

## Trace metals in mangrove seedlings: role of iron plaque formation

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### Abstract

Metal-rich mineral deposits on the roots of aquatic plants, denominated iron plaques, may moderate the uptake of essential, but potentially toxic metals by roots. We investigated the iron plaque formation on the fine, nutritive roots of mangrove seedlings growing in contrasting environments (oxidizing sand flat sediments and reducing mangrove forest sediments) in southeast Brazil. The results indicate that *Avicennia schaueriana*, *Laguncularia racemosa*, and *Rhizophora mangle* seedlings developed an efficient exclusion of Fe, Mn, and Zn through iron plaque formation. This process seems to be influenced substantially by species-specific responses to environmental conditions. While Fe and Zn translocation to leaves appear to be suppressed by accumulation within root tissues, this did not appear to occur for Mn, suggesting that Mn trapping in rhizosphere sediments and iron plaque formation are the main mechanisms responsible for the Mn exclusion from the organism level. In addition to factors well recognized as affecting mangrove seedling development (e.g., salinity stress and nutrient availability), the mediation of trace metal uptake by iron plaque formation possibly contribute to determine the seedling adaptability to waterlogged conditions.

### Introduction

Plants growing in waterlogged sediments are frequently exposed to sediment anoxia, which results in a build up in the porewater concentrations of potentially toxic reduced solutes (e.g., Fe(II), Mn(II), and sulfides). However, many wetland plants are able to induce changes in the sediment chemistry through air transport from aboveground to belowground organs, which promotes oxygen losses from roots, oxidizing rhizosphere sediments (Armstrong 1967; Green and Etherington 1977; Smolders and Roelofs 1996). A process associated with oxygen release by roots that can increase the plant tolerance to flooding conditions is the oxidation of porewater reduced constituents. This

induces a partial precipitation of trace metals under oxidized forms in rhizosphere sediments (Caçador et al. 1996; Doyle and Otte 1997; Sundby et al. 1998) and on the root surfaces, creating iron-rich root coatings, generally called iron plaques (Koch and Mendelssohn 1989; Otte et al. 1989; Lacerda et al. 1992). Metal precipitation in rhizospheres may generate gradients of decreasing metal bioavailability toward roots, while the co-precipitation of different metals on root surfaces may mediate the metal uptake by plants through its retention in iron plaques, which may also act as physical barriers to metal uptake. Several studies have indicated the relevance of factors as the sediment physicochemical conditions and the speciation, amount, and binding strength of metals to sediment solid-phase for the formation of iron plaques

(Mendelssohn et al. 1995; Smolders and Roelofs 1996; St-Cyr and Campbell 1996).

This adaptive mechanism may be presented by a large variety of wetland plants, including those from the mangrove genera *Aegicerus* (Ong Che 1999), *Avicennia* (Lacerda et al. 1993), *Kandelia* (Chiu and Chou 1993) and *Rhizophora* (Silva et al. 1990). Mangrove plants are able to colonize highly diversified environmental conditions, often under strong physicochemical gradients, including areas exposed to trace metal pollution (e.g., Sadiq and Zaidi 1994; Ong Che 1999; Machado et al. 2002). Many studies have been conducted on mangrove seedling adaptability to metal loading (e.g., Walsh et al. 1979; Chiu et al. 1995; MacFarlane and Burchett 2000), but the metal exclusion by seedlings through iron plaque formation has not been investigated in natural conditions. This study evaluates the formation of iron plaques and the concentration of essential, but potentially toxic metals (Fe, Mn, and Zn) by fine, nutritive roots and leaves of *Avicennia schaueriana* Stapf and Leech., *Laguncularia racemosa* (L.) Gaertn., and *Rhizophora mangle* L. seedlings, growing in two contrasting sedimentary environments in Coroa Grande, Sepetiba Bay, southeast Brazil. Comparisons between results from different sites were used in a preliminary evaluation of possible influences of environmental conditions, and species-specific responses to such conditions, on metal exclusion from roots through iron plaque formation.

### Materials and methods

Sepetiba Bay mangrove forests extend over about 35% of the bay perimeter (Barcellos et al. 1997), and are dominated by the three studied mangrove species. Sampling was conducted in dry season (June 1996) in two depositional environments of Coroa Grande, located on the north shore of Sepetiba Bay (Figure 1). This industrialized area experiences a high loading of many anthropogenic metals, particularly Zn and Cd (Barcellos and Lacerda 1994), although anthropogenic Mn loadings has not been identified in Sepetiba Bay, and sources of this element are probably natural (Lacerda et al. 1987). Sepetiba Bay area has an annual rainfall of nearly 2300 mm, with a mean

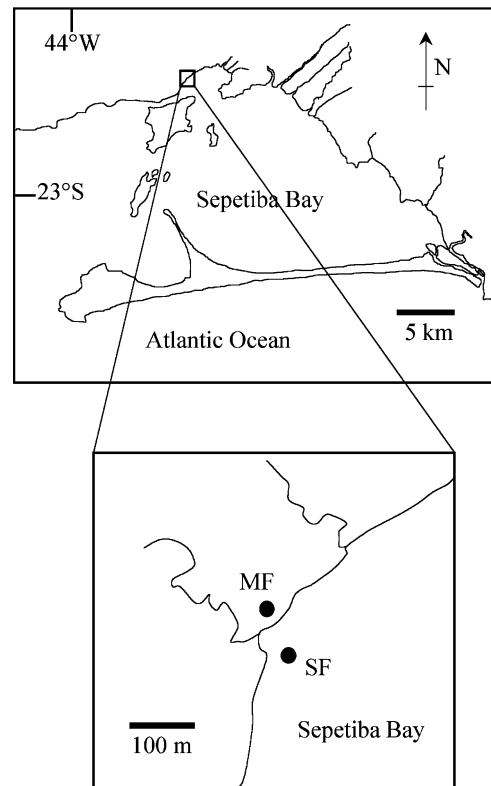


Figure 1. Location of study area in Sepetiba Bay, southeast Brazil. MF: mangrove forest station; SF: sand flat station.

June rainfall of 114 mm. Gueiros et al. (2003) have demonstrated substantial seasonality in porewater physicochemical conditions within Coroa Grande intertidal sediments. For example, lower salinity and acidity have been observed in mangrove-colonized muddy sediments and bare sandy sediments, in the dry season. On the other hand, lower redox potentials have been generally recorded during the rain season, in both environments.

Sampling sites were established inside a mangrove forest (composed by *A. schaueriana*, *L. racemosa*, and *R. mangle*) and an unvegetated sand flat adjacent to the seaward edge of the forest, with an occasional presence of mangrove seedlings. In each site were collected 6–12 seedlings of *A. schaueriana* (22–35 cm height), *L. racemosa* (15–30 cm height), and *R. mangle* (32–62 cm height). Roots were washed with estuarine water and distilled water to remove sediments. Four surface (0–10 cm depth) sediment and porewater samples were collected adjacently to seedling locations. Sediment cores

were collected through acrylic tubes. Porewater was collected through vacuum porewater samplers made of polyethylene tubes with ceramic bottom caps (Lacerda et al. 1993). Porewater redox potential (Eh) and pH were determined with portable electrodes and salinity was measured by refractometry. In the laboratory, leaves and fine roots (<2 mm diameter) were separated from the shoots for analysis and roots with senescence signs or dead were discarded. A root was considered as dead if it was not attached to the plant or showed a limp, necrosed appearance. It was used a ditionite–citrate–bicarbonate (DCB) solution for iron plaque extraction from the roots (Taylor and Crowder 1983). A half of fresh root samples was processed for iron plaque extraction (through agitation in the DCB solution for 3 h at room temperature), while the other half was processed directly for metal analysis. In order to obtain sufficient mass for analysis, composite samples were often made with roots and leaves from different plants. DCB-washed roots were rinsed with distilled water and also processed for analysis. Iron plaque concentrations were considered as the differences between untreated and DCB-washed root concentrations. This indirect procedure was conducted to avoid the interference of sodium compounds from the DCB solution in the metal analysis (Taylor and Crowder 1983; Koch and Mendelsohn 1989). Replicates of root samples (untreated and DCB-washed) and leaf samples were oven-dried (60 °C for 24 h) and ashed (450 °C for 24 h). Ashes were digested in concentrated HNO<sub>3</sub> and concentrations of Fe, Mn, and Zn were determined by atomic absorption spectrophotometry (AAS). DCB-washed roots concentrations are considered as internal root tissue concentrations and the proportion of iron plaque concentrations in relation to untreated roots concentrations is used to evaluate the degree of metal exclusion by iron plaque formation.

In order to allow inter-comparisons between metal concentrations in sediments from the texturally contrasting environments studied here, subsamples of bulk sediments were sieved to separate the fraction smaller than 63 μm (silt and clay particles), minimizing errors due to the presence of roots and sand grains on metal analysis (e.g., Lacerda et al. 1991, 1992, 1993; Gueiros et al. 2003), and dried (60 °C for 24 h). Bulk sediments

were also dried (60 °C for 24 h) and used for gravimetric determination of organic matter content, after combustion (450 °C for 24 h). Extraction procedures were designed to fractionate the metal content according to its binding strength to sedimentary phases (Lacerda et al. 1992, 1993). Sediment subsamples (<63 μm fraction) were submitted to an extraction in a 0.5 N HCl solution. After shaking at room temperature for 16 h, such acid suspensions were filtered. Metals in these extracts were defined as the weakly bound fraction in sediments, assumed as the potentially bioavailable fraction. This fraction probably comprises geochemically reactive carbonates, amorphous oxyhydroxides, amorphous sulfides, and labile organic compounds at different proportions with sediment depth and between different environments. Sediments retained in the filters were submitted to a digestion in a mixture of concentrated HNO<sub>3</sub> and HF (Lacerda et al. 1992, 1993). Metals in these extracts were defined as the strongly bound fraction in sediments, which includes metals in lattice positions, refractory oxyhydroxides, refractory sulfides, and bound to refractory organic matter. Metal concentrations in all extracts were determined by AAS. The sum of weakly and strongly bound fractions was assumed as the total concentrations in sediments.

## Results

### *Sediment porewater and solid phase analyses*

All analyses of porewater variables and contents of organic matter and fine sediments showed significant differences between sites (Table 1). Sand flat porewater was oxidizing, whereas mangrove forest porewater was reducing. A low, but significant difference in porewater acidity was recorded, with slightly lower pH values in mangrove forest sediments. Organic matter content and percentage of fine sediments were significantly higher in the forest environment, as well as salinity was slightly, but significantly greater in mangrove forest porewater. Sand flat sediments showed significantly higher weakly bound concentrations for all elements, but while Mn total concentrations were significantly greater in sand flat sediments, total concentrations of Fe and Zn were not significantly

Table 1. Major physicochemical variables in pore waters, organic matter content (OM), and <63  $\mu\text{m}$  fraction content of Coroa Grande intertidal sediments.

	Sand flat	Mangrove forest	ANOVA <i>P</i> -level
Eh (mV)	+7.0 $\pm$ 1.2	-129 $\pm$ 29	<0.001
pH	7.4 $\pm$ 0.1	7.1 $\pm$ 0.2	<0.05
Salinity	22 $\pm$ 1	25 $\pm$ 1	<0.01
OM (%)	1.9 $\pm$ 0.1	11.2 $\pm$ 1.2	<0.001
<63 $\mu\text{m}$ (%)	3.9 $\pm$ 2.2	25.8 $\pm$ 5.4	<0.001

Means  $\pm$  1 SD and the significance of a comparison of means by one-way ANOVA are given ( $n = 4$ ).

Table 2. Total and weakly bound concentrations of metals in the <63  $\mu\text{m}$  fraction of Coroa Grande intertidal sediments.

	Sand flat	Mangrove forest	ANOVA <i>P</i> -level
Total concentration			
Fe ( $\text{mg g}^{-1}$ )	39.7 $\pm$ 2.7	43.4 $\pm$ 5.0	NS
Mn ( $\mu\text{g g}^{-1}$ )	890 $\pm$ 54	700 $\pm$ 69	<0.001
Zn ( $\mu\text{g g}^{-1}$ )	1060 $\pm$ 69	970 $\pm$ 44	NS
Weakly-bound concentration			
Fe ( $\text{mg g}^{-1}$ )	5.80 $\pm$ 0.22 (15)	3.30 $\pm$ 0.67 (8)	<0.001
Mn ( $\mu\text{g g}^{-1}$ )	610 $\pm$ 27 (69)	390 $\pm$ 30 (56)	<0.001
Zn ( $\mu\text{g g}^{-1}$ )	660 $\pm$ 24 (62)	480 $\pm$ 38 (49)	<0.001

NS = not significant at  $p < 0.05$ . Means  $\pm$  1 SD and the significance of a comparison of means by one-way ANOVA are given ( $n = 4$ ). Percentage of metal concentrations in the fraction potentially bioavailable in relation to total metal concentrations are given in parentheses.

different among sites (Table 2). The potentially bioavailable concentrations constituted a greater portion of total concentrations in sand flat sediments for all metals, particularly for Fe, although the weakly bound fraction of this element present a lower relative contribution for total metal concentrations, in comparison with other metals (Table 2).

#### Metal concentration and exclusion by seedlings

Iron determinations in leaves, untreated roots, and DCB-washed roots, and estimation in iron plaques are shown in Table 3. Iron concentrations in studied plant compartments were similar among sites or higher in sand flat seedlings, as observed for untreated roots of *A. schaueriana*, *R. mangle* root tissues, and leaves of *L. racemosa* and *R. mangle*.

The highest untreated root and iron plaque Fe concentrations were showed by *A. schaueriana* in the sand flat, whereas the lower values of them were presented by the same species in the forest site. *A. schaueriana* roots had a higher degree of Fe exclusion in the sand flat, while this estimation showed close values for *L. racemosa* and for *R. mangle* in the two sites. Root tissue Fe concentrations were one order of magnitude higher than those of leaves.

Manganese determinations in leaves, untreated roots, and DCB-washed roots, and estimation in iron plaques are shown in Table 4. *A. schaueriana* presented higher untreated root and iron plaque Mn concentrations in the sand flat, maintaining similar Mn concentrations in the root tissues among sites. In opposition, *L. racemosa* seedlings from the forest site presented greater untreated root and iron plaque Mn concentrations, but also presented similar root tissue concentrations among sites. *A. schaueriana* roots showed a greater Mn exclusion in the sand flat, in opposition to *L. racemosa* roots. *R. mangle* seedlings did not present distinction in untreated root and iron plaque Mn levels between sites, but its root tissue concentrations did, with higher values in the forest site. Exclusion of Mn by *R. mangle* roots was similar in both sites. Seedling leaves showed Mn levels similar to or greater than root tissues. Only *R. mangle* presented a significant site effect for leaf Mn content, higher in the sand flat.

Zinc determinations in leaves, untreated roots, and DCB-washed roots, and estimation in iron plaques are shown in Table 5. Untreated root and iron plaque Zn contents in *A. schaueriana* seedlings were higher in the sand flat. The same variables did not differ among sites for *L. racemosa*, as observed for untreated root concentrations of *R. mangle*. It was observed a higher Zn accumulation in the plaques of *R. mangle* seedlings from mangrove forest. All species presented significantly higher root tissue levels of Zn in the sand flat. *A. schaueriana* roots presented a slightly greater external proportion of Zn in the sand flat, while this proportion was greater in the forest site for *L. racemosa* and *R. mangle* roots. Leaf Zn concentrations were very lower than respective root tissue levels. Only *L. racemosa* showed a significant site effect for Zn concentrations in leaves, greater in the sand flat.

Table 3. Iron concentrations in leaves, fine roots (untreated and DCB-washed roots), and iron plaques of mangrove seedlings.

	Leaves	Untreated roots	DCB-washed roots	Iron plaque	Percentage in plaque
<i>A. schaueriana</i>					
Sand flat	110 ± 13	14900 ± 1200	2300 ± 1600	12,600	85
Mangrove forest	100 ± 12	3100 ± 14	1200 ± 90	1900	62
ANOVA <i>P</i> -level	NS	<0.001	NS		
<i>L. racemosa</i>					
Sand flat	150 ± 38	8200 ± 1400	1900 ± 590	6400	77
Mangrove forest	65 ± 13	7100 ± 500	1400 ± 90	5700	87
ANOVA <i>P</i> -level	<0.01	NS	NS		
<i>R. mangle</i>					
Sand flat	155 ± 17	9300 ± 890	1600 ± 180	7700	83
Mangrove forest	92 ± 16	7700 ± 140	970 ± 240	6700	87
ANOVA <i>P</i> -level	<0.01	NS	<0.05		

NS = not significant at  $P < 0.05$ . Means ± 1 SD ( $\mu\text{g g}^{-1}$ ) and the significance of a comparison of means by one-way ANOVA are given ( $n = 3$  for sand flat root samples and 4 for forest root samples and leaf samples). Percentage of Fe concentrations in iron plaques in relation to untreated roots concentrations are also given.

Table 4. Manganese concentrations in leaves, fine roots (untreated and DCB-washed roots), and iron plaques of mangrove seedlings.

	Leaves	Untreated roots	DCB-washed roots	Iron plaque	Percentage in plaque
<i>A. schaueriana</i>					
Sand flat	86 ± 29	540 ± 58	84 ± 15	450	84
Mangrove forest	110 ± 25	350 ± 13	100 ± 8.1	250	70
ANOVA <i>P</i> -level	NS	<0.01	NS		
<i>L. racemosa</i>					
Sand flat	92 ± 25	210 ± 70	72 ± 24	140	65
Mangrove forest	71 ± 5.8	450 ± 10	52 ± 4.9	400	88
ANOVA <i>P</i> -level	NS	<0.05	NS		
<i>R. mangle</i>					
Sand flat	162 ± 11	420 ± 28	54 ± 18	360	87
Mangrove forest	100 ± 25	490 ± 56	97 ± 13	390	80
ANOVA <i>P</i> -level	<0.01	NS	< 0.05		

NS = not significant at  $P < 0.05$ . Means ± 1 SD ( $\mu\text{g g}^{-1}$ ) and the significance of a comparison of means by one-way ANOVA are given ( $n = 3$  for sand flat root samples and 4 for forest root samples and leaf samples). Percentage of Mn concentrations in iron plaques in relation to untreated roots concentrations are also given.

## Discussion

### *Environmental conditions*

Diverse metal behavior (and consequent bioavailability) in sediments might be expected between studied sites, which is supported by presented results. Coarser, organic matter-poor sand flat sediments have better percolation of water, allowing a higher pH, lower salinity, and oxidizing conditions, whereas in mangrove forest sediments the lower diffusion of water and gases through fine particles and large amounts of organic matter favor reducing conditions due to bacterial sulfate

reduction (Harbison 1986; Clark et al. 1998). The evapotranspiration of mangrove trees may contribute to a greater salinity (Lacerda et al. 1993) and the production of acidity associated with oxygen release from tree roots (due to enhanced organic matter oxidation, nitrification, and sulfide oxidation; Middelburg et al. (1996)) may contribute for the slightly lower pH observed in mangrove forest sediments.

Sand flat sediments showed higher weakly bound metal concentrations and a slightly greater contribution of the weakly bound fraction for the total concentrations, suggesting a lower metal bioavailability in mangrove forest sediments. This

Table 5. Zinc concentrations in leaves, fine roots (untreated and DCB-washed roots), and iron plaques of mangrove seedlings.

	Leaves	Untreated roots	DCB-washed roots	Iron plaque	Percentage in plaque
<i>A. schaueriana</i>					
Sand flat	39 ± 19	690 ± 280	270 ± 130	420	61
Mangrove forest	35 ± 7.7	140 ± 10	75 ± 8.0	61	45
ANOVA <i>P</i> -level	NS	<0.01	<0.01		
<i>L. racemosa</i>					
Sand flat	100 ± 13	570 ± 180	360 ± 190	210	39
Mangrove forest	44 ± 9.5	350 ± 30	87 ± 15	270	75
ANOVA <i>P</i> -level	<0.001	NS	<0.01		
<i>R. mangle</i>					
Sand flat	16 ± 2.4	370 ± 73	220 ± 31	150	39
Mangrove forest	14 ± 1.2	330 ± 78	32 ± 9.0	300	89
ANOVA <i>P</i> -level	NS	NS	<0.001		

NS = not significant at  $P < 0.05$ . Means ± 1 SD ( $\mu\text{g g}^{-1}$ ) and the significance of a comparison of means by one-way ANOVA are given ( $n = 3$  for sand flat root samples and 4 for forest root samples and leaf samples). Percentage of Zn concentrations in iron plaques in relation to untreated roots concentrations are also given.

assumption is in agreement with major biogeochemical process controlling the availability of the trace metals in reducing mangrove sediments, which are generally bound to insoluble sulfides and organic matter (Lacerda et al. 1991; Clark et al. 1998). As an exception, Mn is preferably accumulated in oxidized forms within sediments (Lacerda et al. 1999), that are susceptible to post-depositional remobilization under reducing conditions and to plant uptake (Alongi et al. 1998). In fact, surface sediment layers frequently have unstable redox conditions, depending on sediment textural and chemical composition, flooding, and season (Harbison 1986; Clark et al. 1998), favoring the occurrence of metastable metal compounds (Lacerda et al. 1991; Gueiros et al. 2003), which may explain the elevated contribution of the weakly bound fraction for the total concentrations of Mn and Zn. Moreover, the greater Mn levels observed in the sand flat are also attributable to a diagenetic Mn remobilization from the reducing deeper sediment layers and accumulation in oxidized surface layers and a Mn transference through tidal fluxing from more reducing sediments adjacent to the sand flat (Harbison 1986; Lacerda et al. 1999). A sequential extraction of Fe performed in mangrove sediments from Sepetiba Bay showed that refractory compounds represent ca 95% of total Fe concentrations, probably in the form of detrital minerals and pyrite, even within the surface layers (Lacerda et al. 1991). This trend probably caused the observed low contribution of

the weakly bound fraction for the total concentrations of Fe.

St-Cyr and Campbell (1996) demonstrated that the sediment geochemistry can be more important for the formation of iron plaques than species-specific (physiological) differences of freshwater submerged plants growing in the same environmental conditions. However, results showed here indicated that the main effects of iron plaque formation (metal accumulation on the root surfaces and exclusion from the root tissues) can be considerably different among mangrove species that co-exist in the same environments. Such differences may be attributed to a coupling between the influence of sediment geochemical heterogeneity within a site and the influence of seedling physiological and anatomical characteristics involved in metal exclusion mechanisms (e.g., Youssef and Saenger 1996).

#### *Mechanisms to moderate deleterious effects of metals*

Wetland plants may present metal precipitates on cell walls and intercellular lacunas of root tissues, probably with an analogous role to that of iron plaques (e.g., Green and Etherington 1977; Ye et al. 1998). Smolders and Roelofs (1996) indicated that internal Fe precipitates outside the root endodermis can prevent Fe toxicity inside the stele and excessive internal Fe precipitation cause early death of root hairs, which probably explains the absence of *Stratiotes aloides* L. in sites with high Fe

levels in porewater. MacFarlane and Burchett (2000) demonstrated that roots and leaves of *Avicennia marina* (Forsk.) Vierh. seedlings concentrated most of their Zn, Cu, and Pb loads in cell walls. Such seedlings displayed an apoplastic metal transport and excreted metals from the leaf tissue. For the studied seedlings, it appears that a preferential accumulation of Fe and Zn within root tissues may partially suppress its translocation to leaves. This did not appear to occur for Mn, which had a greater translocation from nutritive roots to leaves (Tables 3–5). Thus, it is apparent that the formation of iron plaques and the trapping by rhizosphere sediments (both affected by the oxygen release by roots) are the main mechanisms responsible for the Mn exclusion from the organism level. Previous studies have demonstrated a relatively low translocation of most trace metals (Walsh et al. 1979; Chiu et al. 1995; MacFarlane and Burchett 2000), but a higher translocation of Mn (Tam and Wong 1997) from roots to leaves of mangrove seedlings.

The evaluation of the net result of metal retention processes in rhizosphere sediment, iron plaques, and root tissues is essential to elucidate how mangrove plants may tolerate the metal loading in waterlogged conditions. In addition to factors widely recognized as affecting mangrove seedling development, such as sediment nutrient availability (e.g., McKee 1995; Koch 1997; Duarte et al. 1998) and physiological stress related to flooding and porewater salinity (e.g., Jiménez and Sauter 1991; McKee 1993, 1995), the moderation of the uptake of potentially toxic metals, from the organism to the cellular levels (e.g., MacFarlane and Burchett 2000), may possibly contribute to determine the performance of mangrove seedlings. Tanizaki (1994) estimated that over 60% of total Fe, Mn, and Pb concentrations, and considerable fractions of Zn (25–62%) and Cu (18–47%) concentrations, of roots of *A. schaueriana* and *R. mangle* trees growing in Sepetiba Bay were iron plaque deposits, and suggested that the formation of such coatings may be more intense in seedlings, as an adaptation for the colonization of waterlogged substrates. Although our results demonstrated preliminarily that seedlings developed substantial metal exclusion through iron plaque formation on fine roots, further research is necessary to evaluate the relative contribution of metal exclusion mechanisms for the

mangrove seedling adaptability to waterlogged sediments.

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