Journal of Hazardous Materials 190 (2011) 631–638

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Accumulation and partitioning of seven trace metals in mangroves and sediment cores from three estuarine wetlands of Hainan Island, China

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ARTICLE INFO

Article history:
Received 14 January 2011
Received in revised form 18 March 2011
Accepted 24 March 2011
Available online 31 March 2011

Keywords:
Trace metal
Mercury
Mangrove
Wetland
Hainan Island (China)

ABSTRACT

Trace metals in mangrove tissues (leaf, branch, root and fruit) of nine species and sediments of ten cores collected in 2008 from Dongzhai Harbor, Sanya Bay and Yalong Bay, Hainan Island, were analyzed. The average concentrations of Cu, Pb, Zn, Cd, Cr, Hg and As in surface sediments were 14.8, 24.1, 57.9, 0.17, 29.6, 0.08 and 9.7 $\mu g\, g^{-1}$, whereas those in mangrove tissues were 2.8, 1.4, 8.7, 0.03, 1.1, 0.03, and 0.2 $\mu g\, g^{-1}$, respectively. Compared to those from other typical mangrove wetlands of the world, the metal levels in Hainan were at low- to median-levels, which is consistent with the fact that Hainan Island is still in low exploitation and its mangroves suffer little impact from human activities. Metal concentrations among different tissues of mangroves were different. In general, Zn and Cu were enriched in fruit, Hg was enriched in leaf, Pb, Cd and Cr were enriched in branch, and As was enriched in root. The cycle of trace metals in mangrove species were estimated. The biota-sediment accumulation factors (BSAFs) followed the sequence of Hg (0.43) > Cu (0.27) > Cd (0.22) > Zn (0.17) > Pb (0.07) > Cr (0.06) > As (0.02).

1. Introduction

Mangrove ecosystems, the important inter-tidal estuarine wetlands along the coastlines of tropical and subtropical regions, are closely tied to human activities and are subjected to contamination. Mangrove sediments have been shown to have a high capacity to accumulate materials discharged to the nearshore marine environment [1]. Mangroves can tolerate high metal fluxes and often serve as a buffer protecting adjacent marine communities [2]. This is mainly due to the high sulphide and organic matter contents that favour the retention of water-borne trace metals [3]. Over the past few decades, mangrove wetlands have been used for treating municipal, livestock and industrial wastewaters and even mine drainage [4–6]. However, metals can be reintroduced to nearshore waters when they are taken up by mangrove trees and concentrated in exported leaf detritus. Mangrove leaf detritus and associated microbes form the basis of mangrove food web and are also a food source when transported to the adjacent deeper waters [7]. The knowledge of trace metal concentrations in different compartments of mangrove ecosystem is important to understand the fates of these contaminants and, can alert coastal managers of possible impacts upon the detritus driven food web which can potentially lead to the bioaccumulation of contaminants in organisms.

Hainan Island, the second largest Island of China, has mangrove areas of 4772 hm^2, accounting for one third of the total mangrove forest areas of China [8]. There are 26 mangrove plant species distributing in Hainan while 27 species in China [9]. Hainan Dongzhai Harbor Mangrove Protection Zone, as the first National Mangrove Reserve of China, was established in 1986 and was listed as the International Important Wetland in 1992. Since 1978 when China started the reform and opening up policy, the development of coastal zones throughout Hainan Island has put immense pressures on biological communities including mangrove ecosystem. More than 60% mangrove forest has disappeared since 1950s [8], and many mangrove forest areas were developed as culturing ponds and constructing sites. Although many studies on trace metal pollution have been conducted in mangrove wetlands (e.g. [3,10–12]), few data have been published on trace metals of the mangroves in Hainan Island. It has been reported the trace metal concentrations of surface sediments from mangrove wetlands around Haikou and Wenchang, Hainan Island [13]. As an international important wetland, no information is available on the status of trace metals in mangrove ecosystem of Hainan Island. Further, there are very few data on Hg and arsenic concentrations in mangrove tissues around the world so far. The present work therefore aimed (1) to quantify the concentrations of trace metals (Cu, Pb, Zn, Cd, Cr, Hg and As) in nine mangrove species (including in root, trunk, leaf and fruit)

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doi:10.1016/j.jhazmat.2011.03.091

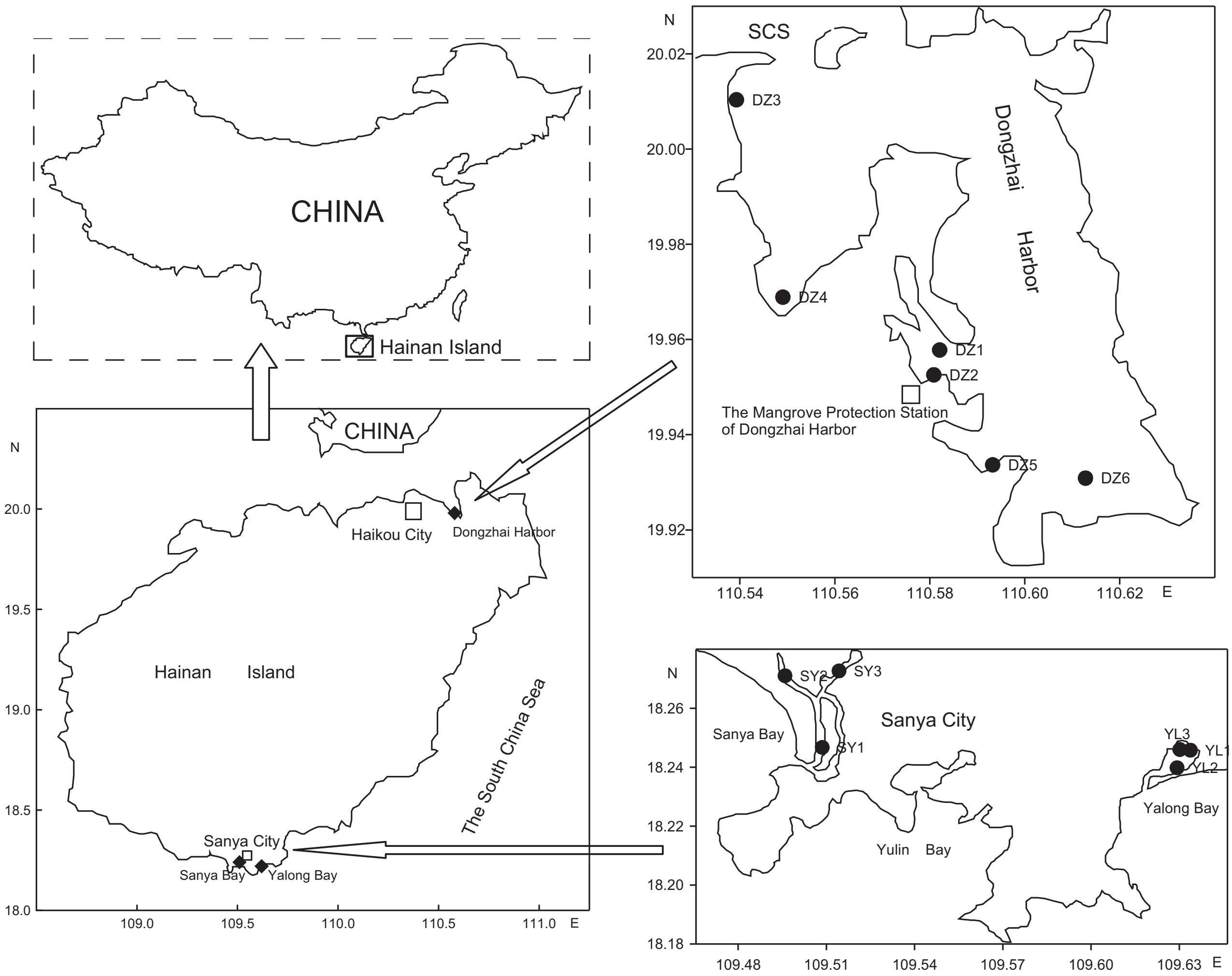

Fig. 1. Sampling locations in three mangrove wetland (Dongzhai Harbor, Sanya Bay and Yalong Bay) of Hainan Island, South China.

from three typical mangrove areas of Hainan Island, i.e., Dongzhai Harbor, Sanya Bay and Yalong Bay (Fig. 1); (2) to determine the distribution of trace metal levels in sediment cores; and (3) to assess the potential risk of trace metals on the mangrove ecosystem in Hainan Island.

2. Materials and methods

2.1. Study site

Of the three studied mangrove areas (Fig. 1), Dongzhai Harbor, in the northern Hainan Island, is the most well-preserved mangrove forest in China and suffers little anthropogenic stress. Sanya Bay, situated in the center of Sanya city of the southern Hainan Island, is subjected to heavy human activities. Yalong Bay, also located in southern Hainan Island, suffers middle-level anthropogenic exploitation. All the three studied areas were predominantly colonized by *Rhizophora stylosa*, *Rhizophora apiculata*, *Bruguiera sexangula*, *Ceriops taga1*, *Aegiceras corniculatum*, *Avicennia marina*, and *Sonneratia apetala* [9].

2.2. Sample collection and processing

Sediment cores and mangrove tissues at six sites of Dongzhai Harbor (DZ1, DZ2, DZ3, DZ4, DZ5 and DZ6), three sites of Saya Bay (SY1, SY2 and SY3), and three sites of Yalong Bay (YL1, YL2 and YL3) (Fig. 1 and Table 1), were collected in October 2008 using pre-determined GPS co-ordinates to accurately locate each station. Sampling sites were selected based on the spatial and the mangrove species community distribution and can be accessible. A stainless steel static gravity corer (8 cm i.d.) with polyvinylchloride (PVC) tubes was employed to collect sediment cores which were then separated at 5 cm intervals, and air dried and weighed to obtain the dry mass. The sediments were disaggregated and ground in an agate mill and sieved through a 100-mesh nylon sieve. Mangrove tissues, including root, perennial branch (diameter about 5–8 cm), leaf and fruit of 9 species, were simultaneously collected. Mangrove samples were washed by deionised water in laboratory to remove the possible dust, and naturally dried, and were then sampled with a thin stainless steel blade. All glasswares were cleaned by soaking in 10% HNO_3 (v/v) for at least two days, followed by soaking and rinsing with water. The mangrove samples covered nine species from four families: *Sonneratia hainanensis*, *Sonneratia caseolaris*, *B. sexangula*, *Bruguiera gymnorrhiza*, *R. stylosa*, *R. apiculata*, *Kandelia candel*, *Lumnitzera racemosa*, and *A. corniculatum*.

2.3. Chemical analysis

Measurements of trace metals followed the procedures described previously [14]. 500.0 mg of sediment was digested with 6 ml concentrated nitric acid (HNO_3) in microwave oven at a temperature of 150 °C for 10 min, 180 °C for 5 min and 200 °C for 10 min.

Table 1
Sampling locations for mangrove species, sediment compositions and the TOC contents in surface sediment of Hainan Island.

Location	Longitude (E)	Latitude (N)	Sediment composition	Species	TOC (mg/g)
Dongzhai Harbor					
DZ1	110°34.744	19°56.927	Silt	*Rhizophora stylosa*	51.1
ZD1	110°34.744	19°56.927	Silt	*Bruguiera gymnorrhiza*	51.1
DZ2	110°34.610	19°56.734	Silt	*Kandelia candel*	55.1
ZD2	110°34.610	19°56.734	Silt	*Aegiceras corniculatum*	55.1
DZ3	110°32.218	20°00.500	Silt	*Rhizophora stylosa*	7.4
DZ4	110°32.943	19°57.833	Clayey silt	*Bruguiera sexangula*	59.0
DZ5	110°35.354	19°55.720	Clayey silt	*Bruguiera sexangula*	30.9
DZ6	110°36.767	19°55.852	Clayey silt	*Sonneratia caseolaris*	13.1
DZ6	110°36.767	19°55.852	Clayey silt	*Sonneratia hainanensis*	13.1
Sanya Bay					
SY1	109°30.529	18°14.427	Sandy silt	*Rhizophora apiculata*	25.6
SY1	109°30.479	18°14.647	Sandy silt	*Sonneratia hainanensis*	25.6
SY2	109°29.631	18°16.240	Clayey silt	*Rhizophora apiculata*	8.8
SY3	109°30.820	18°16.277	Silty sand	*Rhizophora apiculata*	18.5
Yalong Bay					
YL1	109°37.267	18°13.875	Silty sand	*Lumnitzera racemosa*	
YL2	109°37.037	18°13.299	Sandy silt	*Rhizophora stylosa*	39.0
YL3	109°37.250	18°13.548	Sandy silt	*Lumnitzera racemosa*	

Then the solution was diluted to 10 ml with deionised water and analyzed for Cu, Pb, Zn, Cd and Cr. 500.0 mg of sediment was digested with 6 ml HNO_3 in Kjeldahl tube at a temperature of 100 °C (in water both) for 60 min. After cooling, 1 ml 1% $KMnO_4$ was added and deposited for 20 min. Then the solution was diluted to 10 ml with 1% $HOOCCOOH{\cdot}2H_2O$ and analyzed for Hg. 300.0 mg of sediment was digested with 10 ml aqua regia (HCl/HNO_3: 3/1, v/v) in Kjeldahl tube at a temperature of 100 °C (in water both) for 60 min. After cooling, the solution was diluted with deionised water. 5 ml HCl (1:1, v/v) and 2.5 ml the mixed solution (5% sulfocarbamide + 5% ascorbic acid) were added into 1 ml the above solution and diluted to 10 ml with deionised water and analyzed for As. Concentrations of Cu, Pb, Zn, Cd and Cr were determined using atomic adsorption spectrometry (SOLAAR M6, UK), while those of Hg and As were determined by atomic fluorescence spectrometry (AFS-8130, Beijing, China). 100.0 mg mangrove tissue sample was placed into Teflon pot pre-cleaned with high purity nitric acid; then 2.0 ml concentrated nitric acid (HNO_3) was added into the pot lasting for 2 h; and then heated in an electric board at 150 °C for 24 h. After cooling, the solution was diluted by high pure water to 40 g and the concentrations of Cu, Pb, Zn, Cd, Cr, Hg and As were measured using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS model DRC II, Perkin Elmer, USA). All trace metals concentrations in both mangrove tissues and sediments were analyzed in one well-mixed sample and expressed in $\mu g\,g^{-1}$ on dry-weight basis.

500.0 mg sediment was treated with excess acid (HCl, 10%, v/v) to remove inorganic carbon and then oven dried at 60 °C for 24 h. Total organic carbon (TOC) was determined using a CHN Elemental Analyzer (Carlo-Erba model 1108).

The analysis and nomenclature for grain size of sediment were referred to "China National Standard" (GB/T13909-92). Analytical flows of grain size were as follows [15]: sampling, drying, weighing, adding Sodium hexametaphosphate and water, and then soaking, filtering through water sieve with diameter 0.063 mm. The sample on the sieve (>0.063 mm) was analyzed by sieve analysis after drying; and the sample under the sieve (<0.063 mm) was analyzed with granulometry (SKC-2000, Japan).

2.4. Quality assurance and quality control

All glass- and plastic-ware were soaked in 10% nitric acid overnight and rinsed thoroughly with deionized water before use. For quality control, reagent blanks, the Chinese national standard samples of GBW07314 (reference materials for offshore sediment), GBW08571 (reference materials for mussel), GBW08517 (reference materials for kelp) and GBW010016 (reference materials for tea) were used to monitor the analytical quality. The results were consistent with the reference values with relative differences within 10% (mostly within 5%). Blank determinations were carried out for each set of analysis. The determination limits of Cu, Pb, Zn, Cd, Cr, Hg and As in sediment were 0.1, 0.1, 0.2, 0.02, 0.2, 0.002 and 0.06 μg/g dry wt., while for mangrove tissues were 0.02, 0.002, 0.02, 0.02, 0.02, 0.002 and 0.02 μg/g dry wt., respectively.

2.5. Cycling of trace metals in mangroves

Previous studies showed that the total above-ground biomass yield at Dongzhai Harbor was 3.85 $kg\,m^{-2}$ for mixture population of *S. carseolaris* (6-year-old) and *K. candel* (11-year-old) with net production of 0.47 $kg\,m^{-2}\,a^{-1}$ (including 0.42 $kg\,m^{-2}\,a^{-1}$ of stem and 0.05 $kg\,m^{-2}\,a^{-1}$ of leaf) [16]. The biomass of root accounted for 41% of the total biomass and the yearly biomass increment of root accounted for 20% of the total yearly biomass increment for *B. sexangula* (55-year-old) [17]. The mean annual litter production at the three studied areas was about 1.293 $kg\,m^{-2}\,a^{-1}$, with leaf (and flower), branch, and fruit accounting for 78%, 8% and 14%, respectively [18,19]. Based on the average biomass in each compartment in the above studies and the average concentrations of trace metals in the present study, the cycling of trace metals in mangroves can be approximately calculated as follows. The standing stock of trace metals in mangrove tissues was calculated by multiplying metal concentrations in each compartment by its biomass in 1 m^2. The corresponding annual absorption was calculated by multiplying metal concentrations in each compartment by its annual net production in 1 m^2. The annual net retention was estimated by multiplying metal concentrations in each compartment by its annual litter fall in 1 m^2. The annual return was calculated by subtracting the annual net retention from the annual absorption. The turnover period of trace metals was the ratio of the standing stock of trace metals in mangrove tissues and the annual net retention of trace metals.

2.6. Statistical analysis

Pearson correlation was conducted using SPSS for Windows Release 10.0. In order to study the general characteristics of trace metals in mangrove forests of Hainan Island, the concentrations of trace metals and the TOC content in sediment, as well as the concentrations of trace metals in mangrove tissues were used as the input data in the PC.

Table 2
The average concentrations of trace metals ($\mu g\ g^{-1}$ dw) in mangrove sediments of Dongzhai Haibor ($n = 33$), Sanya Bay ($n = 7$), Yalong Bay ($n = 6$) and some mangrove wetlands around the world.

Location	Cu	Pb	Zn	Cd	Cr	Hg	As	Reference
Dongzhai Haibor, Hainan	18	19	57	0.11	40	0.08	13	This study
(±SD)	9	11	32	0.06	14	0.03	4	
Sanya Bay, Hainan	9	18	53	0.13	12	0.06	7	This study
(±SD)	7	8	28	0.08	3	0.03	2	
Yalong Bay, Hainan	5	15	26	0.12	11	0.03	5	This study
(±SD)	1	8	3	0.01	1	0.01	0.5	
Wenchang, Haian, China	27	30	89	ND	109	0.06	15	[13]
Haikou, Hainan, China	27	33	92	ND	122	0.06	13	[13]
Yinglou Bay, Guangxi, China	18.9	10.0	46.6	0.077	9.27	ND	ND	[20]
Mai Po, Hong Kong	78.5	79.2	240	2.62	39.2	ND	ND	[3]
Sungei Buloh, Singapore	7.06	12.28	51.24	0.181	16.61	ND	ND	[21]
Pichavaram, India	43.4	11.2	93	6.6	141.2	ND	ND	[24]
Cienaga Grande, Colombia	23.3	12.6	91	ND	13.2	ND	ND	[23]
The coast of Brazil	98.6	160.8	483	1.32	42.4	ND	1.28	[25]
Punta Mala Bay, Panama	56.3	78.2	105	<10	23.3	ND	ND	[26]
Queensland, Australia	1.0-12	36	23-56	0.6	1-72	ND	ND	[22]
Newington, Australia	71.3	121.9	229.9	ND	ND	ND	ND	[27]

ND: Not detected.

3. Results and discussion

3.1. Metals in sediment

3.1.1. Metals in surface sediment

The average concentrations of trace metals in mangrove sediments of Dongzhai Haorbor, Sanya Bay and Yalong Bay of Hainan are summarized in Table 2. The total mean concentrations of Cu, Pb, Zn, Cd, Cr, Hg and As in surface sediments in all the sites were 15 ± 9, 24 ± 9, 58 ± 37, 0.2 ± 0.1, 30 ± 20, 0.08 ± 0.04 and $10 \pm 4\ \mu g\ g^{-1}$, respectively (Table S1). Generally, the levels of Cu, Cr and As in all sediments followed the order: Dongzhai Harbor > Sanya Bay > Yalong Bay, while the levels of Zn, Cd, and Hg followed the order: Sanya Bay > Dongzhai Harbor > Yalong Bay, and the levels of Pb followed the order Dongzhai Harbor ~ Sanya Bay < Yalong Bay.

Trace metals levels in some typical mangrove wetlands around the world are also shown in Table 2. Generally, levels of mangrove sediment trace metals, except Hg, in the present studied areas were similar to those from Yinglou Bay (China) [20], Sungei Buloh of Singapore [21], and southeast Queensland of Australia [22]; and were slightly lower than those from Haikou and Wenchang of Hainan [13], and Ciénaga Grande de Santa Marta of Colombia [23]; and were much lower than those from Mai Po of Hong Kong [3], Pichavaram mangrove ecosystem in southeast coast in India [24], the tropical coastal estuary and a mangrove in Brazil [25], Punta Mala Bay in Pacific Panama [26], and Newington North estuarine wetlands in Australia [27]. Compared with other trace metals, little information on Hg concentration in mangrove system has been documented. In the present study, Hg levels in surface sediments (0.030–0.140 $\mu g\ g^{-1}$, with mean value of 0.079 $\mu g\ g^{-1}$) was similar to those in another Hainan mangrove areas (Wengchang and Haikou) with mean concentrations of 0.06 $\mu g\ g^{-1}$ [13]. Similar Hg values in sediment from the South Florida estuaries, USA (0.001–0.219 $\mu g/g$, with mean value of 0.020 $\mu g\ g^{-1}$ [28]) and those in the Pearl River Estuary and the surrounding coastal area of South China (0.0015–0.201 $\mu g\ g^{-1}$, with mean value of 0.054 $\mu g\ g^{-1}$ [29]) have also been reported. The Hg levels in surface sediments of the three studying areas were within the Hg background levels (approximately 0.02–0.1 $\mu g\ g^{-1}$) of marine, coastal and estuarine sediments worldwide [30].

Overall, the target metals in sediments from Dongzhai Haorbor, Sanya Bay and Yalong Bay of Hainan were at low levels compared with other mangrove areas around the world, which is consistent with the fact that Hainan Island is still in low exploitation.

3.1.2. Vertical profiles of metals

Previous study based on the stakes dating method showed that a mean sedimentation rate of 4.1 mm/a in mangrove sediments of Dongzhai Harbor [31]. Thus, a 45-cm-long sediment core from Dongzhai Harbor approximately covered the last 110 years. No significant difference for trace metal concentrations vertically was observed from the sediment cores (DZ1, DZ4, DZ6, SY2 and YL2), while the TOC exhibited a decreasing trend with increasing depth in most sediment cores except for core SY-2 (Fig. 2). The decrease of TOC was due to organic matter decomposition with buried times over the past one hundred years. As the length of sediment cores (DZ1, DZ2, DZ3, SY1 and SY3) were shorter compared with the above cores, trace metals were measured in only surface sediment. The sediment in the present study was primarily composed of silt which allowed the metals to migrate in sediment core more easily, leading to a relatively uniform vertical profile. Furthermore, agriculture in Hainan Island was a traditionally dominant economic driving force, and was relatively less impacted by industrial activities compared to other coastal areas in China. Fertilizers and pesticides for agricultural use and sewage were the primary metal sources. Until recently, Hainan Island is still in low exploitation state, which may explain that the metal levels in the core sediments were relatively low.

3.1.3. Potential risk assessment

Marine sediment is often regarded as the ultimate sink for many pollutants including trace metals. Trace metals in sediment may pose hazard to aquatic biota upon released into the overlaying water, or through direct ingestion by deposit feeders. Many metals are biologically essential elements, but they also have potential toxicity to biota if their concentrations surpass certain thresholds. For example, Zn and Cu at low concentrations are essential elements for the growth of organisms, whereas Cd and Pb are non-essential elements and are toxic even at low levels.

In the present study, the guidelines (Table S2) for the estimated sediment safe levels of trace metals recommended by the National Oceanic and Atmospheric Administration (NOAA, 2009) of the United States were used to examine the potential ecological risk of trace metals in sediments. The concentrations of target metals except arsenic in mangrove sediment of Hainan Island were generally below the Effects Range-Low (ERL) values, while concentrations of all the target metals in sediments were below the Effects Range-Median (ERM) values. Among the total 46 samples analyzed, only 32 arsenic samples, and one Pb and one Cu sample, exceeded the ERL values. These assessments suggest that

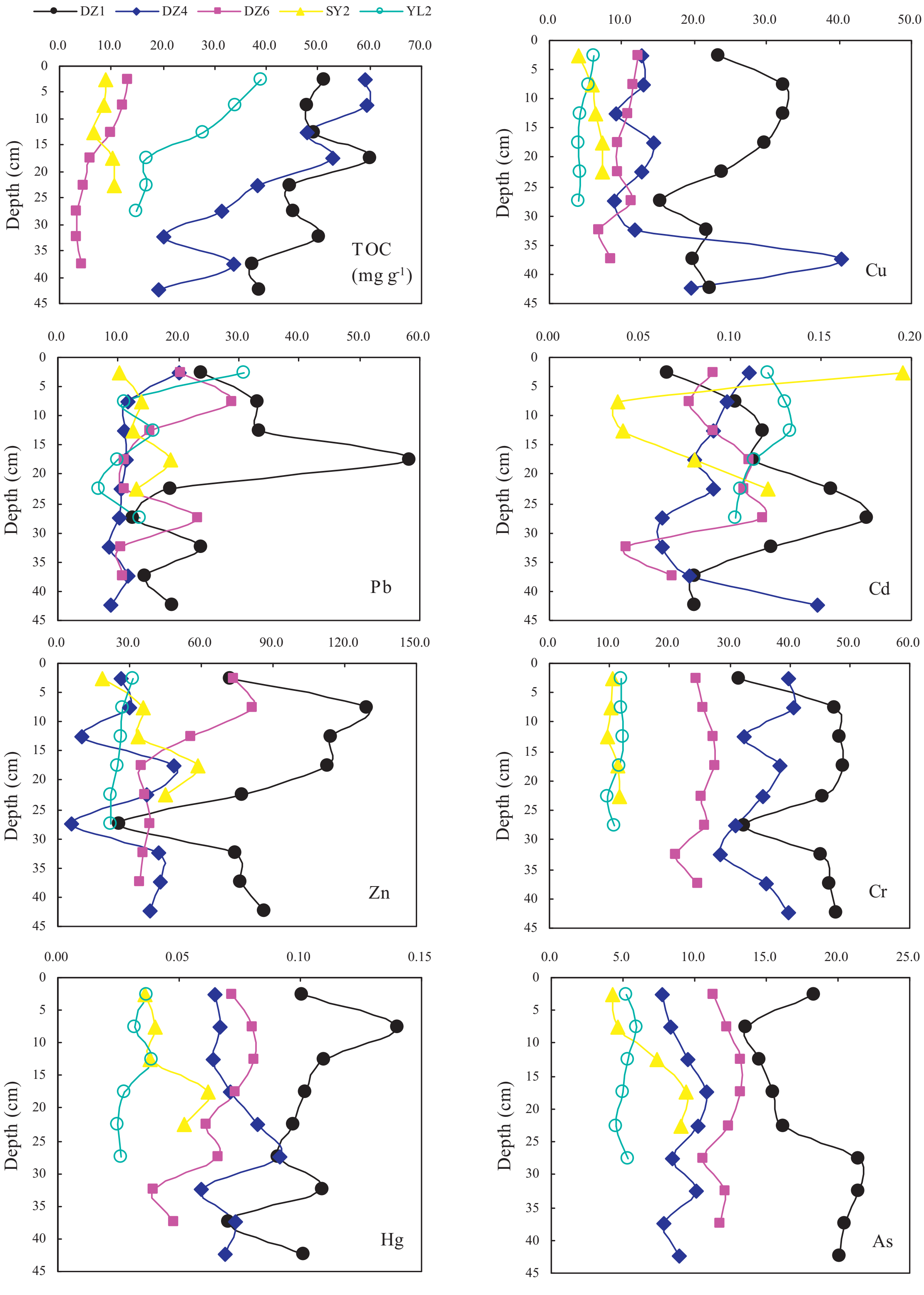

Fig. 2. The vertical profiles of trace metals and TOC concentrations in mangrove sediment cores (DZ1, DZ4, DZ6, SY2 and YL2) of Hainan Island (μg g^{-1}).

arsenic in sediment probably poses potential risk to the mangrove ecological system of Hainan Island, whereas other trace metals are mostly not hazardous to organisms at this stage. Risk assessment showed that the pollution status of all target trace metals except arsenic was still in low level and therefore their ecological and environmental effects on mangroves of Hainan Island were also low.

3.2. Metals in mangroves

3.2.1. Metal concentrations in mangrove tissues

No significant difference was observed for trace metals concentrations in same mangrove species. The average concentrations of Cu, Pb, Zn, Cd, Cr, Hg and As in nine species mangrove tissues (leaf, branch, root and fruit) are shown in Fig. 3. Statistics of trace

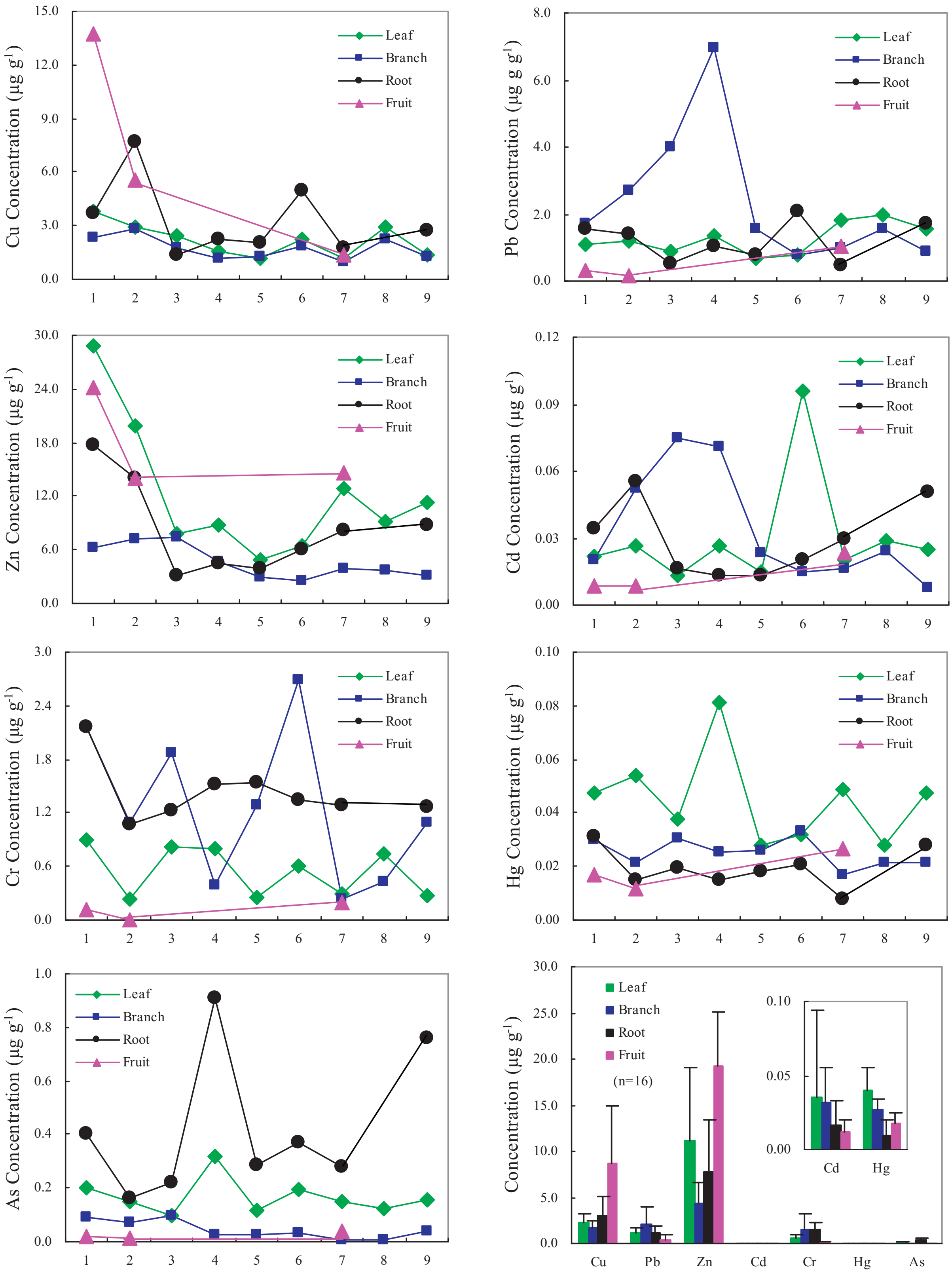

Fig. 3. Distribution of the average concentrations of trace metals in mangrove tissues of Hainan Island ($n = 16$).

metals concentrations in mangrove tissues (leaf, branch, root and fruit) in three typical mangrove areas of Hainan Island are summarized in Table S1. There was not significant difference for trace metals concentrations among mangrove species, but the metal concentrations among different tissues of mangroves were different. In general, concentrations of Zn and Cu were enriched in fruit, Hg was enriched in leaf, Pb, Cd and Cr were enriched in branch, and As was enriched in root. Zn and Cu, the essential elements for the growth of plants, tended to accumulate in fruit, while Hg, a semi-volatile metal, was deposited and accumulated in leaf.

Table 3
The average of the biota-sediment accumulation factors (BSAF) and the cycle of trace metals in mangroves of Hainan Island.

Fraction	Cu	Pb	Zn	Cd	Cr	Hg	As
The biota-sediment accumulation factors (BSAF)							
Leaf	0.22	0.06	0.23	0.22	0.030	0.59	0.018
Branch	0.19	0.11	0.09	0.28	0.090	0.43	0.005
Root	0.30	0.06	0.15	0.20	0.069	0.30	0.039
Fruit	0.61	0.02	0.29	0.08	0.004	0.20	0.002
The standing stock (mg m^{-2})							
Leaf	0.98	0.50	4.90	0.02	0.25	0.02	0.07
Branch	6.05	7.04	15.04	0.11	5.05	0.09	0.15
Root	8.27	3.13	20.61	0.07	3.93	0.05	1.02
Total	15.30	10.66	40.55	0.19	9.23	0.16	1.24
The annual absorption (mg m^{-2} a^{-1})							
Leaf	2.35	1.20	11.80	0.04	0.60	0.04	0.17
Branch	0.93	1.08	2.31	0.02	0.77	0.01	0.02
Root	0.93	0.35	2.31	0.01	0.44	0.01	0.11
Total	4.21	2.63	16.41	0.06	1.81	0.06	0.30
The annual net retention (mg m^{-2} a^{-1})							
Leaf	0.11	0.06	0.56	0.002	0.03	0.002	0.008
Branch	0.74	0.87	1.85	0.013	0.62	0.011	0.018
Root	0.37	0.14	0.91	0.003	0.17	0.002	0.045
Total	1.22	1.06	3.32	0.018	0.82	0.02	0.071
The annual return (mg m^{-2} a^{-1})							
Leaf	2.24	1.14	11.24	0.035	0.57	0.040	0.16
Branch	0.18	0.21	0.46	0.003	0.15	0.003	0.005
Root	0.56	0.21	1.40	0.005	0.27	0.004	0.07
Total	2.99	1.57	13.10	0.043	0.99	0.05	0.23
The turnover period (a)							
	5	7	3	4	9	3	5

Previous study [11] showed that the metal concentrations in trunk of *Rhizophora apiculata* from Leizhou Peninsula, south China were 10.89, 0.51, 14.73, 0.15 and 26.64 μg g^{-1} for Cu, Pb, Zn, Cd and Cr, respectively, which were higher than those in the present study except for Pb. The concentrations of Cu, Pb, Zn, Cd and Cr in roots of three mangrove species (*Acanthus ilicifolius*, *A. corniculatum* and *K. candel*) in Mai Po, Hong Kong were 32.6, 34.4, 137.5, 0.4 and 3.5 μg g^{-1}, respectively [32], which were much higher than the present results. The concentrations of Cu, Pb, Zn, Cd and Cr in tissues (leaf, branch and root) of *Rhizophora mangle* in Natal, Brazil [33] were also higher than those in Hainan Island. Australian mangrove in Port Hacking, situated within a National Marine Park, was deemed a clean and unpolluted mangrove, and its Cu, Pb and Zn concentrations in mangrove (*A. marina*) leaves were 3.2, 1.7 and 14.3 μg g^{-1} [34], which were slightly higher than those in Hainan Island. All above results suggested that Hainan mangrove was in a relatively unpolluted status.

3.2.2. *Accumulation and cycle of trace metals*

Referring to the previous results on biomass, productivity and litter in the present mangrove wetlands [16–19], the average absorption, accumulation, distribution and cycle of trace metals in nine mangrove species at Dongzhai Harbor, Sanya Bay and Yalong Bay of Hainan Island were estimated (Table 3). The average standing stock of seven trace metals (Cu, Pb, Zn, Cd, Cr, Hg and As) in mangrove tissues was 77.33 mg m^{-2}. The annual absorption, annual net retention, annual return, and the turnover period in the community were 25.49 mg m^{-2} a^{-1}, 6.53 mg m^{-2} a^{-1}, 18.96 mg m^{-2} a^{-1} and 5 a, respectively. The biomass, productivity and litter of mangrove forests varied with the age of mangrove, dominant species, and locality.

3.3. *Factors influencing metal distribution*

3.3.1. *Correlations between metals*

Significant positive correlations between trace metals in sediments, except for between Cd–Cr and Cr–As, were observed (Table S3), suggesting the similar sources and deposition mechanism of these metals. Good correlations between trace metals and TOC in sediment were also found. As most mangrove leaf litter will be decomposed and buried in sediment, mangrove sediment is rich in organic materials and favors the retention of the water-borne metals. Mangrove forests are highly efficient carbon sinks in the tropics [35], potentially aiding in the retention of toxic metals and thereby reducing transport to adjacent estuarine and marine systems. Sediment granularity is another important factor regulating metals concentrations. Previous reports stated that metal concentrations in the silt and clay fraction were generally higher than those in the sand-sized fraction in mangrove sediment [3,36]. It was not observed for this pattern in the present study. This may be caused by different pollution sources in the sampling sites.

In mangrove tissues, correlations between trace metals were not good, except for those between Zn–Cu, Pb–Cd and Zn–Hg (Table S4), indicating the different bioaccumulation mechanisms of target metals. Some trace metals like Zn and Cu may share similar absorption mechanism. On the contrary, Pb and Cd may share similar resisting mechanism. Moreover, chemical compositions of mangrove tissues, including carbohydrates, amino acids, lignin-derived phenols, tannins, fatty acids, triterpenoids and n-alkanes [37], may also influence trace metal levels in mangrove tissues.

3.3.2. *BSAF of metals*

Aquatic organism can absorb contaminants from sediment, and its ability can be expressed by the biota-sediment accumulation factors (BSAF), defined as a ratio of the concentration of the chemical in tissue and the concentration of the chemical in sediment. In this study, the BSAFs based on all trace metals data both in sediment and mangroves were calculated and summarized in Table 3. Target metals with descending values of BSAFs (in parentheses) for all mangrove specimens in Hainan Island followed the sequence of Hg (0.43) > Cu (0.27) > Cd (0.22) > Zn (0.17) > Pb (0.07) > Cr (0.06) > As (0.02). Hg exhibited the highest BSAFs values because of its physical property, a semi-volatile metal. The essential metals such as Cu and Zn showed a greater mobility than the non-essential metals such as Pb, Cr and As, similar to the results derived from a synthesis of field-based studies [38]. Cd, a non-essential metal, also exhibited a high BSAF value. This may be explained by its similar chemical behavior as Cu and Zn [39], but the exact reasons still need further study.

4. Conclusions

Trace metals in nine species of mangrove tissues (leaf, branch, root and fruit) and ten sediment cores from Dongzhai Harbor, Sanya Bay and Yalong Bay, Hainan Island, were analyzed, and the results showed that the average concentrations of Cu, Pb, Zn, Cd, Cr, Hg and As in surface sediments were 14.8, 24.1, 57.9, 0.17, 29.6, 0.08 and 9.7 $\mu g\,g^{-1}$, and in mangrove tissues were 2.8, 1.4, 8.7, 0.03, 1.1, 0.03, and 0.2 $\mu g\,g^{-1}$, respectively. Based on the metal concentrations, this study indicated that the pollution status of all target trace metals except arsenic in the study sites were still at relatively low levels, and they have not brought direct stress to the mangroves in Hainan island, China.

Acknowledgments

This work was funded by the commonweal project from the State Oceanic Administration of China (no. 200705026) and National Natural Science Foundation of China (no. 40573061 and no. U0633005). We thank Dr. Xiang Liu with the Guangzhou Institute of Geochemistry for analyzing TOC content in sediment. We also thank the anonymous reviewers for their kind constructive suggestions on the manuscript.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.03.091.

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