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Distribution and Speciation of Some Metals in Mangrove Sediments from Jiulong River Estuary, People's Republic of China

L. Jingchun,[1] Y. Chongling,[1] M. R. Macnair,[2] H. Jun,[1] L. Yuhong[1]

[1] School of Life Sciences, Xiamen University, Xiamen,
Fujian 361005, People's Republic of China
[2] Hatherly Laboratories, School of Biological and Chemical Sciences, University of Exeter, Prince of Wales Road, Exeter, EX4 6EZ, United Kingdom

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Mangroves are important habitats usually found in the inter-tidal zone of tropical and subtropical coasts. They are recognized for playing an important role in protecting embankment against tide, removing pollutants and being good habitats and feeding sites for aquatic organisms (Lin 1997). Previous studies have indicated that mangroves are often at risk from heavy metal pollution due to a range of anthropogenic metal producing activities (MacFarlane 2003; Tam and Wong 2000). However, most of the previous studies (Mackey and Hodgkinson 1995; Tam and Wong 2000) of metal pollutions in mangrove sediments have been limited to the total concentration of metals. It is now widely recognized that the toxicity and the mobility of these pollutants depend strongly on their specific chemical forms and on their binding state (Christine et al. 2002). Therefore, in the present study, a sequential extraction procedure (SEP) was used to investigate some metals' total concentration distribution and chemical form variations through the sediment depth. These will be used to assess the potential bioavailability of sediment heavy metals to mangrove fauna and flora in a subtropical mangrove forest.

MATERIALS AND METHODS

Jiulong river is the second river of Fujian province, south east China, it is some 274 km long, flows north-west to south-east and passes through 13 cities and enters into the Xiamen Harbor. The mangrove forest studied is located at the River estuary (24°24′N, 117°55′E); it is about 233.3 ha, and mainly consists of regrowth and mature *Kandelia candel(L.) Druce* forest, but also has some other mangrove species (*Aepiceras corniculatum* and *Avicennia marina*). It is one of the best *Kandelia candel(L.) Druce* mangrove forests which are protected in China. Alongi et al. (2005) had made a detailed description to environmental condition of this region. Four sample sites in the mangrove forest along the beach were selected. Three replicated sediment cores (0-40 cm) (within a 5 m×5 m area) were collected by using PVC pipes (acid pre-washed with 14% nitric acid) at each site. The sediment in cores were extruded and cut with a plastic knife into 0-2 cm, 2-5 cm, 5-10 cm, 10-15 cm, 15-20 cm, 20-25 cm, 25-30 cm, 30-35 cm and 35-40 cm.

Physicochemical parameters of sediment samples were analyzed based on the published standard methods by using air dried sediment samples (Lu 1999). The pH

Correspondence to: Y. Chongling

(pH-H_2O) values were measured in a 1:5 solid: liquid suspension. Organic matter content was determined by oxidation with potassium dichromate. Total dissolved salt content was measured by the mass method (water: sediment=5:1). The particle size distribution was measured with a hydrometer, and was fractionated into 3 size classes: sand (2 mm–50 μm), silt (50-1 μm) and clay (<1 μm). Freeze-dried sediment particles with diameters less than 2mm were used to measure metals' contents. 0.5 gram was digested with aqua regia and perchloric acid for determination of total metals contents. A sequential extraction procedure proposed by Tessier et al. (1979) was adopted (with some modification to the residue fraction) to reveal the fraction distribution of metals in mangrove sediment cores by using 1.0 gram sediment samples. The details of the sequential extraction procedure are described in Table 1. Between two successive extractions, the extract was separated by centrifugation at 12,000g for 15 minutes. The supernatant was decanted and stored at 4°C in stopper polyethylene vessels until analysis; whereas the residue was washed with 8 mL of deionised water and this second supernatant was discarded.

All metal concentrations were determined by an Agilent 7500I inductively coupled plasma mass spectrometer (ICP-MS) and presented in dry weight basis. Blanks were used in all analyses; all data were the means of the three replicates. The precision and recovery of the procedures used for acid digestion and metal determination were checked using a certified Standard Reference Material namely SRM GBW07310. The metal recoveries from SRM were Cu(87.3%), Pb(91.1%), Zn(85.4%), Cd(93.7%), Ni(109.5%), Mn(96.1%) and Fe(85.5%). All reagents were Merck analytical grade or Suprapur quality, and all materials were acid-cleaned (14% (v/v) nitric acid) and rinsed with deionised water prior to use. The limits of detection (μg.g^{-1}) for Fe, Mn, Cu, Pb, Cd, Ni and Zn were, respectively, 0.44, 0.28, 0.17, 0.41, 0.09, 0.10 and 0.56 in the first fraction; 0.24, 0.11, 0.31, 0.48, 0.06, 0.19 and 0.77 in the second fraction; 0.23, 0.16, 0.05, 0.54, 0.02, 0.30 and 0.41 in the third fraction; 0.18, 0.21, 0.14, 0.21, 0.07, 0.17 and 0.34 in the fourth fraction; and 0.31, 0.13, 0.22, 0.09,0.03, 0.06 and 0.13 in the residual fraction.

Table 1. Operating conditions required in the Tessier sequential extraction method

Stage	Fraction	Reagent	Experimental conditions
1	Exchangeable	8 mL of 1 M $MgCl_2$, pH 7	1 hr at 25℃
2	Bound to carbonate	8 mL of 1 M NaOAc, pH 5 (HOAc)	5 hr at 25°C
3	Bound to Fe–Mn oxides	20 mL of 0.04 M $NH_2OH{\cdot}HCl$ in 25% (v/v) HOAc	6 hr at 96°C
4	Bound to organic matter /sulfide	3 mL of 0.02 M HNO_3/5 mL of 30% H_2O_2 (pH 2) /3 mL of 30% H_2O_2(pH 2 with HNO_3) /5 mL of 3.2 M NH_4OAc in 20%(v/v) HNO_3	2 hr at 85°C 3 hr at 85°C 30 min at 25 °C
5	Residue	aqua regia (HNO_3/HCl=1:3) and perchloric acid	8 hr at 180°C in 30 mL Teflon container

RESULTS AND DISCUSSION

The analysis of some general physicochemical characteristics of sediments at different sites and depths indicated that most layers of the sediment were acidic and showed a decreasing tendency with the sediment depth, except some pH values of the surface samples were higher than 7.0. Organic matter content ranged from 1.27-3.50% of dry weight and showed a high variability among the triplicates (3.73-33.83%), which may be due to micro-scale heterogeneity in the sediment. Particle distribution results indicated that sediments studied were predominantly clay-like.

Table 2. Total metal concentrations of mangrove sediments from Jiulong River Estuary, People's Republic of China

Site	Depth	Cu		Pb		Zn		Cd		Ni		Mn		Fe	
		Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
	(cm)	(mg.kg^{-1})		(mg.kg^{-1})		(mg.kg^{-1})		(mg.kg^{-1})		(mg.kg^{-1})		(mg.kg^{-1})		(%)	
Site 1	0-2	61.0	1.8	71.0	3.4	382.0	19.7	3.8	0.5	15.7	0.3	942.9	9.9	3.8	0.1
	2-5	43.4	0.1	60.5	2.6	376.4	35.6	4.7	0.3	16.3	0.2	888.9	62.5	3.6	0.1
	5-10	44.7	2.2	64.2	7.3	371.5	4.5	5.4	1.1	15.8	0.5	804.6	36.8	3.9	0.2
	10-15	44.3	8.1	65.4	0.9	379.3	12.9	3.4	0.2	15.6	2.2	721.3	25.9	3.6	0.1
	15-20	46.0	4.6	64.0	4.8	403.5	10.7	4.6	1.3	15.5	0.5	707.6	16.7	3.7	0.0
	20-25	36.9	2.5	73.6	18.1	286.1	40.3	3.8	0.2	11.5	0.8	654.3	2.8	3.8	0.0
	25-30	43.7	1.0	67.9	8.2	321.2	15.8	4.3	0.1	13.9	0.1	628.2	13.3	3.3	0.2
	30-35	33.0	6.0	59.2	10.2	356.2	17.3	3.0	0.2	11.5	1.0	614.7	7.5	3.3	0.2
	35-40	29.3	5.4	52.8	6.5	249.6	15.4	2.7	0.0	11.8	0.6	612.2	9.9	3.4	0.3
Site 2	0-2	39.2	3.8	50.8	2.3	375.8	23.6	2.5	0.3	14.7	0.0	959.2	41.7	3.7	0.1
	2-5	40.9	0.8	56.0	0.6	381.9	0.4	2.9	0.2	14.5	0.1	747.6	57.9	3.6	0.1
	5-10	37.9	5.0	58.4	4.2	350.5	10.6	2.7	0.2	13.7	0.2	647.6	30.0	3.4	0.1
	10-15	38.1	3.1	62.3	1.9	341.0	2.4	2.5	0.4	12.0	0.1	780.3	44.6	3.5	0.1
	15-20	32.3	2.3	50.7	4.0	308.8	18.5	2.0	0.0	12.6	0.5	813.9	16.7	3.4	0.1
	20-25	29.8	1.1	44.6	3.0	303.6	19.7	1.9	0.4	13.3	1.1	746.9	22.4	3.5	0.1
	25-30	25.1	2.6	39.3	0.1	256.8	9.1	1.4	0.1	12.9	0.0	712.2	22.3	3.1	0.1
	30-35	27.2	3.0	42.2	0.6	273.7	6.9	1.4	0.0	12.3	0.5	639.2	1.4	3.5	0.1
	35-40	25.9	1.1	41.1	1.6	263.3	3.2	1.1	0.0	11.4	0.5	601.7	27.7	3.3	0.0
Site 3	0-2	46.3	5.1	71.0	0.7	355.5	6.1	3.0	0.5	14.2	0.9	1026.0	41.9	3.6	0.2
	2-5	40.1	5.3	58.2	7.2	321.2	26.3	3.8	0.5	15.3	0.4	757.9	26.2	3.3	0.1
	5-10	43.2	2.5	66.3	1.9	353.8	9.6	3.3	0.2	13.9	0.5	793.8	36.9	3.4	0.1
	10-15	40.4	2.6	73.7	0.3	364.7	46.1	2.8	0.4	14.8	1.0	733.8	47.9	3.2	0.1
	15-20	39.1	1.3	69.3	0.7	320.8	8.2	3.2	0.4	14.2	0.2	650.6	31.8	2.8	0.2
	20-25	40.8	3.0	65.6	2.3	295.7	19.0	2.4	0.2	13.3	0.9	724.7	2.7	3.2	0.2
	25-30	35.1	7.7	56.6	6.8	300.0	60.7	2.1	0.4	12.5	0.6	666.2	23.4	2.9	0.2
	30-35	28.9	3.0	42.4	5.9	256.8	23.3	2.2	0.6	11.8	0.7	630.4	49.7	2.9	0.2
	35-40	34.8	0.9	46.5	0.1	278.6	9.3	1.7	0.2	13.3	1.2	675.5	2.4	2.7	0.1
Site 4	0-2	40.6	2.3	49.2	2.7	394.1	6.6	2.9	0.1	13.5	0.2	991.3	6.5	3.8	0.1
	2-5	42.6	3.0	51.9	3.5	410.2	23.2	2.9	0.2	16.1	0.6	895.5	10.2	3.4	0.0
	5-10	37.2	0.3	48.9	0.5	396.2	4.3	2.5	0.4	13.9	1.3	742.1	3.6	3.3	0.1
	10-15	35.6	0.5	45.4	1.8	384.7	6.9	2.4	0.1	12.5	0.6	642.6	15.9	3.5	0.1
	15-20	38.6	0.6	51.2	0.0	382.4	6.5	2.8	0.4	12.2	0.7	605.0	31.6	3.3	0.1
	20-25	39.0	2.1	51.5	0.9	377.1	10.9	3.2	0.7	12.9	0.9	728.8	26.1	3.2	0.1
	25-30	40.8	2.1	49.4	0.4	388.1	9.3	2.6	0.2	11.4	0.7	695.1	7.7	3.0	0.2
	30-35	39.6	0.2	54.4	0.8	369.7	0.4	2.6	0.4	12.0	0.7	676.4	21.5	3.3	0.2
	35-40	40.2	5.5	62.8	4.2	391.6	3.1	3.5	0.1	12.2	0.5	686.2	31.2	3.2	0.2

S.D.=Standard deviation

The orders of total metal concentrations in different sediment profiles showed an identical trend (Table 2): Fe>Mn>Zn>Pb>Cu>Ni >Cd. The high concentrations of iron and manganese may be related to its native rock type, which is either basalt or granite. Due to the influence of the subtropical climate, soils has a strong weathering process and undergo significant desilicification and allitization, and forms the high iron and aluminum red earth (Chen et al. 1995). However, the high concentrations of cadmium, zinc, lead and copper would be derived from anthropogenic inputs from industrial activities around the estuary. Further investigation is needed to identify the possible pollution sources of these metals.

Although fluctuations were observed, most of the metal concentrations from site 1 to site 3 decreased with increasing sediment depth (Table 2). In contrast, at site 4, concentrations of copper, zinc and cadmium did not decrease with depth but remained rather stable. Lead concentration at site 4 increased at 30-40cm, this may result from human activities in years past. Enrichment of metals at the surface of the profile may reflect the impacts of contaminant inputs from recent industrial development around the estuary. However, the fluctuations of metal concentration in certain depths may be attributed to factors besides the input from natural and anthropogenic sources, such as leaching, and post-depositional remobilization (Ramanathan et al. 1996), the effect of scavenging of trace metals onto manganese and iron hydroxides, bioturbation in upper sediment layers and metal uptake by vegetation (Clark et al. 1998). The different concentrations of a certain metal at different sites in this study may due to variation in hydraulic condition, which may result in different deposition rates of sediment particles (Mackey and Hodgkinson, 1995).

Table 3. Correlations between total concentration of metals and some parameters of mangrove sediments from Jiulong River Estuary

	Total Fe	Total Mn	Total Ni	Total Cu	Total Cd	Total Pb	Total Zn
Total Mn	0.510**						
Total Ni	0.379*	0.588**					
Total Cu	0.415*	0.543**	0.648**				
Total Cd	0.469*	0.251	0.580**	0.709**			
Total Pb	0.295	0.21	0.398*	0.703**	0.684**		
Total Zn	0.377*	0.438**	0.465**	0.683**	0.504**	0.286	
Organic matter	0.278	-0.115	-0.027	-0.131	0.054	0.143	-0.307
Salt content	0.480**	0.271	0.558**	0.319	0.451**	0.472**	-0.093
Particle content (<50 μ m)	0.407*	0.637**	0.603**	0.424*	0.346*	0.261	0.22

Correlations were based on 36 mangrove sediment samples. * and ** indicate correlation is significant at the 0.05 and 0.01 probability levels, respectively

Table 3 shows no correlations between organic matter content and the total concentrations of metals, which is consistent with the results of Jain and Sharma (2001). However, positive correlations were found between total Ni, Cu, Cd, Zn and Fe, Mn; Fe, Mn, Ni, Cu, Cd and sediment particles (<50μm). This suggested that Fe, Mn and fine sediment particles played an important role in transport of these metal ions. Meanwhile, positive correlations were found between dissolved salt content and total metal concentrations for Fe, Ni, Cd and Pb.

The results (Figure 1) of the sequential extraction procedure indicated that different metals resulted in different partitioning patterns among the secondary mineral phases; there was a different variation tendency with sediment depth. The same trace metal showed somewhat identical trends of binding fractions with variation in sediment depth in all sediment cores from the four sites. Thus, only the analytical results obtained from site 1 are selected and the concentrations in percent (%) of the elements determined at each extraction step are illustrated in Figure1.

The two dominant fractions of iron in the sediment were in the residue and bound to Fe-Mn oxides that comprise 41-56% and 39-54% of the total Fe concentration, respectively. Iron bound to organic matter/sulfide was less than 10%. The portion of exchangeable and bound to carbonate were very low, these did not represent any significant fractions of iron in the sediments.

A large amount of Mn (31-51%) was extracted in Fe-Mn oxides fraction. Exchangeable Mn was another important portion (20-40%). Significant high concentrations of exchangeable Mn in sediments have already been reported by Tessier et al. (1979). It was suggested that in most natural waters, Mn(Ⅱ) oxidation is a much slower process than Fe(Ⅱ) oxidation (Tessier et al.1979).

The lead fraction of bound to Fe-Mn oxides was the predominant portion throughout the depth of the core, representing about 51-72% of the total lead concentration. The residue was the second most important fraction with 17-32% of total lead. The remainder is distributed more or less between bound to carbonate and bound to organic matter/sulfide fraction. The exchangeable fraction is lower than 1%. This may be attributed to the high Fe-Mn oxides content of the sediment; it is known that lead can form stable complexes with Fe-Mn oxides (Ramos et al. 1994). Analysis of the data revealed a positive correlation coefficient between Pb and Fe, Mn concentrations bound to Fe-Mn oxides (Table 4, (b)).

A major portion of the Cu was associated with Fe-Mn oxides. Bound to organic matter/sulfide was the next most important with a range from 19-37% to the total Cu; followed by the residue fraction. It is not surprising that a significant amount of Cu was found in the organic matter/sulfide fraction as Cu forms highly stable complexes with organics (Li et al. 2001). Correlation analysis indicated that the Cu concentration bound to Fe-Mn oxides had positive correlation with Fe and Mn concentration bound to Fe-Mn oxides (Table 4, (b)). The Cu concentration bound to organic matter/sulfide also had a positive correlation with organic matter content (Table 4, (c)).

High percentages of Cd were extracted at each stage: 4-15%, 16-21%, 21-33%, 15-23%, 20-33% of total Cd were obtained from steps 1 to 5 (Figure 1). Strong correlations existed between the concentrations of Cd-Fe and Cd-Mn in the bound to Fe-Mn oxides stage (Table 4, (b)). Meanwhile, a positive correlation was found between Cd concentration bound to carbonate fraction and sediment pH value (Table 4, (a)). This result, together with the toxicity of Cd to organisms and humans, suggests that we should pay more attention to the high concentration of cadmium in the study area.

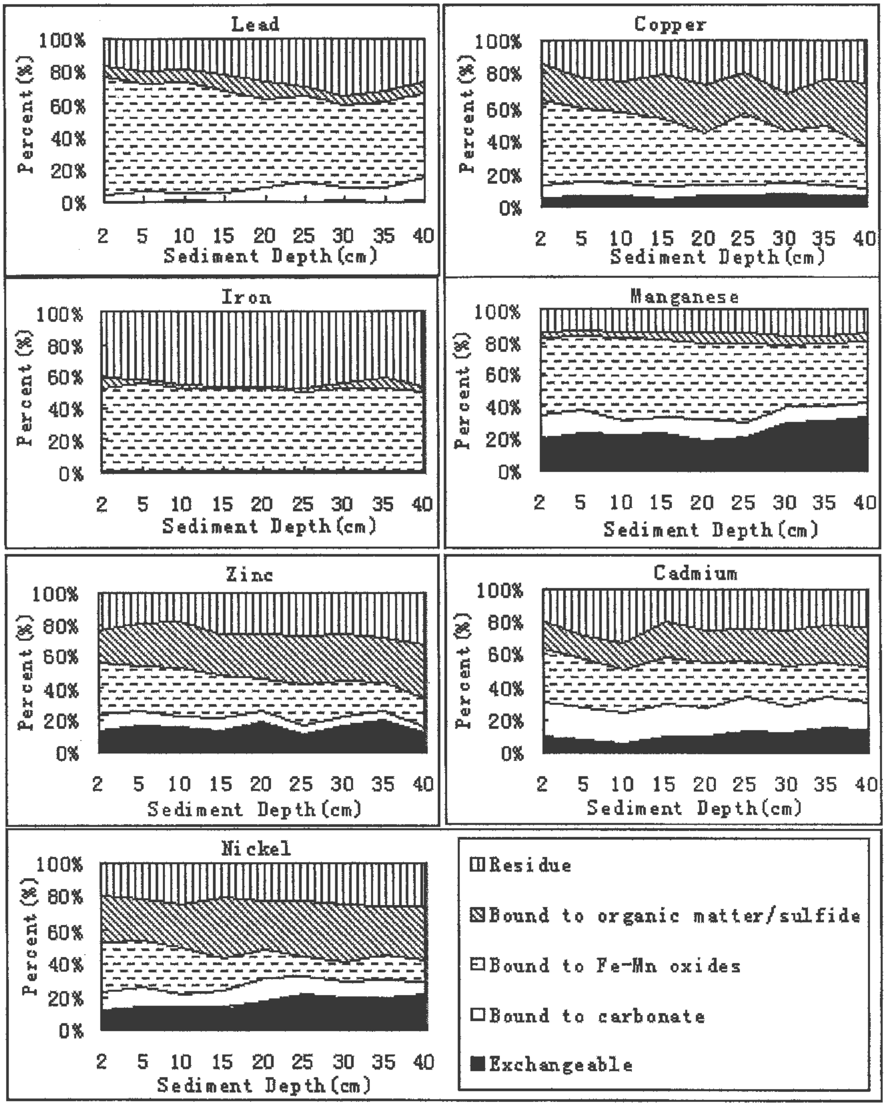

Figure 1. Speciation distribution of metals with mangrove sediment depth in Jiulong River Estuary

Zn and Ni were distributed in a similar manner, with a major portion of the metals bound to Fe-Mn oxides, organic matter/sulfide and the residual fraction (Figure 1). The association of Zn and Ni with Fe-Mn oxides in sediment has been widely recognized (Jones and Turki, 1997). The significant correlations between Zn/Ni and Fe-Mn in the fraction bound to Fe-Mn oxides (Table 4, (b)) may be attributed to the adsorption of Zn/Ni onto Fe-Mn oxides. The concentration of residual Zn and Ni changed little with depth, probably reflecting the natural background level. The positive correlation between Ni concentration bound to organic matter/sulfide with organic matter content (Table 4, (c)) indicated that the vertical distribution of Ni was related to sediment organic matter content.

Table 4(a). Correlation between metal concentrations bound to carbonate and pH Values

	pH	Ni	Cu	Cd	Pb	Zn	Fe
Ni	0.501**						
Cu	0.479**	0.634**					
Cd	0.540**						
Pb							
Zn	0.666**	0.727**	0.789**	0.470**			
Fe							
Mn	0.563**	0.557**				0.497**	

Table 4(b). Correlation between metal concentrations bound to Fe-Mn oxides

	Ni	Cu	Cd	Pb	Zn	Fe
Cu	0.753**					
Cd	0.543**	0.424**				
Pb	0.679**	0.697**	0.633**			
Zn	0.675**	0.748**		0.398*		
Fe	0.437**	0.347*	0.593**	0.420*	0.443**	
Mn	0.701**	0.562**	0.580**	0.563**	0.573**	0.669**

Table 4(c). Correlation between metal concentrations bound to organic matter/sulfide and organic matter

	Organic matter	Ni	Cu	Cd	Pb	Zn	Fe
Ni	0.427**						
Cu	0.424**	0.627**					
Cd			0.458**				
Pb		0.675**	0.892**	0.530**			
Zn				0.579**			
Fe						0.410*	
Mn	0.408*	0.400*	0.786**	0.655**	0.759**		

Correlations were based on 36 mangrove sediment samples. * and ** indicate correlation is significant at the 0.05 and 0.01 probability levels, respectively

In this study, a large proportion of trace metals in the sediment were associated with Fe-Mn oxides. This is in agreement with the results of some other studies in south China (Chen et al. 2000; Li et al. 2001), and may partly be due to the excellent scavenging properties of Fe-Mn oxides for trace metals. The concentrations of most studied metals in the residue fraction were relatively low compared to Fe. This may be attributed to the intensity of chemical weathering of the primary minerals under a subtropical climate and high precipitation of the south China.

According to the total concentrations in sediments, the study area was polluted with certain metals. In the case of Cd, Zn, Pb and Cu, the sum of each metal associated with the first three fractions (exchangeable, bound to carbonate and bound to Fe-Mn oxides) was considerably high. This is a concern because these fractions represent the proportion of heavy metals that can be easily remobilized by changes in environmental conditions such as pH or bioturbation.

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