Ecological risk assessments and context-dependence analysis of heavy metal contamination in the sediments of mangrove swamp in Leizhou Peninsula, China

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ABSTRACT

Sediments in eight types of mangroves were sampled in the Leizhou Peninsula. Heavy metals were analyzed to investigate the effects on metal distribution of mangrove communities, to evaluate contamination levels, identify sources and relationships between the two. Results showed that mangrove communities have effects on most heavy metal distributions in sediments, especially in the sediment with shrub communities of *Aegiceras corniculatum* where the contents of many metals are highest. As, Cr and Ni were identified as metal pollutants of primary concern, while Cd was of no concern. Zn, Pb, As mainly originated from anthropogenic source while the other metals are geogenic. Heavy metal distributions were affected by the independent and joint effects of landscape and sediment context; landscape context explains more variations in heavy metals than does sediment physicochemical variables. Total sulfur, total phosphorus and total potassium in sediment, and the existence of paddy field and forest land within 2000 m around the sampling sites are significant variables also.

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1. Introduction

Mangrove forests are diverse vegetation communities that commonly thrive in the intertidal zones of tropical and subtropical coastal rivers, estuaries and bays (Yim and Tam, 1999). Mangrove ecosystems provide food sources, diverse ideal habitats for residents and migratory organisms, and maintain stabilization for adjacent coastal landforms (MacFarlane et al., 2007). It is well known that mangroves have the capacity to act as a sink or buffer to remove or immobilize metals before they reach nearby aquatic ecosystems (Macfarlane and Burchett, 2001). However, the rapid development of agriculture, industrial and traffic practices bring large numbers of heavy metal pollutants to estuarine wetlands, which exert damaging effects on mangrove biodiversity and human health with its persistence, non-biodegradation, toxicity and bio-availability (Agoramoorthy et al., 2008; Tam and Wong, 2000). Therefore, metal contamination in mangrove swamp has received more concern.

Heavy metals derived from either weathering of rock and soil or the main anthropogenic activities, such as mining and smelting activities, disposal of untreated and partially treated effluents contain toxic metals, as well as metal chelates from different industries and indiscriminate use of heavy metal-containing fertilizer and pesticides in agricultural fields (Macklin et al., 2006; Nouri et al., 2008; Reza and Singh, 2010; Varol and Şen, 2012). In addition, there are many explainable variables for metal immobilization, deposition or accumulation, including organic matter,

carbonates, phosphates, pH and sulfur compound in sediment (Bai et al., 2011; Cui et al., 2009; Kumpiene et al., 2008; Macfarlane and Burchett, 2001), and the land use at landscape scales (Xin et al., 2014). It is well-known that these explainable variables are often highly inter-correlated (Castrignanò and Buttafuoco, 2004; Facchinelli et al., 2001; Lin and Chang, 2000; Mico et al., 2006; Slavković et al., 2004). Thus, for effective control of heavy metals in mangrove swamp, it is necessary to identify the essentially important variables and gain an understanding of the interaction between these variables accounting for the variation of heavy metals, except to get the whole comprehension of heavy metal extent.

Multivariate statistical methods become very helpful to assess the interrelationships among the measured data. Principle component analysis (PCA) has been an effective tool for source identification of heavy metals (Bai et al., 2011; Han et al., 2006; Mico et al., 2006). Constrained ordination combined with variation partitioning among sets of explanatory variables was applied to examine the relative importance of these explanatory variables and their independent and joint effects on heavy metals (Borcard et al., 1992; Matthews et al., 2009; Wang et al., 2013).

Leizhou Peninsula harbors about 33% of Chinese mangroves (Gao et al., 2009). Although great efforts have been undertaken to monitor metal pollution level in mangrove swamp in Leizhou Peninsula (Zhang et al., 2006; Zhu et al., 2014), very few studies have considered the extent of heavy metal contamination in sediments with different mangrove vegetation. Several studies showed that mangroves have high capacity to accumulate heavy metals (Liu et al., 2014; MacFarlane et al., 2003; Qiu et al., 2011), while available heavy metals in the sediment could be reintroduced to water or be uptaken by plants (DeWolf and

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Rashid, 2008; Liu et al., 2014; MacFarlane et al., 2003). To understand the fate of heavy metals in a mangrove swamp, it is important to explore the difference of heavy metals in the sediments with different vegetation cover. Thus, the primary objectives of this study are: (1) to investigate heavy metal contamination in the sediments with different mangrove vegetation in Leizhou Peninsula; (2) to evaluate the potential ecological risks of heavy metals; (3) to identify the pollution sources and context dependence of these heavy metals using multivariate analysis.

2. Materials and methods

2.1. Study sites and sampling

The Leizhou Peninsula is located on the northern boundary of the tropics in South China with longitude 109°30'–110°55'E and latitude 20°12'–21°35'N. The mangrove area recorded by local governments

was 7 305.8 ha in 2001, comprising 33% of total mangrove area in China and 80% in Guangdong Province (Gao et al., 2009). The field survey and sample collection at low tide were conducted in October and November 2012. Fourteen representative sampling sites were selected for this study (Fig. 1), including eight communities: dominated by tree community of *Avicennia marina*, *Phizophora stylosa*, *Kandelia candel*, *Sonneratia apetala* and *Aegiceras corniculatum* and shrub community of *A. marina*, *K. candel* and *A. corniculatum*. A community is here defined as having a certain, often monospecific, floristic composition, and covering an area above 300 m² for a tree community and 75 m² for a shrub community. Additionally, the tree community of *A. corniculatum*, *A. marina* and *K. candel* are all native vegetation, while most of their shrubs community have been planted. On every site, a sample transect was established parallel to the shoreline and three sub-sample plots (10 × 10 m size for tree community or 5 × 5 m size for shrub community) were established.

Fig. 1. Location of sampling sites in mangrove swamp in Leizhou Peninsula, China.

At each sub-sample plot, three sediment cores were randomly collected around the roots of mangroves by using a self-made stainless sediment core sampler, 15 cm deep and 5 cm in diameter, and mixed to obtain one homogenized sample. All samples were packed in plastic bags and transported immediately to the lab. The samples were air-dried and sieved through a 2-mm plastic sieve, and stones and plant debris were removed with tweezers. Then, approximately 20 g of each sample was ground in an agate mortar and passed through a 150- μ m polyethylene sieve. Samples were sealed in polyethylene bags and stored in a desiccator prior to chemical analyses.

2.2. Analytical methods

2.2.1. Heavy metal analysis in sediment samples

Approximately 0.2 g of a sample was digested by a microwave oven (Anton-Paar PE Multiwave 3000) with a highly purified concentrated acid mixture of 4 ml nitric acid (HNO_3 ; 68%), 1.5 ml perchloric acid (HClO_4) and 2 ml hydrofluoric acid (HF). The solution of the digested samples was analyzed with the inductively coupled plasma-optical emission spectrometry (ICP-OES, 7000 DV, Perkin Elmer, USA) for the content of Fe and Mn. While the contents of As, Cu, Pb, Zn, Cr, Cd and Ni were analyzed with the inductively coupled plasma-mass spectrometer (ICP-MS, 7500 CX, Agilent, USA). The metal analysis was conducted in triplicate. The analytical quality was assessed using standard reference materials (GBW 07401 from Chinese Academy of Measurement Sciences) and reagent blanks. All results showed good agreement with the certified data and were verified with accuracy and precision.

2.2.2. Determination of sediment variables

Sediment variables include salinity, electrical conductivity (EC), total organic carbon (TOC), total sulfur (TS), total phosphorus (TP), total nitrogen (TN) and total potassium (TK). Salinity and EC of sediment were measured with a hand-held conductivity/TDS meter (Oakton, CON110). TOC was measured with a TOC analyzer (LiquiTOC II, Elementar). TN was determined by the elemental analyzer (vario MAX CN, Elementar). TP was analyzed with the inductively coupled plasma-mass spectrometer (ICP-MS, 7500 CX, Agilent, USA). TK and TS were also measured using the inductively coupled plasma-optical emission spectrometry (ICP-OES, 7000 DV, Perkin Elmer, USA).

2.2.3. Determination of landscape variables

Explanatory landscape variables were described by a percentage of land use in 2000-m scale around sampling sites. Combined with the ground survey, environmental satellite images of the year 2010 were used to interpret landscape maps of the study area. Before identifying remote sensing images and marking land utilization types, based on the Chinese “Current Land Utilization Classification” (GB/T 21010-2007), as well as the actual situation of coastal wetlands, eight kinds of land use were set: forest land, dry cropland, paddy field, impervious area, water area, aquaculture pond, mangrove swamp and mudflat.

2.2.4. Statistical analyses

All statistical analyses, including one-way analysis of variance (ANOVA) followed by a least significant different test (LSD), principal component analysis (PCA) and constrained ordination, were conducted using the software R (version 3.0.3) (R Core Team development 2013) with “agricolae” (Mendiburu, 2013), “GPArotation” (Bernaards and Jennrich, 2005) and “Vegan” (Oksanen et al., 2013) packages. Before constrained ordination, initial detrended correspondence analyses (DCA) were carried out to determine the most appropriate ordination method, with the gradient length as the criterion (Ter Braak and Prentice, 1988). In this study, DCA indicated that gradient in metal data among sites was short (<3) (Lepš and Šmilauer, 2003). Therefore, redundancy analysis (RDA) was used to determine the relation between metal concentrations and two sets of explainable variables (sediment variables and landscape variables). The statistical significance of each

analysis was tested by a permutation test involving 999 permutations. To determine significant variables, forward selection by permutation of residuals at the 5% significance level was applied. Variation partitioning was performed using only these significant variables. The results are presented in an ordination diagram in which all of the variables are represented by arrows. A smaller angle between arrows represents a high correlation between variables, the direction of the arrows represents positive or negative correlations, and the length of the arrows corresponds to their importance in explaining the variation of metals.

3. Results and discussion

3.1. Heavy metal concentrations in surface sediment with different mangrove communities

Table 1 shows the mean concentrations of total Cd, Cr, Cu, Ni, Pb, As, Zn, Mn and Fe in surface sediments under eight types of mangrove vegetation in mangrove swamp in Leizhou Peninsula. Generally, Fe showed the highest mean concentration, followed by Mn, Zn, As, Cr, Pb, Ni, Cu and Cd. The results of one-way ANOVA analysis for the mangrove communities showed that there was a significant difference among different types of mangrove vegetation for the contents of Cu, Cd, Cr, Ni, As, Fe and Mn. The concentrations of As were much higher in sediments of *R. stylosa* community compared with sediments of shrub community of *K. candel*, *A. corniculatum*, and tree community of *A. marina*, *K. candel* and *S. apetala*. The higher concentrations of Cr, Cd, Fe, Ni and Cu were found in sediments with the shrub community of *A. corniculatum*. For Mn, sediments of *S. apetala* community have high concentrations compared with the shrub community of *A. marina* and the tree community of *A. corniculatum*. However, no significant differences were found in Zn and Pb concentrations among different mangrove vegetation. Furthermore, there were no differences for metals in the sediment of tree and shrub *A. marina* community, same with *K. candel* community, while the sediments of the tree community of *A. corniculatum* had significantly lower concentrations of Cd, Mn and Ni ($p < 0.05$) than the ones in the shrub community.

Mangrove vegetation increases fine particle and organic matter content in the upper sediment layers, which can trap heavy metals from overlying water (Zhou et al., 2010). The accumulation of fine particles in the upper sediment layers may directly contribute to the increase in metal concentrations, because fine particles usually include more metals than coarse particles (>0.063 mm) in an estuarine environment (Deely and Fergusson, 1994). Thus mangroves have the capacity to act as a sink or buffer to remove or immobilize metals before they reach nearby aquatic ecosystems. On the other hand, mangrove results in rapid acidification of sediments. This may be caused by the microbial decomposition of mangrove litter and oxidation of FeS_2 and FeS (Zhou et al., 2010), and the secretion of root exudates. Different carboxylic acids, strong organic acids, alcohols, carbohydrates and proteins are components of root exudates, especially the range of low-molecular-weight organic acids, which were responsible for increasing bioavailability of metals in sediments near the rhizosphere (Liu et al., 2014). Furthermore, preferential uptake of metals from the soil to the aboveground biomass actively mobilizes the metals and transports them to the crown canopy and the litter layer (Mertens et al., 2007). However, plant species differ in their effect on the biogeochemical cycles of metals through organic acid input, cation uptake and change of soil pH and redox (Evimer and Chapin, 2003; Wang et al., 2011). Zhang et al. (2010) showed that *S. apetala* species was more effective in the removal of nutrients and heavy metals, while Akshayya et al. (2007) showed that *A. marina* in comparison with other mangrove species is evident of its adaptability even under polluted conditions. In this study, the concentrations of As, Cr, Cd, Cu, Fe and Ni have no difference between those of *A. marina* and *S. apetala* communities, except that the latter has the highest concentration of Mn. The highest contents of Cd, Cr, Fe, Ni and Cu were found in

Table 1Heavy metal concentrations in different mangrove vegetation communities in Leizhou Peninsula (mg kg⁻¹ wt.)^a.

Vegetation	As	Cd	Cr	Cu	Fe (wt.%)	Mn	Ni	Pb	Zn
<i>Avicennia marina</i> (S)	41.29 ± 2.97 ^{ab}	0.11 ± 0.03 ^b	32.47 ± 12.70 ^{ab}	11 ± 2.14 ^{ab}	1.39 ± 0.70 ^b	61.31 ± 32.36 ^{cd}	10.49 ± 4.17 ^b	41.93 ± 6.69	61.75 ± 9.76
<i>Avicennia marina</i> (T)	36.39 ± 3.95 ^b	0.19 ± 0.06 ^{ab}	24.58 ± 13.22 ^b	11.14 ± 7.23 ^{ab}	2.29 ± 0.95 ^{ab}	121.8 ± 32.96 ^{bcd}	12.36 ± 8.46 ^b	30.99 ± 9.41	51.81 ± 20.16
<i>Rhizophora stylosa</i>	48.18 ± 3.2 ^a	0.15 ± 0.07 ^{ab}	42.56 ± 16.25 ^{ab}	15.4 ± 7.17 ^{ab}	2.01 ± 0.75 ^{ab}	81.81 ± 24.86 ^{bcd}	15.84 ± 5.08 ^b	27.48 ± 22.98	78.02 ± 26.61
<i>Kandelia candel</i> (S)	33.8 ± 4.01 ^b	0.21 ± 0.01 ^{ab}	25.19 ± 3.53 ^{ab}	5.83 ± 1 ^b	2.12 ± 0.26 ^{ab}	233.2 ± 60.94 ^{ab}	12.07 ± 2.46 ^b	21.98 ± 2.89	50.32 ± 11.02
<i>Kandelia candel</i> (T)	40.79 ± 5.49 ^{ab}	0.2 ± 0.06 ^{ab}	50.15 ± 16.07 ^{ab}	16.73 ± 7.56 ^{ab}	2.61 ± 0.53 ^{ab}	89.74 ± 32.58 ^{bcd}	20.89 ± 4.76 ^{ab}	20.68 ± 18.59	90.37 ± 39.44
<i>Aegiceras corniculatum</i> (T)	38.14 ± 2.65 ^b	0.09 ± 0.03 ^b	26.39 ± 16.6 ^{ab}	6.79 ± 3.87 ^{ab}	0.91 ± 0.38 ^b	22.75 ± 15.12 ^d	7.22 ± 5.44 ^b	20.01 ± 8.93	51.63 ± 13.23
<i>Aegiceras corniculatum</i> (S)	39.05 ± 3 ^b	0.26 ± 0.12 ^a	74.58 ± 50.85 ^a	22.26 ± 11.76 ^a	4.1 ± 2.72 ^a	194.9 ± 120.58 ^{abc}	51.61 ± 45.33 ^a	18.86 ± 7.5	76.39 ± 7.12
<i>Sonneratia apetala</i>	36.8 ± 5.65 ^b	0.22 ± 0.03 ^{ab}	35.82 ± 3.02 ^{ab}	10.74 ± 2.53 ^{ab}	2.77 ± 0.37 ^{ab}	307.4 ± 111.91 ^a	19.55 ± 1.88 ^{ab}	14.79 ± 4.24	66.9 ± 10.14

Abbreviations are: S, the shrub community; T, the tree community.

^a The mean and standard deviation values of each metal concentration followed by different letter superscripts within each column indicated that there were significant differences in sediment under different mangrove vegetation communities at a probability level of 0.05 according to ANOVA test.

the sediment with the shrub community of *A. corniculatum*. The reason for these is that heavy metal accumulation in sediments are complicated and often controlled by an array of factors, such as sediment physicochemical characteristics, metal bioavailability, rhizosphere process, mechanism of plant uptakes, the change of land use and pollution sources (Bai et al., 2011; Clemens, 2006; Klavinš et al., 2000; Liu et al., 2014; Remon et al., 2013; Xin et al., 2014). Additionally, the biomass of a plant species plays an important role in the removal of nutrients and heavy metals from mangrove wetlands (Zhang et al., 2010). In all, the interactions of sediment and mangrove plants will influence the distribution of heavy metals in sediment.

3.2. Ecological risk assessment

The extent of metal pollution was assessed by comparing metal concentrations in sediment with mangrove cover to the consensus-based sediment quality guidelines (SQGs) developed by MacDonald (MacDonald et al., 2000), the SQGs developed by USEPA (Pekey et al., 2004), the proposed Interim Sediment Quality Values (ISQVs) of Hong Kong (Chapman et al., 1999), and the soil quality thresholds (SQTs) of China (State Administration for Quality Supervision and Inspection, 2002) (Table 2). The guidelines developed by MacDonald indicated that all samples for As exceeded a threshold effect concentration (TEC, below which adverse effects are not expected to occur), and 4% to 30% of the sediment samples for Cr, Zn, Ni, Pb and Cu exceeded the TEC, which demonstrated that adverse toxic impact to benthic organisms might be expected. However, no sample exceeded the TEC for Cd. Seemingly, almost all samples for Zn, Cd, Cu and Pb did not exceed the probable effect concentration (PEC, above which adverse effects are expected to occur more often than not), except that 88% (for As) and 7% (for Cr and Ni) of the sediment samples exceeded PEC and may cause severe effects on benthic organisms. The USA EPA guidelines, on the other hand,

indicated that the Cd pollution in all the samples were not serious, while 100% (for As) and 7.14% (for Cr and Ni) of sediment samples were heavily polluted, and 7.14% to 69% of the samples were moderate-polluted by Zn, Cr, Ni, Cu and Pb. In comparison of the metal data with the ISQVs of Hong Kong, about 7.14% of sediment samples for Cr and Ni were above the low value of ISQVs, and no metals exceeded the high value of ISQVs. Similarly, all the samples had As concentrations above the limit value based on soil quality standards of China, and had Zn, Cd, Cu and Pb concentrations below the limit values, while there are 93% of sediment samples that exceeded the limit values for Ni. Overall, As, Cr and Ni were identified as metal pollutants of primary concern, especially for As. Zn, Pb and Cu were of moderate concern and Cd was of no concern.

3.3. Multivariate analysis for context dependence of heavy metals

3.3.1. PCA analysis

The results of PCA analysis in this study to assist the source identification of heavy metals were shown in Table 3. Based on eigenvalues (eigenvalue > 1), two principal components (PCs) explained 81% of the total variance. The first PC1, explaining 57% of the total variance, was strongly and positively related to Cd, Cr, Cu, Ni, Fe and Mn. The second PC2, explaining 24% of the total variance, showed highly positive factor loadings on Zn, As and Pb. These degrees of covariance are strongly suggestive of common sources for the metals.

Several studies have proved that the association of these metals with the PCs can be indicated by the anthropogenic activities or diagenetic processes (Bai et al., 2011). Fe and Mn are well known to geogenic (Mico et al., 2006), and Cr and Ni are also geogenic (Brumelis et al., 2002; Hanesch et al., 2001). Gan et al. (2014) showed that Cu and Cr were from diagenetic processes, while Cd was anthropogenic. In this study, Cd was considered as metal pollutants of no concern and its contents in all sampling sites were all below the TEC. Therefore, Cd was also

Table 2Comparison of sediment quality guidelines with the range of heavy metals in Leizhou Peninsula (mg kg⁻¹ wt.).

		As	Cd	Cr	Cu	Fe (wt.%)	Mn	Ni	Pb	Zn
SQGs ^a	TEC	9.79	0.99	43.40	31.60	–	–	22.70	35.80	121
	PEC	33.30	4.98	111	149	–	–	48.60	128	459
SQGs of US EPA ^b	Non-polluted	<3	–	<25	<25	–	–	<20	<40	<90
	Moderate-polluted	3–8	–	25–75	25–50	–	–	20–50	40–60	90–200
	Heavily-polluted	>8	>6	>75	>50	–	–	>50	>60	>200
Hong Kong OSQVs ^c	ISQV-low	–	1.50	80	65	–	–	40	75	200
	ISQV-high	–	9.60	370	270	–	–	–	218	410
MSQGs ^d		–	0.50	80	35	–	–	–	60	150
The range of heavy metals in this study		29.20–52.06	0.05–0.36	8.37–126.20	3.37–33.44	0.06–6.70	13.56–439.23	2.89–96.07	7.26–59.44	26.67–134.56

^a Sediment quality guidelines developed by MacDonald (MacDonald et al., 2000).^b Sediment quality guidelines developed by USEPA (Pekey et al., 2004).^c Interim sediment quality values of Hong Kong (Chapman et al., 1999).^d Marine sediment quality guidelines of China (State Administration for Quality Supervision and Inspection, 2002).

Table 3

Total variance explained and rotated component matrix (two principal components selected) for heavy metal contents.

	Initial eigenvalues			Element	Rotated component matrix	
	Total	% of variance	Cumulative %		PC1	PC2
	Total variance explained				Component matrixes	
1	5.0876	0.5653	0.5653	Cd	0.84	0.06
2	2.1904	0.2434	0.8087	Cr	0.88	0.35
3	0.81321	0.09036	0.89902	Ni	0.95	0.06
4	0.50088	0.05565	0.95468	Cu	0.77	0.57
5	0.26294	0.02922	0.98389	Fe	0.97	0.14
6	0.07933	0.00881	0.99271	Mn	0.7	−0.2
7	0.04392	0.00488	0.99759	Zn	0.37	0.88
8	0.01771	0.00197	0.99955	As	−0.17	0.82
9	0.004013	0.00045	1	Pb	0.09	0.86

Bold letters means first two principal component cumulative variance and factor load of the heavy metals on the former two principal components.

geogenic, the same with Fe, Mn, Cu, Cr, and Ni. Thus PC1 could be defined as a geogenic component mainly from weathering of rocks (Gan et al., 2014). For PC2, Zn, As and Pb are typically anthropogenic. Zn, Pb and their compounds were mainly used in agricultural fertilizers (Mico et al., 2006), and As has been used for agriculture pesticide (Andrew and Jeanette, 2002). Thus PC2 could be defined as anthropogenic component, especially agriculture. Additionally, Leizhou Peninsula is mineral-rich, and the higher concentrations of As are related with mining (Gan et al., 2014).

These results could be explained by the regional social and economic conditions of the study areas. Heavy metals are the productions from textile, steel and food industries. Wastewater, discharged from these industries into the coastal area, could lead to high levels of heavy metals such as Cu, Cd, Ni and Cr (Raj and Jayaprakash, 2008). However, agriculture is the primary economic activity in Leizhou Peninsula, and Zinc, Pb, As and their compounds were used in agricultural fertilizers and pesticides, suggesting that they are mainly from agriculture-activities.

3.3.2. Redundant analysis of explainable variables

Significant correlations were found between metal concentrations and sediment variables in mangrove swamp ($p = 0.047$). The eigenvalues of the first two RDA axes accounted for 63.70% of the variance of metal concentration (Fig. 2A). The results of the permutation tests revealed that three variables had statistically significant effects: total sulfur (TS, $p = 0.003$), total phosphorus (TP, $p = 0.001$) and total potassium (TK, $p = 0.001$). Along RDA axis 1, Zn, Pb and Cu stand out with a positive RDA axis 1 and negative axis 2 and are thus associated with TP. Cd shows a positive score correlating with TK. Along axis 2, As stands out with a positive RDA axis 1 and negative axis 2 and is associated with TS. According to the length of arrows in RDA triplot, the importance of significant variables in turn is TP, TK, TS.

Several studies have proved that there are high concentrations of Zn in phosphate deposits in fertilizer (Adriano, 1986; Eriksson et al., 1995; Nan et al., 2002). Correlations of Cd and total potassium obtained in this study might be expected on the basis of their common affinity for clay minerals in sediment (Van der Graaf et al., 2007). Sulfur is a key element in the biogeochemistry of estuarine soils and sediments (Nobrega et al., 2013). Rich sulfides were widely believed to be the main factors responsible for the retention of As in mangrove ecosystem with the form of sulfur–arsenic mixtures (Esther et al., 1997; Liu et al., 2014). Furthermore, several studies showed that soil organic matter played a fundamental role in the control of Pb, Cu, Cr and other metals (Calvert et al., 1985; Lee et al., 1998; McLaren et al., 1983). However, TOC is not a significant factor contributing to metals in this study. The reason for this

Fig. 2. Triplots from redundancy analysis (RDA) showing the relationship of heavy metal concentrations with variables of sediment (A) and landscape (B). Abbreviations are: TP, total phosphorus; TK, total potassium; TS, total sulfur.

discrepancy is, perhaps, the absence of significant variations in TOC among sampling sites.

Redundant analysis predicting metal distribution using landscape variables produced a triplot similar to that of the RDA of metal distribution based on sediment physicochemical variables ($p = 0.009$). RDA axis 1 and axis 2 both support a significant effect on the variability of sediment metal (Fig. 2B) and accounted 72.52% of variance in landscape variables. Imperative area ($p = 0.034$), paddy field ($p = 0.002$), forest land ($p = 0.001$) and mudflat ($p = 0.004$) are significant factors that influence sediment metal concentrations. According to the length of arrows in RDA triplot, the importance of significant variables in turn is forest land, paddy field, imperative area and muddy flat. Along RDA axis 1, Cd, Fe, Ni and Cr stand out with positive axis 1 and axis 2 scores significantly correlated with forest land. While, along RDA axis 2, As, Pb and Zn showed positive axis 1 and negative axis 2 indicative of close relationships with high percentages of paddy fields. Mn has a positive score significantly correlated with imperative areas and mudflat.

The impact of the proportion of agricultural area on heavy metal concentration could be related to the input of agricultural chemicals. The runoff of fertilizer and pesticides from agricultural lands is a key concern. Previous study showed that organic fertilizer significantly increased the total Zn and Pb contents (Wang et al., 2008). Intensive use

of water from these As-contaminated aquifers, mining activities and arsenic-containing pesticides have led to an As buildup in paddy soils. Arsenic chemistry in paddy soils is extremely complex, because soils are subject to frequent redox cycles in both time and space (Chen et al., 2008). Results obtained by the RDA are confirmed by analyzing the PCA, which showed that As, Zn and Pb came from anthropogenic activities, especially agriculture. However, there are no presences of significant variations in dry croplands among sampling sites; dry croplands had no significant effects on the variations of metal concentrations.

Forests are mainly plantation forest with *Pinus* plants around the coast. The secretion of *Pinus* root exudates and the microbial decomposition can increase mobility of metals in sediments. However, soil organic matter content is low in the sediment of *Pinus* community for their less litter, which lessens heavy metal accumulation and lead to metal run off with soil withering (Tang, 2003).

Main residential areas are located within a 2000 m width zone along the coast line (Xin et al., 2014). Therefore, the imperative areas in this study include a large percentage of residential areas and less percentage of industrial land and traffic land. Manganese (Mn) is a redox sensitive element and its distribution may reflect the redox potential of environment. The soil of residential areas and the sediments of mudflat are in oxidation state, which make high contents of Mn (Qiao and Huang, 2009). Furthermore, the content of Mn is higher in the sediment of *S. apetala* community in studies, just as in China most of *S. apetala* are planted in the upper intertidal zone far from the coastline (Wang and Wang, 2007). The sediments in the upper intertidal zone were in oxidation state for longer times than the ones in the lower intertidal zone.

Aquaculture ponds at buffer scale contributed significantly to Cu and Zn contents, for they were widely used as feeds (Cai et al., 2010). It was reasonable to think that feed additives were one of the most important sources for metals in aquaculture sewage. However, aquaculture pond is not a significant factor contributing to metals in this study. The reason for this discrepancy is, perhaps, the absence of significant variations in aquaculture ponds among sampling sites. Additionally, RDA results also showed that many metals, such as Ni, Cr, Cd and Cu, have a correlation with Fe. Several studies have proved that Fe oxy-hydroxides are a major controlling factor for trace metal accumulation (Banerjee et al., 2012).

Variation partitioning showed that landscape variables accounted for 72% of total variations of metal concentrations, larger than those of sediment variables (57% of total variations of metal concentrations). Furthermore, a large amount of variation (41%) attributed to sediment variables could be explained by landscape variables. These results have proved that there is no single, simple cause or scale important for sediment metal contamination in a mangrove swamp. Heavy metals are affected by processes operating from sediment scale to landscape scale. In this study, landscape variables, in contrast, were more of an important context in affecting metal concentrations. More importantly, large amounts of the variations were shared between sediment and landscape variables. These further revealed that the larger scale context (landscape variables) constrained local variables (sediment variables), which directly control accumulation, mobility and bioavailability of heavy metals. And these also agreed with the facts that intensive human modification of landscapes alters hydrology and increases sediment, nutrient, and pollutant inputs, which facilitate the increase of sediment metal concentrations (Kercher et al., 2006; Sillimani and Bertness, 2003).

4. Conclusions

The present study analyzed nine heavy metals in the sediments with different types of mangrove vegetation. Significant differences among mangrove communities were found for the contents of Cu, Cr, Cd, Ni, As, Mn and Fe in the sediments, indicating that vegetation was an important factor influencing heavy metal concentrations in mangrove sediments. Especially in the sediment with the shrub community of

A. corniculatum, the contents of many kinds of metals are highest. By comparing the concentrations of heavy metals in sediments with four SQGs, As, Cr and Ni are identified as metal pollutants of primary concern, Cu, Pb and Zn are of moderate concern, and Cd is of no concern. Various assessment results are based on different SQGs, highlighting the need of establishing baseline value for heavy metals in mangrove ecosystems.

Principal component analysis shows that Zn, Pb, As mainly originate from anthropogenic sources, while Cr, Cu, Cd, Ni, Fe and Mn are controlled by rocks. These results are confirmed by the part of redundancy analysis for metals. Redundancy analysis shows that heavy metal distributions are affected by the independent and joint effects of landscape and sediment context. Landscape context explains more variations of heavy metals than sediment physicochemical variables, and landscape contexts have effects on heavy metal distribution probably by changing sediment physicochemical characteristics. Total sulfur, total phosphorus and total potassium in sediment and imperative area, paddy field, forest land and mudflat in landscape in 2000 m around sampling sites are significant variables for controlling heavy metals in mangrove sediments. Therefore, the results of this investigation are important to further research and will find use in the effective protection of the mangrove swamp. Further investigation of the characteristics of these heavy metals, the mechanisms of metal uptake by mangrove vegetation and the mechanisms of these explainable variables from sediment and landscape are required in order to reduce heavy metal pollution in mangrove swamp ecosystems.

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