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ORIGINAL ARTICLE

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Five heavy metals in propagules of ten mangrove species of China

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Abstract Five heavy metals in the propagules of 10 mangrove species in China have been investigated. The results revealed that the levels of five heavy metals in most of the propagules were lower than the background levels of the soil. The levels of copper, manganese, zinc, cadmium, and lead in the propagules varied at about 2.1–7.8 μg/g, 3.9–28.0 μg/g, 5.7–60.0 μg/g, 0.014–0.057 μg/g, and 0.018–0.038 μg/g, respectively. On average, the levels of five heavy metals were in the order Zn > Mn > Cu > Cd > Pb. The biological absorption coefficients were 0.02–1.30 for copper, manganese, zinc, and cadmium and about 0.0007–0.0020 for lead in propagules, showing the following order: Zn > Cd > Cu > Mn > Pb. The above results indicate that the five heavy metals have low accumulation in most of the propagules of 10 mangrove species and are at safe levels for the effective utilization of mangrove resources.

Key words Heavy metals · Accumulation · Biological absorption coefficient · Mangrove plants

Introduction

The residue and accumulation of heavy metals in the environment often cause problems.[1–4] In a plant–soil system, strong absorption and fixation of heavy metals by soil can easily cause residual accumulation in the soil, resulting in overabsorbtion of heavy metals by growing plants. These plant products are then harmful to the health of humans. For this reason, it is important and necessary to study the relation between the content of heavy metals in soil and the absorption and accumulation by plants. This is not only a problem of geochemistry circulation but also an approach for preventing heavy metal pollution of plant products.

Mangrove is a woody community that plays an important role in the ecological balance of estuaries and seashores in tropical and subtropical zones. It is also an important natural resource awaiting effective utilization because of its vast amount of biomass materials. For example, mangrove plants provide timber for furniture, pulp for paper, firewood, edible fruits, feed for livestock, and so on. They are also a source of traditional Chinese medicines, tannin for dyestuff, fishnets, and materials for the leather-making industry. Therefore, preliminary phytochemical investigations are needed to provide basic information on their effective utilization. Unfortunately, there is not much information available on mangrove pollution ecology, especially from the viewpoint of resource exploitation of mangrove propagules. In a previous paper[5] we reported lipids and carbohydrates in propagules of 10 mangrove species of China. In this paper we started an investigation of five heavy metals in propagules of mangrove plants, with a view to providing new evidence on the effective utilization of the mangrove resources.

Materials and methods

Propagules from 10 mangrove species were used in this investigation, (Table 1) as in our previous study.[1] The propagule samples of mangrove plants (nos. 1–9) were collected from the Dongzhai Harbor National Nature Reserve of Hainan Island of China. A site about 150 m long and 30 m wide (site A) within the mangrove swamp was chosen for the experimental work. About 500 g of propagules was collected at random from each of five trees of every species of mangrove plant. Meanwhile, about 500 g of triplicate surface soil samples (sampling depth 0–20 cm) from five plots at regular intervals were collected from the same experimental site. The propagules of *Acanthus ilicifolius* (no. 10) were collected from a mangrove community loc-

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Table 1. Contents of heavy metals in the propagules of 10 mangrove species

No.	Sample	Cu	Mn	Zn	Cd	Pb
1	*Ceriops tagal* (Perr.) C.B.Rob.	5.4 (0.16)	14 (1.8)	6.8 (1.0)	0.033 (0.0022)	0.029 (0.0027)
2	*Aegiceras corniculatum* (L.) Blanco	7.7 (0.14)	5.1 (0.61)	27 (1.4)	0.024 (0.0016)	0.018 (0.00096)
3	*Bruguiera sexangula* (Lour.) Poir	7.8 (0.53)	20 (0.99)	30 (1.6)	0.031 (0.0018)	0.026 (0.0011)
4	*Sonneratia caseolaris* Engl.	6.8 (0.53)	18 (0.70)	36 (2.5)	0.031 (0.0020)	0.027 (0.0012)
5	*Rhizophora stylosa* (L.) Griff.	2.4 (0.38)	22 (0.96)	5.7 (0.85)	0.047 (0.0013)	0.036 (0.0015)
6	*Bruguiera gymnorrhiza* (L.) Lamk.	7.8 (0.68)	3.9 (0.75)	5.7 (0.98)	0.014 (0.0017)	0.021 (0.0015)
7	*Kandelia candel* (L.) Druce	3.1 (0.58)	27 (2.2)	9.8 (1.4)	0.057 (0.0017)	0.038 (0.0019)
8	*Avicennia marina* (Forsk.) Vierh.	6.3 (0.60)	5.1 (0.36)	20 (1.6)	0.019 (0.0011)	0.023 (0.0017)
9	*Sonneratia ovata* Backer	7.4 (0.40)	28 (1.6)	19 (1.1)	0.041 (0.0016)	0.021 (0.0013)
10	*Acanthus ilicifolius* L.	2.1 (0.35)	11 (1.3)	60 (2.7)	0.041 (0.0014)	0.028 (0.0014)

Results are based on oven-dried samples and are means with standard deviations in parentheses. The units are micrograms per gram

ated in Longhai County of Fujian Province, where a sample area about 3000 m^2 (100 × 30 m, site B) was chosen for collection of propagules and soil samples. The sampling method was the same as that used in the Dongzhai Harbor National Nature Reserve. All samples of propagules and soil were air-dried for 10 days, heated in an electrical oven at 105°C for 3 h, and then ground by a mortar carefully to pass through a 100-mesh (ϕ 0.149 cm) sieve. The final material was used in the preparation for atomic absorption spectrophotometry.

Preparation of samples

Dry digestion was performed for cadmium and lead. Each ground sample was carbonized at 200°C for 1 h and then linearly programmed at 1°C/min to 560°C for 12 h. The ash was digested first with nitric acid/perchloric acid (1:1, v/v) to dissolve it in chloric acid; it was then diluted to a certain volume and extracted with 4-methyl-2-pentanone in the presence of chloric acid, potassium iodide, and ascorbic acid. The residual organic layer in a funnel was separated for the following determination. At the same time, the standard solutions for each element were carefully prepared under the same conditions.

Wet digestion was used to determine the contents of copper, manganese, and zinc in the samples. Each sample powder was immerged overnight with concentrated nitric acid and then heated carefully with concentrated nitric acid and perchloric acid until the solution became pink. After cooling down, the solution was diluted to a certain volume for the following determination. To avoid the possible interference of silicon in the sample, 1% lanthanum solution was added to both the standard and sample solutions.[6]

Determination of heavy metals

The contents of these heavy metals of the samples were determined by an atomic absorption spectrophotometer (Perkin-Elmer 3030B, USA). The wavelengths used to determine the presence of copper, manganese, zinc, cadmium, and lead were 324.8, 279.5, 213.9, 228.8, and 217.0 nm, respectively. All determinations were conducted on duplicate samples. Using the present extraction conditions, the values of heavy metals of the soils were acid-soluble contents. The results were calculated from calibration curves of each standard element and expressed as the mean and standard deviation (SD) of the samples based on 105°C oven-dried weight.

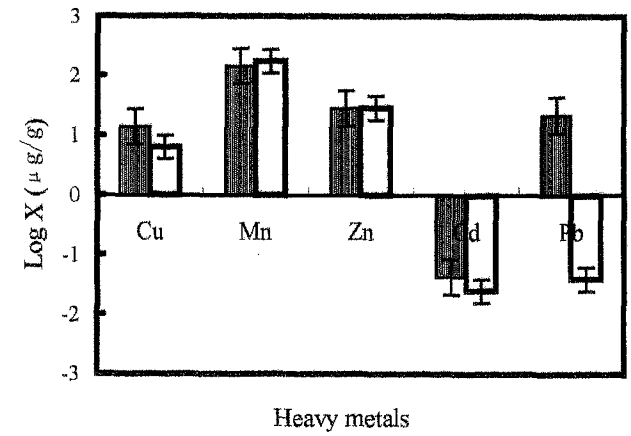

Fig. 1. Background contents of five heavy metals in the soil and plants of Hainan Island. *Filled bars* represent the contents of soil; *open bars* represent the contents of plants

Results and discussion

Background levels of five heavy metals in the soil and plants of Hainan Island

Plants absorb chemical elements from soil to meet their physiological needs. Consequently, all plants are dependent on and adaptable to the level of chemical elements in their inhabited surroundings.

The background levels of these five heavy metals in the soil of Hainan Island[7] are shown in Fig. 1. As can be seen, their concentrations differ greatly. On average, the level of these elements were, in the following order: Mn (150 μg/g) > Zn (29 μg/g) > Pb (22 μg/g) > Cu (14 μg/g) > Cd (0.043 μg/g).

Table 2. Acid-soluble contents of five heavy metals at sampling sites A and B

Site	Cu	Mn	Zn	Cd	Pb
A	14.00 ± 0.48	130.0 ± 1.9	28.00 ± 0.48	0.0480 ± 0.0051	25.00 ± 0.44
B	29.00 ± 0.33	570.0 ± 5.6	110.00 ± 3.30	0.0900 ± 0.0080	18.00 ± 0.70

Results are means ± SD (micrograms per gram)

The levels of copper, zinc, and manganese in general were lower in the soil of Hainan Island than those in mainland China soil. For example, the background level of copper was about 14 µg/g and zinc about 29 µg/g in Hainan Island, whereas their corresponding values in the eastern suburb of Beijing were about 40 µg/g and 120 µg/g, respectively.[8]

The background levels (averaged from 77 species of plants) of the five heavy metals in the plants of Hainan Island [7] could be arranged in the order of Mn (170 µg/g) > Zn (29 µg/g) > Cu (6.3 µg/g) > Pb (0.040 µg/g) > Cd (0.025 µg/g). These data showed that the level of zinc was the same for soil and plants of Hainan Island, whereas the level of manganese in soil was less than that in plants. However, the copper, cadmium, and lead levels in soil were much higher than those in plants, especially that of lead, which was 550 times that in plants.

The above results are different from those of subtropical plants in China. Generally speaking, the contents of chemical elements in tropical plants of Hainan Island are rather lower than those in either the temperate zone or the warm temperate zone. For example, the content of copper in Hainan Island averaged 6.3 µg/g (mostly in 5–10 µg/g) and zinc 29 µg/g, whereas the contents of copper and zinc were 12 µg/g and 45 µg/g in the warm temperate zone and 14 µg/g and 120 µg/g in the temperate zone. The manganese content was 170 µg/g in Hainan Island but 92 µg/g in the warm temperate zone and 16 µg/g in the temperate zone.[7]

The acid-soluble contents of copper, manganese, zinc, cadmium, and lead in the soil of site A are shown in Table 2. Apparently, the contents of copper, zinc, cadmium, and lead in the soil of site A were almost identical to the background values for Hainan Island soil. As for the two sample plots, the contents of copper, manganese, zinc, and cadmium of site B were much greater than those at site A, and there was less lead at site B than at site A.

These results imply that these heavy metals had not accumulated in high concentrations in the soil of the sample plot or the plants of Hainan Island compared to that in mainland China.

Contents of five heavy metals in propagules of 10 mangrove species

The contents of five heavy metals in the propagules of 10 mangrove species are listed in Table 1. With two or three exceptions, most were present at lower level in the plants than in the soil of the sample plot. On average, the contents of five heavy metals in the propagules showed the order Zn > Mn > Cu > Cd > Pb.

Copper. The content of copper in most propagules of the mangrove species fluctuated between 2 and 8 µg/g, and five of nine propagules had values about half of the background values of the soil from site A. The propagules of *Rhizophora stylosa* (no. 5), *Kandelia candel* (no. 7), and *A. ilicifolius* (no. 10) showed lower amounts of copper (ca. 2–3 µg/g) than the others.

Manganese. A comparison of the contents of manganese between the soil of the sample plots and the propagules demonstrated that the soil content was much greater than the propagule content. As a whole, the levels ranged from about 4 to 28 µg/g. *Sonneratia ovata* (no. 9) showed the largest amount (28 µg/g) followed by *K. candel* (no. 7; 27 µg/g), and *Bruguiera gymnorrhiza* (no. 6) had the least amount (4 µg/g.)

Zinc. On the whole, zinc had the highest concentration among the five heavy metals in these propagules. *A. ilicifolius* (no. 10) contained the largest amount (60 µg/g), about half the background concentration in the soil of site B. In *Aegiceras corniculatum* (no. 2), *Bruguiera sexangula* (no. 3), and *Sonneratia caseolaris* (no. 4), the zinc content of the propagules was approximately similar to that of the soil of the sample plots, whereas those of *Ceriops tagal* (no. 1), *R. stylosa* (no. 5), *B. gymnorrhiza* (no. 6), and *K. candel* (no. 7) were less than or equal to 10 µg/g.

Cadmium. The cadmium content in the propagules varied from 0.014 to 0.057 µg/g. *B. gymnorrhiza* (no. 6) had the least and *K. candel* (no. 7) the most cadmium. All except *K. candel* (no. 7) had less than that in the soil of the sample plots. The propagules of *R. stylosa* (no. 5), *S. ovata* (no. 9), and *A. ilicifolius* (no. 10) had contents of about 0.041–0.047 µg/g.

Lead. The contents of lead in these propagules were lower than that of the background content of the soil. They ranged from about 0.018 to 0.038 µg/g.

Propagules from some mangrove plants traditionally have been utilized in China as edible fruits (from *R. stylosa* and *A. marina*) or for traditional Chinese medicine (*A. ilicifolius* and *B. gymnorrhiza*). There have also been reports that although most mangrove plants are resistant to pollution to some degree a number of heavy metals have accumulated in the soil or sediment of mangrove plants.[9,10] Therefore, the content of heavy metals in the propagules of mangrove plants is a noteworthy problem in regard to their utilization. Fortunately, the above results demonstrated that the five heavy metals investigated had not accumulated in most propagules of 10 mangrove species in large amounts, with higher background values found in some of the soil from the sample plots. The reason for this is discussed further in the following sections.

Relation of heavy metal content in the soil with that in mangrove propagules

Plants show different absorption and accumulation of various chemical elements. They selectively accumulate some elements in certain tissues or organs.[11–13] Therefore, the absorption and accumulation of a chemical element by a plant is related not only to the physiologically necessary amount in the plant itself but also to the element's content and its existing state in the soil. To compare the differences in accumulation in plants, we introduced a parameter called biological absorption coefficient (BAC) to express this geochemical effect of plants. The BAC indicates the ratio of an element's content in a plant to that in the soil in which the plant grows.[7] In this paper, we discuss only the absorption and accumulation trend of chemical elements in plants under the present comprehensive conditions. The BACs of five heavy metals for the mangrove propagules are shown in Table 3, which shows a relatively low level for these mangrove propagules. For example, the BAC of copper was generally less than 0.6 and manganese mostly less than 0.2 in these propagules. Furthermore, the BAC of zinc for most propagules was less than 1.0, except in *A. corniculatum* (no. 2), *B. sexangula* (no. 3), and *S. caseolaris* (no. 4). On average, the BACs for mangrove propagules can be arranged in the following order: Zn > Cd > Cu > Mn > Pb.

Lead is known to be an inactive element. Usually it accumulates in roots and does not easily translocate to the reproductive organs of plants.[14,15] In contrast, cadmium is thought to enter the roots easily, and to move slowly to the stem, leaves, and reproductive organs of plants.[16–18] Because of marked toxicity, the higher BAC of cadmium implies much more possibility of causing an environmental problem. The BAC of cadmium, especially lead, in this investigation showed less accumulation in the propagules of the 10 mangrove species.

Table 3. Biological absorption coefficients of five heavy metals for mangrove propagules

No.	Cu	Mn	Zn	Cd	Pb
1	0.39	0.110	0.24	0.69	0.00120
2	0.56	0.040	0.95	0.50	0.00072
3	0.56	0.160	1.10	0.65	0.00100
4	0.49	0.140	1.30	0.65	0.00110
5	0.18	0.170	0.20	0.98	0.00140
6	0.57	0.031	0.20	0.29	0.00085
7	0.23	0.210	0.34	1.20	0.00150
8	0.46	0.040	0.70	0.40	0.00092
9	0.54	0.220	0.68	0.85	0.00084
10	0.07	0.020	0.57	0.46	0.00160

The biological absorption coefficient is the ratio of the content of an element in the ash of mangrove propagules to that of the element in soil of the sample plot

Heavy metals and hydrogen sulfide in acid sulfate soils from the mangrove swamp[19] combine to form sulfides in the strongly reductive soil environment; thus, rather large amounts of sulfides are insoluble in the soil, resulting in inhibition of the absorption of heavy metals by plants. On the other hand, the sulfides are acid-soluble under the present extraction conditions, so it is presumed that the BACs of these heavy metals are smaller for the propagules of mangrove plants than for land plants. For example, the BACs of copper, manganese, and zinc were 6.7, 5.8, and 4.4, respectively, for *Casuarina equisetifolia* and 5.2, 11.0, and 7.7, respectively, for *Hevea brasiliensis* in Hainan Island.[7] They were larger than those of the mangrove plants.

The BAC of manganese in plants usually ranges between 1 and 10. Commonly the BAC of manganese for swamp plants such as rice (*Oryza sativa*) or reed (*Phragmites communis*) is higher than 10. The content and BAC of manganese in the mangrove plants in this investigation were lower, however, which plainly implies less accumulation in their propagules. The results here may be explained by the role of the absciss layer between the mother tree and the propagules, which would regulate the redistribution of heavy metals before the propagules are dropped from the mother tree.

Conclusions

The results showed that the contents of heavy metals in the propagules, in most cases, were lower than those of the background contents of site A and site B soils. It is assumed that the absciss layer between the mother tree and the propagules protected the propagules from large accumulation of heavy metals. From the viewpoint of mangrove pollution ecology, the contents of five heavy metals in propagules accounts for only a small proportion of the accumulation of total heavy metals in a mangrove community. This investigation provided evidence that the propagules of mangrove plants can be safely utilized. Combining these results with the data on lipids and carbohydrates in propagules of the same 10 mangrove species leads to the conclusion that mangrove plants, especially the propagules, are not only worthy but also safe for utilization as natural resources.

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