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Metal phytoremediation potential of *Rhizophora mucronata* (Lam.)

V Pahalawattaarachchi, C S Purushothaman & A Vennila

Division of Aquatic Environmental Management, Central Institute of Fisheries Education, Versova, Mumbai, 400 061, India
[E-mail: vasa_lanka@yahoo.com]

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The present study consist the absorption, accumulation and partitioning of eight metals in order to find out the phytoremediation potential of the mangrove species *Rhizophora mucronata* (Lam.) in Alibag, Maharashtra, India. The concentrations of Cu, Cd, Ni, Mn, Cr, Zn, Fe and Pb in the sediments of the mangrove area were determined to be 92.59, 5.31, 63.29, 1020.00, 545.00, 78.18,68164.26 and 19.51 ppm, respectively on dry weight basis. Metal concentrations were different in specific parts of the plant, and the highest concentration (in ppm on dry weight basis) of each metal was found in the following pattern: leaves for Ni (1.74 ± 0.58) and Cr (16.78 ± 7.06; senescent leaves for Zn (6.29 ± 0.80); bark for Cd (1.34 ± 0.04) and Pb (7.35 ± 0.45), and roots for Fe (1236.69 ± 754.69) and Mn (618.31 ± 186.08). There were different translocation rates for each metal from root to shoots. The translocation ratios of Cd, Cr and Pb (1.53, 1.66 and 1.08, respectively) exceeded one in the case of senescent leaves, as these metals were being accumulated in leaves before falling off and thus eliminated. The trend of the phytostabilization capacity of *R. mucronata* in the Alibag mangrove ecosystem is confined to only the highly abundant metals in nature and the phytoremediation capacity of *R. mucronata* varies from metal to metal.

[**Key words**: mangrove, translocation, bioaccumulation, absorption, sediment, bivariate]

Introduction

Mangrove ecosystems are considered as highly productive ecosystems and functioning remarkably in various ecological processes. *Rhizophora mucronata* (Lam.) is one of the widely distributed mangrove species that has been identified as a desirable species for silvicultural practices and in planting programmes because of its noteworthy qualities such as fast growing rate and viviparous seeds, which are easy to plant.

Metal contaminants are common pollutants in urban ecosystems, arising from industrial effluents, industrial wastes and urban runoff[1]. They are harmful to humans and animals, and tend to bioaccumulate in the food chain. Mangrove systems have the capacity to act as a sink or buffer and remove/immobilize metals before reaching the nearby aquatic ecosystems. Due to a large proportion of fine clays, organic matter and low pH, mangrove mud effectively sequester metals, often immobilized as sulfides in anaerobic sediments[2]. Bioaccumulation of chromium has been addressed in limited studies[3]. Little adverse effect was observed on the growth of treated and established *R. mucronata* seedlings in sediment, with lead (50-250 mg/ml) and zinc (l0-50 mg/ml) additions twice over a 10-week period[4]. The accumulation of both the metals was much higher in *Avicennia alba* than in *R. mucronata*[4]. There was no effect of Pb on the final weight and size of hypocotyls, stems, roots or leaves of *R. mucronata*[5]. Many studies have been carried out to evaluate the potential of terrestrial plants in the phytoremediation of metals. However the studies on the metal extraction potential of mangroves *in situ* are rare. Therefore, an attempt was made to understand the metal phytoremediation capability of *R. mucronata* in a mangrove ecosystem at Alibag, Maharashtra, India, in view of generating baseline data that would benefit in the wise-management and utilization of this ecosystem. The present study presents data on the concentrations of eight metals (Cu, Cd, Ni, Mn, Fe, Cr, Zn and Pb) in leaves, senescent leaves, bark and roots of *R. mucronata.*

Material and Methods

The study was carried out in a mangrove ecosystem at Alibag (Raigad district of Maharashtra) India. Alibag is situated on the West coast of India. The area extends between latitudes 18° 56' N and 18° 29' N and longitudes 72° 50' E and 73° 04' E. The highest maximum temperature of the study area is 38°C and the lowest minimum is 8.4°C. Relative humidity is on an average over 80% during the southwest monsoon season. In the rest of the year, the relative humidity is between 65 and 75%. The average annual rainfall is

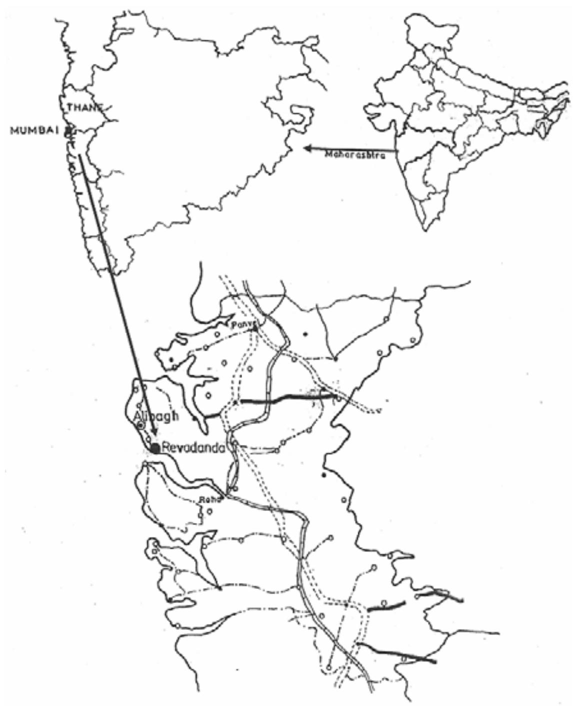

Fig. 1—Map showing the study area

between 2000 and 2200 mm[6]. The mangrove species found in the area comprised of *Avicennia marina* and *Acanthus illicifolius, Aegiceras cornicu!atum, Excoecaria agga!acha, Ceriops tagal, Brugeira cylindrical. R. mucronata. R. mucronata* was found around the waterfronts of the small streams. The trees were less than 2.5 m in stature and comparatively stunted in nature.

Sampling and analysis

Live plant parts (young leaves, leaves at senescent stage, bark and roots) were collected from three randomly selected *R. mucronata* trees in January 2007. Root tissue was sampled from what was considered to be nutritive roots for absorptionother than anchoring roots. Root samples were washed thoroughly in tap water followed by distilled water in order to get rid of attached soil and debris. All the samples were air-dried for three days. The samples were oven-dried at 60°C temperature to a constant weight and ground to powder. Three replicates of dried samples were digested with a mixture (3:1) of conc. nitric acid and hydrofluoric in microwave assisted Kjeldhal digestion (Anton Parr, USA). Each microwave extraction vessel was added with 6 ml of nitric acid and 2 ml of hydrofluoric acid together with 0.8 g of plant sample. The vessels were capped and heated in a microwave unit at 800 W to a temperature of 190°C for 20 min with a pressure of 25 bar. The digested samples were diluted to 50 ml and subjected to analysis of the eight metals (Cu, Cd, Ni, Mn, Fe, Cr, Zn and Pb) by atomic absorption spectrophotometer (A Analyst 800, Perkin Elmer, USA) using flame atomization. Results are expressed on dry weight basis of each component. Metal translocation ratios were calculated to illustrate the metal mobility from roots to the aerial parts of the plant using the following formula[7].

Translocation Ratio $= (HM_{1eaf} \text{ or } HM_{s.leaf} \text{ or } HM_{bark}) / HM_{root}$

Where; HM = Metal concentration (mg/kg plant dry weight), s. leaf- senescent leaf

Sediment analysis

Sediment samples were collected in triplicate and were dried at 105°C to constant weight. Three replicates of 0.25 g sediments were acid-digested in microwave assisted Kjeldhal digester. Each microwave extraction vessel was added with 5 ml of conc. nitric acid, 2 ml hydrochloride acid and 1 ml of hydrofluoric acid. The vessels were capped and heated in a microwave unit at 800 W to a temperature of 210°C for 20 min with pressure of 40 bar. The digested samples were analysed for the eight metals by atomic absorption spectrophotometer using flame atomization. Results are expressed on dry weight basis. In order to compare the degree of storage of the metals, concentration factors (CF) were calculated as concentrations of metals per tissue (g) over the concentration of metal per (g^-) in sediment[8].

The efficiency of the analytical method and instrumentation was verified by the analysis of the reference materials obtained from National Research Council of Canada for Marine sediments (MESS -3) and Estuarine water (SLEW-3) using five replicates. The obtained percentage recovery for the metal in sediment reference ranged from 91.00-112.00.

Statistical analysis

The mean, standard deviation and the range of the metal concentrations were calculated using SPSS 15.0 statistical package. The differences among metal concentrations in plant parts were tested by analysis of variance and post-hoc Duncan multiple range test. Person's bivariate correlation analysis was carried out to determine the extent of the relationship between the elements investigated.

Results

Concentrations of metals accumulated by leaves, senescence leaves, bark and roots of *R. mucronata* are shown in Table 1, while Fig. 2 presents the percentage accumulation of each metal in each plant part. Correlation coefficients obtained among the eight total metals in the whole plant is presented in Table 2. All the eight metals were accumulated in the tissues of *R. mucronata*. The weighted means of whole plant increased in order of Cd (0.93 ppm) < Ni (1.36 ppm) < Zn (4.99 ppm) < Cu (5.39 ppm) < Pb (6.02 ppm) < Cr (I 1.69 ppm) < Mn (329.63 ppm) < Fe (839.92 ppm).

Of the metals measured in the study, Fe showed the highest concentration many times than those of other metals. Accumulation of Cu was the highest in roots although it does not show any significant difference from the level observed in senescent leaves or in bark (Table 1, Fig. 2). Non-senescent leaves exhibited the lowest copper level (Table 1, Fig. 2). Accumulation of Cu in senescent leaves is 3.4 times greater than in non-senescence leaves. Accumulation of Mn in different plant parts showed a similar pattern to Cu accumulation showing the significant highest level in roots when compared to leaves, senescent leaves or bark (Table 1, Fig. 2). Significant positive relationship (Table 2) was observed between the levels of Cu and Mn (r^2 = 0.76; $P<0.05$) and highly

Table 1—Partitioning of average metal concentrations (ppm) in *R. mucronata*

	Leaves		Senescent leaves		Bark		Roots		Weighted
	Mean ± S.D.	Range	Mean ± S.D.	Range	Mean ± S.D.	Range	Mean ± S.D.	Range	Mean Total
Cu	$2.78^{a} \pm 1.63$	1.48-4.60	$4.04^{ab} \pm 1.15$	3.23-4.85	$5.32^{ab} \pm 1.23$	5.45-7.19	$9.43^{b} \pm 3.43$	6.29-13.05	5.39
Cd	$1.00^{b} \pm 0.16$	0.88-1.18	$1.00^{b} \pm 0.20$	0.79-1.18	$1.34^{b} \pm 0.04$	1.31-1.37	$0.63^{a} \pm 0.15$	0.52-0.74	0.93
Ni	$1.74^{b} \pm 0.58$	1.25-2.39	$1.53^{ab} \pm 0.34$	1.13-1.80	$0.67^{a} \pm 0.06$	0.62-0.71	$1.50^{ab} \pm 0.46$	1.00-1.90	1.36
Mn	$114.19^{a} \pm 18.08$	98.64-134.03	$291.96^{a} \pm 143.75$	123.70-410.64	$294.05^{a} \pm 67.15$	246.56-341.53	$618.31^{b} \pm 186.08$	468.53-826.62	329.63
Cr	$16.78^{a} \pm 7.06$	8.62-21.04	$10.40^{a} \pm 2.30$	8.36-12.89	$9.91^{a} \pm 0.57$	9.50-10.31	$9.33^{a} \pm 1.47$	8.41-11.02	11.61
Zn	$4.67^{a} \pm 0.48$	4.12-5.02	$6.29^{a} \pm 0.80$	5.82-7.21	$4.89^{a} \pm 1.48$	3.84-5.93	$4.09^{a} \pm 1.82$	3.03-6.02	4.99
Fe	$661.42^{a} \pm 211.41$	496.72-899.81	$735.50^{a} \pm 85.97$	657.62-827.75	$726.05^{a} \pm 106.81$	650.62-801.57	$1236.69^{a} \pm 754.69$	709.62-2101.23	839.92
Pb	$3.76^{a} \pm 0.98$	2.96-4.85	$7.23^{b} \pm 0.36$	6.99-7.65	$7.35^{b} \pm 0.45$	7.03-7.67	$5.73^{ab} \pm 1.60$	4.05-7.23	6.02

Values within a row with different superscripts are significantly different ($p < 0.05$)

Table 2—Person correlation matrix average metals in whole plant

		Cu	Cd	Ni	Mn	Fe	Zn	Cr	Pb
Cu	R^2	1							
	P	.							
	N	10							
Cd	R^2	-0.40	1						
	P	0.29	.						
	N	9	10						
Ni	R^2	0.05	-0.68(*)	1					
	P	0.89	0.03	.					
	N	10	10	11					
Mn	R^2	0.76(*)	-0.51	-0.11	1				
	P	0.01	0.13	0.74	.				
	N	10	10	11	11				
Fe	R^2	0.86(**)	-0.37	0.35	0.46	1			
	P	0.01	0.29	0.29	0.16	.			
	N	10	10	11	11	11			
Zn	R^2	-0.06	0.25	0.26	-0.36	0.24	1		
	P	0.86	0.50	0.436	0.28	0.47	.		
	N	10	10	11	11	11	11		
Cr	R^2	-0.32	0.22	0.31	-0.40	-0.02	0.11	1	
	P	0-.37	0.54	0.34	0.22	0.96	0.75	.	
	N	10	10	11	11	11	11	11	
Pb	R^2	0.44	0.23	-0.41	0.29	0.29	0.47	-0.40	1
	P	0.20	0.52	0.21	0.39	0.39	0.14	0.23	.
	N	10	10	11	11	11	11	11	11

significant positive relationship was found between Cu and Fe levels (r^2 = 0.86; P<O.O1). The mean level of Cd content in plant parts decreased in the order of bark> leaves = senescence leaves> roots. Accumulation of Cd in bark/leaves/senescent leaves was significantly greater than in the roots, of the tree (Table 1). Ni showed inverse accumulation pattern to Cu and Cd with increasing trends in order of leaves > roots ~ senescence leaves > bark. A negative relationship was observed between Ni and Cd accumulation (r^2 = -0.68) in the tree. Percentage accumulation of Fe by different plant parts showed a similar trend as those of Cu and Mn. There was no significant difference observed among the levels of Fe in different parts of the tree. Zn and Cr accumulation in different plant parts were not significantly different (Table 2). Pb accumulation level in leaves was significantly lower than the levels observed in senescent leaves, bark or roots.

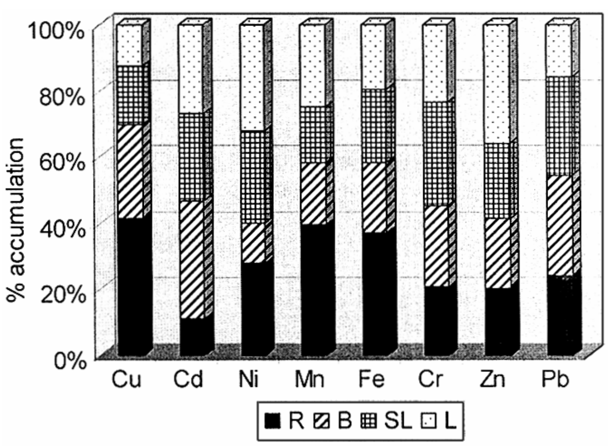

Fig. 2—Percentage accumulation of metals by each plant component (R = roots; B = Bark; SL = Senescent leaves; L = Leaves)

Table 3 presents the translocation ratios ([HM_{1eaf} or $HM_{s.leaf}$ or HM_{bark}]/HM_{roots}]) of detected metals from root to bark, leaves or senescent leaves. The translocation ratio from root to the aerial parts was the highest for Cd in all the three parts of the plant studied (Table 3). In the case of leaves, the mean (± SD) calculated translocation ratios increased in the order of Mn (0.16 ± 0.05) < Cu (0.31 ± 0.19) < Pb (0.49 ± 0.02) < Fe (0.62 ± 0.54) < Ni (1.16 ± 0.46) = Cr (1.16 ± 0.70)< Cd (1.51 ± 0.46) < Zn (1.60 ± 1.15) while it was in the increasing order of Mn (0.30±0.22)< Cu (0.3 7± 0.0) < Fe (0.56± 0.35) < Zn (0.94±0.05) < Ni (0.97±0.21) < Pb (1.08 ± 0.] 5) < Cd (1.53 ± 0.66) < Cr (1.66 ± 1.02) in the senescent leaves. The metal translocation ratios increased in the order of Ni (0.38 ± 0.01) < Mn (0.45 ± 0.22) < Fe (0.60 ± 0.41) < Cu (0.62 ± 0.29) < Zn (1.02 ± 0.12) < Cr (1.1] ± 0.22) < Pb (1.14 ± 0.235) < Cd (2.] 8 ± 0.48) in bark.

Total metal concentration in sediment

The total concentrations of the eight metals studied are presented in Table 4. The study site contains elevated average concentrations of Fe (68164 ppm) followed by Mn (1020 ppm). The metal concentration in sediments showed a decreasing order of Fe> Mn > Cr > Cu > Zn> Ni > Pb> Cd.

Ability of *R . mucronata* to absorb metal in sediment

The weighted average concentration factors of *R. mucronata* in the eight elements studied In Alibag were in the order of Pb > Cd > Mn > 2n > Cu > Ni = Cr > Fe (Table 5). Except Pb, Cd and Mn other metals were showed a CF of lower than 0.1. However for all the metals, *R. mucronata* showed a concentration factor of less than one. When the individual plant components are considered, the

Table 3—Translocation ratios of detected metals to leaves, senescent leaves and bark of *R. mucronata*

	Cu	Cd	Ni	Mn	Cr	Zn	Fe	Pb
Leaves								
Range	1.7-0.53	1.19-1.84	0.84-1.49	0.12-0.20	0.67-1.66	0.78-2.4 I	0.24-1.00	0.48-0.50
Mean±	0.31	1.51	1.16	0.16	1.16	1.60	0.62	0.49
SD	0.19	0.46	0.46	0.05	0.70	1.15	0.541	0.02
Senescent leaves								
Range	0.37-0.37	1.06-1.99	0.82-1.22	0.15-0.45	0.94-2.37	0.90-0.98	0.3-0.80	0.98-1.18
Mean	0.37	1.53	0.97	0.30	1.66	0.94	0.56	1.08
SD	0.00	0.66	0.21	0.22	1.02	0.05	0.35	0.15
Bark								
Range	0.42-0.83	1.85-2.53	0.37-0.39	0.29-0.66	0.96-1.27	0.93-1.11	0.31-0.89	0.97-1.30
Mean	0.62	2.18	0.38	0.45	1.11	1.02	0.60	1.14
SD	0.29	0.48	0.0]	0.22	0.22	0.12	0.41	0.235

accumulation factor for Pb is the highest in bark and senescent leaves, while bark showed the highest values of Cd and Ni.

Discussion

In terms of environmental restoration and management, mangrove communities may provide effective traps to immobilize waste-water borne metals[9,10]. In the present study, higher percentages of Cu, Mn and Fe were in roots, while the higher percentages of the other five metals studied were accumulated in the aerial parts such as leaves, senescent leaves and bark. Higher accumulation of Mn and Fe are justifiable when considered with the highest abundance of Fe and Mn in the planet earth and the lithosphere[11]. In the present study, maximum metal concentrations in sediments were shown by Fe followed by Mn reflecting the lithogenic origin of these metals. The values recorded higher than the values recorded in some other mangrove sediments in India[12,13]. Many mangrove species contained very high concentrations of certain metals such as Fe and Mn[14]. Most of the studies have proved this phenomenon regarding accumulation of Fe and Mn by mangrove roots[4].

It has been demonstrated that the translocation of Cu from root to shoot is low[15]. The plants have the capacity to be extremely tolerant to such metals, with preferential accumulation mainly in the root tissue, and through the barrier to translocation, imparting the minimal physiological effects to the species[16]. The study conducted for the determination of resistance capacity of *R. mucronata* seedlings to Pb, Cu, Cd and Hg has shown that the seedlings do not translocate Pb but Cd is translocated into aerial parts[5]. Contrasting results were obtained in the present study, regarding the translocation of Cd and Pb. In the present study each metal exhibited different extent of translocation rates from root to shoots. These results are probably related to the differences in the solubility and the availability of each metal ion. Higher translocation ratios were observed in the case of senescent leaves for Cr, Cd, Pb, Ni and Zn ranging from 0.94 ± 0.05 for Zn to 1.66 ± 0.70 for Cr. Cd, Cr and Pb exceeded a translocation ratio of I, as these metals were being accumulated in leaves before falling off and thus eliminated. With the progression of young leaves to old ones, Ni and Cr are translocated and reabsorbed by the plant before defoliation. This act shows the special capability of mangrove species *R. mucronata* to retain non-essential metals in aerial parts of the tree. Although the difference is not statistically significant, these two metal levels in the younger leaves were higher than those in the senescent leaves. All the metals except Ni, Cr and Cd showed higher concentrations in senescent leaves. Out of these, only Pb showed a significantly difference in senescent leaves. Similar observations were also reported for translocation of metals in *Rhizophora stylosa*[17]. The change in Cd concentration in leaves, senescent leaves or bark was not evident in this study. The mobility of metals to leaves were in the order of Mn < Cu < Pb < Fe < Cr = Ni < Zn. Zn is one of the essential nutrients for plant systems so the higher translocation ratio of Zn in this study is explainable. The non-essential metal Cd has the maximum translocation ratio from root to bark suggesting that Cd is excluded from roots and foliage, as well as accumulated in dead tissues.

Accumulation or concentration factors (CF) of metals are rather low (« 0.50) for every metal studied. This is due to the fact that the CF was calculated on the basis of total metal concentration in sediment rather than that of bioavailable fraction. The high

Table 4—Concentration (ppm) of total metals in sediments (0-30 cm) of the study area

	Minimum	Maximum	Mean	SD
Cu	73.15	104.58	92.59	10.28
Cd	4.46	6.10	5.31	0.61
Ni	54.83	75.30	63.29	6.44
Mn	907.57	1134.20	1020.13	71.59
Cr	221.70	1168.89	545.16	377.49
Zn	58.85	112.25	78.18	15.22
Fe	66.89×10^3	69.46×10^3	68.16×10^3	1046.87
Pb	16.06	24.78	19.51	3.45

Table 5—Metal concentration factors (CF) of *R. mucronata*

	Cu	Cd	Ni	Mn	Cr	Zn	Fe	Pb
Leaves	0.030	0.187	0.027	0.109	0.030	0.059	0.010	0.191
S. leaves	0.041	0.178	0.022	0.242	0.018	0.078	0.010	0.350
Bark	0.061	0.250	0.012	0.295	0.020	0.081	0.01	0.369
Root	0.091	0.107	0.021	0.055	0.015	0.047	0.044	0.265
Weighted average	0.056	0.180	0.021	0.175	0.021	0.066	0.018	0.294

values observed were for Pb (0.3), Cd (0.18) and Mn (0.18). These results indicate that the absorption and accumulation abilities of *R. mucronata* for metals are rather low. The estimation of CF on the basis of bioavailable fraction of metals would serve as a real indicator to evaluate the plant for its phytoremediation purpose. With the fallen leaves, considerable quantities of metals enter the detritus and after the process of decomposition, these metals may be prone to different fates such as reentering the biogeochemical cycle or transport to the adjacent water bodies. Significant higher concentrations of Cu, Mn and Fe were found in the roots than in the aerial parts of the tree, indicating that the root acts as a barrier for metal translocation and protects the sensitive parts of the plant from metal contamination. Observations on the cycling of Zn, Mn and Fe through production, decomposition and export of litter carried out at the Itacurussá Experimental Forest, a red mangrove forest in Southeast Brazil reveled that the export of metals through leaf fall represents less than 0.01% of the total sediment reservoir[18]. Hence, it could be suggested that mangrove ecosystems are probably efficient biogeochemical barriers to the transport of metal contaminants in tropical coastal areas.

Conclusion

All the metals studied showed mobility in *R. mucronata* at different extents. Cu, Mn and Fe showed restricted mobility, while the other metals had greater mobility. Hence, the trend of phytostabilization capacity of *R. mucronata* in the Alibag mangrove system is confined to only highly abundant metals in nature. Phytostabilization can be used to reduce the migration of contaminants in soil. As the accumulation or concentration factors are rather low, the phytoextraction capacity of *R. mucronata* is limited. Non-essential metals such as Pb and Cd are removed through defoliation and enter to the biogeochemical cycle while Ni and Cr are translocated and reabsorbed by the plant before defoliation. The toxic metal Pb tends to be accumulated in bark and would decrease the transfer probabilities to secondary consumers. The study reveals that phytoremediation capacity of *R. mucronata* varies from metal to metal.

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