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The Biogeochemistry and Trace Metals Distribution of Mangrove Rhizospheres¹

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ABSTRACT

Soils and porewater of the rhizosphere of mangrove trees, *Rhizophora mangle* L. and *Avicennia schaueriana* Stapf & Leech., of the salt marsh grass *Spartina alterniflora* Loisel, and of unvegetated mud flats, were analyzed for pH, salinity, platinum electrode redox potential, organic matter content, sulfide concentrations, and the total and exchangeable concentrations of trace metals (Fe, Zn, Cu, Pb and Cd). The study was conducted in a fringe mangrove forest in Sepetiba Bay, Rio de Janeiro, Brazil. The rhizospheres differed in their biogeochemistry. Mud flats and *Rhizophora* soils were very reducing, with highest concentrations of sulfide. *Avicennia* soils showed the highest variability of the variables measured, with the rhizosphere changing from oxic to anoxic conditions. *Spartina* soils, on the other hand, were generally oxic, with very low sulfide concentration.

The distribution of trace metals in these soils varied with the major physical and chemical characteristics. Mud flat soils presented the highest total trace metal concentrations followed by mangrove soils and *Spartina* soils. However, exchangeable trace metals were similar among the different soils with the exception of *Avicennia* soils, which due to their characteristic instability of redox conditions, presented much higher exchangeable trace metals concentrations.

RESUMO

Solos e águas intersticiais sob a influência da rizosfera de árvores de mangue (*Rhizophora mangle* L. e *Avicennia schaueriana* Stapf & Leech.), de gramínea de marisma *Spartina alterniflora* Loisel, e de áreas sem vegetação em planícies de lama, foram analisados em relação ao pH, potencial redox, salinidade, teor de matéria orgânica e concentração de sulfetos, e das concentrações totais e trocáveis de metais traço (Fe, Zn, Cu, Pb e Cd), em uma floresta de mangue de franja na Baía de Sepetiba, Rio de Janeiro. Os resultados mostraram que a rizosfera das diferentes plantas mostraram diferenças significativas em sua biogeoquímica. Os solos de planície de maré e sob *Rhizophora* apresentaram-se mais redutores e com altas concentrações de sulfetos. Os solos sob *Avicennia* mostraram as maiores variações dos parâmetros medidos, alternado condições óxicas e anóxicas. Por outro lado, os solos sob *Spartina* apresentaram-se geralmente óxicos, com baixas concentrações de sulfetos.

As concentrações de metais traço também foram diferentes entre os diferentes solos, variando de acordo com as principais características físico-químicas. Os solos de planície de maré apresentaram as maiores concentrações de metais totais, seguindo-se os solos de mangue e por último os solos sob *Spartina*. Entretanto, as concentrações trocáveis de metais traço foram semelhantes para todos os solos, menos aqueles sob *Avicennia*, que devido a sua típica instabilidade de potencial redox, apresentou a maiores concentrações de metais trocáveis.

Key words: *Avicennia schaueriana*; *biogeochemistry*; *Brazil*; *mangrove*; *Rhizophora mangle*; *rhizosphere*; *roots*; *soil chemistry*; *Spartina alterniflora*; *tropics*.

PLANTS GROWING IN WATERLOGGED SOILS FREQUENTLY EXCRETE AIR THROUGH ROOTS creating oxidized rhizospheres within the anaerobic soil environment and therefore creating specific biogeochemical conditions in the soils under their influence; thus, in general, differ greatly from the conditions present in the surrounding soils. The typical trees of New World mangrove forests, the genera *Rhizophora* (Rhizophoraceae) and *Avicennia* (Avicenniaceae), are com-

monly found in waterlogged, anaerobic soils. They translocate air, through lenticels located on the aerial parts of *Rhizophora* (proproots) and pneumatophores of *Avicennia*, to underground roots (Scholander *et al.* 1955, Thibodeau & Nickerson 1986). The activity of mangrove roots creates rhizospheres with completely different physical-chemical conditions from the surrounding soil (Nickerson & Thibodeau 1985, Carlson *et al.* 1983).

Differences between *Rhizophora* and *Avicennia* rhizospheres however, have been consistently reported and are common knowledge in areas where rice farmers use mangrove soils for cultivation. *Rhi-*

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zophora soils tend to develop adverse conditions for rice growth after empoldering (Mongia & Ganeshamurthy 1989).

The *Avicennia* rhizosphere tends to be richer in organic matter and has a higher pH (Naidoo 1980); it can be highly oxidized to an extent that sulfide is virtually absent (Nickerson & Thibodeau 1985). *Rhizophora* rhizospheres, on the other hand, have little effect on the general conditions of mangrove soils, being highly sulphidic, and therefore generating high acidity after empoldering (Thibodeau & Nickerson 1986, Mongia & Ganeshamurthy 1989).

Recently, mangrove forests have been shown to play an important role in the biogeochemistry of trace metal contaminants in tropical coastal areas, either as sources or sinks for these contaminants (Harbinson 1984, 1986a, b; Lacerda & Rezende 1991; Silva *et al.* 1990). However, the behavior of trace metals in mangrove ecosystems is highly dependent on the physical-chemical conditions of mangrove soils and porewaters (Harbinson 1986a, Lacerda *et al.* 1988). Therefore, if different plant covers result in differences in soil conditions, this may also affect trace metal behavior in mangrove ecosystems.

In the present study we investigated the biogeochemical conditions and the trace metal distribution in soils and pore waters in the rhizosphere of mangrove plants in Sepetiba Bay, SE Brazil. This is an industrialized area highly contaminated by trace metals. In Sepetiba Bay, mangrove forests, which cover over 35 percent of the Bay's coast, play an important role in trace metal cycling (Lacerda *et al.* 1988). Detailed descriptions of the Bay's environmental situation and of the ecology of the local mangrove forests are published elsewhere (Lacerda *et al.* 1987, Silva *et al.* 1990, Ovalle *et al.* 1990).

MATERIALS AND METHODS

Samples were collected from a mixed (*Rhizophora mangle* L. and *Avicennia schaueriana* Stapf & Leech.), fringe mangrove forest along the NE coast of Sepetiba Bay. Hereafter these samples are called *Rhizophora* and *Avicennia* soils. Inside the forest we chose areas where only one species occurred homogeneously. These areas should also present the same microtopography, distance to sea water and tidal creeks. And in these areas the trees, at least visually, were healthy adults. We also collected samples hereafter called mud flats soils, in nearby un-vegetated mud flats and inside *Spartina alterniflora* Loisel. (Gramineae) banks, hereafter called *Spartina*

soils, which occur adjacent to the mangrove fringe in this area.

In each chosen area, sediments were carefully collected by inserting plastic tubes into the soil close to major root systems to a depth of 15 cm. The tubes with the soil sample were closed with plastic films, stored in ice, and transported to the laboratory. In the holes left by the tubes, we inserted porewater collectors immediately after taking out the soil samplers, which were made of polyethylene tubes with ceramic bottoms. Vacuum was created immediately after inserting the tubes by using a hand pump. With this procedure it took from 20 to 40 min to collect 100 ml of pore water and kept disturbance of soil conditions to a minimum. Porewater subsamples were collected sequentially with 20 ml plastic syringes. For sulfide analysis, 5 ml of zinc acetate were present in the syringe. The other variables (salinity, pH, and Eh, the platinum electrode redox potential) were determined directly in the field with portable equipment. All other laboratory analysis of soils and porewater were performed no later than 24 hr after collection.

In the laboratory, pore water sulfide concentrations were analyzed colorimetrically. Bulk soil subsamples were used for gravimetric determination of organic matter, after combustion at 450°C for 24 hr. The remaining soil samples were sieved to separate the fraction <63 μm for trace metal analysis, therefore avoiding errors due to presence of large root pieces and sand grains. Extraction procedures were designed to fractionate trace metals according to their binding strength to soil particles. Four grams of dried soil were first leached with a weak acidic solution (0.1 N HCl, 40 ml), after shaking at room temperature for 4 hr. The mixture was filtered and the metals present in the acid extract were considered as the exchangeable fraction. Subsamples (2 g of dry soil) were submitted to a concentrated acid extraction (conc. HNO₃ + conc. HF) for the extraction of total trace metals present, including the fraction strongly bound to sediment particles (metal sulfides, oxides, and organic matter complexes). For a complete discussion of such methods and occurrences of trace metals in soils and sediments, see Fiszman *et al.* (1984). All trace metal analyses were performed through conventional flame atomic absorption spectrophotometry.

Sediment and porewater sample number were different for the different parameters and plant cover. Therefore number of samples and/or determinations are shown separately in Tables 1, 2 and 3. One-way analyses of variance and Student *t*-tests were used to compare the results when appropriate.

TABLE 1. Major physical-chemical variables of porewaters, and soil organic matter content (OM) in a fringe mangrove forest in Sepetiba Bay, Rio de Janeiro, Brazil. Same superscript letter means no significant difference between means of a given variable, ANOVA $P < 0.01$. SD = one standard deviation; N = number of samples or determinations under different plant cover.

Plant cover		HS ⁻ (mg/l)	Eh (mV)	pH	Salinity (ppt)	OM (%)
<i>Avicennia</i> N = 13	mean	0.33 ^a	-63 ^a	6.8 ^a	32.8 ^a	24.7 ^a
	SD	0.49	92	0.6	6.5	11.8
<i>Rhizophora</i> N = 17	mean	15.6 ^b	-173 ^b	6.8 ^a	31.2 ^a	12.5 ^b
	SD	4.6	125	0.2	4.9	4.3
<i>Spartina</i> N = 16	mean	0.58 ^a	+5 ^a	6.9 ^a	25.2 ^b	5.5 ^c
	SD	0.09	102	0.2	0.8	7.6
Mud flat N = 13	mean	47.1 ^c	-204 ^b	7.1 ^a	26.4 ^b	20.5 ^a
	SD	16.3	95	0.3	2.7	7.9

RESULTS AND DISCUSSION

Major characteristics of porewater chemistry and soil organic matter content are presented in Table 1. The different soils showed differences in all variables except pH. Unvegetated mud flats and *Avicennia* soils were similar in organic matter content (20.5 and 24.7%, respectively; $P > 0.01$) and significantly richer than *Rhizophora* (12.5%) and *Spartina* soils (5.5%) ($P < 0.01$, $df = 24$ and $P < 0.01$). Sulfide concentrations were similar and very low in *Avicennia* (0.33 mg/liter) and *Spartina* (0.58 mg/liter) soils. This is probably a reflection of the capacity of these plant species to oxidize their rhizospheres contrary to *Rhizophora* and mud flat soils which presented sulfide concentrations up to two orders of magnitude higher than the former ones (15.6 and 47.1 mg/liter, respectively). This oxidizing capacity is clearly seen in the redox potential of porewaters under the different vegetation. Soils under *S. alterniflora*, which is a grass well-known for its high capacity of soil aeration (Otte *et al.* 1987), presented a positive redox potential (+5.0 mV) notwithstanding the general reducing conditions of the surrounding environment. The least reducing conditions were found in *Avicennia* forest soils (-63 mV). However, this average presented a very high standard deviation, and during various collections the redox potential of *Avicennia* soils was very high and oxidic. Also, due the large standard deviation found, *Avicennia* and *Spartina* soils were not significantly different (Table 1). *Rhizophora* forest soils (-173 mV) and unvegetated mud flat soils (-204 mV) presented significantly lower ($P < 0.01$) redox potential than the two former soils and were not significantly different between themselves ($P < 0.01$). Sulfide concentrations seem to reflect the overall mean Eh values of each soil.

Differences in pH were very small and not significant, although vegetated soils were slightly more acidic than mud flats soils. Also, mangrove soils, both under *Avicennia* and *Rhizophora*, were significantly more saline than unvegetated mud flats and *Spartina* soils, probably as a reflection of water consumption and evapotranspiration by mangrove trees and of longer residence times of water inside the mangroves. This allowed stronger evaporation and higher salt concentration in the soils (Ovalle *et al.* 1990).

Naidoo (1980), studying South African mangroves, also found that *Avicennia* soils contained higher organic matter, higher cation exchange capacity, and exchangeable bases when compared to *Bruguiera* (Rhizophoraceae) soils. Nickerson and Thibodeau (1985) found similar sulfide distribution in Bahamas mangroves, with unvegetated and *Rhizophora* soils showing much higher sulfide content than *Avicennia* soils. These authors showed that *Avicennia* is able to oxidize its rhizosphere in a manner similar to *S. alterniflora*, resulting in comparatively high redox potentials (Thibodeau & Nickerson 1986), while *Rhizophora* soils were not different from the surrounding nonvegetated soil.

Interesting to note is the very high variability of redox conditions and sulfide concentrations in *Avicennia* soils when compared to the other soils. Standard deviations of Eh and HS⁻¹ means were over 145 percent, suggesting constant shifts from oxidic to anoxic conditions. These changing conditions will keep unstable various chemical constituents, particularly trace metals, of the porewater and soils.

Table 2 presents total trace metal concentrations in the different soils studied. The results showed the highest concentrations of all metals occurred in unvegetated mud flat soils and the lowest occurred in

TABLE 2. Total trace metal concentrations ($\mu\text{g/g}$ dry weight) and iron (% dry weight) in mangrove soils compared to salt marsh and mud flats soils in Sepetiba Bay, Rio de Janeiro, Brazil. SD = one standard deviation; N = number of samples of each soil type. Same superscript letter means no significant difference between means of a given metal.

Plant cover		Fe	Zn	Pb	Cu	Cd
<i>Avicennia</i> N = 9	mean	3.3 ^a	311 ^a	17.8 ^a	12.4 ^a	2.8 ^a
	SD	0.3	180	4.7	5.3	1.4
<i>Rhizophora</i> N = 9	mean	3.6 ^a	191 ^a	21.5 ^a	12.5 ^a	3.1 ^a
	SD	0.3	140	2.4	1.2	1.1
<i>Spartina</i> N = 6	mean	1.5 ^b	155 ^b	8.0 ^b	6.3 ^b	1.3 ^b
	SD	0.3	55	1.6	1.2	0.4
Mud flats N = 6	mean	4.5 ^c	823 ^c	39.4 ^c	23.9 ^c	6.9 ^c
	SD	0.4	24	1.7	1.4	0.4

Spartina soils. Soils under both mangrove species showed similar, intermediate concentrations of trace metals. However, they are significantly different from the two other soils.

Trace metals enter these mangrove forests in oxidized forms, in particular iron and manganese oxo-hydroxides, associated with suspended particles during high tide. When reaching the reducing environment inside mangrove forests, they are desorbed from particles and precipitated as sulfides (Lacerda & Rezende 1991, Lacerda *et al.* 1988). Therefore, the more reducing conditions the more efficient is the precipitation and accumulation of trace metals in mangrove soils, at least for those metals that form stable sulfides in reducing environments like the ones studied here (Harbinson 1986a, b; Lacerda *et al.* 1988). This fact explained the higher concentration of trace metals in mud flat and mangrove soils when compared to *Spartina* soils. In the latter, aeration capacity of the grass would dissociate recently-formed metal sulfides, liberating trace metals to the water column (Lacerda

& Rezende 1991). The low organic matter content of *Spartina* soils could render difficult the re-adsorption of the released metals (Lacerda & Abr ao 1984). In fact, metals present in the rhizosphere of this grass are more likely to be fixed in the iron-plaque typical of its roots (Otte *et al.* 1987). Comparing the two mangrove rhizospheres, however, no significant difference is found in the total metal concentrations between *Rhizophora* and *Avicennia* soils, notwithstanding the large differences in both sulfide and redox potentials between the two rhizospheres. These differences, however, are not large enough to affect strongly bound metals. From the results presented in Table 1 a possible explanation for these apparently paradoxical results is the organic matter content of *Avicennia* soils; this is twice the values found for *Rhizophora* soils (24.7 vs 12.5%). This organic matter could act as an adsorbing surface for the trace metals eventually released from sulfides dissociated by the oxidizing activity of *Avicennia* roots. Also, metal-rich iron plaques may form preferentially in *Avicennia* roots rather than in *Rhizophora*

TABLE 3. Exchangeable trace metal concentrations ($\mu\text{g/g}$ dry weight) in mangrove soils compared to salt marsh and mud flats soils in Sepetiba Bay, Rio de Janeiro, Brazil. SD = one standard deviation; N = number of samples of each soil type. Same superscript letter means no significant difference between means of a given metal.

Plant cover		Fe	Zn	Pb	Cu	Cd
<i>Avicennia</i> N = 4	mean	172 ^a	6.6 ^a	0.5 ^a	0.1 ^a	0.1 ^a
	SD	47	1.7	0.1	0.01	0.01
<i>Rhizophora</i> N = 3	mean	35 ^b	1.1 ^b	0.1 ^b	0.01 ^b	0.01 ^b
	SD	6.7	0.7	0.01	0.01	0.01
<i>Spartina</i> N = 5	mean	44 ^b	1.9 ^b	0.1 ^b	0.06 ^b	0.01 ^b
	SD	19	0.9	0.1	0.01	0.01
Mud flats N = 4	mean	43 ^b	2.9 ^b	0.1 ^b	0.01 ^b	0.01 ^b
	SD	4.7	0.7	0.01	0.01	0.01

ra roots (Tanizaki, *pers. comm.*). These iron plaques are well known for their capacity in adsorbing and accumulating trace metals under conditions of waterlogging (Taylor & Crowder 1983, Otte *et al.* 1987, St-Cyr & Crowder 1990). Preliminary research developed in the area showed that over 60 percent of the trace metal content of *Avicennia* roots is bound to iron plaque (Tanizaki, *pers. comm.*). However, this hypothesis is weakened by the low trace metal content of *Spartina* soils which are known to present intense formation of iron plaques (Otte *et al.* 1987). Finally, the redox conditions of *Avicennia* soils were the most variable among all soils studied, suggesting a permanent shift from oxic to anoxic conditions. Since trace metals will constantly move from oxidizable to reduced substrates, this will result in a more dynamic state of trace metal species in *Avicennia* rhizosphere.

Table 3 shows exchangeable trace metal concentrations in the studied soils. Although concentrations in this fraction are very low, particularly for Cu, Pb, and Cd, and therefore difficult to compare statistically, exchangeable trace metal concentrations were significantly higher in *Avicennia* soils than in all other soils which presented similar concentrations of exchangeable trace metals.

The changing redox conditions found for *Avicennia* soils, the higher content of organic matter, and the different stability of iron plaques under such conditions would affect the stability of the trace metal complexes precipitated in *Avicennia* soils. This results in higher trace metal concentrations under exchangeable form. But since these concentrations are much lower than the strongly bound metal concentrations, this phenomenon can not be detected by analyzing for total trace metal concentrations. Previous studies on trace metal concentrations in mangrove plants (Lacerda *et al.* 1986) showed that

Avicennia systematically presents higher concentrations of trace metals in its leaves than *Rhizophora*. This has been accounted for by the salt-filtrating mechanism present in *Rhizophora* roots and by its absence in *Avicennia* (Scholander *et al.* 1955). The present results, however, suggest that trace metals are much more available for plant uptake in *Avicennia* soils and this may also explain the differences in trace metal contents of mangrove leaves previously reported.

The more stable conditions, either oxic in *Spartina* soils, or anoxic in *Rhizophora* and mud flat soils, will result in higher stability of the trace metal complexes precipitated at the rhizospheres, and therefore will decrease exchangeable trace metal concentrations.

In conclusion, we confirm previous reports on the significant differences in porewater chemistry of mangrove soils under different vegetation cover as well as between soils under mangrove and under other vegetation types and unvegetated mud flats. However, although these differences result in different trace metal accumulations between mangrove and salt marsh and unvegetated tidal soils, they are not large enough to create differences between total trace metal concentrations in *Avicennia* and *Rhizophora* soils. However, they were large enough to affect exchangeable trace metal concentrations and therefore their availability to plant uptake.

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