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Author(s): Carlos Augusto R. Silva, Luiz D. Lacerda and Carlos E. Rezende

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Metals Reservoir in a Red Mangrove Forest[1]

Carlos Augusto R. Silva, Luiz D. Lacerda,[2] and Carlos E. Rezende

Programa de Pós-Graduação em Geoquímica, Instituto de Química, Universidade Federal Fluminense,
Morro Do Valonguinho S/N°, Niterói 24.210, Rio De Janeiro, Brazil

ABSTRACT

This study presents heavy metal concentrations and distributions in a mangrove forest in Sepetiba Bay, Rio de Janeiro. Sediments are the main reservoir of the total metal contained in mangrove studied: 99 percent for Mn; 100 percent for Fe; 100 percent for Zn; 99 percent for Cu; 100 percent for Cr and 100 percent for Pb and Cd. *Rhizophora mangle* biomass contained less than 1 percent of reservoir. Within the biotic compartment, perennial tissues accounted for almost all of the metals present in biomass. The results indicate that mangrove may act as an efficient metal trap in tropical coastal environments.

RESUMEN

Reservatório de metais em uma floresta de mangue vermelho: Este estudo apresenta a concentração de metais pesados e sua distribuição em uma floresta de manguezal da Baía de Sepetiba, Rio de Janeiro. O sedimento foi o principal reservatório de metais, com 99 por ciento do Mn; 100 por ciento de Fe; 100 por ciento de Zn; 99 por ciento do Cu; 100 por ciento do Cr e 100 por ciento do Pb e do Cd. A biomassa de *Rhizophora mangle* contribuiu com menos de 1 por ciento do reservatório. Dentro do compartimento biótico, os tecidos perenes acumularam a quase totalidade dos metais presentes na biomassa. Os resultados indicam que os manguezais podem atuar como eficientes barreiras biogeoquímicas ao trânsito de metais pesados em áreas costeiras tropicais, através da imobilização de metais nos sedimentos sob formas não-biodisponíveis que, juntamente com certas adaptações fisiológicas típicas de árvores de mangue, decrescem sensivelmente a absorção de metais pelas plantas.

MANGROVE FORESTS PLAY AN IMPORTANT ROLE in energy and nutrient cycling on most tropical coasts. With growing industrial activity in many such areas, these ecosystems can also contribute to the cycling of certain pollutants in the local environment (Murray 1985), either as sinks or conveyors of pollutants to marine food chains (Harbison 1981, Lacerda *et al.* 1988). In the Sepetiba Bay region of Rio de Janeiro mangroves dominate the coastline and are subjected to high inputs of heavy metals from a large metallurgical park located along the Bay's coast.

The extent of mangrove's role in the cycling of such metals in the Bay will depend on the balance between metal immobilization in the system and export through plant litter and particulate organic matter (Lacerda & Rezende 1987). Reducing conditions in mangrove sediments will favor metal precipitation and immobilization as sulphides (Lacerda & Abrão 1984). On the other hand, mangrove plants can be considered, in a more general ecological sense, as opportunistic species of early succession (Odum *et al.* 1982). Therefore, a tendency to accumulate trace metals also may occur in these ecosystems at the plant level.

The present work aims to quantify the distribution of the trace metals (Fe, Zn, Mn, Cu, Cr, Pb and Cd) in biotic and abiotic compartments of a red mangrove (*Rhizophora mangle* L.) forest in Sepetiba Bay, Rio de Janeiro, in order to quantify metal accumulations within the forest and their mobility among the different mangal compartments.

STUDY SITE

The study site is located along the North shore of Sepetiba Bay at the Itacuruçá municipality, approximately 100 km from Rio de Janeiro. The forest has an area of approximately 4 ha, and is limited by two tidal creeks running almost perpendicular to the shore and landward, by transitional vegetation of nonmangrove species. The dominant species is the red mangrove (*Rhizophora mangle* L.), although isolated trees of the black mangrove (*Avicennia shaueriana* Stpaf and Leech.) and of the white mangrove (*Laguncularia racemosa* Gaerth.) occur throughout the forest.

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[2] To whom any correspondence and reprint request should be sent.

Forest structure has been studied by Silva *et al.* (1990). Mean plant density is 4510 trees/ha, with mean height of 6.1 m and mean diameter (DBH) of 7.8 cm. All trees sampled in this study presented height and diameter as close as possible to these mean values.

Freshwater inputs to the forest are from subsurface runoff and the inundation pattern is controlled by tidal amplitude (Ovalle *et al.* 1987). These characteristics classify the study area as a typical fringe forest according to the general classification of Lugo and Snedaker (1974).

Heavy metals enter the forest through tides, mostly bound to suspended matter originating in the Bay, which receives large inputs of metals from metallurgical industries located on the NE coast, approximately 20 km from the study site (Lacerda *et al.* 1987).

MATERIAL AND METHODS

The concentrations of Fe, Mn, Zn, Cu, Cr, Pb, and Cd were analyzed in plants (leaves, branches, trunks, flowers, and aerial and below ground roots) and in sediments of different depths. Plant samples were collected from five trees representative of the dominant class of tree diameter in the forest. Below ground roots were collected from sediment cores taken in polyethylene tubes of 3.4 and 6.4 cm in diameter. Core sections (10.0 cm) were cut and thoroughly washed with distilled water in a sieve (1 mm mesh size to separate fine live root material).

Plant samples were oven dried (80°C, 24 hr) and ashed (450°C, 16 hr). Ashes were then dissolved in hot 0.1 N HCl. This solution was used for any other further dilutions.

Heavy metal reservoirs in sediments were estimated from 5 cores to a total depth of 50.0 cm. The sediment cores were cut in layers of 3.0 cm in the first 15.0 cm and subsequent layers of 5.0 cm. The results from the 3.0 cm and 5 cm layers were pooled and presented a mean concentration of 10 cm intervals to be directly compared with root biomass data. Sediment samples were oven dried (80°C, 24 hr) and sieved through 1 mm pore sieves. Samples were then leached with 0.1 N HCl for 16 hr at room temperature, for the extraction of the weakly bound metal fraction (Fiszman *et al.* 1984). Strongly bound metal concentrations were determined in the residual sediment sample retained in filters, after digestion with 30 percent H_2O_2 + HCl conc. + HNO_3 conc. + $HClO_4$ conc. (3:3:1:1 V/V) till dry in a hot plate, and redissolved in 0.1 N HCl. Total metal concentration was considered as the sum of the weakly and strongly bound fractions. All digestion procedures for metal determinations in plant and sediment samples were tested in reference material: NBS "Tomato Leaves" for plants and IAEA "Marine Sediments" for sediments. Differences between certified and measured results were always less than 10 percent (Silva 1988).

All acidic extracts were analyzed for the metals studied by conventional flame atomic absorption spectrophotometry. Deuterium background correction was used for Zn, Pb and Cd.

The standing stock of metals in plants were calculated by multiplying metal concentrations in each compartment by its biomass, determined in the area by Silva *et al.* (in press). The stock of metals in sediments was calculated by multiplying mean metal concentration in the sediment by the total weight of sediment per ha and 50 cm of depth.

RESULTS

Table 1 shows metal concentrations in mangrove sediments to a total depth of 50.0 cm and the respective metal concentrations in roots. The relative concentration in sediments found were: Fe > Mn > Zn > Cr > Pb > Cu > Cd for both the strong and weakly bound fractions. However, weakly bound concentrations of Cd, Pb, Cu, and Cr were below the detection limit of the method. Significant differences of Mn, Cu, and Cr strongly bound concentrations occurred between different depths: Mn $- H = 13.96$, $P < 0.05$; Cu $- H = 20.17$, $P < 0.05$ and Cr $- H = 15.12$ $P < 0.05$. Strongly bound Mn increased with depth while weakly bound Zn decreased ($H = 11.28$; $P < 0.05$). Strongly and weakly bound Fe, Cd and Pb didn't show significant variations with depth ($P > 0.05$). Metal concentrations in roots did not show significant variations with depth ($P > 0.05$) with the exception of Fe which presented significantly higher concentrations at 50 cm of depth (Table 1).

Mean concentrations of metals in different parts of *R. mangle* are presented in Table 2. Branches and leaves contained the highest concentrations of Mn (67 and 101 ppm). Below ground roots contained the highest concentrations of Fe (1011 ppm), Zn (19.9 ppm) and Cu (5.1 ppm). Cu concentrations were below the detection limit in fruits, flowers, and leaves. Cr was only detected in perennial tissues (branches and trunks), and Pb and Cd were below the detection limit in all plant parts.

Below ground fine root biomass decreased sig-

TABLE 1. *Metal concentrations in sediment profiles in the Sepetiba Bay red mangrove forest. S—Strongly bound fraction; W—Weakly bound fraction; R—Roots (n = number of samples). Detection limits—Cu < 0.05 ppm; Cr < 0.06 ppm; Pb < 0.15 ppm; Cd < 0.02 ppm.*

		Metals concentrations ($\mu g \cdot g^{-1}$ d.w., ppm)						
Depth (cm)	(n)	Mn	Fe	Zn	Cu	Cr	Pb	Cd
0–10	S (5)	52 ± 11	4856 ± 1429	18 ± 5	2.8 ± 0.8	10.8 ± 4.3	9.4 ± 3.9	0.6 ± 0.2
	W (5)	9.2 ± 5.3	247 ± 33	26.5 ± 12.7	ND	ND	ND	ND
	R (2)	18.3	637	24	2	ND	ND	ND
10–20	S (5)	55 ± 6.0	6994 ± 939	16 ± 3	2.1 ± 0.5	12 ± 6.0	8.6 ± 1.1	0.5 ± 0.1
	W (5)	10.4 ± 4.0	255 ± 8	15.7 ± 9.0	ND	ND	ND	ND
	R (2)	11.8	797	19.6	7.7	ND	ND	ND
20–30	S (5)	65 ± 8	7134 ± 934	19 ± 4	2.4 ± 0.5	14.8 ± 7.1	9.0 ± 2.0	0.4
	W (5)	14.2 ± 2.9	255 ± 2	0.8 ± 2.0	ND	ND	ND	ND
	R (2)	13.6	868	16.9	1.6	ND	ND	ND
30–40	S (5)	82 ± 11	8279 ± 290	22 ± 3	3.3 ± 0.5	17.2 ± 4.8	10.8 ± 1.9	0.5
	W (5)	12.9 ± 4.6	228 ± 33	6.2 ± 0.5	ND	ND	ND	ND
	R (2)	8.8	618	30.0	7.5	ND	ND	ND
40–50	S (2)	90	6405	21	2.8	16.5	12	0.5
	W (2)	14.2	236	4.5	ND	ND	ND	ND
	R (2)	23.9	2134	9.1	6.7	ND	ND	ND

TABLE 2. *Heavy metal concentration in* R. mangle *from the Sepetiba Bay mangrove forest. Mean and standard deviation. Detection limit: Cu < 0.05; Cr < 0.06; Cd < 0.02; Pb < 0.15.*

Plant parts	Mean metal concentrations ($\mu g \cdot g^{-1}$ D.W.)				
	Mn	Fe	Zn	Cu	Cr
Fruits	17.8 ± 5.5	3.2 ± 0.6	1.2 ± 0.1	—	—
Flowers[a]	59.0	67.0	9.0	—	—
Leaves	101 ± 39	37.2 ± 8.9	7.2 ± 0.8	—	—
Branches[a]	67.0	19.4	6.2	0.6	1.2
Trunks	20.4 ± 5.8	12.4 ± 7.3	3.4 ± 0.8	0.5 ± 0.3	0.2 ± 0.1
Aerial roots	15.5 ± 3.2	8.2 ± 3.2	7.2 ± 2.4	0.4 ± 0.2	—
Below ground roots (0–50 cm)	15.3 ± 5.9	1011 ± 637	19.9 ± 7.8	5.1 ± 3.0	—

[a] Only one composed sample was analyzed in duplicate.

nificantly with depth, from 89.1 g/m^2 at the sediment surface to 12.5 g/m^2 at 50 cm (Silva *et al.* in press).

The quantity of metals in the sediment and in the biomass of *R. mangle* trees are summarized in Table 3. The sediment was the main reservoir of the heavy metals: Mn (99%), Fe (~100%), Zn (~100%), Cu (99%), Cr (~100%), Pb (~100%) and Cd (~100%). *R. mangle* contained a much smaller fraction (~1%) of the heavy metals. Within the biotic compartments, perennial tissues accounted for the major pool of Mn (84%), Fe (99%), Zn (95%), Cu (~100%) and Cr (~100%) while deciduous tissues, (leaves and flowers), accounted for an insignificant portion of the total metal content, notwithstanding the fact that deciduous tissues account for nearly 5 percent of the total biomass.

DISCUSSION

The dominance of the strongly bound fraction of metals in sediments of the forest, over 95 percent of the total concentrations for Fe, Cu, Cd, Pb, and Cr, shows the low availability of these metals for plant uptake. All of them, except Cr, form highly stable sulphide compounds in the anoxic mangrove sediments (Aragon 1986, Lacerda & Rezende 1987). Chromium complexes with high molecular weight organic substances in mangrove sediments, which immobilize it in a manner similar to the sulphides (Souza 1987).

The most mobile metals in this study were Mn and Zn with a significant portion and 39 percent of the total concentration in the weakly bound fraction. Sulphidic compounds of Mn have low stability; under anoxic conditions reduced, soluble Mn^{2+} occurs (Giblin *et al.* 1980). The high input of anthropogenic Zn reaching the area associated with suspended particulate matter (Lacerda *et al.* 1987); as confirmed by the concentration peak at the sediment surface, accounts for the high mobility found for this element. This element enters the mangal weakly bound to oxi-hydroxides of Fe and Mn present in the suspended particulate matter, then these bounds are rapidly broken in the reducing mangal sediments (Lacerda *et al.* 1988). The dissociated Zn, and probably Mn, complex with colloidal and dissolved organic substances which render them higher in solubility and therefore in mobility (Lacerda & Rezende 1987).

Harbison (1981), Lacerda *et al.* (1987), Lacerda and Abrão (1984), Lacerda *et al.* (1988), Rezende (1988) and Silva (1988) have shown that mangrove sediments operate as a biogeochemical sink for heavy metals, mainly due to the high concentrations of organic matter and sulphides under permanently reducing conditions. Iron is generally considered the principal metal that precipitates in several sulphidic compounds (Howarth 1979, Berner 1984). Elderfield *et al.* (1979) suggested that trace metals precipitate with Fe forming polysulphide minerals, in particular Cu, Zn, and Pb. Polysulphides have been reported to be formed in less than 24 hr in salt marsh sediments under similar conditions to those found in mangroves (Howarth 1979). In the forest studied, Aragon (1986) reported highly significant correlations between sulfide sulphur (which reached concentrations of up to 3% dry weight) and heavy metal concentrations in sediments, confirming that sulphides are the major sink for heavy metals in the area.

The strongly bound metal fraction dominates over the weakly bound fraction in the studied sediment. Consequently, the major portion of metals are probably unavailable for *R. mangle* uptake. Highest Zn and Mn concentrations, however, occur in weakly bound forms, and this higher mobility is

TABLE 3. *Mass distribution and heavy metal reservoirs in biotic and abiotic compartments in the red mangrove forest of Sepetiba Bay. (The number between parentheses are percentages.) Biomass data are from Silva* et al. *(in press).*

	Kg·ha^{-1}	Mn	Fe	Zn	Cu	Cr	Pb	Cd
Total sediment to 50 cm depth	4,799,604 (98)	390 (99)	33,492 (≈100)	150 (≈100)	12.96 (99)	69 (~100)	48 (~100)	2.39 (~100)
Weakly-bound		59	1171	59	ND	ND	ND	ND
Strongly bound		331	32,321	91	12.96	69	48	2.39
Total biomass	81,707 (2)	2.44 (1)	17.45 (<1)	0.67 (<1)	0.12 (1)	0.03 (<1)	ND (<1)	ND (<1)
Underground roots to 50 cm depth	16,334	0.25	16.51	0.33	0.08	ND	ND	ND
Aereal roots	16,762	0.26	0.14	0.12	0.01	ND	ND	ND
Trunks	31,422	0.64	0.39	0.11	0.02	0.01	ND	ND
Branches	12,912	0.87	0.25	0.08	0.01	0.02	ND	ND
Leaves	4202	0.42	0.16	0.03	ND	ND	ND	ND
Flowers	22.1	<0.01	<0.01	<0.01	ND	ND	ND	ND
Fruits	53.2	<0.01	<0.01	<0.01	ND	ND	ND	ND

reflected in the concentrations of these metals in *R. mangle* biomass.

It has been suggested that several salt marsh plants transfer oxygen from aerial parts to roots, and may release it through the roots into the anoxic sediment (Mendelsshon & Postek 1982, Barlett 1961, Armstrong 1978). This mechanism helps to supply oxygen to meet the physiological requirements of the roots (Armstrong 1978), and decreases the concentrations of several phytoxins such as Fe^{2+}, Mn^{2+} and SH^{-} and others (Mendelsshon & Postek 1982).

Releasing of oxygen by mangrove roots has been studied by Thibodeau and Nickerson (1986) who documented oxidation of sediments by mangrove roots. Scholander *et al.* (1962) commented that mangrove roots are well ventilated through pneumatic tissues, which would facilitate oxygen transport. On the other hand, mangrove trees have similar environmental constraints as salt marsh plants and thus it is possible that these trees use the same mechanisms present in salt marsh macrophytes.

Our results show higher Fe, Mn and Cu concentrations in fine roots of *R. mangle* in relation to the weakly bound fraction of these metals present in the surrounding sediment. This may indicate the presence of an oxidant geochemical microenvironment caused by the releasing of oxygen by mangrove roots. This would oxidize soluble Fe^{2+} and Mn^{2+} to insoluble Fe (OH)$_3$ and MnO$_2$ (Barlett 1961). The oxide–hydroxides of Fe and Mn strongly coprecipitates other metals. In salt marsh plants the presence of an "iron plate" is frequent and is responsible for the precipitation of various metals at the roots' surface (Otte *et al.* 1987).

The peak concentrations of Fe, Mn, and Cu in fine roots around 40 cm depth (Table 1) may be due to a process involving the release of oxygen by mangrove roots.

It is interesting to note that the mangrove studied showed higher total concentrations of most heavy metals in the sediment than the concentrations found by Golley *et al.* (1978) in tropical moist forest. For example, in the strongly bound fraction in the sediment, the Fe concentrations (100 ×) and Mn (60 ×) were higher than concentrations found by Golley *et al.* (1978), while Zn and Cu were in the same range (10.0–51.0 ppm and 1.0–2.0 ppm) found for Panama forest (Golley *et al.* 1978). However, our results are within the range found by Lacerda *et al.* (1987) in 18 mangal sediments along the SE Brazilian coast. Thus, it seems that these forests generally contain higher metal content in their soils than other tropical forests.

Notwithstanding the hither metal concentrations in sediments, our mangal forest showed the lowest quantity per area of heavy metals in the biotic compartments when compared to moist tropical (Golley *et al.* 1978) and temperate forests (Whittaker *et al.* 1979, Pastor *et al.* 1984) (Table 4). In addition, the concentrations of metals in mangrove leaves are lower than in leaves of tropical and temperate forest trees (Table 4). These results confirm the lower bioavailability of metals in mangrove ecosystems.

Most of the metals measured in the *R. mangle*

TABLE 4. *Reservoir and heavy metal concentrations in different forests: mangrove, moist tropical and temperate. a. Sample collected in September; b. Mean of aspen and maple trees; c. Mean of Hubbard Brook trees.*

Forests	Heavy metals (Kg·ha^{-1}) Fe	Mn	Zn	Cu	Author
Mangrove					This work
Perennial tissues	17.29	2.02	0.64	0.12	
Deciduous tissues	0.16	0.42	0.03	—	
Leaf concentration (ppm)	37.2	101	7.2	<0.05	
Tropical (a)					Golley *et al.* 1978
Perennial tissues	12.3	27.7	7.1	1.5	
Deciduous tissues	0.7	0.5	0.2	0.1	
Leaf concentration (ppm)	96	68	22	5.5	
Temperate (b)					Pastor *et al.* 1984
Perennial tissues	4.6	—	2.2	—	
Deciduous tissues	0.3	—	0.2	—	
Leaf concentration (ppm)	130	—	97	—	
Temperate (c)					Whittaker *et al.* 1979
Perennial tissues	32.8	42.1	6.3	0.6	
Deciduous tissues	0.4	5.2	0.3	0.03	
Leaf concentration (ppm)	111	—	96	9.0	

forest accumulate in perennial tissues of trees. Vitousek and Reiners (1975), Bormann and Likens (1979), and Boring *et al.* (1981) suggested that plants of early successional stage can be more efficient as nutrient reservoir than late successional species, due to higher productivity, higher nutrient uptake, and preferential retention of nutrients into perennial tissues. This model seems to apply to the mangal forest studied. Therefore, also at the plant level, this forest could represent a long term sink for metals in the area.

CONCLUSION

The cycling of trace metals in mangal ecosystems has been poorly studied in contrast, for instance, with salt marsh ecosystems. Studies on metal export from mangals showed that plant litter is very poor in trace metal content, leading to very low export rates (Lacerda *et al.* 1988). This is in agreement with the low metal content in deciduous tissues found in the present study. Salt marsh plants however, are annuals and actively "mine up" metals from sediments (DeLaune *et al.* 1981), eventually exporting them associated with detritus much more efficiently than mangroves (Odum & Drifmeyer 1978, Lacerda *et al.* 1979).

Our results show that notwithstanding their high environmental concentrations, heavy metals show a low bioavailability to mangrove trees, due to their strong chemical bonding with sediment compounds. Although some metals (*e.g.*, Mn and Zn) show a certain mobility within the sediment plant system, they are preferentially incorporated in plant tissues of very low mobility such as trunks and aerial roots. These findings confirm the proposition that mangrove forests are efficient barriers to heavy metal transport in tropical coastal areas and may be considered in management plans of industrial pollution in the tropics.

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