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Speciation Changes of Cadmium in Mangrove (*Kandelia candel* (L.)) Rhizosphere Sediments

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Abstract The speciation distribution of cadmium (Cd) in mangrove (*Kandelia candel* (L.) *Druce*) rhizosphere sediment was investigated after different contents of Cd being loaded. The study results indicated that root induced changes of Cd bioavailability in the rhizosphere. Exchangeable and carbonate bound Cd in the rhizosphere sediments were lower than these in the bulk sediments, whilst an increase in Fe–Mn oxides bound and O.M/sulfide bound fractions occurred in the rhizosphere sediment. Increased levels of Cd in sediments resulted in higher Cd concentrations in mangrove plants, and the order of accumulation was: roots > hypocotyls > stems and leaves.

Keywords Cadmium · *Kandelia candel* (L.) · Rhizosphere · Speciation

Mangroves are one of the major types of habitats found in the inter-tidal zone of tropical and subtropical coasts, and are recognized as playing an important role in removing heavy metal pollutants from waste water. Heavy metal speciation difference between plant rhizosphere and bulk soil has been reported by Wang et al. (2002). For mangrove plants, this difference is expected to be more markedly due to the presence of aerenchyma and because waterlogged soils are mostly anaerobic, this may result in a great difference in redox potential (Eh), pH value and aerobic microbial activity between the rhizosphere and bulk sediment (Philippe et al. 2003). In this study, mangrove (*Kandelia candel* (L.)) seedlings were cultivated in the rhizobox under different cadmium (Cd) concentrations. The Cd speciation change between plant rhizosphere and bulk sediment was studied by using sequential extraction procedures (SEPs), in an attempt to understand its availability and accumulation by mangrove plants.

Materials and Methods

The sediment sample used in the study was collected from a mangrove forest of the Jiulong River estuary in Fujian Province, China. Surface sediment (5–20 cm) was collected, and thoroughly mixed. The general properties of the sediment were pH 6.52, CEC 16.23 me.100 g^{-1}, organic carbon 24.4 g kg^{-1}, total salt content 16.7‰, moisture content 43.68%, more than 90% of the sediment particles were silt particle. The metal concentrations were Cd 1.07 mg kg^{-1}, Pb 53.61 mg kg^{-1}, Cu 39.63 mg kg^{-1}, Zn 300.30 mg kg^{-1}, Fe 3.54%, Mn 764.69 mg kg^{-1}. Sediment samples were divided into seven parts, packed in plastic barrel separately, and different amounts of Cd^{2+} were added by using $CdCl_2$, separately as 0 (control), 5, 10, 20, 30, 40, 50 mg kg^{-1} fresh sediment. The treated sediments were kept fresh by adding distilled water and homogenized by mixing thoroughly each week for 56 days. Before use, the sediments were sampled and freeze-dried to measure the factual content and fraction distribution of Cd under the treatments.

A laboratory rhizobox (Fig. 1) used to plant the mangrove seedlings, was adopted from Wang et al. (2002) but with some adjustments to make it suitable for mangrove seedlings and cultivation over a long time. The rhizobox was divided into five sections by nylon cloth (500 meshes). A central zone (S1) (20 mm in width) was designed to

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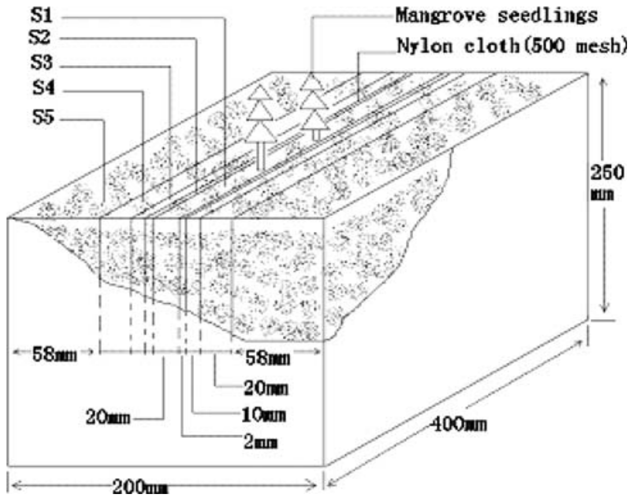

Fig. 1 Sketch diagram of rhizobox

plant mangrove seedlings, and next to this central zone, four sections were further separated within both left and right zones, referred to as S2 (2 mm), S3 (10 mm), S4 (20 mm) and S5 (58 mm) according to distance from the central zone to the boundary of the rhizobox. Considering that there will be many mangrove roots, a root network should be formed after a long cultivation period, and ultimately it will fill in the central zone, S2, which borders on the central zone and is designed as the rhizosphere zone. In turn, S3, S4, S5, were designed as near rhizosphere, near bulk sediment and bulk sediment zones. About 13 kg of the treated sediment was added to each rhizobox, each treatment had three replicates. Fifteen *K. candel* seedlings were planted in the central zone of the box and grown under greenhouse conditions.

After 8 months of cultivation, the rhizobox was dismantled. Sediments within different zones (except S1) were collected, freeze dried and then powdered in an agate mortar and sieved through a nylon sieve (250 μm) for analysis. Sediment within the central zone could not be collected without damaging the roots, as the root network formed and occupied nearly all the space of the central zone. The roots remained completely in the central zone, and were washed out with tap water to remove sediment. Roots, hypocotyls, leaves and stems were separated and then dried at 60°C in the oven until a constant weight was obtained. The dried samples were finely ground in an agate mortar for analysis.

The sequential extraction procedures proposed by Tessier et al. (1979) were adopted to reveal the Cd fraction distribution in these sediments. The details of the sequential extraction procedures have been described by Liu et al. (2006). The concentration of Cd in each fractionation solution was measured by atomic absorption spectrophotometer (AAS: Model AA-6800, Shimadzu, Kyoto). The concentration of Cd in leaves, stems, hypocotyls and roots were also determined by AAS after samples were microwave digested with HNO_3 and H_2O_2.

All results presented and discussed are based on mean values and standard deviation (SD) of three replications. All statistical analysis was carried out by using the SPSS statistical software, and statistically significant differences between groups were tested using the Ducan and LSD multiple comparison tests.

Results and Discussion

The results from speciation analysis of Cd in sediments, after different concentrations of added Cd^{2+} and incubation for 56-days, are shown in Table 1. In the controlled sediment (CK), a high concentration of Cd was found in different bond phases (except the residue fraction). This partly attributed to the intensity of natural chemical weathering of the primary minerals in southeast China (Chen et al. 2000). It also indicated that the sediment has been polluted anthropogenically by Cd. Except those bound to the residue fraction, the concentrations of Cd presented in each fraction, increased significantly with the total increase in concentration. This indicates that both the organic and inorganic fractions are responsible for Cd sorption, and under elevated metal concentrations, Cd is mainly associated with secondary mineral phases

Table 1 Speciation distribution of cadmium in mangrove sediment after different concentration of Cd^{2+} added for 56 days

Treat	Exchangeable	Bound to carbonate	Bound to Fe/Mn oxides	Bound to O.M/sulfide	Residue
CK	0.15 ± 0.01	0.34 ± 0.01	0.30 ± 0.02	0.24 ± 0.02	0.07 ± 0.02
5	2.81 ± 0.12	2.39 ± 0.26	3.41 ± 0.27	2.64 ± 0.31	0.15 ± 0.01
10	7.16 ± 0.20	4.81 ± 0.16	7.80 ± 0.13	4.45 ± 0.18	0.20 ± 0.02
20	14.49 ± 0.77	6.10 ± 0.31	16.01 ± 0.44	7.16 ± 0.35	0.29 ± 0.05
30	25.34 ± 1.42	7.11 ± 0.64	24.91 ± 1.10	11.07 ± 0.66	0.31 ± 0.04
40	35.30 ± 0.71	10.49 ± 0.72	30.20 ± 1.78	12.63 ± 0.64	0.50 ± 0.05
50	48.87 ± 0.62	13.48 ± 1.02	36.10 ± 1.34	16.28 ± 0.11	0.55 ± 0.01

Values expressed as mean ± SD (mg kg^{-1} dry weight, n = 3)

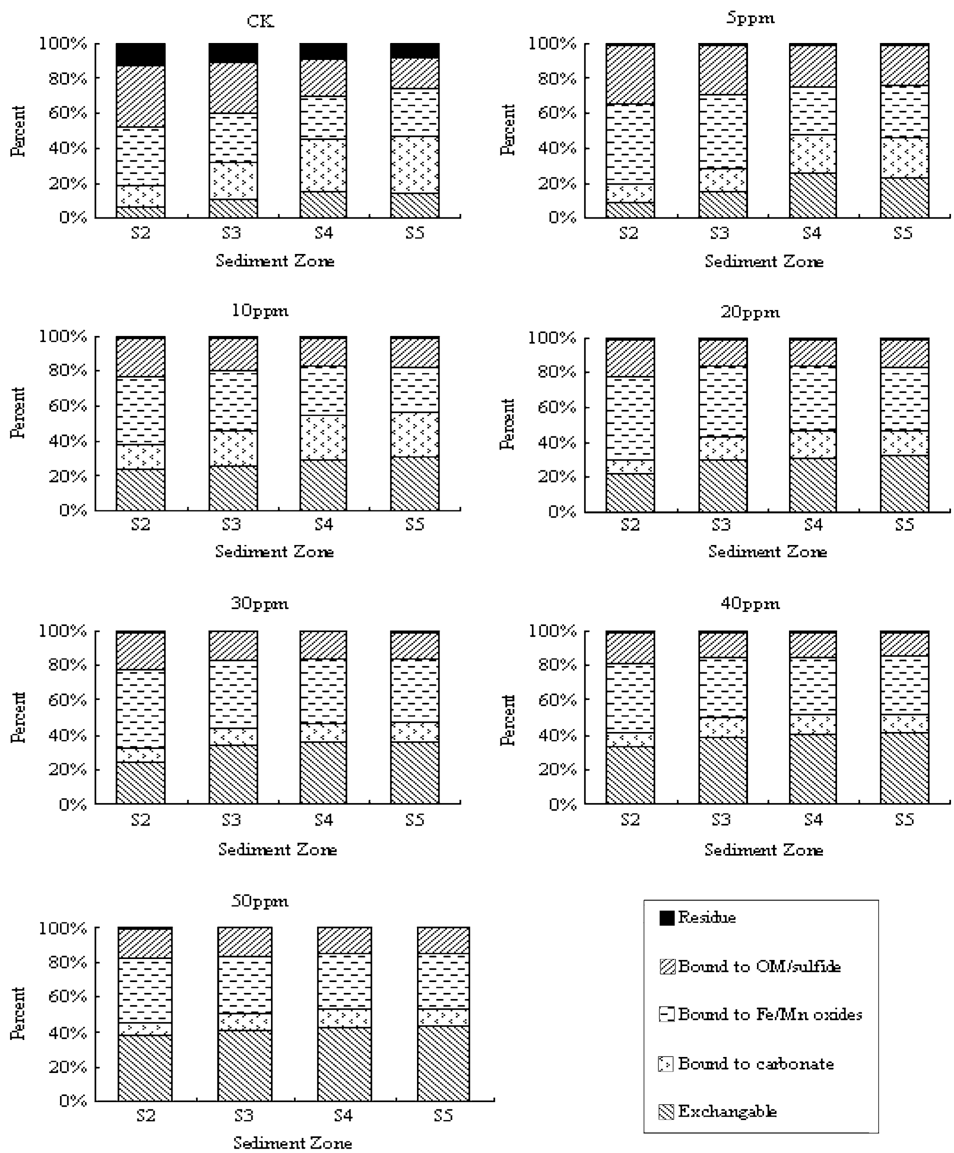

Fig. 2 Fractionation difference of cadmium in different sediment zones

(carbonate, iron and manganese oxides, organic matter) instead of the primary mineral phase (Wang et al. 1997).

However, there is a different change characteristic in the percentage of the bound fraction with increase of Cd in the total concentration. The percentage of Cd in exchangeable fraction increased with the increasing treatment concentration (from 14.02% to 42.39%), whilst carbonate and O.M/sulfide bound decreased from 30.39% to 11.70%, and 21.47% to 14.12% separately. The percentage of Cd bound to Fe–Mn oxides increased gradually when the treatment concentration was 0–20 ppm, and then decreased with continued concentration treatment. This decrease may due to the adsorptive capacity of secondary minerals being exceeded in environments containing elevated concentrations of Cd. This revealed that exchangeable and bound to Fe–Mn oxides were two dominant forms when elevated Cd was loaded in the mangrove sediment. Adsorption of heavy metals onto Fe–Mn oxides has been recognized as an important reaction for the immobilization of these compounds (Ainsworth et al. 1994). Fe–Mn oxides is one of the most important metal binding components in the mangrove sediment of China has also been reported by Liu et al. (2006). However, the significant amount of Cd present in the exchangeable fraction when high concentrations of Cd^{2+} were added, suggested that Cd may be easily taken up by organisms living in the mangrove forest.

Figure 2 shows the percentage ranges of Cd in different fractions to the total concentration in the different zones of mangrove sediment by use of the sequential extraction procedure. The difference comparisons among mean concentrations of the same solid binding fraction at same Cd stress conditions are given in Table 2. The results illustrate that the total concentration of Cd in different sediment zones showed some difference when the treatment

Table 2 Multiple comparison results of Cd concentration among different sediment zones by using Ducan and LSD

Treat	Zone	F1	F2	F3	F4	F5	Total
CK	S2	c	d	b	ab	a	c
	S3	b	c	b	a	a	b
	S4	a	b	ab	bc	a	a
	S5	a	a	a	c	a	a
5	S2	c	b	a	a	a	c
	S3	b	b	a	ab	a	bc
	S4	a	a	b	c	a	a
	S5	a	a	b	bc	a	ab
10	S2	c	c	a	a	a	b
	S3	b	b	a	b	a	a
	S4	a	a	ab	b	a	a
	S5	a	a	b	b	a	a
20	S2	b	b	a	a	a	b
	S3	a	a	ab	b	a	a
	S4	a	a	b	b	a	a
	S5	a	a	b	b	a	a
30	S2	b	b	a	a	a	b
	S3	a	a	b	b	a	ab
	S4	a	a	b	b	a	ab
	S5	a	a	b	b	a	a
40	S2	b	a	a	a	a	a
	S3	a	a	b	b	a	a
	S4	a	a	c	b	a	a
	S5	a	a	bc	b	a	a
50	S2	b	b	a	a	a	a
	S3	a	a	b	a	a	a
	S4	a	a	b	b	a	a
	S5	a	a	b	b	a	a

F1, F2, F3, F4, F5 separately denote the exchangeable, bound to carbonate, bound to Fe–Mn oxides, bound to O.M/sulfide, and residue fraction of Cd, lowercase expresses the difference at 0.05 probability level

concentration is from 0 to 20 mg kg^{-1} wet sediment. This change should be mainly attributed to the accumulation of the mangrove seedlings. Under more concentrated Cd treatment, no significant difference was found, although the mangrove seedlings accumulated much more Cd (Table 3). This may partly because the quantity of Cd accumulated by plants is too little compared to its total concentration in the sediment. It may also be partly ascribed to the possible transport of Cd by diffusion (Youssef and Chino 1989) from the adjacent zone to rhizosphere zone for a significant difference to be detected between the exchangeable concentration of rhizosphere and other zones. Significant differences also were found between near rhizosphere zone (S3) and bulk sediment (S5) or near bulk sediment (S4) zone in the controlled experiment. Although variation in analyses of mean concentration (Table 2) indicated that no significant difference existed for bound to Fe–Mn oxides or bound to O.M/sulfide between S2 and S4/S5 in the controlled and 10 ppm treatment, integrating the proportional distribution of Cd fraction with the total concentration difference among the different zones, one can draw a conclusion that the rhizosphere sediments (S2) had rather lower fractions of exchangeable and bound to carbonate, and higher Fe–Mn oxides and bound to O.M/sulfide fractions compared to the bulk (S5) or near bulk sediments (S4). Meanwhile, no difference existed for the residue fraction. No difference was found between S4 and S5 in both the mean concentration and metal speciation distribution for all treatments; however, some differences existed between S3 and S4/S5, especially in the low level stress treatments (0–10 ppm). In these treatments, lower exchangeable, bound to carbonate, and higher bound to Fe–Mn oxides, O.M/sulfide were found, as well as a decrease in total concentration at controlled and 5 ppm treatment of Cd compared to bulk sediments.

The speciation difference among the different zones is more complex and may attributed to many factors, such as pH, Eh, water-extractable organic, and some other factors. Many studies have been conducted on metal speciation transformation between rhizosphere and bulk soil, and unsurprisingly, different study results have been reported on metal speciation transformation, due to the difference of metal, plant and cultivation conditions (Lin et al. 2003; Véronique et al. 2004; Wang et al. 2002). The decrease in exchangeable and carbonate bound forms in the rhizosphere has been reported previously (Lin et al. 2003; Wang et al. 2002). They attributed this change to plant uptake, complexing and chelating by soluble exudates of roots. In the present study, pH decreasing in the rhizosphere sediments was found compared to the bulk sediment (Table 4). The Eh value was not measured for it is somewhat problematic to be determined outside the laboratory. But visible red iron plaque was seen in the roots of seedlings and indicated the oxidation of Fe^{2+} to Fe^{3+} in the rhizosphere. Results also indicated that a significant difference existed for both dissolved organic matter and low-molecular-weight organic matter between rhizosphere and non-rhizosphere sediments (Lu et al. 2007). Therefore, the transfer of Cd from bound to carbonate and exchangeable into the Fe–Mn oxides should be one of the important reasons for the difference between rhizosphere and non-rhizosphere sediments. The difference of bound to O.M/sulfide, however, is mainly attributed to the change of organic matter content.

To reveal the accumulation rate of Cd by *K. candel* seedlings with different levels of Cd loaded, the ratios of concentration of plant tissue to total concentration in the rhizosphere zone were analyzed as the concentration factor 1 (CF1). These results are shown in Table 3, as well as the ratios of concentration of plant tissue to extractable Cd in

Table 3 Concentration of Cd in different components of *K. candel* seedlings and concentration factors by plants

Treat	Leaf			Stem			Root			Hypocotyl		
	Concentration	CF1	CF2	Concentration	CF1	CF2	Concentration	CF1	CF2	Concentration	CF1	CF2
CK	0.03 ± 0.01	0.02	0.58	0.04 ± 0.00	0.03	0.88	3.06 ± 0.29	2.48	65.2	0.23 ± 0.02	0.19	4.89
5	0.27 ± 0.04	0.02	0.32	0.39 ± 0.05	0.03	0.45	35.61 ± 2.75	3.17	41.6	1.22 ± 0.05	0.11	1.42
10	0.86 ± 0.11	0.04	0.17	0.99 ± 0.14	0.04	0.2	86.85 ± 2.46	3.55	17.5	2.41 ± 0.08	0.10	0.48
20	1.58 ± 0.08	0.04	0.17	2.05 ± 0.12	0.05	0.22	142.20 ± 10.20	3.21	15.3	4.18 ± 0.06	0.09	0.45
30	2.91 ± 0.33	0.04	0.16	3.16 ± 0.16	0.04	0.18	222.08 ± 8.54	3.16	12.5	6.95 ± 0.47	0.10	0.39
40	4.27 ± 0.23	0.05	0.15	4.69 ± 0.43	0.05	0.16	273.89 ± 12.64	3.05	9.51	10.31 ± 0.85	0.11	0.36
50	5.32 ± 0.13	0.05	0.13	5.59 ± 0.28	0.05	0.13	356.97 ± 35.87	3.17	8.55	13.95 ± 0.63	0.12	0.33

Concentrations expressed as mean ± SD (mg kg^{-1} dry weight, n = 3), CF1 = concentration of plant component/total concentration in rhizosphere, CF2 = concentration of plant component/exchangeable concentration in rhizosphere

Table 4 pH values of sediment in different rhizosphere zones of *K. candel* seedlings (values expressed as mean ± SD, n = 3)

Zone	Treat						
	CK	5	10	20	30	40	50
S2	6.43 ± 0.05	6.39 ± 0.04	5.94 ± 0.08	6.08 ± 0.02	6.16 ± 0.06	6.27 ± 0.03	6.24 ± 0.08
S3	6.45 ± 0.04	6.47 ± 0.06	6.23 ± 0.06	6.42 ± 0.05	6.33 ± 0.04	6.31 ± 0.07	6.03 ± 0.04
S4	6.54 ± 0.07	6.19 ± 0.05	6.35 ± 0.07	6.37 ± 0.06	6.28 ± 0.05	6.34 ± 0.04	6.47 ± 0.06
S5	6.47 ± 0.05	6.49 ± 0.07	6.40 ± 0.06	6.33 ± 0.03	6.32 ± 0.09	6.37 ± 0.05	6.33 ± 0.03

the rhizosphere zone as the concentration factor 2 (CF2). Table 3 also shows the Cd accumulation and distribution within different components of *K. candel* seedlings under different concentrations of Cd stress. The results indicate that increased levels of Cd in sediments resulted in higher Cd concentrations in mangrove plants. Most of this Cd was accumulated in the roots, with little transportation to the aboveground portions. The order of accumulation was: root > hypocotyls > stem and leaf. For CF1, a gradually increasing trend in leaves and stems was found, and no relationship was observed in roots and hypocotyls, but for CF2, it decreased with the increase of exchangeable Cd concentration. Significant positive relationships were found between Cd concentration in different plant components and total concentration or exchangeable Cd in rhizosphere sediment (S2) ($r = 0.963$–0.995, n = 21).

The majority of studies show few significant correlations between metal levels in sediment and metals in tissues, which suggests that mangroves actively avoid metal uptake and/or most metals are present below the sediment bioavailability threshold (MacFarlane et al. 2003). The significant positive correlations between Cd accumulation by different plant components and total concentration or exchangeable concentration in the present study, may due to a higher concentration, and that most of the Cd is bioavailable. The concentration factor in the present study (CF1) was higher than that reported by Che (1999), but lower compared to the results of Tam and Wong (1997) by treating with waste water on the same mangrove species. This difference may be partly attributed to the different metal concentrations. Naturally, most metal is unavailable for uptake by plants, and present below the sediment bioavailability threshold (MacFarlane et al. 2003). The reported higher concentration factor by Tam and Wong (1997) may be related to the nutrient difference for mangrove treated with waste water. The different change trends between CF1 and CF2 with the increasing of loaded Cd, may be due to a more rapid increase of exchangeable speciation compared to the total Cd concentration increase, as well as the uptake by plants decreasing with increasing input concentrations.

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