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Effects of freshwater leaching on potential bioavailability of heavy metals in tidal flat soils

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Abstract Leaching experiments were conducted to investigate the effects of desalination levels and sediment depths on potential bioavailability of heavy metal (Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) in tidal flat soils. The data showed that both the desalination levels ($p < 0.001$) and soil depths ($p < 0.001$) had significant effects on the concentrations of acid-volatile sulfide (AVS). AVS concentrations generally exhibited increasing trends with an increase in depth and decreasing trends with enhanced desalination levels. The desalination levels had significant ($p < 0.05$) effects on the concentrations of simultaneously extracted metal (SEM; Cd, Cr, Cu, Fe, Mn, Pb, and Zn). Moreover, the concentrations of SEM (Cd, Cr, Cu, Fe, Mn, Pb, and Zn) generally tended to decrease with an increase in the desalination level. The desalination treatment significantly reduced the ratios of SEM/AVS compared with control. However, the ratios of SEM/AVS increased with enhanced desalination levels in treatments. Results reveal that low desalination treatment is better for reducing toxicity to benthic organisms than high desalination treatment. Since these reclaimed tidal flats with low desalinisation are suitable for saline water aquaculture, transforming the present land use of reclaimed tidal flats from fresh water aquaculture into saline water aquaculture may reduce health risk of heavy metals remained in sediments. These results will also contribute to our understanding of the dynamic behavior of heavy metals in the reclamation of tidal flats during leaching and the role of the ratio of SEM/AVS predictions on assessing the ecological risks of reclaimed tidal flats.

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Introduction

Transforming tidal flats into aquaculture land is considered as a main strategy in coastal area of the world, although this may result in the loss of natural marine ecosystems and water buffering capacity. Meanwhile, tidal flats are considered as the important ultimate sink of heavy metals. For example, estuarine and coastal tidal flats in the Pearl River estuary, China,

have been contaminated by heavy metals in the last three decades as a result of massive economic growth and urban development, and many of them were reclaimed into aquaculture ponds (Li et al. 2007). Heavy metals in these reclaimed tidal flats have become potential sources of health risks through aquaculture (Leung et al. 2014). It is therefore important to explore methods for decreasing the toxic metals in reclaimed tidal flats to grow safe aquaculture products for human consumption.

Varying salinities are expected to affect metal mobility in the sediments and have a major impact on their bioavailabilities. Chloride ions at high salinities in coastal tidal flat sediments could form strong aqueous chloro-complexes and could lead to heavy metal mobilization (Norvell et al. 2000; Tampouris et al. 2001). High salinity can also increase the concentrations of major cations (e.g., Na, K, Ca, and Mg) that compete with heavy metals for sorption sites of the solid phase, thus leading to desorption of heavy metals and promotion of their bioavailabilities (Du Laing et al. 2002). This phenomenon has been demonstrated in both laboratory (Du Laing et al. 2008) and field experiments (Hatje et al. 2003). Since most aquacultures in reclaimed tidal flats of estuaries are fresh water culture, saline tidal flats must be leached with fresh water from rivers to meet the requirements of aquatic culture. Therefore, such a leaching process could affect the environmental behavior of heavy metals in tidal flats (Li et al. 2011).

Acid-volatile sulfide (AVS) is defined as the amount of sulfides volatilized during cold hydrochloric acid (HCl) extraction (Di Toro et al. 1992; Allen et al. 1993). Simultaneously extracted metal (SEM) is the amount of heavy metal (e.g., Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) released during the extraction used for AVS. The relationship between AVS and SEM has been proposed as a possible indicator of heavy metal toxicity in anaerobic sediments (Long et al. 1998; He et al. 2011). When the ratio of the molar concentrations of SEM to AVS is <1, all reactive metals are assumed to exist in the form of their respective metal sulfides, which are not bioavailable. These results suggest that acute toxicity by metals may not be present in these sediments. On the contrary, sediments may be considered potentially toxic when the ratio of SEM to AVS > 1. However, the other metal-binding phases can be present in sediments (e.g., Fe and Mn hydroxides and particulate organic carbon), which can

additionally bind excess SEM and reduce their bioavailability (Poot et al. 2009; Van den Berg et al. 1998). Therefore, the SEM–AVS method only predicts potential bioavailability. Researches on spiked and field-contaminated sediments demonstrated that the SEM–AVS method is successful at predicting potential metal bioavailability (Di Toro et al. 1992; Poot et al. 2009; Van Griethuysen et al. 2004; Yin and Fan 2011; Yang et al. 2012). In the assessment of environmental quality regarding certain metals in sediments, the SEM–AVS relationship has been used as the primary method for evaluating their potential bioavailability (Nizoli and Luiz-Silva 2012). Therefore, in the present study, the molar concentrations of SEM and AVS are used to predict heavy metal bioavailability and to assess the ecological risks of reclaimed tidal flats.

Although there is a potential health risk of heavy metals to residents living in reclaimed tidal flats (Li et al. 2012), leaching with fresh water can remove a fraction of heavy metal contamination (Li et al. 2011). Thus far, most studies on tidal flats focus mainly on heavy metal distribution and risk assessment of estuarine sediments (Fang et al. 2005; Zhang et al. 2011). Little information is available on heavy metal bioavailability and the potential risk assessment of reclaimed tidal flats under the influence of various desalination levels. Our previous research has evaluated the behavior of heavy metals during the reclamation of tidal flats (Li et al. 2011). Therefore, the major objectives of the present study include (1) determination of the bioavailability of heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) in reclaimed tidal flats, (2) assessment of the ecological risks of reclaimed tidal flats by using the SEM–AVS method, and (3) investigation of the effects of sediment depth and desalination treatment on heavy metal potential bioavailability and the ecological risks on benthic organisms.

Materials and methods

Collection and preparation of sediment

Sediment samples were collected at depths of 0–20 cm from a 10 m^2 area from a tidal mudflat of Qi'ao Island at low tide, located at the mouth of the Pearl River estuary, Zhuhai, China. The samples were

stored in cooler PVC vessels and were transported to the laboratory. After all sediment samples were sieved through a 2-mm mesh to remove coarse debris and stones, the sediments were mixed together randomly and settled, and the supernatants were removed. One month was required for the sediments to be mixed together thoroughly until the electrical conductivity (EC) values in all sediments were nearly the same. The mixed sediment was placed into 24 organic glass columns, each with an internal diameter of 19 cm and a height of 1 m, at an 80 cm depth. The bottom of the column was covered with a nylon sieve upon which a 5-cm-thick layer of coarse sand was placed (Li et al. 2011).

Desalination treatments

A platinum conductivity electrode was installed 10 cm below surface in each column and was used to monitor the salinity decrease during the leaching process. The electrical conductivity (EC) value of each column was measured once every day. Eight treatments were defined by the following target EC values of sediment samples after leaching: 8000 μS cm^{-1} (T1), 7000 μS cm^{-1} (T2), 6000 μS cm^{-1} (T3), 5000 μS cm^{-1} (T4), 4000 μS cm^{-1} (T5), 3000 μS cm^{-1} (T6), 2000 μS cm^{-1} (T7), and 1000 μS cm^{-1} (T8). Each treatment was repeated in triplicate. The initial EC value of the sediment before leaching was 15,250 $\pm$ 200 μS cm^{-1}. Distilled water was added to the sediment surface in each column, and the water depth above the sediment surface was maintained at 1–4 cm. No additional water was added until the EC was reduced to the target value. The leaching process lasted for 65 days for treatment T1 and up to 224 days for treatment T8. At the end of the leaching process, the sediment depths were 70–75 cm due to compaction.

Chemical analyses

Five sediment samples collected randomly from the PVC vessels prior to the leaching process were used as controls. After leaching, wet sediments were sampled from each column at depth intervals of 0–10 cm (D1), 10–20 cm (D2), 20–35 cm (D3), 35–50 cm (D4), and 50–65 cm (D5). Determination of AVS and SEM was conducted according to the method described by Allen et al. (1993) and Fang et al. (2005). The experimental setup consisted of a reaction vessel connected to a trapping vessel containing 100 mL of 0.5 M sodium hydroxide (NaOH) solution. Approximately 90 mL of deionized water was added to the reaction vessel and was sparged with nitrogen (N$_2$) for 10 min. Approximately 10 g of the wet sediment sample was added to the deionized water and was sparged with N$_2$ for an additional 10 min. The sediment suspension was stirred and acidified for 45 min with 20 mL of 6 M hydrochloric acid (HCl) at room temperature to form H$_2$S, which was subsequently collected in the trapping vessels with a continuous N$_2$ flow. The dissolved sulfide concentration in the NaOH solution was determined by using an ultraviolet (UV) spectrophotometer with the methylene blue method at a wavelength of 670 nm. The acidified sediment suspension in the reaction vessel was filtered through a 0.45-μm membrane, and the concentrations of heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) in the filtrate were determined by using atomic absorption spectrometry (FAAS; Shimadzu AA-7000, Japan) and graphite furnace atomic absorption spectrometry (GFAAS; Shimadzu AA-7000, Japan). Analytical reagent blanks were prepared with each batch of digestion and analyzed for the same elements as the samples. Two soil standard reference materials [GBW07401 (GSS-1) and GBW07404 (GSS-4)] were carried through the digestion and analyzed as a part of the quality control protocol. 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.

Statistical analyses

All results were tested by one- or two-way analysis of variance (ANOVA) by using the SPSS 16.0 statistical package, and all figures were drawn by the PC-based Origin 8 program. Duncan's multiple range tests at a probability level of 5 % were used for post hoc comparison to separate the treatment differences.

Results

AVS in sediments

The results of the two-way ANOVA for the AVS are summarized in Table 1. Concentrations of AVS in sediments at various depths prior to and following the

Table 1 Significance levels of two-way ANOVA for acid-volatile sulfide (AVS) and simultaneously extracted metals (SEM) (Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) between soil depth and desalination level

	Desalination levels	Depths	Interaction
AVS	$p < 0.001$	$p < 0.001$	NS[a]
Cd	$p < 0.05$	NS	NS
Cr	$p < 0.001$	NS	NS
Cu	$p < 0.001$	NS	$p < 0.05$
Fe	$p < 0.05$	NS	NS
Mn	$p < 0.001$	$p < 0.01$	NS
Ni	NS	$p < 0.001$	$p < 0.01$
Pb	$p < 0.001$	NS	NS
Zn	$p < 0.01$	$p < 0.05$	$p < 0.05$

[a] NS represents no significance at the 5 % level

leaching process are presented in Table 2. Desalination levels ($p < 0.001$) and soil depths ($p < 0.001$) both had profound effects on AVS concentration (Table 1). The EC values from T1 to T8 were 8000–1000 $\mu S\ cm^{-1}$, indicating that the desalination levels increased from T1 to T8. The concentrations of AVS, in units of $\mu mol\ g^{-1}$, were 0.1 before soil leaching, 0.2–0.5 from D1 to D5 in T1, 0.17–0.46 in T2, 0.17–0.41 in T3, 0.14–0.43 in T4, 0.05–0.34 in T5, 0.03–0.27 in T6, 0.01–0.25 in T7, and 0.004–0.18 in T8 (Table 2). Table 2 also shows that the concentrations of AVS tended to decrease with enhanced desalination levels and increase with an increase in soil depth. The concentration of AVS was highest (0.5 $\mu mol\ g^{-1}$) in D5 under the T1 desalination level

and lowest (0.004 $\mu mol\ g^{-1}$) in D1 under the T8 desalination level.

SEM in sediments

Concentrations of SEM at the various sediment depths prior to and following the leaching process are listed in Tables 3 and 4, respectively. Desalination levels had significant effects ($p < 0.05$) on the concentrations of SEM-Cd, SEM-Cr, SEM-Cu, SEM-Fe, SEM-Mn, SEM-Pb, and SEM-Zn (Table 1). Furthermore, the concentrations of SEM (Cd, Cr, Cu, Fe, Mn, Pb, and Zn) exhibited decreasing trends with enhanced desalination levels at various soil depths (Tables 3, 4). For example, the concentrations of SEM-Cd, in units of $\mu mol\ g^{-1}$, were 3.8×10^{-3} before soil leaching, 3.4–2.7×10^{-3} from T1 to T8 in D1, 3.4–2.8×10^{-3} from T1 to T8 in D2, 3.2–2.8×10^{-3} from T1 to T8 in D3, 3.2–2.9×10^{-3} from T1 to T8 in D4, and 3.2–2.8×10^{-3} from T1 to T8 in D5 (Table 3). Soil depths had a profound influence ($p < 0.05$) on the concentrations of SEM-Mn, SEM-Ni, and SEM-Zn (Table 1). For Cd, Pb, and Zn, the soil desalination treatment significantly decreased the SEM concentrations in sediments ($p < 0.05$) when compared with the control samples with no leaching (Tables 3, 4). In addition, it was noted that the average concentration of SEM-heavy metal under various desalination treatments followed the order of Cd < Cr < Ni < Pb < Cu < Zn < Mn < Fe (Tables 3, 4). The SEM concentrations in the desalination sediments ranged, in units of $\mu mol\ g^{-1}$, from 2.7 to 3.4×10^{-3} for Cd, 0.09–0.16 for Cr, 0.51–0.60 for Cu, 146–174 for Fe,

Table 2 Concentrations of acid-volatile sulfide (AVS) in the various sediment depths before leaching (CK) and after leaching (T1, T2, T3, T4, T5, T6, T7, and T8) ($\mu mol\ g^{-1}$)

	D1	D2	D3	D4	D5
CK	$0.10 \pm 0.007bc$	$0.10 \pm 0.007ab$	$0.10 \pm 0.007a$	$0.10 \pm 0.007a$	$0.10 \pm 0.007a$
T1	$0.20 \pm 0.026e$	$0.26 \pm 0.009c$	$0.38 \pm 0.019d$	$0.45 \pm 0.006e$	$0.50 \pm 0.013e$
T2	$0.17 \pm 0.014de$	$0.26 \pm 0.014c$	$0.35 \pm 0.026cd$	$0.42 \pm 0.002e$	$0.46 \pm 0.016de$
T3	$0.17 \pm 0.039de$	$0.23 \pm 0.021c$	$0.33 \pm 0.019cd$	$0.41 \pm 0.009e$	$0.41 \pm 0.037de$
T4	$0.14 \pm 0.018cd$	$0.22 \pm 0.013c$	$0.33 \pm 0.013cd$	$0.40 \pm 0.014e$	$0.43 \pm 0.006de$
T5	$0.05 \pm 0.010ab$	$0.15 \pm 0.032b$	$0.24 \pm 0.028bc$	$0.28 \pm 0.021d$	$0.34 \pm 0.031cd$
T6	$0.03 \pm 0.012a$	$0.12 \pm 0.033ab$	$0.18 \pm 0.059ab$	$0.23 \pm 0.035cd$	$0.27 \pm 0.028bc$
T7	$0.01 \pm 0.003a$	$0.10 \pm 0.033ab$	$0.18 \pm 0.080ab$	$0.18 \pm 0.030bc$	$0.25 \pm 0.094bc$
T8	$0.004 \pm 0.004a$	$0.05 \pm 0.018a$	$0.10 \pm 0.030a$	$0.16 \pm 0.048ab$	$0.18 \pm 0.040ab$

Data are presented as mean values $\pm$ SD ($n = 3$). Means followed by the same letter within the same column are not significantly different determined by the Duncan's multiple range tests at the 5 % level

Table 3 Concentrations of simultaneously extracted metals (SEM) (Cd, Cr, Cu, and Fe) in various sediment depths before leaching (CK) and after leaching (T1, T2, T3, T4, T5, T6, T7, and T8) (μmol g^{-1})

	D1	D2	D3	D4	D5
Cd (10^{-3} μmol g^{-1})					
CK	3.8 ± 0.08c	3.8 ± 0.08c	3.8 ± 0.08c	3.8 ± 0.08b	3.8 ± 0.08d
T1	3.4 ± 0.06b	3.4 ± 0.02b	3.2 ± 0.05ab	3.2 ± 0.04a	3.2 ± 0.13bc
T2	3.1 ± 0.21ab	3.2 ± 0.09ab	3.1 ± 0.21ab	3.0 ± 0.11a	3.1 ± 0.16abc
T3	3.2 ± 0.29ab	3.1 ± 0.20ab	3.1 ± 0.13ab	3.2 ± 0.24a	2.8 ± 0.23a
T4	3.0 ± 0.23ab	3.2 ± 0.11ab	3.2 ± 0.02ab	3.2 ± 0.17a	3.0 ± 0.10abc
T5	3.1 ± 0.24ab	2.9 ± 0.17a	3.3 ± 0.13b	3.2 ± 0.06a	3.4 ± 0.10cd
T6	3.0 ± 0.21ab	2.9 ± 0.07a	3.2 ± 0.19ab	3.2 ± 0.11a	2.8 ± 0.07ab
T7	2.7 ± 0.13a	2.8 ± 0.20a	2.8 ± 0.04a	3.1 ± 0.07a	3.0 ± 0.10abc
T8	2.7 ± 0.15a	2.9 ± 0.16a	2.9 ± 0.09ab	2.9 ± 0.16a	2.9 ± 0.01ab
Cr (μmol g^{-1})					
CK	0.17 ± 0.002c	0.17 ± 0.002c	0.17 ± 0.002c	0.17 ± 0.002c	0.17 ± 0.002c
T1	0.15 ± 0.005bc	0.13 ± 0.004abc	0.13 ± 0.002b	0.14 ± 0.001bc	0.14 ± 0.002bc
T2	0.12 ± 0.006ab	0.13 ± 0.009abc	0.12 ± 0.008ab	0.14 ± 0.007bc	0.14 ± 0.011bc
T3	0.14 ± 0.014abc	0.14 ± 0.013bc	0.15 ± 0.007bc	0.15 ± 0.010bc	0.16 ± 0.010bc
T4	0.14 ± 0.012abc	0.14 ± 0.012bc	0.14 ± 0.016bc	0.14 ± 0.014bc	0.14 ± 0.010bc
T5	0.13 ± 0.019abc	0.14 ± 0.013abc	0.14 ± 0.015b	0.14 ± 0.017bc	0.14 ± 0.015bc
T6	0.13 ± 0.026abc	0.13 ± 0.029abc	0.14 ± 0.018b	0.13 ± 0.022ab	0.14 ± 0.018bc
T7	0.13 ± 0.010ab	0.12 ± 0.006ab	0.12 ± 0.002ab	0.12 ± 0.008ab	0.13 ± 0.011ab
T8	0.10 ± 0.009a	0.10 ± 0.005a	0.09 ± 0.004a	0.09 ± 0.004a	0.10 ± 0.002a
Cu (μmol g^{-1})					
CK	0.59 ± 0.012c	0.59 ± 0.012d	0.59 ± 0.012b	0.59 ± 0.012bc	0.59 ± 0.012c
T1	0.60 ± 0.017c	0.57 ± 0.006bcd	0.56 ± 0.012ab	0.60 ± 0.015c	0.58 ± 0.010c
T2	0.59 ± 0.009bc	0.59 ± 0.013d	0.59 ± 0.012b	0.59 ± 0.011c	0.56 ± 0.007abc
T3	0.60 ± 0.006c	0.58 ± 0.011bcd	0.57 ± 0.013ab	0.57 ± 0.010abc	0.57 ± 0.005bc
T4	0.55 ± 0.015ab	0.58 ± 0.015cd	0.57 ± 0.014ab	0.55 ± 0.014abc	0.57 ± 0.011c
T5	0.54 ± 0.008a	0.56 ± 0.006abcd	0.56 ± 0.015ab	0.58 ± 0.031bc	0.58 ± 0.017c
T6	0.60 ± 0.011c	0.55 ± 0.009abc	0.54 ± 0.010a	0.52 ± 0.006a	0.53 ± 0.012ab
T7	0.54 ± 0.019a	0.54 ± 0.006ab	0.53 ± 0.014a	0.51 ± 0.017a	0.53 ± 0.008ab
T8	0.52 ± 0.011a	0.53 ± 0.009a	0.53 ± 0.016a	0.54 ± 0.010ab	0.53 ± 0.010a
Fe (μmol g^{-1})					
CK	171 ± 5.4a	171 ± 5.4a	171 ± 5.4a	171 ± 5.4a	171 ± 5.4a
T1	171 ± 2.4a	174 ± 13a	171 ± 2.9a	174 ± 11a	165 ± 6.5a
T2	162 ± 5.0a	165 ± 11a	168 ± 6.4a	173 ± 5.6a	172 ± 8.1a
T3	167 ± 13a	167 ± 8.4a	165 ± 8.4a	163 ± 12a	166 ± 3.4a
T4	161 ± 5.6a	159 ± 7.9a	161 ± 12a	164 ± 11a	166 ± 2.7a
T5	166 ± 7.5a	161 ± 11a	164 ± 12a	166 ± 8.3a	166 ± 3.2a
T6	161 ± 16a	161 ± 2.6a	162 ± 8.3a	162 ± 14a	162 ± 3.0a
T7	161 ± 5.7a	156 ± 3.9a	157 ± 6.4a	159 ± 12a	157 ± 8.3a
T8	146 ± 7.9a	148 ± 4.8a	148 ± 5.7a	150 ± 7.9a	157 ± 7.9a

Data are presented as mean values ± SD (n = 3). Means followed by the same letter within the same column are not significantly different determined by the Duncan's multiple range tests at the 5 % level

Table 4 Concentrations of simultaneously extracted metals (SEM) (Mn, Ni, Pb and Zn) in the different depth of sediments before leaching (CK) and after leaching (T1, T2, T3, T4, T5, T6, T7, and T8) (µmol g^{-1})

	D1	D2	D3	D4	D5
Mn (µmol g^{-1})					
CK	13 ± 0.12d	13 ± 0.12d	13 ± 0.12d	13 ± 0.12d	13 ± 0.12e
T1	12 ± 0.02c	12 ± 0.03c	12 ± 0.01c	13 ± 0.05cd	12 ± 0.04d
T2	12 ± 0.12c	12 ± 0.15c	12 ± 0.21c	13 ± 0.06cd	12 ± 0.31cd
T3	12 ± 0.17c	12 ± 0.30c	12 ± 0.36c	12 ± 0.53bc	12 ± 0.05bc
T4	11 ± 0.20bc	12 ± 0.21bc	12 ± 0.31bc	12 ± 0.34bc	12 ± 0.15cd
T5	11 ± 0.40c	12 ± 0.16bc	11 ± 0.24abc	12 ± 0.14bc	11 ± 0.33abc
T6	11 ± 0.21bc	11 ± 0.25b	11 ± 0.45abc	11 ± 0.01ab	12 ± 0.18bcd
T7	11 ± 0.26ab	11 ± 0.21b	11 ± 0.10ab	11 ± 0.26ab	11 ± 0.30ab
T8	10 ± 0.01a	10 ± 0.01a	11 ± 0.14a	11 ± 0.40a	11 ± 0.07a
Ni (µmol g^{-1})					
CK	0.15 ± 0.001b	0.15 ± 0.001a	0.15 ± 0.001ab	0.15 ± 0.001abc	0.15 ± 0.001b
T1	0.14 ± 0.003ab	0.15 ± 0.005a	0.15 ± 0.001ab	0.16 ± 0.002d	0.14 ± 0.001ab
T2	0.14 ± 0.004ab	0.15 ± 0.005a	0.15 ± 0.001bc	0.15 ± 0.001abc	0.15 ± 0.003ab
T3	0.14 ± 0.005ab	0.15 ± 0.003a	0.15 ± 0.004ab	0.15 ± 0.002ab	0.14 ± 0.003ab
T4	0.14 ± 0.001ab	0.14 ± 0.002a	0.14 ± 0.002a	0.16 ± 0.004cd	0.15 ± 0.002bc
T5	0.15 ± 0.005ab	0.14 ± 0.005a	0.15 ± 0.002ab	0.15 ± 0.002abcd	0.16 ± 0.003c
T6	0.14 ± 0.003a	0.14 ± 0.004a	0.15 ± 0.003bc	0.15 ± 0.001a	0.16 ± 0.001c
T7	0.14 ± 0.003ab	0.15 ± 0.002a	0.15 ± 0.002b	0.15 ± 0.002bcd	0.15 ± 0.001ab
T8	0.14 ± 0.001ab	0.15 ± 0.003a	0.16 ± 0.002c	0.15 ± 0.003abcd	0.14 ± 0.001a
Pb (µmol g^{-1})					
CK	0.19 ± 0.002b	0.19 ± 0.002b	0.19 ± 0.002d	0.19 ± 0.002d	0.19 ± 0.002b
T1	0.17 ± 0.002a	0.16 ± 0.000a	0.17 ± 0.001ab	0.16 ± 0.001ab	0.16 ± 0.002a
T2	0.17 ± 0.001a	0.17 ± 0.004a	0.17 ± 0.002bc	0.18 ± 0.001c	0.17 ± 0.003a
T3	0.17 ± 0.002a	0.17 ± 0.010a	0.18 ± 0.001c	0.17 ± 0.001bc	0.17 ± 0.001a
T4	0.17 ± 0.001a	0.17 ± 0.000a	0.16 ± 0.002ab	0.17 ± 0.002abc	0.16 ± 0.006a
T5	0.17 ± 0.000a	0.17 ± 0.003a	0.16 ± 0.001ab	0.17 ± 0.001abc	0.17 ± 0.002a
T6	0.17 ± 0.003a	0.16 ± 0.003a	0.17 ± 0.005abc	0.16 ± 0.001ab	0.16 ± 0.001a
T7	0.16 ± 0.001a	0.16 ± 0.003a	0.16 ± 0.005a	0.16 ± 0.008a	0.16 ± 0.004a
T8	0.17 ± 0.002a	0.17 ± 0.007a	0.17 ± 0.002abc	0.16 ± 0.003ab	0.17 ± 0.004a
Zn (µmol g^{-1})					
CK	1.1 ± 0.023c	1.1 ± 0.023d	1.1 ± 0.023c	1.1 ± 0.023c	1.1 ± 0.023d
T1	0.79 ± 0.004b	0.79 ± 0.008c	0.83 ± 0.005b	0.81 ± 0.034ab	0.74 ± 0.056abc
T2	0.73 ± 0.006ab	0.67 ± 0.009a	0.75 ± 0.024a	0.87 ± 0.007b	0.81 ± 0.001bc
T3	0.72 ± 0.010ab	0.74 ± 0.006bc	0.78 ± 0.001ab	0.79 ± 0.045ab	0.78 ± 0.020abc
T4	0.73 ± 0.020ab	0.71 ± 0.024ab	0.76 ± 0.003ab	0.75 ± 0.078a	0.84 ± 0.048c
T5	0.77 ± 0.036b	0.74 ± 0.009bc	0.72 ± 0.008a	0.72 ± 0.032a	0.71 ± 0.006ab
T6	0.74 ± 0.007ab	0.76 ± 0.011bc	0.76 ± 0.008ab	0.69 ± 0.011a	0.79 ± 0.028abc
T7	0.66 ± 0.064a	0.71 ± 0.027ab	0.74 ± 0.045a	0.73 ± 0.003a	0.78 ± 0.043abc
T8	0.72 ± 0.013ab	0.72 ± 0.014ab	0.71 ± 0.034a	0.71 ± 0.014a	0.69 ± 0.027a

Data are presented as mean values ± SD ($n = 3$). Means followed by the same letter within the same column are not significantly different determined by the Duncan's multiple range tests at the 5 % level

10–13 for Mn, 0.14–0.16 for Ni, 0.16–0.18 for Pb, and 0.66–0.87 for Zn (Tables 3, 4). It is suggested that the concentration of SEM-Cd was least compared with that of the other metals (Cr, Cu, Fe, Mn, Ni, Pb, and Zn).

SEM/AVS ratios in sediments

The SEM/AVS ratio of heavy metals in the sediments prior to and following the leaching process is presented in Fig. 1; that at five various depths of sediment is presented in Fig. 2. The average SEM/AVS ratios under the eight desalination treatments were all less than 1 for Cd (0.01–0.04) and Cr (0.38–0.96). However, the average SEM/AVS ratios were all more than 1 for Cu (1.6–5.4), Fe (477–1513), Mn (34–106), and Zn (2.2–7.1) (Fig. 1). Figure 1 also indicates that the SEM/AVS ratios increased from 0.42 to 0.88 for Ni and from 0.46 to 0.98 for Pb in T1–T6, which were all less than 1, whereas the ratios increased from 1.0 to 1.5 for Ni and from 1.1 to 1.7 for Pb in T7–T8, which were more than 1. Under the five soil depth treatments, the ratios of SEM/AVS for Cd (0.01–0.03) were all less than 1; those for Cu (5.7–1.7), Fe (1635–507), Mn (116–36), and Zn (7.8–2.5) were all more than 1 (Fig. 2). The average SEM/AVS ratios were more than 1 for Cr in D1 (1.3), Ni in D1 (1.4), and Pb in D1 and D2 (1.7–1.02) and were less than 1 for Cr in D2–D5 (0.80–0.43), Ni in D2–D5 (0.89–0.46), and Pb in D3–D5 (0.70–0.52). In summary, the desalination treatment in T1 reduced the ratios of SEM/AVS dramatically compared with control (without desalination), and the ratios of SEM/AVS decreased with soil depth and increased with enhanced desalination levels (Figs. 1, 2). The sum of the molar concentrations of heavy metals ($\sum$SEM) compared with the molar concentration of AVS in sediments was significantly more than 1 under the eight desalination treatments.

Discussion

The desalination levels ($p < 0.001$) and soil depths ($p < 0.001$) both had significant effects on the concentrations of AVS (Table 1). Furthermore, the concentrations of AVS tended to decrease with enhanced desalination levels (from T1 to T8) and increase with an increase in soil depth (Table 2). Concentrations of AVS within sediments depend on several factors including organic matter supply, particle size, rate of sulfate reduction, and sediment redox condition (Oehm et al. 1997; Prica et al. 2008, 2010; Liu et al. 2010). The sediment oxidation–reduction potential (ORP) measured at a 5 cm depth in the sampling field was -122.2 ± 16.1 mV and at 15 cm was -136.0 ± 20.7 mV. When the sediment columns were prepared, the initial redox potential was -133.6 ± 9.3 mV. It was noted that the ORP value of sediments decreased dramatically and became more reduced after leaching due to long-term flooding conditions (Li et al. 2011), whereas the concentrations of AVS increased after leaching (T1) (Table 2). The SO_4^{2-} reduction is regarded as an important factor for AVS formation in sediments. Under such conditions, SO_4^{2-} transfers into high concentrations of S^{2-}, and more AVS is produced. In addition, the ORP value tends to enhance (Li et al. 2011), whereas AVS decreased during the leaching treatments from T1 to T8 (Table 2). These results can be explained by the transfer of S^{2-} into SO_4^{2-} from T1 to T8, which caused an increase in the ORP value. The AVS concentrations were very low in the top 0–10 cm of sediment leaching and increased gradually with depth from D1 to D5, which is consistent with the results of Fang et al. (2005). The depth of O_2 penetration in the sediments is attributed to its downward diffusion from surface water. A reduction in O_2 penetration with an increase in sediment depth can lead to a decrease in ORP value and the formation of AVS by SO_4^{2-} reduction (Fang et al. 2005; Li et al. 2011). Therefore, the ORP value strongly influenced the AVS concentration.

The distribution of heavy metals among various sediment profiles includes water-soluble, exchangeable, carbonate-bound, reducible, oxidizable, and residual fractions (Yu et al. 2001; Zhang and Zhang 2007). In oxic sediments, metal bioavailability is related to binding mechanisms onto organic C, Fe, and Mn oxyhydroxides (Yu et al. 2001). In anoxic sediments, the mobility of divalent metals can be controlled by the formation of stable sulfide complexes, and the availability of divalent metals to organisms living nearby is related to AVS (Di Toro et al. 1992; Zhang and Zhang 2007; Ankley et al. 1996; Cooper and Morse 1998). The average SEM/AVS ratios were all less than 1 for Cd and Cr under the eight desalination treatments (Fig. 1), indicating that the AVS in the sediments was sufficient for binding the Cd or Cr. In contrast, the SEM/AVS ratios were all more
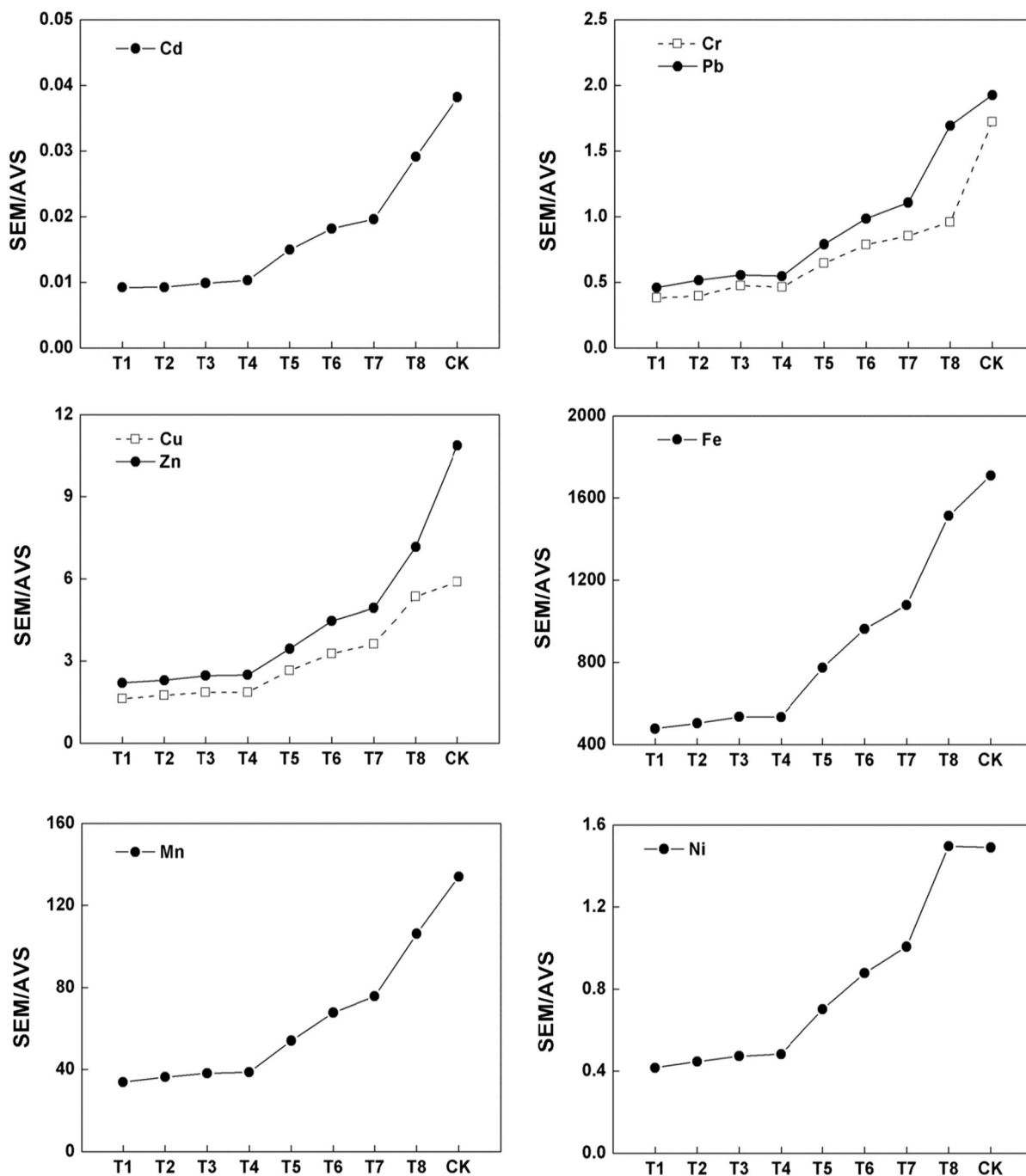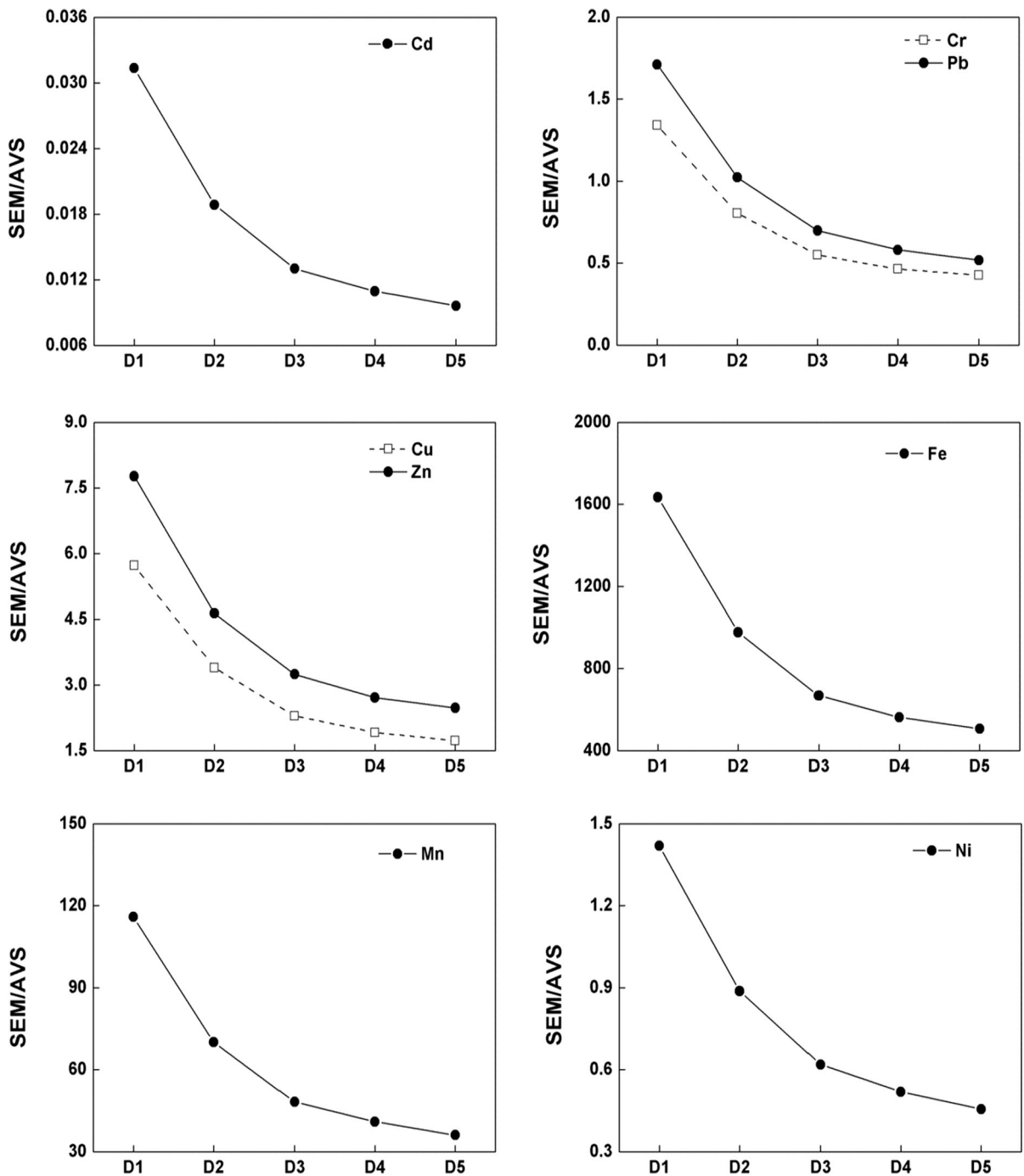
Fig. 1 Average simultaneously extracted metal/acid-volatile sulfide (SEM/AVS) ratios of heavy metals in sediments before leaching (CK) and after leaching (T1, T2, T3, T4, T5, T6, T7, and T8)

than 1 for Cu, Fe, Mn, and Zn under the same treatments (Fig. 1), which shows that Cu, Fe, Mn, and Zn may be available to benthic organisms. On the basis of our previous study (Li et al. 2011), the SEM of

Cu and Zn was lower than the total concentration of four nonresidual fractions in Tessier's sequential extraction and more than the concentration of oxidizable fractions, respectively. These results suggest the

Fig. 2 Average simultaneously extracted metal/acid-volatile sulfide (SEM/AVS) ratios of heavy metals in five various depths of sediment

SEM from the AVS extraction represented different chemical forms for different heavy metals, depending on the reactions of the metal with HCl in the AVS procedure. Compared with Tessier's sequential extraction method (Tessier et al. 1979), HCl used in the AVS extraction procedure is a stronger reagent than

those used in the exchangeable ($MgCl_2$) and carbonate fractions (NaOAc). Metals bound to these two fractions could be extracted by the AVS extraction procedures.

The present results showed that desalination levels ($p < 0.001$) had profound effects on the concentrations of SEM (Cd, Cr, Cu, Fe, Mn, Pb, and Zn) (Table 1), which generally exhibited decreasing trends with enhanced desalination levels after leaching (Tables 3, 4). These trends can be explained by the following facts: (1) The S^{2-} and sulfide decreased because the ORP value enhanced when the desalination level increased (Fang et al. 2005); (2) the carbonate fraction was reduced owing to the dissolution of carbonates in the sediment during leaching (Chen et al. 1998; Jiang et al. 2006); (3) the desorption of some exchangeable metals from solid phases increased as the leaching time was extended (Loser et al. 2007).

The solubilities of metal sulfides differ according to the sequences of their Ksp values, which largely affects the ability of metals to form SEM in sediment. In sediments, divalent metals that form less soluble sulfides follow the order of: Cu > Pb > Cd > Ni > Zn > Fe > Mn > Cr, and are retained in the sediment as their respective metal sulfides (Cooper and Morse 1998). In environmental research, the sum of the molar concentrations of heavy metals ($\sum$SEM) is usually compared to the molar concentration of AVS to evaluate the potential effects of those metals on benthic organisms. In the present study, the $\sum$SEM/AVS ratio in the sediments was significantly higher than 1. This assessment theoretically suggests that SEM, apart from binding with AVS, can exist in pore water and may be available to benthic organisms (Liu et al. 2010; Ankley et al. 1996; Gao et al. 2013). However, not all sediments can actually cause increased toxicity when the $\sum$SEM/AVS ratio > 1 because many other metal-binding phases occur in sediments, such as organic matter, the carbonate phase, and Fe and Mn oxides (Ankley et al. 1996; Chapman et al. 1998; McGrath et al. 2002). Yu et al. (2001) have identified that the presence of a range of adsorptive phases, such as the organic phase, the carbonate phase, and the Fe and Mn oxyhydroxide phase, can influence SEM concentration. Therefore, the total SEM concentration does not correspond to only metals bound to AVS. SEM/AVS predictions may overestimate metal bioavailability if a significant quantity of metals bound to other phases can be leached out during HCl extraction (Allen et al. 1993; Ankley et al. 1996; O'day et al. 2000). Therefore, although the $\sum$SEM/AVS ratio is >1, the other binding phases, such as organic complexing ligands and Fe and Mn oxides, may limit the bioavailabilities of heavy metals (Yang et al. 2012). Desalination refers to the removal of salts and minerals (such as Ca^{2+}, Mg^{2+}, and Na^+) in soil, leading to the decrease in acidic buffering capacity of soil. Thus, the bioavailabilities of heavy metals in soil can be enhanced by the rainwater leaching in the field conditions. In the present study, the pH of distilled water used for leaching was higher than the rainwater normally used in the field. Moreover, the water flow rate was faster in this study than in the field. Therefore, the effects of leaching on particular metals under field conditions may differ from those observed in this study. However, the results obtained in this study can still provide references for the application of leaching for soil desalinization in field conditions.

Conclusions

Desalination level ($p < 0.001$) and soil depth ($p < 0.001$) both had significant effects on the concentrations of AVS, which generally exhibited increasing trends with an increase in depth and decreasing trends with enhanced desalination levels. The desalination levels had significant ($p < 0.05$) effects on the concentrations of SEM (Cd, Cr, Cu, Fe, Mn, Pb, and Zn). The concentrations of SEM (Cd, Cr, Cu, Fe, Mn, Pb, and Zn) decreased with an increase in desalination level. The average SEM/AVS ratios were less than 1 for Cd and Cr and more than 1 for Cu, Fe, Mn, and Zn under eight desalination treatments. In addition, the desalination treatment significantly reduced the ratios of SEM/AVS compared with control (without desalination), and the ratios of SEM/AVS increased with desalination levels, indicating that low desalination treatment is better for reducing toxicity to benthic organisms than high desalination treatment. Although all of the $\sum$SEM/AVS ratios in the sediments were more than 1 during leaching under the eight desalination treatments, these results do not necessarily suggest that the sediment is potentially toxic because the other binding phases such as organic matter, the carbonate phase, and Fe and Mn oxides can

limit the bioavailabilities of heavy metal and reduce the ecological risks. Since the reclaimed tidal flats with low desalinisation are suitable for saline water aquaculture, transforming the present land use of reclaimed tidal flats from fresh water aquaculture into saline water aquaculture may reduce health risk of heavy metals remained in sediments. This research contributes to an understanding of the dynamic behavior of heavy metals in the reclamation of tidal flats during the leaching process and the role of the ratio of SEM/AVS prediction on assessing the environmental quality of reclaimed tidal flats.

References

Allen, H. E., Fu, G., & Deng, B. (1993). Analysis of acid-volatile sulfide (AVS) and simultaneously extracted metals (SEM) for the estimation of potential toxicity in aquatic sediments. *Environmental Toxicology and Chemistry, 12*(13), 1441–1453.

Ankley, G. T., Ditoro, D. M., & Hansen, D. J. (1996). Technical basis and proposal for deriving sediment quality criteria for metals. *Environmental Toxicology and Chemistry, 15*(11), 2056–2066.

Chapman, P. M., Wang, F. Y., Janssen, C., Persoone, G., & Allen, H. E. (1998). Ecotoxicology of metals in aquatic sediments: binding and release, bioavailability, risk assessment, and remediation. *Canadian Journal Fisheries and Aquatic Science, 55*(23), 2221–2243.

Chen, W., Chen, B. B., & Fang, M. (1998). Studies on the increasing of pH value and alkalization of seashore saline soil during its desalting in Liaodong Peninsula. *Journal of Nanjing Agricultural University, 21*(6), 59–64.

Cooper, D. C., & Morse, J. W. (1998). Extractability of metal sulfide minerals in acidic solutions: Application to environmental studies of trace metal contamination within anoxic sediments. *Environmental Science and Technology, 32*(3), 1076–1078.

Di Toro, D. M., Mahony, J. D., Hansen, D. J., Scott, K. J., Carlson, A. R., & Ankley, G. T. (1992). Acid volatile sulfide predicts the acute toxicity of cadmium and nickel in sediments. *Environmental Science and Technology, 26*(6), 96–101.

Du Laing, G., Bogaert, N., Tack, F. M. G., Verloo, M. G., & Hendrickx, F. (2002). Heavy metal contents (Cd, Cu, Zn) in spiders (Pirata piraticus) living in intertidal sediments of the river Scheldt estuary (Belgium) as affected by substrate characteristics. *Science of the Total Environment, 289*(11), 71–81.

Du Laing, G., De Vos, R., Vandecasteele, B., Lesage, E., Tack, F. M. G., & Verloo, M. G. (2008). Effect of salinity on heavy metal mobility and availability in intertidal sediments of the Scheldt estuary. *Estuarine Coastal and Shelf Science, 77*(14), 589–602.

Fang, T., Li, X. D., & Zhang, G. (2005). Acid volatile sulfide and simultaneously extracted metals in the sediment cores of the Pearl River Estuary, South China. *Ecotoxicology and Environmental Safety, 61*(12), 420–431.

Gao, X. L., Li, P. M., & Chen, C. T. A. (2013). Assessment of sediment quality in two important areas of mariculture in the Bohai Sea and the northern Yellow Sea based on acid-volatile sulfide and simultaneously extracted metal results. *Marine Pollution Bulletin, 72*(8), 281–288.

Hatje, V., Payne, T. E., Hill, D. M., McOrist, G., Birch, G. F., & Szymczak, R. (2003). Kinetics of trace element uptake and release by particles in estuarine waters: effects of pH, salinity, and particle loading. *Environment International, 29*(11), 619–629.

He, J., Lü, C. W., Fan, Q. Y., Xue, H. X., & Bao, J. H. (2011). Distribution of AVS-SEM, transformation mechanism and risk assessment of heavy metals in the Nanhai Lake in China. *Environmental Earth Science, 64*(13), 2025–2037.

Jiang, M., Lu, X. G., Yang, Q., & Tong, S. Z. (2006). Iron biogeochemical cycle and its environmental effect in wetlands. *Acta Pedologica Sinica, 43*(7), 493–499. (in Chinese).

Leung, H. M., Leung, A. O. W., Wang, H. S., Ma, K. K., Liang, Y., Ho, K. C., et al. (2014). Assessment of heavy metals/metalloid (As, Pb, Cd, Ni, Zn, Cr, Cu, Mn) concentrations in edible fish species tissue in the Pearl River Delta (PRD), China. *Marine Pollution Bulletin, 78*(11), 235–245.

Li, Q. S., Chen, X. J., Luo, X., Cui, Z. H., Shi, L., Wang, L. L., et al. (2012). Phytoavailability of heavy metals in tidal flat soils after fresh water leaching. *Ecotoxicology and Environmental Safety, 79*(6), 22–27.

Li, Q. S., Liu, Y. N., Du, Y. F., Cui, Z. H., Shi, L., Wang, L. L., et al. (2011). The behavior of heavy metals in tidal flat sediments during fresh water leaching. *Chemosphere, 82*(5), 834–838.

Li, Q. S., Wu, Z. F., Chu, B., Zhang, N., Cai, S. S., & Fang, J. H. (2007). Heavy metals in coastal wetland sediments of the Pearl River Estuary, China. *Environmental Pollution, 149*(7), 158–164.

Liu, J. C., Yan, C. L., Spencer, K. L., Zhang, R. F., & Lu, H. L. (2010). The distribution of acid-volatile sulfide and simultaneously extracted metals in sediments from a mangrove forest and adjacent mudflat in Zhangjiang Estuary, China. *Marine Pollution Bulletin, 60*(8), 1209–1216.

Long, E. R., Field, J. J., & MacDonald, D. D. (1998). Predicting toxicity in marine sediments with numerical quality guideline. *Environmental Toxicology and Chemistry, 17*(14), 714–727.

Loser, C., Zehnsdorf, A., Hoffmann, P., & Seidel, H. (2007). Remediation of heavy metal polluted sediment by suspension and solid-bed leaching: Estimate of metal removal efficiency. *Chemosphere, 66*(7), 1699–1705.

McGrath, J. A., Paquin, P. R., & Di Toro, D. M. (2002). Use of the SEM and AVS approach in predicting metal toxicity in sediments. *Fact Sheet on Environmental Risk Assessment,*

International Council on Mining and Metals, London, UK, 10, 1–7.

Nizoli, E. C., & Luiz-Silva, W. (2012). Seasonal AVS–SEM relationship in sediments and potential bioavailability of metals in industrialized estuary, southeastern Brazil. *Environmental Geochemistry and Health, 34*(10), 263–272.

Norvell, W. A., Wu, J., Hopkins, D. G., & Welch, R. M. (2000). Association of cadmium in durum wheat grain with soil chloride and chelate-extractable soil cadmium. *Soil Science Society of Amercia Journal, 64*(7), 2162–2168.

O'day, P. A., Carroll, S. A., Randall, S., Anderson, S. L., Jelinski, J., & Knezovich, J. P. (2000). Metal speciation and bioavailability in contaminated estuary sediments; Alameda naval air station, California. *Environmental Science & Technology, 34*(9), 3665–3673.

Oehm, N. J., Luben, T. J., & Ostrofsky, M. J. (1997). Spatial distribution of acid-volatile sulfur in the sediments of Canadohta Lake, PA. *Hydrobiology, 345*(7), 79–85.

Poot, A., Meerman, E., Gillissen, F., & Koelmans, A. A. (2009). A kinetic approach to evaluate the association of acid volatile sulfide and simultaneously extracted metals in aquatic sediments. *Environmental Toxicology and Chemistry, 28*(7), 711–717.

Prica, M., Dalmacija, B., Dalmacija, M., Agbaba, J., Krcmar, D., Trickovic, J., et al. (2010). Changes in metal availability during sediment oxidation and the correlation with the immobilization potential. *Ecotoxicology and Environmental Safety, 73*(8), 1370–1377.

Prica, M., Dalmacija, B., Roncevic, S., Krcmar, D., & Becelic, M. (2008). A comparison of sediment quality results with acid volatile sulfide (AVS) and simultaneously extracted metals (SEM) ratio in Vojvodina (Serbia) sediments. *Science of the Total Environment, 389*(10), 235–244.

Tampouris, S., Papassiopi, N., & Paspaliaris, I. (2001). Removal of contaminant metals from fine grained soils, using agglomeration, chloride solutions and pile leaching techniques. *Journal of Hazardous Materials, 84*(23), 297–319.

Tessier, A., Campbell, P. G. C., & Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry, 51*(8), 844–851.

Van den Berg, G. A., Loch, J. P. G., Van der Heijdt, L. M., & Zwolsman, J. J. G. (1998). Vertical distribution of acid-volatile sulfide and simultaneously extracted metals in a recent sedimentation area of the river meuse in The Netherlands. *Environmental Toxicology and Chemistry, 17*(6), 758–763.

Van Griethuysen, C., Van Baren, J., Peeters, E. T. H. M., & Koelmans, A. A. (2004). Trace metal availability and effects on benthic community structure in floodplain lakes. *Environmental Toxicology and Chemistry, 23*(14), 668–681.

Yang, Y. F., Chen, F. R., Zhang, L., Liu, J. S., Wu, S. J., & Kang, M. L. (2012). Comprehensive assessment of heavy metal contamination in sediment of the Pearl River Estuary and adjacent shelf. *Marine Pollution Bulletin, 64*(9), 1947–1955.

Yin, H., & Fan, C. (2011). Dynamics of reactive sulfide and its control on metal bioavailability and toxicity in metal-polluted sediments from Lake Taihu, China. *Archives of Environmental Contamination and Toxicology, 60*(11), 565–575.

Yu, K. C., Tsai, L. J., Chen, S. H., & Ho, S. T. (2001). Chemical binding of heavy metals in anoxic river sediments. *Water Research, 35*(9), 4086–4094.

Zhang, H. G., Cui, B. S., & Zhang, K. J. (2011). Heavy metal distribution of natural and reclaimed tidal riparian wetlands in south estuary, China. *Journal of Environmental Science-China, 23*(10), 1937–1946.

Zhang, X. S., & Zhang, L. J. (2007). Acid volatile sulfide and simultaneously extracted metals in tidal flat sediments of Jiaozhou Bay, China. *Journal of Ocean University of China, 6*(6), 137–142.