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ORIGINAL ARTICLE

Accumulation and partitioning of heavy metals in mangrove rhizosphere sediments

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Abstract A field study was conducted to clarify the effect of rhizosphere processes on the accumulation and partitioning of heavy metals (Pb, Zn, Cu, Cr, Cd and Ni) in mangrove sediments. Metals were fractionated by a sequential extraction procedure into three chemically distinct fractions: water soluble, exchangeable and carbonate bound (B1), Fe–Mn oxide bound (B2), and organic and sulfide bound (B3). Results indicate that rhizosphere processes tend to increase the metal concentrations in the rhizosphere sediments. However, plant uptake may result in the decrease of the metal concentrations in the rhizosphere sediments when the metal concentrations are relatively low in the bulk sediments. Compared with the bulk sediments, the rhizosphere sediments have low concentrations of heavy metals in the B1 and B2 fractions and high concentrations in the B3 fraction. Either an increase or decrease in the residual fraction of heavy metals in the rhizosphere sediments may appear, depending on whether the formation of the refractory metal-organic compounds or the activation of the residual fractions dominates. Results also indicate that mangrove plants absorb and store non-essential metals in the perennial tissues, thus reducing the export of non-essential metals via leaf litter transport. Mangrove plants are excellent candidates for phytostabilization of heavy metals in intertidal substrates.

Keywords Accumulation · Heavy metals · Rhizosphere processes · Sediment · Speciation

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Introduction

Mangrove ecosystems, one of the most important intertidal wetlands, are commonly situated in tropical and sub-tropical coastal regions. Because mangrove sediments are anaerobic, reduced and rich in sulfide and organic matter, they tend to retain water-borne heavy metals (Silva et al. 1990; Tam and Wong 1995, 2000) and usually act as sinks for anthropogenic contaminants (especially heavy metals) in coastal areas. Mangrove ecosystems can be considered a "green barrier" because they can efficiently reduce the transport of heavy metals to adjacent marine systems (Machado et al. 2002; Silva et al. 2006). Given the rapid urbanization and industrialization in coastal regions, mangrove ecosystems will play an increasingly important role in controlling heavy metal pollution.

Mangrove plants have a high tolerance for heavy metals (Peters et al. 1997; MacFarlane and Burchett 2002) and act as long-term sinks for most heavy metals (Silva et al. 1990; Yim and Tam 1999; Silva et al. 2006). Mangrove colonization increases the content of fine particles and organic matter in the intertidal sediments (Madkour and Mohammed 2008; Perry and Berkeley 2009). Thus, mangrove sediments are particularly effective in sequestering potentially toxic heavy metals (Peters et al. 1997; Ramanathan et al. 1999). Mangrove plants affect the migration and accumulation of heavy metals and also their bioavailability and mobility, particularly through rhizosphere processes. Previous studies have found that radial oxygen loss (ROL) may lead to precipitation of iron oxyhydroxides in the rhizosphere and on the root surface as iron plaques, consequently decreasing the mobility of heavy metals (Otte et al. 1989, 1995; Mortimer and Rae 2000). However, other studies indicate that ROL could significantly increase the mobility of heavy metals and decrease the concentration of acid-volatile sulfides (AVS) (Clark et al. 1998; Jacob and Otte 2004). Mangrove roots can exude many low-molecular weight organic acids (Lu et al. 2007), which may induce partial activation of heavy metals in rhizosphere sediments (Bennett 1991; Welch and Ullman 1996). Moreover, the oxidation of sulfides and microbial decomposition of root exudates may result in a decrease in pH, which would cause partial dissolution of Fe–Mn oxides and carbonates. The role of mangrove ecosystems on the immobilization of heavy metals is unclear.

The goal of this study is to clarify the effect of rhizosphere processes on the accumulation and partitioning of heavy metals in mangrove sediments. Comparison of the concentrations and distribution patterns of heavy metals between rhizosphere sediments and bulk sediments was conducted under field conditions. Knowledge of these processes is important for understanding how mangrove ecosystems function for utilizing mangrove ecosystems as a "green barrier."

Materials and methods

Description of study areas

Two representative mangrove forests, the *Sonneratia apetala* forest (latitude 23°33′N and longitude 116°53′E) and the *Aegiceras corniculatum* forest (latitude 23°19′N and longitude 116°43′E) were selected as study areas in the Shantou Coastal Wetland of Guangdong Province, China (Fig. 1). The former thrives in the non-enclosed intertidal zone of the Yifeng Estuary, while the latter survives in an enclosed shrimp pond that was reclaimed from the Rongjiang Estuary. The *S. apetala* forest is an artificial mangrove wetland with an area of around 80 ha. Because of its rapid growth, *S. apetala* has been widely used for mangrove restoration in southeastern China since 1985. Mature trees in this wetland are around 10 years old and are characterized by their mean tree density (7,200 ± 3,857 ind./ha), high tree canopy (6.42 ± 0.51 m) and very high pneumatophore density (around 180–240/m^2). Most mature trees are located in a small delta with tidal flushing twice a day. The largest tidal range is 2.1 m. The *A. corniculatum* forest is a natural secondary forest with an area of around 10 ha. *A. corniculatum* has been planted and used to purify the water of the shrimp pond in some areas. The mean tree density of the *A. corniculatum* forest is 9,800 ± 1,450 ind./ha, and the mean canopy height is 2.46 ± 0.45 m. Water exchanges from the pond vary according to the stage of tidal cycle. Inpouring occurs through a relatively wide inlet, and outpouring occurs through a narrow outlet at the other end during high tide. No exchange occurs at low tide.

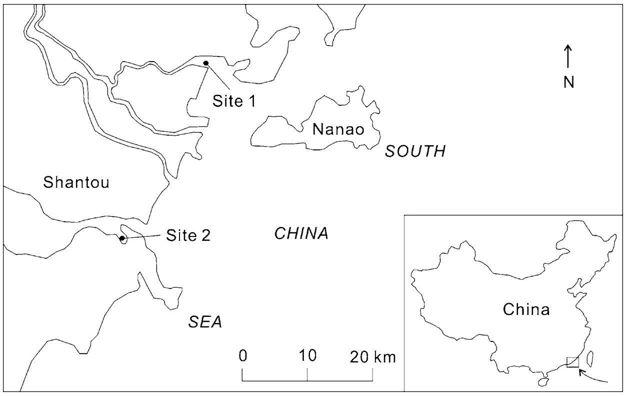

Fig. 1 Study area with location of the two sampling sites. *Site 1 Sonneratia apetala* forest (23°33′N, 116°53′E), *Site 2 Aegiceras corniculatum* forest (23°19′N, 116°43′E)

Sample collection and pretreatment

Rhizosphere and bulk sediments were sampled from the *S. apetala* and *A. corniculatum* forests in October 2007. Six replicated sediment cores were collected by using acid-washed PVC pipes (40-cm long, 8-cm internal diameter) in both mangrove wetlands. All sampled cores were immediately closed with plastic films, stored in a homemade ice box and transported to the laboratory on the same day. When samples arrived at the laboratory, the cores were immediately processed to recover the surface 15 cm sediments and then to separate the rhizosphere sediments from the bulk sediments with a plastic knife. The rhizosphere sediments were taken as the 1 mm of sediments surrounding the live roots (Wang et al. 2009), and the remainder was treated as bulk sediments. The subsampling process was conducted inside a glove box with a nitrogen atmosphere. Each subsample was divided into two portions. The portion for metal analysis was freeze dried, powdered and sieved through a 0.25 mm nylon sieve. The other portion was air-dried and used for analysis of physicochemical parameters.

To investigate the role of mangrove trees on metal storage and metal export, the root, branch and leaf samples from six different trees in the two regions were collected on the same day. Root samples were collected from the feeding and cable roots of *S. apetala*, while pneumatophores and anchor roots were avoided (MacFarlane et al. 2003). Plant samples were stored separately in polythene bags before reaching the laboratory. In the laboratory, plant samples were washed in distilled water, oven dried until the weight was constant (70°C, 48 h), and then powdered and sieved through a 0.25-mm nylon sieve.

Physicochemical analysis

The physicochemical parameters of the sediment samples were analyzed using standard methods (Lu 1999). The organic content was determined by oxidation with potassium dichromate. The total dissolved salt content was determined by the mass method with a ratio of 1:5 (sediment to water). Sediment texture was determined by wet sieving (0.063 mm), and the sediments were fractionated into two parts in samples previously treated with hydrogen peroxide. The pH values of the samples were determined in deionized water with a mass ratio of 1:5 (sediment to water) using a pH meter. Soil redox potential measurements were taken in the forests at a depth of 10 cm using a portable redox meter.

Heavy metal analysis

The BCR (Community Bureau of Reference) three-step sequential extraction procedure (Ure et al. 1993), one of the most widely applied methods for speciation analysis, was used. This method is also known as the Standard Measurement and Testing Program of the European Community (STM). Metals were fractionated into three chemically distinct fractions: water soluble, exchangeable and carbonate bound (B1), Fe–Mn oxide bound (B2) and organic and sulfide bound (B3) (Table 1). Microwave digestion in a mixture of 4 ml HNO_3, 2 ml H_2O_2 and 2 ml HF was performed to dissolve all metals in the sediment samples. Microwave digestion in a mixture of 7 ml HNO_3 and 1 ml H_2O_2 was used to extract the metals from the plant samples. All reagents were of analytical reagent grade or better.

The concentrations of Pb, Zn, Cu, Cr and Ni were determined by inductively coupled plasma–atomic emission spectrometry (ICP–AES). Graphite furnace atomic absorption spectrometry (GFAAS) was used for the determination of Cd because of the low concentration of this element. To study the accuracy of the sequential extraction procedure, the certified reference material CRM 701 was used. The recoveries of Pb, Zn, Cu, Cr, Ni and Cd in B1, B2 and B3 fractions ranged from 96 to 109%, 82 to 99% and 100 to 120%, respectively. Another reference sediment material (GBW-07310) was used to check the recovery of total digestion. Recoveries for all metals studied were greater than 89%. The precision and accuracy of the plant sample analysis were ensured using a shrub reference material (GBW07603) for all metals. The results were found to be within ±15% of the certified value. All reference samples were run in four replicates and standard errors were always less than 3%.

Table 1 Extractant and procedure used for fractionation of BCR

Step	Phase	Procedure
1	B1: water soluble, exchangeable and carbonate bound	0.11 M CH_3COOH, 20 ml, room temperature, shake for 16 h
2	B2: Fe–Mn oxide bound	0.5 M $NH_2OH \cdot HCl$ (pH 1.5 with HNO_3), 20 ml, room temperature, shake for 16 h
3	B3: Organic matter and sulfide bound	30% H_2O_2, 5 ml, room temperature, 1 h, followed 85°C, 1 h, occasionally shake; add 5 ml 30% H_2O_2, 85°C, 1 h; add 1 M CH_3COONH_4 (pH 2 with HNO_3) 25 ml, room temperature, shake for 16 h

Statistical analysis

Statistic analysis was performed using the software SPSS 11.0. Concentrations of all metals in the residual fraction (B4) were calculated by subtraction (B4 fraction = total content − B1 fraction − B2 fraction − B3 fraction). All data presented and discussed are mean values.

Results

Physicochemical characteristics of rhizosphere and bulk sediments

The major characteristics of rhizosphere and bulk sediments are presented in Table 2. *A. corniculatum* bulk sediments had higher total sulfur content and lower pH values than *S. apetala* bulk sediments. No significant difference was found in fines (silt + clay) content, salinity, organic content or Eh values between these two mangrove bulk sediments. All variables were significantly different between the rhizosphere and the bulk sediments in both mangrove forests. Rhizosphere sediments had higher fines content, organic content and salinity, and lower total sulfur content and pH values than bulk sediments.

Heavy metal concentrations in rhizosphere and bulk sediments

The heavy metal concentrations in the rhizosphere and bulk sediments are presented in Table 3. Mean metal concentrations in all the sediments decreased in the order Zn > Pb > Cr > Cu > Ni > Cd. *S. apetala* bulk sediments had significantly higher concentrations of Pb, Zn, Cu and Cr ($P < 0.01$), and slightly higher concentrations of Ni and Cd than *A. corniculatum* bulk sediments. Compared with bulk sediments, rhizosphere sediments in the *S. apetala* forest had higher concentrations of all metals studied except for Cd, which was lower. In the *A. corniculatum* forest, the

Table 2 Comparison of some physicochemical properties between rhizosphere sediments and bulk sediments

	OC (%)	S (g/kg)	Salinity (‰)	Fines (%)	pH	Eh (mV)
S. apetala sediment						
Rhizosphere	4.14 ± 0.22	1.47 ± 0.09	13.81 ± 0.63	90.44 ± 1.87	5.30 ± 0.08	ND
Bulk	3.26 ± 0.18	2.36 ± 0.12	12.16 ± 0.82	86.22 ± 1.62	5.54 ± 0.07	240 ± 32
Sig.	**	**	*	*	**	ND
A. corniculatum sediment						
Rhizosphere	5.25 ± 0.31	4.33 ± 0.17	14.59 ± 0.98	89.18 ± 2.04	3.58 ± 0.06	ND
Bulk	3.05 ± 0.16	7.04 ± 0.28	11.20 ± 0.77	84.49 ± 1.96	3.71 ± 0.07	189 ± 28
Sig.	**	**	**	*	*	ND

Data are mean ± standard deviations of three replicates. Significant difference is determined by paired *t* test

ND not determined

* Significant at the 0.05 level

** Significant at the 0.01 level

Table 3 Comparison of heavy metal concentrations between rhizosphere sediments and bulk sediments (μg g^{-1})

	Pb	Zn	Cu	Cr	Ni	Cd
S. apetala sediment						
Rhizosphere	77.7 ± 2.9	129.0 ± 7.8	38.0 ± 3.1	46.2 ± 1.7	21.3 ± 1.2	0.14 ± 0.01
Bulk	73.5 ± 2.6	119.1 ± 6.2	31.9 ± 2.9	39.0 ± 1.6	19.2 ± 1.2	0.18 ± 0.02
Sig.	*	**	**	**	*	**
A. corniculatum sediment						
Rhizosphere	51.0 ± 3.1	88.9 ± 8.4	22.1 ± 1.5	32.5 ± 1.4	15.8 ± 1.4	0.10 ± 0.01
Bulk	59.7 ± 3.8	101.2 ± 7.6	23.7 ± 1.6	32.8 ± 2.0	17.8 ± 1.3	0.16 ± 0.01
Sig.	**	**	*	–	*	**

Data are mean ± standard deviations of six replicates. Significant difference is determined by paired *t* test

* Significant at the 0.05 level

** Significant at the 0.01 level

– Nonsignificant

rhizosphere sediments had lower concentrations of Pb, Zn, Cu, Ni and Cd than the bulk sediments, and no significant difference was found in the Cr content.

Partitioning of heavy metals in rhizosphere and bulk sediments

The concentrations of metals in B1, B2, B3 and B4 fractions are shown in Figs. 2 and 3. The different metals showed different distribution patterns in both mangrove forests, but the distribution pattern of any individual metal was similar between the two mangrove forests. The highest percentages of Zn (55–62%), Cr (64–76%) and Ni (65–75%) were in the B4 fraction. The second-highest percentages of Zn (17–25%), Cr (21–33%) and Ni (16–25%) were in the B3 fraction. Pb was predominantly in the B2 fraction (55–71%). Around 75–86% of the total Cu was found in the B3 and B4 fractions, and around 72–82% of the total Cd was found in the B1 and B4 fractions. The mean metal concentrations decreased in the order Pb > Zn > Cu > Cr > Ni > Cd in the non-residual fractions (B1 fraction + B2 fraction + B3 fraction) of both mangrove sediments.

In B1 and B2 fractions of both mangrove forests, the concentration of all metals studied was lower in the rhizosphere sediments than in the bulk sediments. In B3 fraction, the opposite was true for all metals except for Cd in the *A. corniculatum* forest, which was lower in the rhizosphere sediments. In B4 fraction, the concentration of all metals studied in the *A. corniculatum* forest was lower in the rhizosphere sediments than in the bulk sediments. In the *S. apetala* forest, the opposite was true for all metals except Cd.

Concentrations and bioconcentration factors of heavy metals in plant tissues

The heavy metal concentrations in the roots, branches and leaves of *S. apetala* and *A. corniculatum* are shown in

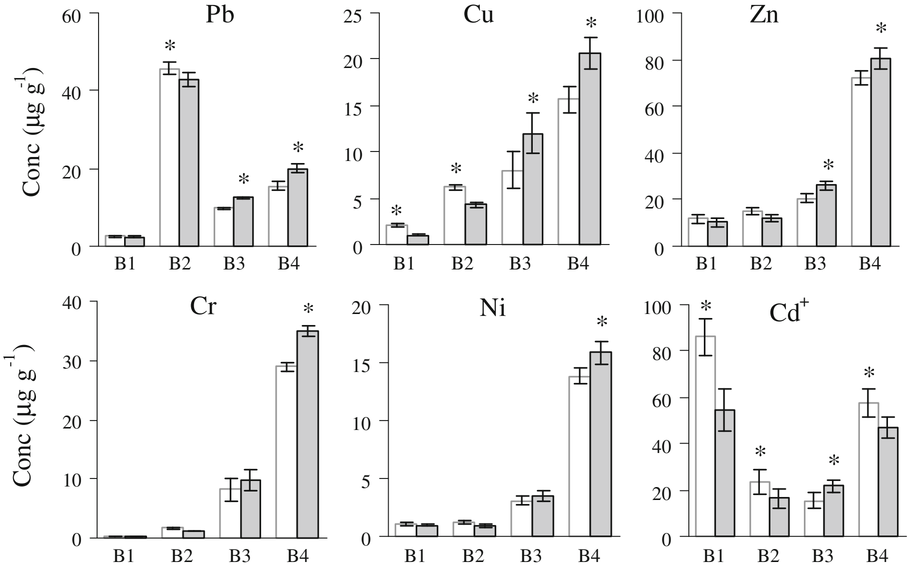

Fig. 2 Comparison of element concentrations in B1, B2, B3 and B4 fractions between rhizosphere sediments and bulk sediments in *S. apetala* forest. Bulk sediments (*open bars*), Rhizosphere sediments (*filled bars*). *Asterisks* indicate significant in paired *t* test ($P < 0.05$), *plus symbol* indicates units: ng g^{-1}

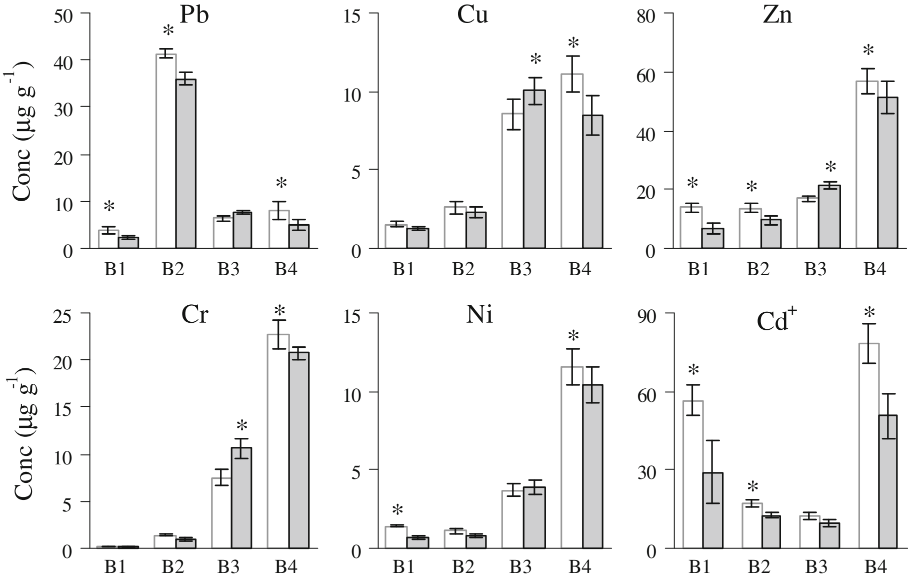

Fig. 3 Comparison of element concentrations in B1, B2, B3 and B4 fractions between rhizosphere sediments and bulk sediments in *A. corniculatum* forest. Bulk sediments (*open bars*), Rhizosphere sediments (*filled bars*). *Asterisks* indicate significant in paired *t* test ($P < 0.05$), *plus symbol* indicates units: ng g^{-1}

Table 4. The bioconcentration factor (BCF), the ratio of structural metal concentration to rhizosphere sediment metal concentration, is also given for each metal. The mean concentrations of all metals studied in different structures of *A. corniculatum* decreased in the order roots > branches > leaves. In *S. apetala*, the different metals had different partitioning patterns. The highest concentrations of the essential metals, Cu and Zn, were found in the leaves, the highest concentrations of the non-essential metals, Pb, Cr, and Ni, were found in the roots and Cd was found in branches. The mean metal concentrations in the *A. corniculatum* roots decreased in the order Pb > Zn > Cu > Cr > Ni > Cd, and in *S. apetala* roots the concentrations decreased in the order Pb > Zn, Cr > Ni > Cu > Cd. The highest BCFs for Pb (1.30 ± 0.07), Zn (0.28 ± 0.01), Cu (0.93 ± 0.07), Cr (0.58 ± 0.06), and Ni (0.34 ± 0.02) were found in the roots of *A. corniculatum*. Relatively high Cd BCFs were obtained for the branches (2.10 ± 0.15) and roots (1.39 ± 0.12) of *S. apetala* and for the roots (1.85 ± 0.16) of *A. corniculatum*.

Discussion

Effects of mangrove rhizosphere processes on physicochemical properties

The results show that *A. corniculatum* bulk sediments had higher sulfur content and lower pH values than *S. apetala* bulk sediments. This may result from the older age of the

Table 4 Heavy metal concentrations (μg g^{-1}) and bioconcentration factors (BCF; ratio of structural metal concentration to rhizosphere sediment metal concentration) of plant structures

Element	Structures	Concentation		BCF	
		S. apetala	*A. corniculatum*	*S. apetala*	*A. corniculatum*
Pb	Roots	21.25 ± 1.51	66.05 ± 3.24	0.27 ± 0.03	1.30 ± 0.07
	Branches	1.00 ± 0.13	4.09 ± 0.20	0.01 ± 0.00	0.08 ± 0.00
	Leaves	0.55 ± 0.08	0.62 ± 0.04	0.01 ± 0.00	0.01 ± 0.00
Zn	Roots	16.75 ± 1.31	23.85 ± 0.94	0.13 ± 0.02	0.28 ± 0.01
	Branches	10.33 ± 0.62	16.18 ± 0.98	0.08 ± 0.01	0.19 ± 0.01
	Leaves	25.76 ± 1.72	6.24 ± 0.18	0.20 ± 0.02	0.07 ± 0.00
Cu	Roots	4.75 ± 0.34	20.54 ± 1.52	0.13 ± 0.01	0.93 ± 0.07
	Branches	6.32 ± 0.57	7.10 ± 0.44	0.17 ± 0.02	0.32 ± 0.02
	Leaves	12.95 ± 1.02	5.88 ± 0.29	0.34 ± 0.04	0.27 ± 0.01
Cr	Roots	16.93 ±2.09	18.71 ± 1.72	0.37 ± 0.05	0.58 ± 0.06
	Branches	1.18 ± 0.07	1.86 ± 0.08	0.03 ± 0.00	0.06 ± 0.00
	Leaves	2.88 ± 0.19	1.41 ± 0.11	0.06 ± 0.00	0.04 ± 0.00
Ni	Roots	5.45 ± 0.28	5.32 ± 0.32	0.26 ± 0.01	0.34 ± 0.02
	Branches	0.85 ± 0.06	1.05 ± 0.07	0.04 ± 0.00	0.07 ± 0.00
	Leaves	0.90 ± 0.04	0.68 ± 0.03	0.04 ± 0.00	0.04 ± 0.00
Cd*	Roots	194.56 ± 13.35	188.53 ± 12.39	1.39 ± 0.12	1.85 ± 0.16
	Branches	293.70 ±17.39	33.37 ± 3.58	2.10 ± 0.15	0.33 ± 0.03
	Leaves	27.85 ±3.43	15.18 ± 1.77	0.20 ± 0.02	0.15 ± 0.02

Data are mean ± standard deviations of six replicates

* Units: ng g^{-1}

A. corniculatum forest. Mangrove plants absorb SO_4^{2-} from seawater and return organic sulfur to sediments by litterfall. On the other hand, the SO_4^{2-} may be converted into S^{2-} by sulfate-reducing bacteria and form sulfides. Thus, the sulfur content may increase gradually with the development of a mangrove forest. At the same time, the pH may decrease because of the partial oxidation of sulfides.

The rhizosphere sediments were very different from the bulk sediments in both mangrove forests (Table 2). The high organic content in rhizosphere sediments may be due to the accumulation of root exudates. The breakdown of dead roots may also increase the organic content. The large fine particle content may have resulted from strong transpiration that transported soil water from bulk sediments to rhizosphere sediments. The salinity was markedly higher in rhizosphere sediments than in bulk sediments, especially for *A. corniculatum* rhizosphere sediments, which were 30% more saline than the bulk sediments. This large difference may result from a combination of strong transpiration in mangrove trees and high fines and organic content in the rhizosphere. The total sulfur content was 38% lower in rhizosphere sediments than in bulk sediments in both mangrove forests, possibly because of the large consumption of S by mangrove trees. The decrease in pH in the rhizosphere may be due to the oxidation of FeS_2 and FeS caused by ROL. The accumulation of organic acids exuded by the mangrove roots may also have contributed to the pH decrease.

Effects of mangrove rhizosphere processes on the accumulation of heavy metals

Metals move in soil by mass flow and diffusion (Barber 1984). The enrichment of Pb, Zn, Cu, Cr and Ni in the *S. apetala* rhizosphere sediments may be due to the strong transpiration of mangrove trees. This transpiration transported soil water and associated metals from the bulk sediments to the rhizosphere (the mass flow process). The high fines and organic content in the rhizosphere may also play an important role in metal accumulation. The organic and clay colloids have a high specific surface area and can efficiently trap heavy metals diffused from the bulk sediments. The low concentration of Cd in the S. *apetala* rhizosphere sediments may be a result of Cd uptake by mangrove trees. The *S. apetala* root and branch tissues had higher Cd concentrations than either the rhizosphere or bulk sediments (Tables 3, 4). The absorption rate of Cd by *S. apetala* is higher than the accumulation rate of Cd in rhizosphere sediments.

The low concentrations of Pb, Zn, Cu, Ni and Cd in the *A. corniculatum* rhizosphere sediments may also be a result of plant uptake. Given that some root residues passed through the 0.25 mm sieve, they could dilute or concentrate metal concentrations in rhizosphere sediments (Caçador et al. 1996). In this study, *A. corniculatum* roots had higher concentrations of Pb and Cd and lower concentrations of Zn, Cu, Ni and Cr than bulk sediments (Tables 3, 4), but rhizosphere sediments had lower concentrations than bulk sediments for all studied metals except Cr. This result suggests that the contribution of root residues to decreasing metal concentrations in rhizosphere sediments may be insignificant. Due to the relatively low metal concentrations in bulk sediments, the accumulation of heavy metals in rhizosphere sediments may not compensate for the uptake by the plant. The large decrease in Zn, Pb and Cd concentrations in *A. corniculatum* rhizosphere sediments corresponds to the high concentrations in *A. corniculatum* structures (Tables 3, 4). The similar Cr concentrations between rhizosphere and bulk sediments may be attributed to a balance of plant absorption and rhizosphere accumulation. This interpretation is in accordance with the low bioavailability and mobility of Cr.

Effects of mangrove rhizosphere processes on the partitioning of heavy metals

A large proportion of the Zn, Cr, Ni and Cu in both mangrove bulk sediments was in the residual fraction. Similar results were obtained in the Pearl River Estuary (Li et al. 2000). The second-largest amount of these metals was in the B3 fraction (organic and sulfide bound). The low concentrations of Zn, Cr, Ni and Cu in B2 fraction (Fe–Mn oxide bound) may be attributed to the dissolution of Fe–Mn oxides as a result of the low pH in both mangrove sediments. The B2 fraction was the predominant geochemical phase of Pb in this study. This result reflects the dominance of anthropogenic influence over natural processes, because heavy metals derived from atmospheric deposition and water runoff are found mainly in the Fe–Mn oxide fraction. Some studies suggest that Pb can form stable complexes with Fe–Mn oxides (Ramos et al. 1994). Cd is a pH-sensitive element, and the high percentages of Cd in B1 fraction (water soluble, exchangeable and carbonate bound) may be due to the low pH values in both mangrove sediments (Stephenson and Mackie 1988).

The rhizosphere sediments had low B1 and B2 fractions and high B3 fraction compared to the bulk sediments. The low B1 fraction in rhizosphere sediments may be primarily a result of plant uptake. Complexation and chelation by organic materials may also contribute to the decrease of the B1 fraction (Wang et al. 2002). The decrease in the B2 fraction in rhizosphere sediments is inconsistent with previous studies that found that mangrove roots can diffuse oxygen to create an oxidized rhizosphere (Youssef and Saenger 1996; Suzuki 2004; Pi et al. 2009). This phenomenon may be explained by the pH decrease in rhizosphere sediments, because a pH decrease may result in the dissolution of Fe–Mn oxides and release of metal ions. Root exudates can result in reduction or dissolution of Fe–Mn oxides (Godo and Reisenauer 1980; Jauregui and Reisenauer 1982). The increase in the B3 fraction may be due to the abundance of organic material in the rhizosphere. The ROL may lower the concentration of sulfides, decreasing the contribution of sulfides to the B3 fraction. The lower total sulfur content in the rhizosphere sediments may indirectly reflect the oxidation of the metal sulfides and their subsequent consumption by the mangrove trees. The concentrations of Cd in B3 fraction of the rhizosphere sediments were lower than that in the bulk sediments in the *A. corniculatum* forest, because the total Cd concentrations were much lower in the rhizosphere sediments due to plant uptake.

This study reports for the first time that mangrove rhizosphere sediments contained fewer immobile heavy metals than the bulk sediments. Mangrove trees can secrete various low-molecular weight organic acids including citric acid, malic acid, lactic acid, acetic acid, etc. (Lu et al. 2007). Organic acids (e.g., citric acid, oxalic acid and malic acid) can increase the dissolution rate of primary minerals (e.g., quartz and feldspar), especially in acidic conditions (Lundström and Öhman 1990; Bennett 1991; Welch and Ullman 1996; Blake and Walter 1999). A variety of nutrient stresses (e.g., N, P or Fe deficiency) can enhance organic acid efflux (Jones 1998), possibly accelerating the dissolution of minerals and release of metal ions. Organic material is abundant in the rhizosphere sediments. Metals can be bound to the organic material, forming refractory metal-organic compounds that are difficult to decompose with a mixture of H_2O_2/HNO_3 (Tessier et al. 1979; Caçador et al. 1996). In this study, the decrease of metal concentrations in the residual fraction in *A. corniculatum* rhizosphere sediments might be a result of the activation rate of the residual fractions being higher than the formation rate of the refractory metal-organic compounds. In the *S. apetala* rhizosphere sediments, the high concentrations of Pb, Zn, Cu, Ni and Cr in residual fraction might be a result of the formation rate of the refractory metal-organic compounds surpassing the activation rate of the residual fractions. The bulk sediments had relatively high concentrations of Pb, Zn, Cu, Ni and Cr and could provide sufficient metal irons to the rhizosphere sediments to allow the formation of these refractory compounds.

Uptake and distribution of heavy metals in mangroves

This study compares *A. corniculatum* (a secreting species) and *S. apetala* (a non-secreting species). The mean metal concentrations in *A. corniculatum* roots decreased in the order Pb > Zn > Cu > Cr > Ni > Cd. This pattern is different from the pattern of total meal concentrations in the rhizosphere sediments, but in agreement with the pattern of the non-residual fractions. This result indicates that the non-residual fraction, but not the total content, can efficiently reflect the bioavailability and potential biotoxicity of heavy metals. In addition, the *A. corniculatum* roots may be used as an environmental bioindicator. In *S. apetala* roots, the mean metal concentrations showed a different pattern of Pb > Zn, Cr > Ni > Cu > Cd. This phenomenon may be due to a large portion of the essential metals Cu and Zn being transported from the roots to the aboveground tissues.

Metal distribution patterns were different between *A. corniculatum* and *S. apetala*, especially for the essential metals Cu and Zn. Mean concentrations of Cu and Zn in different structures of *A. corniculatum* decreased in the order roots > branches > leaves. In *S. apetala*, Cu decreased in the order leaves > branches > roots, and Zn decreased in the order leaves > roots > branches. These differences may be due to the variations of physiology and accumulation strategies of different plant species (Defew et al. 2005). The highest concentrations of non-essential elements were found in roots for both mangrove species. The exception was Cd, which was concentrated in the branches of *S. apetala*. Pb, Cr and Ni in both mangrove trees were one to two orders of magnitude more concentrated in root tissues than in leaf and branch tissues. The non-essential metals Pb, Cr and Ni were predominantly accumulated and immobilized in the mangrove roots. This phenomenon might be interpreted by cell wall immobilization and/or sequestering of the epidermal layers (MacFarlane and Burchett 2002; MacFarlane et al. 2007).

Compared with *S. apetala* roots, *A. corniculatum* roots had high BCFs for all metals studied, especially for Pb and Cu. This phenomenon may be due to *A. corniculatum* rhizosphere sediments having lower pH values than *S. apetala* rhizosphere sediments (3.58 ± 0.06 vs. 5.30 ± 0.08). Differences in physiology and accumulation strategies may also result in different BCFs. Due to its relatively high Cd BCFs in the branches (2.10 ± 0.15) and roots (1.39 ± 0.12) and large biomass, *S. apetala* may be used for Cd remediation in intertidal substrates. Notably, for the non-essential metals, both mangrove species had low leaf BCFs (Table 4). Similar results have been reported in many other species, such as *Avicennia marina* (MacFarlane et al. 2003), *Kandelia candel* (Miao and Chen 1998) and *Rhizophora mangle* (Silva et al. 2006). These results suggest that metal export through leaf litter transport is very small. Mangrove plants are long-term sinks for non-essential heavy metals.

Conclusion

This study shows that rhizosphere processes modify the rhizosphere sediment properties and consequently influence the concentration and speciation of heavy metals in mangrove sediments. Rhizosphere processes tend to increase metal concentrations in the rhizosphere sediments through a combination of strong transpiration and high organic and fines content of rhizosphere sediments. However, plant uptake may result in the decrease of metal concentrations in the rhizosphere sediments when the metal concentrations are relatively low in the bulk sediments. Compared with the bulk sediments, the rhizosphere sediments have low concentrations of heavy metals in the B1 and B2 fractions and high concentrations in the B3 fraction. Either an increase or a decrease in the residual fraction of heavy metals in the rhizosphere sediments may appear, depending on whether the formation of the refractory metal-organic compounds or the activation of the residual fractions dominates. Results also indicate that metal distribution patterns are different between *A. corniculatum* and *S. apetala*, especially for the essential metals Cu and Zn. However, both mangrove plants absorb and store non-essential metals in the perennial tissues, thus reducing the export of non-essential metals via leaf litter transport. Mangrove plants are excellent candidates for phytostabilization of heavy metals in intertidal substrates.

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