measured. Small portions of all soil samples were mixed together and used in the experiment to simulate the field conditions. The remaining soil samples were then air-dried, ground, and sieved through a 2 mm nylon sieve. The sieved soil was tested for chemical properties and Cd, Cr, Cu, Ni, Pb, and Zn content. The chemical properties of the soil samples were measured following the methods

Table 1. Selected soil chemical properties from the Pearl River estuary soils.

Soil properties	Values
soil redox potential (mV)	−40.3 ± 2.9
pH	6.40 ± 0.15
soil moisture (%)	57.9 ± 2.4
CEC (cmol kg^{-1})	10.11 ± 0.61
organic matter content (g kg^{-1})	66.50 ± 4.3
$CaCO_3$ content (g kg^{-1})	3.50 ± 0.13
amorphous iron oxides (g kg^{-1})	15.0 ± 0.91
salt content (g kg^{-1})	0.60 ± 0.04
concentration of AVS (mmol kg^{-1})	0.21 ± 0.02

described in [20]: soil pH and salt content were measured in a 1:5 soil–water suspension, soil cation exchange capacity was measured by the ammonium acetate method, soil organic matter content was measured by the combustion method, $CaCO_3$ content was measured by the gasometric method, and amorphous iron oxide content was measured by the ammonium oxalate extraction method. Analyses of acid-volatile sulfide (AVS) concentrations in soils were done by the cold-acid purge-and-trap method described in [21]. AVS recovery of the experimental procedure was checked using sodium sulfide solution with a known concentration and was found to be greater than 90%. Selected soil properties are listed in Table 1.

2.2. *Experiment design*

An orthogonal experiment design was conducted using six salinity levels and five heavy metal concentration levels. Each salinity treatment group includes five heavy metal concentration levels. The salinity treatment groups were 0 g/kg, 2 g/kg, 4 g/kg, 6 g/kg, 8 g/kg, and 10 g/kg. Since NaCl is the major component of wetland salinity, NaCl was used instead of seawater for salinity treatment. Five initial heavy metal concentration levels were selected: control (CT), concentration1 (C1), concentration 2 (C2), concentration 3 (C3), and concentration 4 (C4). Each treatment and control was replicated three times. The initial concentrations for each metal are listed in Table 2. These concentrations were selected to cover the possible concentration ranges occurring in the studied area. The following salts were added: $CuSO_4$, $Zn(NO_3)_2 \cdot 6H_2O$, $Pb(AcO)_2 \cdot 3H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $K_2Cr_2O_7$, and $3CdSO_4 \cdot 8H_2O$. Two and a half kilograms of soil were placed in a glass vessel, and appropriate amounts of heavy metals and NaCl were added to achieve the desired metal and salt concentrations. The soil and the solution in the vessel were thoroughly mixed. The recipient was open to the air, and deionised water was added periodically to keep the soil saturated. The vessels were kept at room temperature. Eight months later, the soils were collected again to determine fractionation of heavy metals in the soil.

2.3. *Determination of heavy metals*

The sieved soils were ground using a mortar and pestle until all particles passed through a 100-mesh nylon sieve. For fractionation studies, soil samples were only sieved and not ground in order to keep the soil property unchanged. The total heavy metal content of the prepared soil was determined by HCl-HNO_3-HF-$HClO_4$ extraction. A total of 0.5 g of soil sample was digested in a Teflon reactor on a heating plate using 10 mL HCl, 5 mL HNO_3, 5 mL HF and 3 mL $HClO_4$. After evaporation to dryness, the residue was completely re-dissolved in 1 mL HNO_3 on a heating plate and brought to 25 mL in a volumetric flask using deionised water. The species of each heavy metal was extracted by Tessier's sequential extraction method.[22] The trace metals were derived into

Table 2. The concentration of heavy metals in each fraction in the soils tested without additional salinity. (mg kg^{-1}).

Element	Concentration levels	Initial concentration of metals	Exchangeable	Carbonate bound	Reducible	Oxidisable	Residual	Apparent recovery (%)
Cd	CT	0.94	0.15A	0.21A	0.49A	0.11A	0.25	129
	C1	3.94	1.31B	1.63B	1.97B	0.10A	0.14	131
	C2	6.94	2.41C	1.94C	3.52C	0.21B	0.26	120
	C3	9.94	2.98D	3.19D	4.65D	0.28C	0.21	114
	C4	12.94	3.75E	4.65E	5.79E	0.59D	0.26	116
Cr	CT	98.3	0.00A	1.69A	17.34A	13.07A	71.46	105
	C1	158.3	1.72B	4.15B	50.01B	30.20B	60.42	93
	C2	218.3	3.08C	9.78C	84.79C	49.83C	69.86	100
	C3	278.3	3.64E	12.53D	121.16D	67.18D	73.96	100
	C4	338.3	3.34D	13.30E	154.02E	80.57E	77.04	97
Cu	CT	56.6	0.09A	1.34A	7.71A	10.79A	41.69	111
	C1	77.6	0.13B	3.98B	23.42B	21.89B	38.85	117
	C2	97.6	0.22C	6.19C	31.45C	29.37C	41.81	114
	C3	117.6	0.22C	9.73D	41.57D	37.42D	43.90	115
	C4	137.6	0.35D	13.54E	53.02E	45.82E	44.55	116
Ni	CT	54.6	0.00A	0.58A	7.32A	3.22A	37.61	89
	C1	74.6	0.00A	2.67B	23.73B	7.97B	38.16	97
	C2	94.6	1.19B	5.20C	38.24C	10.21C	37.69	98
	C3	114.6	2.55C	8.39D	52.91D	15.65D	37.95	102
	C4	134.6	3.53D	9.20E	59.20E	20.53E	43.90	101
Pb	CT	57.6	0.00A	3.67A	13.85A	10.12A	25.42	92
	C1	77.6	1.64E	6.59B	26.07B	15.29B	25.41	97
	C2	97.6	0.69B	8.90C	35.83C	19.02C	32.31	99
	C3	117.6	1.21C	12.23D	44.39D	26.41D	26.96	95
	C4	137.6	1.34D	17.86E	51.12E	33.13E	32.33	99
Zn	CT	163.0	0.15A	7.62B	33.25A	12.75A	116.6	105
	C1	203.0	1.59B	6.92A	63.69B	23.50B	123.7	108
	C2	243.0	3.79C	10.02C	93.11C	30.50C	81.57	90
	C3	283.0	4.18D	10.94D	113.3D	35.00D	127.0	103
	C4	323.0	6.25E	13.39E	143.1E	43.25E	113.1	99

Notes: Upper case letters A, B, C, D, E indicate significant differences at $p < 0.01$ within column of each metal for a specific fraction. CT represents control samples, and C1-C4 represents different initial concentrations of metals.

five fractions: exchangeable (EXC), carbonate bound (CAR), reducible (RED), oxidisable (OXI), and residual (RES). Each of the chemical fractions was extracted with the following: 8.0 mL of 1.0 M $MgCl_2$(pH 7); 8 mL of 1.0 M NaOAc (pH 5); 20 mL of 0.04 M NH_2OH/HCl in 25% acetic acid (v/v); 6 mL of 30% H_2O_2 (pH 2, adjusted using concentrated HNO_3); and HF-$HClO_4$, in a sequential extraction procedure. The heavy metal concentration in each solution was determined by atomic absorption spectrometry (F-AAS, Shimadzu AA-7000, Japan). In cases in which the sensitivity of F-AAS was insufficient, metal concentrations were determined by graphite furnace AAS (GF-AAS, Shimadzu AA-7000, Japan).

Analytical reagent blanks were prepared with each batch of digestion. These blanks were set and analysed for the same elements as the samples. Two soil standard reference materials [GBW07401 (GSS-1) and GBW07404 (GSS-4)] underwent digestion and were analysed to comply with quality control protocols. The results of the analyses were only accepted when the measured concentrations in the reference materials were within one standard deviation of the certified values. Accuracy of the sequential extraction procedure was evaluated by comparing the sum of concentrations determined from five fractions with the total concentration data. Apparent recoveries (%) of metals are listed in Table 2.

2.4. *Data statistics*

Data were analysed by conducting Duncan's multiple range test using Statistical Analysis Software (SAS 1999). Statistical differences among the concentrations of heavy metals in each fraction in testing soils without additional salinity were assessed at the 5% ($p < 0.05$) and 1% ($p < 0.01$) significance levels.

3. Results and discussion

3.1. *The proportion of heavy metal in the each fraction*

The proportion of heavy metal in the each fraction in soils without additional salinity is presented in Figure 1.

The highest cadmium content in the control soil was found in the RED fraction (40.6%). Amorphous iron oxide content in the sampled soil was 15.0 g kg^{-1} and could contribute to Cd binding, as iron and manganese oxides may be important sinks for Cd.[23,24] The proportions of EXC fraction (12.2% to 25%) and CAR fraction (17.3% to 31.7%) were much higher than those of other metals (≤5.0%) for all initial metal concentrations, indicating that Cd had higher mobility and bioavailability than the other heavy metals studied. The high percentage of Cd carbonate-bound fraction was likely because the soil contained high concentration of HCO_3^-, which came from the karst area in the upper Pearl River and formed $CdCO_3$ under neutral pH conditions. The OXI fraction only existed in small proportions (4% to 9%). Cd binds organic matter to a lesser extent than it binds Fe-Mn oxides.[23,25] Meanwhile, since the Ksp of metal sulfides is in the order CuS < PbS < CdS < NiS < ZnS, Cu and Pb preferably bind with S^{2-}.[26] The soil AVS was 0.21 mmol kg^{-1} and the total oxidisable content of Cu and Pb was 0.219 mmol kg^{-1} in control soil and 0.88 mmol kg^{-1} in C4 soil. This indicates that very few Cd could bind to sulfides. The RES fraction accounted for 20.6% of the total Cd in the control soil and existed only in minor proportions in soils with added Cd. This result shows that formation of the residual fraction was slow. Unlike the RES fraction, the proportions of the EXC and CAR fractions increased with the addition of Cd. Cd adsorption in the soil is usually characterised by rapid initial processes followed by a slow process.[12] Tang *et al.*[27] found that freshly spiked Cd primarily existed in the EXC fraction (53.4% to 71.8%) after two months of incubation.

On the other hand, Cr existed primarily in the RES fraction (69%) in the control soil. The proportion of each fraction followed the order RES > RED > OXI > CAR > EXC. The concentrations of the EXC and CAR fractions were very low in the control soil. This result indicates that the mobility and bioavailability of Cr were low in the control soil. Nurcan [28] studied Cr speciation in agricultural soils in Turkey and also found Cr primarily in the RES fraction. In the treatment soil, most of the spiked Cr was found to have bound to the RED and OXI fractions. The high contents of amorphous iron oxide and organic matter in the soil may have contributed to transformation of the spiked Cr.

Copper existed in the control soil primarily in the RES fraction (67.7%), followed by the OXI fraction (17.5%) and the RED fraction (12.5%). The CAR and EXC fractions were very low in the control soil (0.1% and 2.2%, respectively). Pénilla *et al.*[29] found that Cu was most associated with the RES fraction in goethite-clay mineral systems. This finding suggests that Cu has a strong ability to form stable species in soils. This may explain why the mobility and the bioavailability of Cu in the control soil are low. Ramos *et al.*[30] and Balasoiu *et al.*[31] found that Cu content in soil systems was low in the EXC fraction and high in the OXI fraction in their study of soils from the Ebro River in Spain and of synthetic soils with high organic content, respectively. Wu *et al.*[32] examined the sorption of Cu on soil clay components and found that Cu was preferentially retained

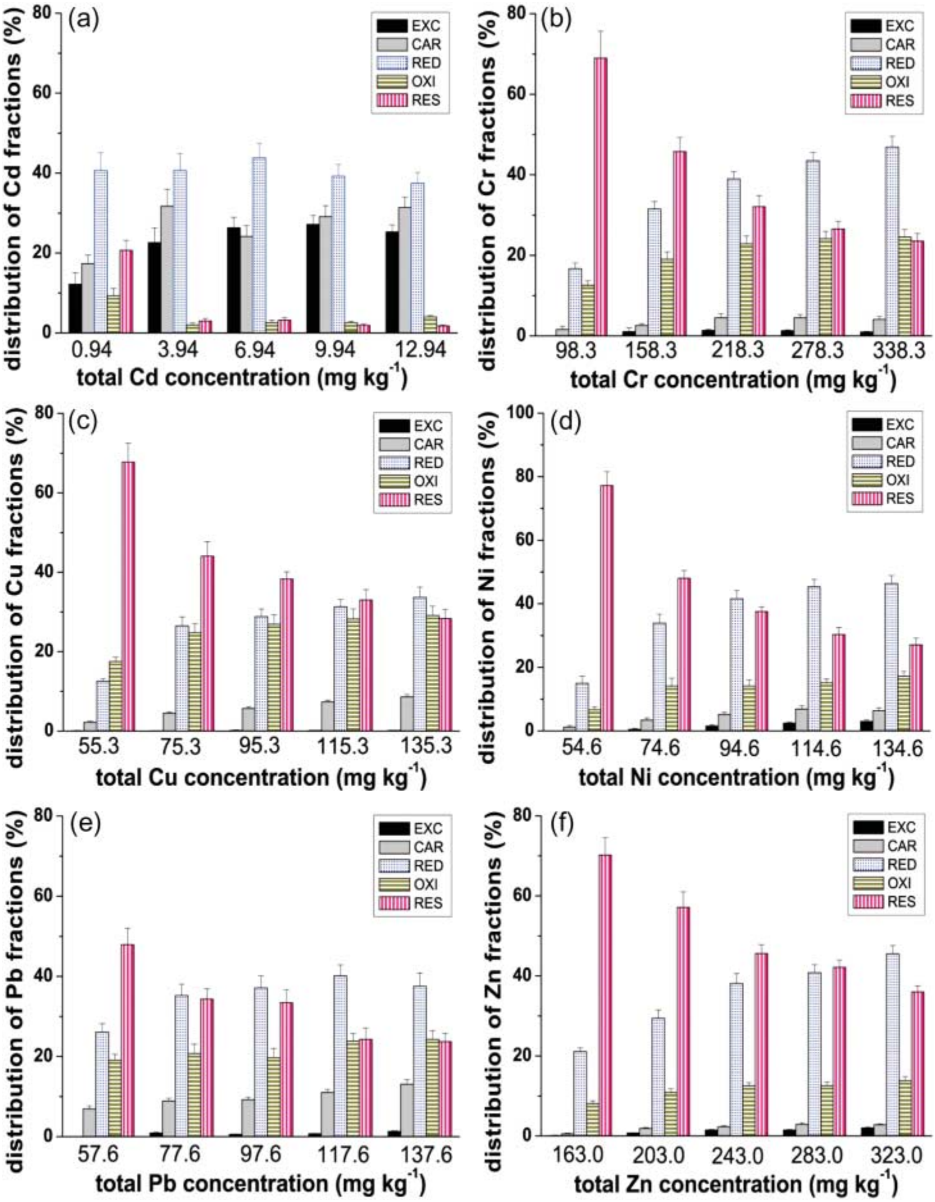

Figure 1. The proportion of heavy metal in the each fraction in soils without additional salinity.

in organic matter associated with the coarse clay fraction. Cu is also associated the strongest with sulfide among the six metals tested in the current experiment. Therefore, Cu bound to the OXI fraction could include some copper sulfide. In addition, our results indicated that the RED fraction of Cu was comparable to the OXI fraction. Karthikeyan *et al*.[33] demonstrated that aside from sorption, Cu can precipitate on the surface of iron and aluminium oxides. In the current study, an increase in the initial Cu concentration resulted in a high proportion of non-residual fractions and low residual fraction of Cu. Most of the spiked Cu was also found in the RED and OXI fractions over the middle (8 month) term, suggesting that formation of residual Cu was relatively slow. Thus, the potential bioavailability of Cu increased with Cu concentration.

The nickel RES fraction was the predominant species (77.2%) in the control soil, followed by RED (15.0%) and OXI (6.6%) fractions. No EXC fraction was detected in the control soil, implying that Ni mobility and bioavailability were low. These results are in agreement with those of Ma and Rao,[34] who found that residual Ni was by far the most important fraction in soils contaminated by heavy metals. In the current study, the proportions of all non-residual fractions increased, and the proportion of RES fraction decreased as the initial Ni concentration increased. A large input of Ni enhanced the accumulation of the RED and OXI fractions of Ni.

Lead existed in the control soil primarily in the RES fraction (47.9%), followed by the RED fraction (26.1%), the OXI fraction (19.1%), and the CAR fraction (6.9%). No exchangeable fractions were detected in the control soil. Most of the spiked Pb was transformed into the RED and OXI fractions over the middle (8 month) term. A part of the spiked Pb was bound to the CAR fraction, while few were bound to the EXC fraction. Dollar *et al*.[35] reported that the Fe-Mn oxide fraction was important for Pb, particularly at the drained site, and that the oxidisable fraction was most important for Pb. Ogunfowokan *et al*.[36] also reported that the organic matter fraction and the Fe-Mn oxide fraction are important for Pb in roadside dust along major roads in South Western Nigeria.

Zinc in the control soil was primarily associated with the RES fraction (70.2%), followed by the RED fraction (21.1%) and the OXI fraction (8.1%). The EXC and CAR fractions in the soil were minor ($\leq$0.5%), indicating that bioavailability of Zn in the control soil was low. Ma and Rao [34] also found up to 98% of Zn to have strongly bound with the residual fraction in their study. Kabala and Singh [37] found that among the non-residual fractions, oxide-bound and organically complexed Zn fractions occurred at the highest proportions. In the current study, the proportions of non-residual fractions generally increased with the initial Zn concentration, whereas the RES fraction decreased. Most of the spiked Zn (69%) was found to be bound to the RED fraction. Although the RED fraction is not generally thought of as bioavailable and metals associated with the RED fraction are relatively stable under normal conditions, they would be released when the soil became more reduced under long-term inundation.

3.2. *Concentration of heavy metal in each fraction without additional salinity*

Table 2 shows the concentrations of the five fractions at different initial levels of heavy metal content in soils without added salinity. Compared with the controls, the EXC, CAR, and RED fractions increased as the initial concentrations of the heavy metals increased. Results of Duncan's multiple range test demonstrated that across the EXC, CAR, RED, and OXI species, the concentration of each fraction became significantly higher ($p < 0.01$) as the initial concentration increased. This was true for nearly all heavy metals tested, whereas no significant difference was found in the RES fraction concentrations. These results indicate that the added heavy metals remained potentially bioavailable after an eight-month-long incubation.

Time is an important factor in the bioavailability of heavy metals in soils – bioavailability usually decreases the longer a metal stays in the soil.[38–40] Lu *et al*.[12] reported that the EXC fraction of heavy metals increased in the first three hours and then decreased, while reducible and oxidisable metals, but not the RES fraction, increased consistently over an eight-week incubation period. They concluded that heavy metal distribution was biphasic, with an initial rapid process followed by a slow process. The results of a 48-week incubation period showed that Cd transformed from the EXC to the CAR fraction, Cr transformed from the CAR to the OXI fraction, and Pb, Ni, Cu, and Zn transformed to the RED fraction.[41] Taken together, these results support our interpretation that heavy metals in the Pearl River estuary wetland soils remained potentially bioavailable after an eight-month period.

3.3. *Effects of salinity on heavy metal speciation*

Figures 2–4 show the effects of salinity on the fractionation of Cd, Pb, and Zn. The effects of salinity on the fractionation of Cu, Cr, and Ni were not statistically significant (data not shown). The EXC fraction of Cd increased slightly with increase in salinity. However, the changes were not statistically significant at low Cd concentrations. Concentration of the CAR fraction decreased as the salinity increased. A number of studies suggest that chloride ions in the soil may form strong aqueous Cd chloro-complexes under conditions of high salinity.[42–44] These stable chloro-complexes can hinder the formation of other non-EXC forms of Cd. Increased ionic strength can

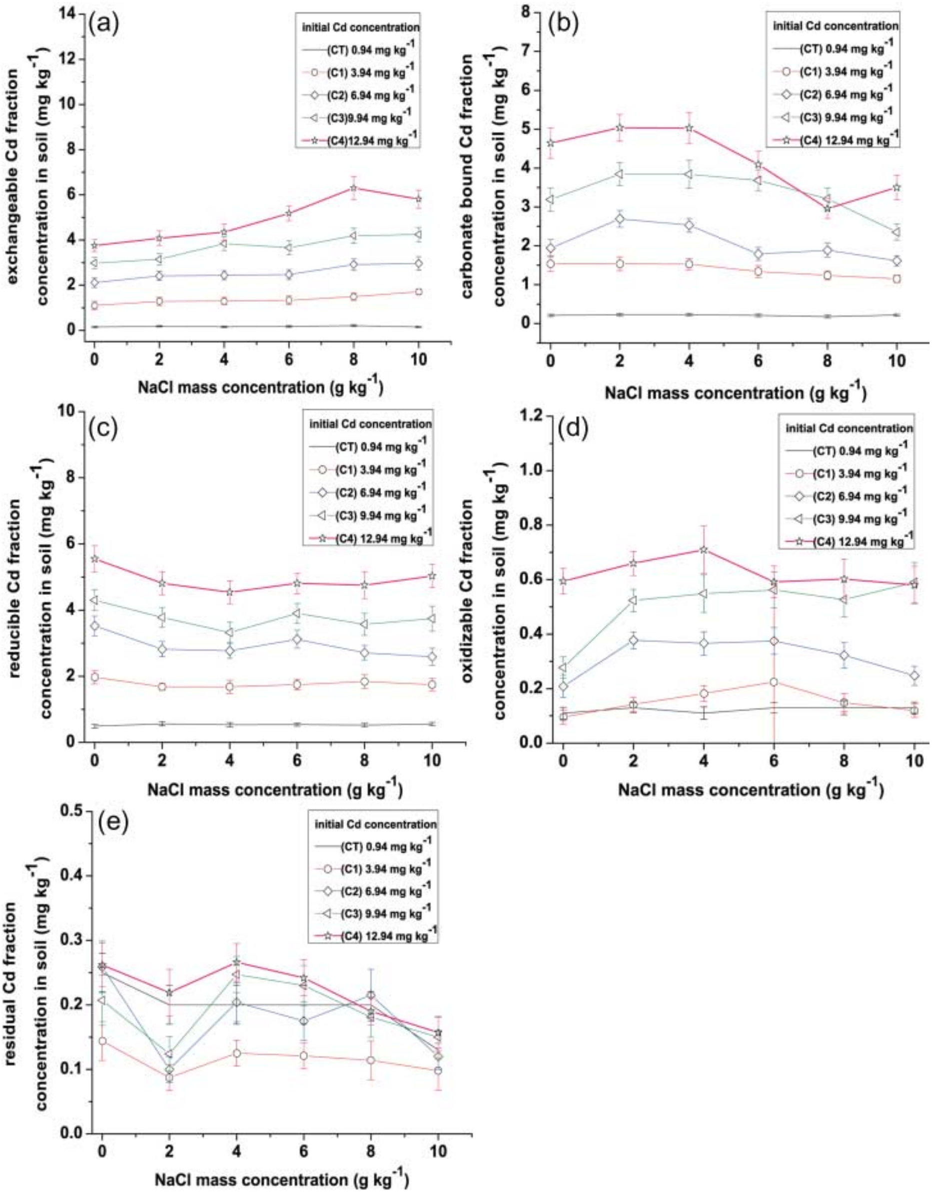

Figure 2. Salinity effect on Cd fractionation. (a) exchangeable fraction, (b) carbonate bound fraction, (c) reducible fraction, (d) oxidisable fraction, and (e) residual fraction.

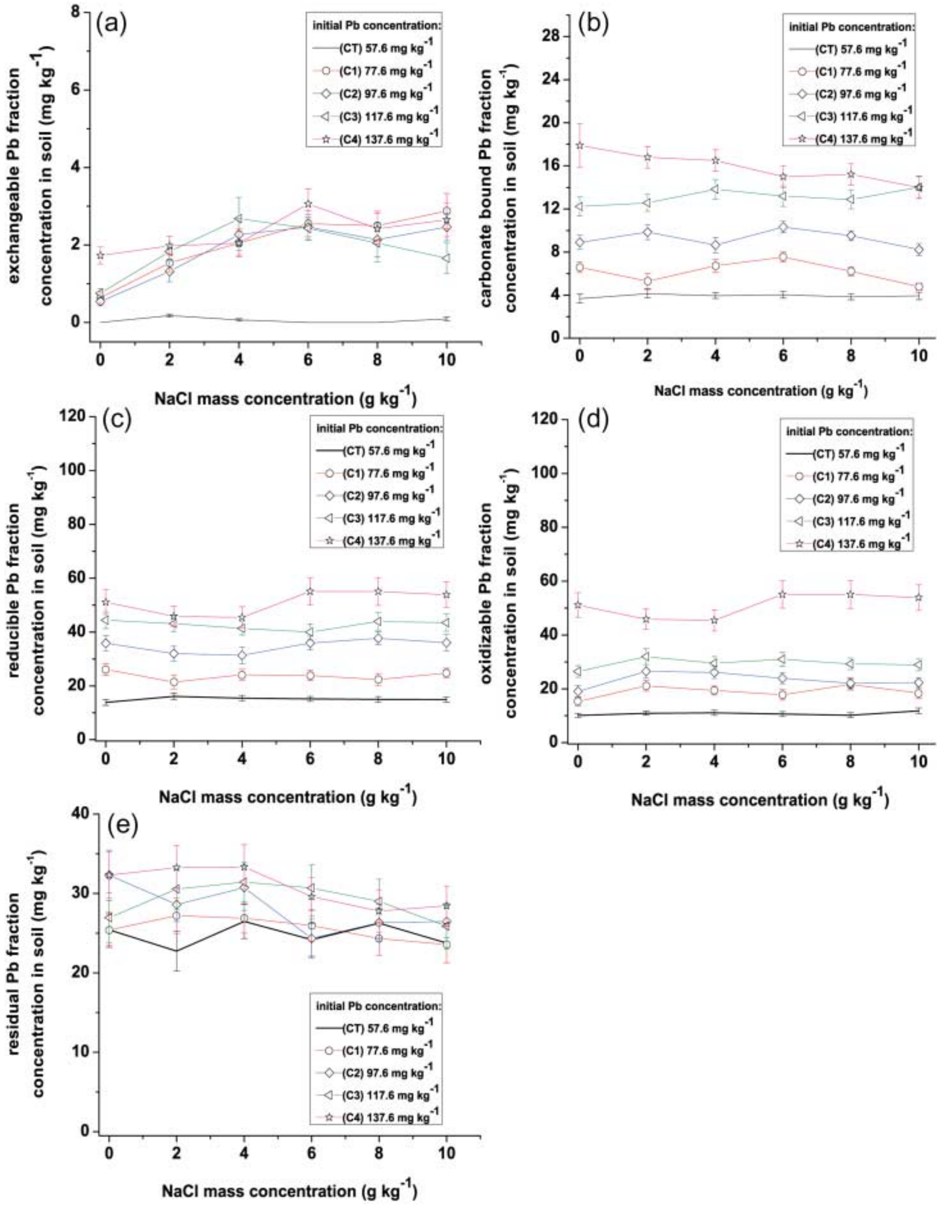

Figure 3. Salinity effect on Pb fractionation. (a) exchangeable fraction, (b) carbonate bound fraction, (c) reducible fraction, (d) oxidisable fraction, and (e) residual fraction.

also result in competitive sorption of Na^+ for sorption sites of Cd.[45] Therefore, increase in solubility of Cd would increase its mobility and bioavailability.[46] These results are consistent with previous findings that high salinity resulted in increased uptake of cadmium by plants.[43,47,48]

The EXC Pb and Zn fractions increased, and the CAR fraction decreased slightly as salinity increased (Figures 3 and 4). Stevens *et al.*[49] found that increased salinity increased the Pb and Zn concentrations in soil solutions and increased toxicity in plants. In the current study, the OXI Pb fraction also showed a decreasing trend with increasing salinity. Pinheiro *et al.*[50] found that ionic strength reduced Pb binding to humic acid, which suggests that electrostatic binding of Pb

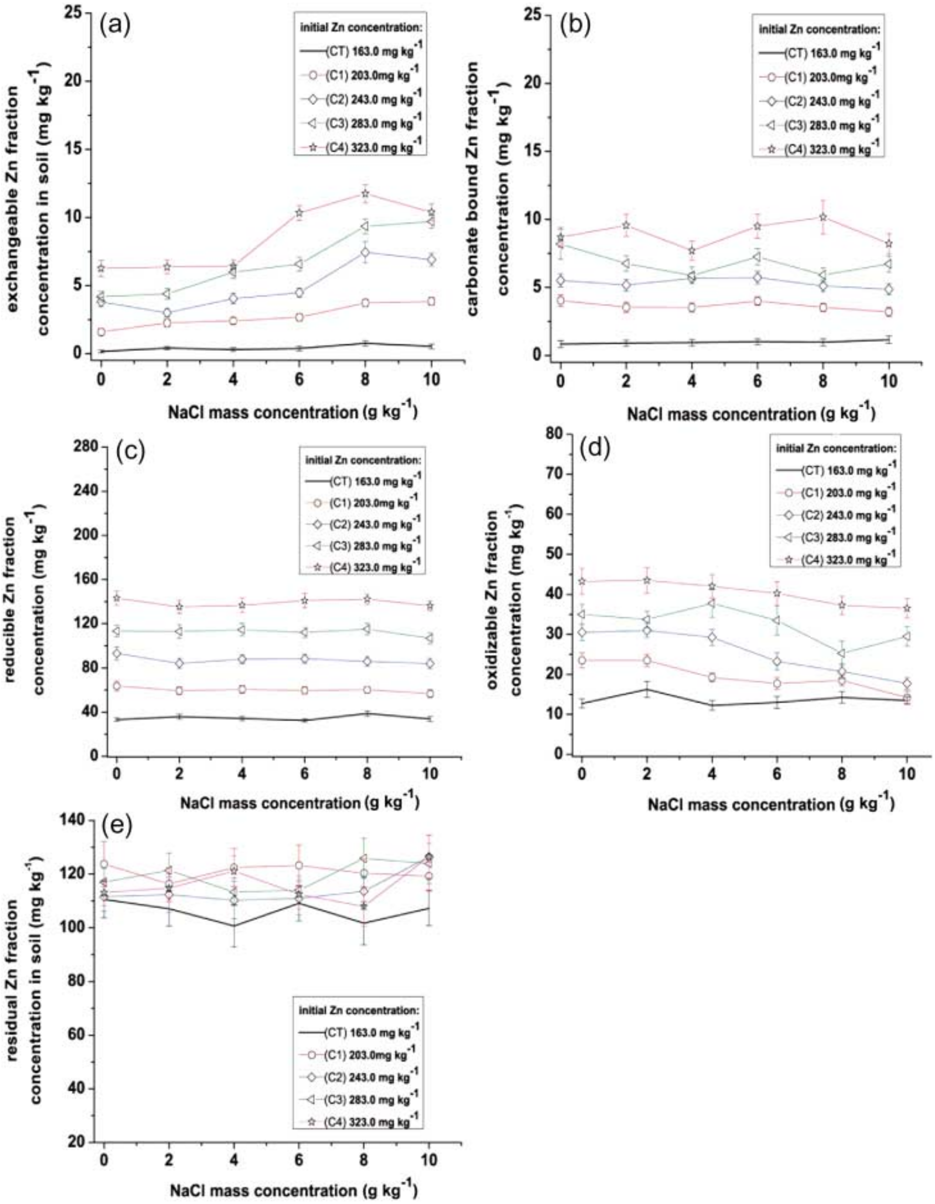

Figure 4. Salinity effect on Zn fractionation. (a) exchangeable fraction, (b) carbonate bound fraction, (c) reducible fraction, (d) oxidisable fraction, and (e) residual fraction.

with organic matter may be important in saline or estuarine soils. Acosta *et al*.[17] also found that increased salinity increased the mobility of Pb. In our study, the OXI Zn fraction decreased slightly, and changes in salinity did not affect the rest of the Zn fractions. By contrast, Du Laing *et al*.[46] did not find significant effects of NaCl on Zn mobility, probably because Zn can be mobilised in low salinity conditions via chloride complexation.[17] The decrease of OXI Zn fraction observed in the current study indicates that OXI Zn complexed with Cl in salinity conditions.[51]

No apparent effect on Cr, Cu, and Ni fractions was observed with changes in salinity in the current study. Consistent with this result, Du Laing *et al*.[46] also found that Cu and Ni mobility did not change with increase in ionic strength of NaCl, likely because of low solubility of Cu and Ni sulphides and strong association of Cu with organic matter.

The Pearl River estuary is characterised by its unique tidal movements and water circulation.[52] The wetlands in this area are frequently subjected to tidal changes and constant mixing of fresh and saltwater. The saline tide can intrude landward far from the estuary along the river in the dry season. Therefore, heavy metals accumulated in wetlands of this area may pose significant ecological risk owing to their potential for exposure to salinity. Besides, tidal movements can also cause the redox potential of soil to change. The water table level is the main factor that controls fluctuations in redox conditions.[53] Low tide increases soil aeration and redox potential, which results in the oxidisable fractions of heavy metals being released from the soil. By contrast, high tide decreases soil redox potential and may result in the release of reducible fractions of heavy metals.

4. Conclusions

Results of the transformation experiment conducted in the current study showed that after eight months of incubation, large amounts of heavy metals were still in bioavailable or potentially bioavailable forms owing to slow formation of the residual fractions. Among the metals studied, Cd had the highest proportion of readily bioavailable fraction. The rest of the metals were strongly associated with reducible and oxidisable fractions, and may be re-released during tidal movements because of variations in the redox potential of the soil. Furthermore, our results revealed that increase in salinity may enhance the mobility of Cd, Pb, and Zn, indicating that these metals may be remobilized during saline tidal flooding. These findings suggest that input of heavy metals in the Pearl River estuary wetland soils may pose high ecological risks.

Acknowledgements

We also acknowledge the contributions of the reviewers of this manuscript.

Funding

We are grateful to the National Science and Technology Support Program of China [2012BAC07B05], and the National Natural Science Foundation of China [U0833002, 40871154] for the financial support provided to conduct the experiment.

References

[1] Cui WZ. Study on protection of mudflat wetland in the Pearl River estuary. Wetland Sci. 2004;2:26–30. (in Chinese)
[2] Administration of Ocean and Fisheries of Guangdong Province. Public report of marine environmental quality in guangdong province. Guangzhou (China): Administration of Ocean and Fisheries of Guangdong Province; 2011.
[3] Tang CWY, Ip CCM, Zhang G, Shin PKS, Qian PY, Li XD. The spatial and temporal distribution of heavy metals in sediments of Victoria Harbour, Hong Kong. Mar Pollut Bull. 2008;57:816–825.
[4] Schützendübel A, Polle A. Plant responses to abiotic stresses: heavy metal induced oxidative stress and protection by mycorrhization. J Exp Bot. 2002;53:1351–1365.
[5] Järup L. Hazards of heavy metal contamination. Br Med Bull. 2003;68:167–182.
[6] Tack FM, Verloo MG. Chemical speciation and fractionation in soil and sediment heavy metal analysis: a review. Int J Environ Anal Chem. 1995;59:225–238.
[7] Naidu R, Bolan NS, Kookana RS, Tiller KG. Ionic-strength and pH effects on the sorption of cadmium and the surface charge of soils. Eur J Soil Sci. 1994;45:419–429.
[8] Fernandes LL, Nayak GN. Heavy metals contamination in mudflat and mangrove sediments (Mumbai, India). Chem Ecol. 2012;28:435–455.
[9] McLaughlin MJ. Ageing of metals in soils changes bioavailability. Environ Risk Assess. 2001;4:1–6.

[10] Jalali M, Khanlari ZV. Effect of aging process on the fractionation of heavy metals in some calcareous soils of Iran. Geoderma. 2008;143:26–40.

[11] Lu AX, Zhang SZ, Qin XY, Wu WY, Liu HL. Aging effect on the mobility and bioavailability of copper in soil. J Environ Sci. 2009;21:173–178.

[12] Lu AX, Zhang SZ, Shan XQ. Time effect on the fractionation of heavy metals in soils. Geoderma. 2005;125:225–234.

[13] Li XD, Shen ZG, Wai OWH, Li YS. Chemical forms of Pb, Zn and Cu in the sediment profiles of the Pearl River estuary. Mar Pollut Bull. 2001;42:215–223.

[14] Ip CCM, Li XD, Zhang G, Farmer JG, Wai OWH, Li YS. Over one hundred years of trace metal fluxes in the sediments of the Pearl River estuary, South China. Environ Pollut. 2004;132:157–172.

[15] Ip CCM, Li XD, Zhang G, Wai OWH, Li YS. Trace metal distribution in sediments of the Pearl River estuary and the surrounding coastal area, South China. Environ Pollut. 2007;147:311–323.

[16] Shilla D, Dativa J. Speciation of heavy metals in sediments from the Scheldt estuary, Belgium. Chem Ecol. 2011;27:69–79.

[17] Acosta JA, Jansen B, Kalbitz K, Faz A, Martínez-Martínez S. Salinity increases mobility of heavy metals in soils. Chemosphere. 2011;85:1318–1324.

[18] Norvell WA, Wu J, Hopkins DG, Welch RM. Association of cadmium in durum wheat grain with soil chloride and chelate-extractable soil cadmium. Soil Sci Soc Am J. 2000;64:2162–2168.

[19] Du Laing G, Rinklebe J, Vandecasteele B, Meers E, Tack FMG. Trace metal behavior in estuarine and riverine floodplain soils and sediments: a review. Sci Total Environ. 2009;407:3972–3985.

[20] Dewis J, Freiras F. Physical and chemical methods of Soil and water analysis. Rome, Italy: Food and Agricultural Organization of the United Nations; 1976.

[21] Allen HE, Fu G, Deng B. Analysis of acid volatile sulfide (AVS) and simultaneously extracted metals (SEM) for the estimation of potential toxicity in aquatic sediment. Environ Toxicol Chem. 1993;12:1441–1453.

[22] Tessier A, Campbell PGC, Bisson M. Sequential extraction procedure for the speciation of particulate trace metals. Anal Chem. 1979;51:844–851.

[23] Dong D, Nelson YM, Lion LW, Shuler ML, Ghiorse WC. Adsorption of Pb and Cd onto metal oxides and organic material in natural surface coatings as determined by selective extractions: new evidence for the importance of Mn and Fe oxides. Water Res. 2000;34:427–436.

[24] Turner A, Le Roux SM, Millward GE. Adsorption of cadmium to iron and manganese oxides during estuarine mixing. Mar Chem. 2008;108:77–84.

[25] Dong D, Liu L, Hua X, Lu Y. Comparison of lead, cadmium, copper and cobalt adsorption onto metal oxides and organic materials in natural surface coatings. Microchem J. 2007;85:270–275.

[26] Dean JA. Lange's handbook of chemistry. New York: McGraw-Hill Inc; 1998.

[27] Tang XY, Zhu YG, Cui YS, Duan J, Tang L. The effect of ageing on the bioaccessibility and fractionation of cadmium in some typical soils of China. Environ Int. 2006;32:682–689.

[28] Nurcan K. Speciation of chromium in 12 agricultural soils from Turkey. Chemosphere. 2004;57:1473–1478.

[29] Pénilla S, Bordas F, Bollinger JC. Sequential heavy metals extraction from polluted solids: influence of sulfate overconcentration. J Colloid Interface Sci. 2005;292:20–28.

[30] Ramos L, González MJ, Hernández LM. Sequential extraction of copper, lead, cadmium, and zinc in sediments from Ebro River (Spain): relationship with levels detected in earthworms. Bull Environ Contam Toxicol. 1999;62:301–308.

[31] Balasoiu CF, Zagury GJ, Deschênes L. Partitioning and speciation of chromium, copper, and arsenic in CCA-contaminated soils: influence of soil composition. Sci Total Environ. 2001;280:239–255.

[32] Wu J, Laird DA, Thompson ML. Sorption and desorption of copper on soil clay components. J Environ Qual. 1999;28:334–338.

[33] Karthikeyan KG, Elliott HA, Chorover J. Role of surface precipitation in copper sorption by the hydrous oxides of iron and aluminum. J Colloid Interface Sci. 1999;209:72–78.

[34] Ma L, Rao G. Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soils. J Environ Qual. 1997;26:259–264.

[35] Dollar NL, Souch CJ, Filippelli GM, Mastalerz M. Chemical fractionation of metals in wetland sediments: Indiana Dunes National Lakeshore. Environ Sci Technol. 2001;35:3608–3615.

[36] Ogunfowokan AO, Oyekunle JAO, Durosinmi LM, Akinjokun AI, Gabriel OD. Speciation study of lead and manganese in roadside dusts from major roads in Ile-Ife, South Western Nigeria. Chem Ecol. 2009;25:405–415.

[37] Kabala C, Singh BR. Fractionation and mobility of copper, lead, and zinc in soil profiles in the vicinity of a copper smelter. J Environ Qual. 2001;30:485–492.

[38] Joner EJ, Leyval CL. Time-course of heavy metal uptake in maize and clover as affected by root density and different mycorrhizal inoculation regimes. Biol Fertil Soils. 2001;33:351–357.

[39] Lock K, Janssen CR. Influence of ageing on zinc bioavailability in soils. Environ Pollut. 2003;126:371–374.

[40] Ma YB, Uren NC. Transformations of heavy metals added to soil – application of a new sequential extraction procedure. Geoderma. 1998;84:157–168.

[41] Han FX, Banin A. Long-term transformation and redistribution of potentially toxic heavy metals in arid-zone soils: II. Incubation at the field capacity moisture content. Water Air Soil Pollut. 1999;114:221–250.

[42] Comans RNJ, Van Dijk CPJ. Role of complexation processes in cadmium mobilization during estuarine mixing. Nature. 1988;336:151–154.

[43] Khoshgoftar AH, Shariatmadari H, Karimian N, Kalbasi M, van der Zee SEATM, Parker DR. Salinity and zinc application effects on phytoavailability of cadmium and zinc. Soil Sci Soc Am J. 2004;68:1885–1889.

[44] Paalman MAA, Weijden CH, Loch JPG. Sorption of cadmium on suspended matter under estuarine conditions; competition and complexation with major sea-water ions. Water Air Soil Pollut. 1994;73:49–60.
[45] Petruzzelli G, Guidi G, Lubrano L. Ionic strength effect on heavy metal adsorption by soil. Commun Soil Sci Plant Anal. 1985;16:971–986.
[46] Du Laing G, De Vos R, Vandecasteele B, Lesage E, Tack FMG, Verloo MG. Effect of salinity on heavy metal mobility and availability in intertidal sediments of the Scheldt estuary. Estuarine Coastal Shelf Sci. 2008;77:589–602.
[47] Weggler-Beaton K, McLaughlin MJ, Graham RD. Salinity increases cadmium uptake by wheat and Swiss chard from soil amended with biosolids. Soil Res. 2000;38:37–45.
[48] Mühling KH, Läuchli A. Interaction of NaCl and Cd stress on compartmentation pattern of cations, antioxidant enzymes and proteins in leaves of two wheat genotypes differing in salt tolerance. Plant Soil. 2003;253:219–231.
[49] Stevens DP, McLaughlin MJ, Heinrich T. Determining toxicity of lead and zinc runoff in soils: salinity effects on metal partitioning and on phytotoxicity. Environ Toxicol Chem. 2003;22:3017–3024.
[50] Pinheiro JP, Mota AM, Benedetti MF. Effect of aluminum competition on lead and cadmium binding to humic acids at variable ionic strength. Environ Sci Technol. 2000;34:5137–5143.
[51] Amrhein C, Strong JE, Mosher PA. Effect of deicing salts on metal and organic matter mobilization in roadside soils. Environ Sci Technol. 1992;26:703–709.
[52] Mao Q, Shi P, Yin K, Gan J, Qi Y. Tides and tidal currents in the Pearl River estuary. Cont. Shelf Res. 2004;24:1797–1808.
[53] Seybold C, Mersie W, Huang J, McNamee C. Soil redox, pH, temperature, and water-table patterns of a freshwater tidal wetland. Wetlands. 2002;22:149–158.