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Manganese Behavior at the Sediment-Water Interface in a Mangrove Dominated Area in Sepetiba Bay, SE Brazil

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ABSTRACT

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We investigated the behavior of Mn in intertidal environments in a mangrove dominated area in Sepetiba Bay, southeast Brazil, to characterize the contribution of diagenetic remobilization to the Mn cycling and bioavailability near the sediment-water interface. Sediment cores and pore water were collected in a mixed mangrove forest and in adjacent unvegetated mud and sand flats, during the rain season (November 1995) and the dry season (June 1996). Redox conditions control the distribution of solid-phase Mn in sediment, associated with diffusional and non-diffusional dissolved Mn transport in pore water. Diverse conditions observed in the studied environments (*e.g.* mangrove forest rhizosphere and high permeability of sand flat sediments), may remarkably affect the Mn vertical distribution within sediments, and contribute to its seasonal variability. Solid-phase Mn variability was strongly associated with weakly-bound (0.5 M HCl-extractable) phases, which composed most of solid-phase Mn in surface Mn-enriched sediment layers and nearly half of solid-phase Mn in sub-surface Mn-depleted layers, in all environments. The dynamic nature of Mn in this study, particularly in muddy sediments, suggests that: (i) Mn transference from sediments to overlying waters and its transport to adjacent environments occurs, (ii) Mn is present as bioavailable forms within the sediments, and (iii) Mn may potentially have a strong influence on the behavior of other elements (*e.g.* metal pollutants) within intertidal sediments.

ADDITIONAL INDEX WORDS: *Bioavailability, biogeochemistry, diagenesis, intertidal sediments, pore water, remobilization.*

INTRODUCTION

The reducing conditions that develop in mangrove sediments, because of microbial decomposition of organic matter, high sediment accretion rates, high content of organic matter, and high content of fine sediment particles, result in potentially high accumulation of trace metals. Although the importance of mangrove ecosystems on trace metal biogeochemistry has been demonstrated, and many studies have characterized possible factors which affect the trace metal distribution in sediments colonized by mangrove vegetation (HARBISON, 1984, 1986; CHIU and CHOU, 1991; LACERDA *et al.,* 1993; SPRATT and HODSON, 1994; TAM *et al.,* 1995; MACKEY and MACKAY, 1996; BADARUDEEN *et al.,* 1996; CLARK *et al.,* 1997, 1998), the post-depositional mobility of trace metals in these environments is still poorly understood.

Much interest has been focused on Mn cycling in response to diagenetic processes in sedimentary environments (LANDING and BRULAND, 1980; SUNDBY *et al.,* 1981; THAMDRUP *et al.,* 1994; BRYANT *et al.,* 1997) and on the behavior of other trace elements coupled to Mn geochemistry (CORNWELL, 1987; SHAW *et al.,* 1990; GAGNON *et al.,* 1997; DONAHOE and LIU, 1998). Sediment redox stratification may result in remobilization of Mn from reducing subsurface sediment layers and its enrichment in the oxidizing surface layers (*e.g.* GOBEIL *et al.,* 1997). This may cause an upward co-migration and concentration of other elements into the upper oxidized layer (*e.g.* Co, Cu, Zn, Ni and Mo), where they may coprecipitate with Mn oxides (SHIMMIELD and PEDERSEN, 1990). The upward diagenetic remobilization and sediment resuspension processes may result in Mn mobilization from sediments to overlying waters (LANDING and BRULAND, 1980; HUNT, 1983; THAMDRUP *et al.,* 1994), where Mn transport between adjacent sedimentary environments may occur (SUNDBY *et al.,* 1981; HARBISON, 1986; LACERDA *et al.,* 1999). Furthermore, diagenetic remobilization may setup an internal recycling of Mn (LACERDA, 1994).

The Mn migration and accumulation near the sediment-

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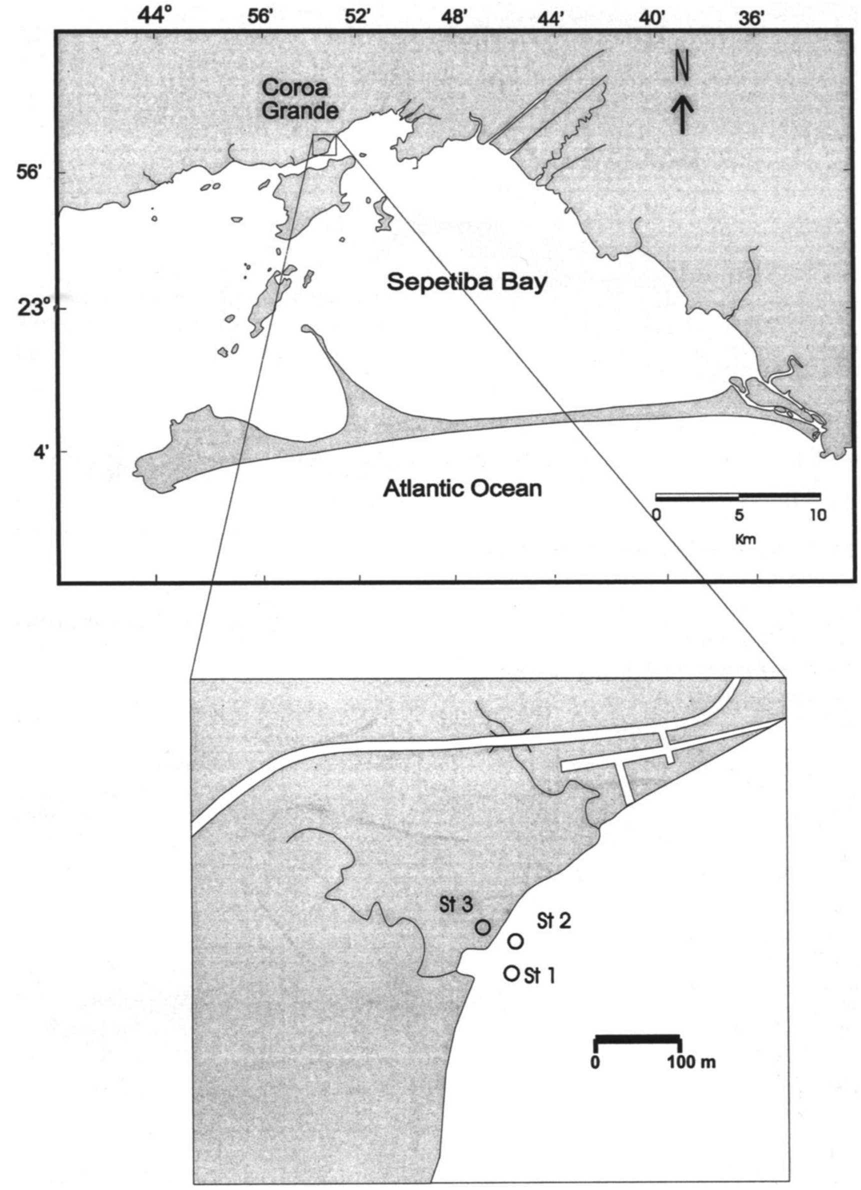

Figure 1. Location of study area and sampling stations in Coroa Grande, Sepetiba Bay, Southeastern Brazil. St 1: sand flat station, St 2: mud flat station, St 3: mangrove forest station.

water interface may make Mn within sediments available for biotic uptake (LACERDA, 1994). Because Mn sulfides are generally unstable in reduced sediments (FÖRSTNER and WITTMAN, 1979), Mn commonly presents an atypical behavior in mangrove sediments, with a higher mobility and bioavailability than most other trace metals, that form more stable metal sulfides (LACERDA, 1998).

This paper investigates the behavior of Mn in short profiles of sediments and pore water to characterize the contributions of diagenetic remobilization in Mn cycling and bioavailability within the sediment-water interface of intertidal environments of a mangrove dominated area in Sepetiba Bay, southeast Brazil.

MATERIAL AND METHODS

Study Area

Sampling was conducted in rain season (November 1995) and in dry season (June 1996), in three depositional environments of Coroa Grande, located on the North shore of Sepetiba Bay (Figure 1), Rio de Janeiro State, Southeastern Brazil. The Sepetiba Bay area has a high seasonality in rainfall. An annual rainfall of nearly 2,300 mm is recorded, with a mean November rainfall of 305 mm, and a mean June rainfall of 114 mm (DENAEE, 1997). This industrialized area experiences high trace metal loads (LACERDA *et al.,* 1987; PATCHINEELAM and SOUZA, 1987; BARCELLOS *et al.,* 1997). However, anthropogenic Mn loadings has not been identified in Sepetiba Bay water and sediments, and sources of this element are probably natural (LACERDA *et al.,* 1987).

The Sepetiba Bay mangrove forests extend over about 35% of the Bay perimeter (BARCELLOS *et al.,* 1997), and are dominated by *Avicennia schaueriana* Stapf & Leech., *Laguncularia racemosa* (L.) Gaertn.f. and *Rhizophora mangle* L. Sediment and pore water sampling stations were established inside a typical fringe mangrove forest (with mixed vegetation of the three dominant species), and in unvegetated areas of a mud flat and a sand flat adjacent to the seaward edge of the mangrove fringe (Figure 1).

Sampling and Physicochemical Analysis

During the low tide, pore water was collected by vacuum pore water samplers made of polyethylene tubes with ceramic bottom caps (see LACERDA *et al.,* 1993; ARAGON *et al.,* 1999). At each sampling station, three different depths were sampled: surface (0–5 cm), subsurface (10–15 cm) and deep (25–30 cm). The method used allows a sequential sampling of pore water, without sediment disturbance between sampling extractions (ARAGON *et al.,* 1999). Vacuum was created immediately after inserting the tubes, by means of hand pumps. A 30–40 min sampling time gave approximately 100–200 mL of pore water. Duplicate samples of the pore water were taken for analysis of dissolved Mn and physicochemical characterization. Pore water samples used for Mn analysis were stored in acid-cleaned polyethylene flasks and acidified (1% equivalent volume of 6 M HCl; GUEIROS, 1997; LACERDA *et al.,* 1999). Pore water redox potentials (Eh) and pH were measured with portable electrodes and salinity was estimated by refratometry. Analytical errors of pH and salinity analysis were better than 6%, while Eh determinations generally showed errors within 20%. Two sediment cores were collected at each station by the insertion of acid-cleaned acrylic tubes (8 cm i.d.) into the sediment. Sediment cores were visually examined, subsampled and the subsamples were packed in acid-cleaned plastic bags. Sediments and acidified pore water samples were kept frozen prior to analysis.

Dissolved Mn Analysis

Dissolved Mn determinations in some sand flat pore water samples required a pre-concentration step. To pre-concentrate the samples, Mn concentrations of duplicate 100-mL samples were complexed with 8-hidroxiquinoline (0.06%) in chloroform, followed by extraction into 7 M HNO_3, resulting a final volume of 10 mL (LANDING and BRULAND, 1980; RESING and MOTTL, 1992; LACERDA *et al.,* 1999). Dissolved Mn concentrations in duplicate 100-mL samples of mangrove forest and mud flat pore water were analyzed without pre-concentration. Dissolved Mn concentrations in all samples were analyzed by conventional flame atomic absorption spectrophotometry (AAS). Detection limit was derived from the calibration curves, according to Miller and Miller (1993). The detection limit of the pre-concentration method was 1.8 $\mu g\ L^{-1}$, and samples were within 11% from each other.

Solid-Phase Mn Analysis

To characterize sediments, samples of the surface layers (integrated to a depth of 10 cm) were dried at 60 °C for 24 h, and the organic matter content was estimated gravimetrically after combustion at 450 °C for 24 h (LACERDA *et al.,* 1993; GUEIROS, 1997). Fresh sediments were sieved to separate and determine the fraction smaller than 63 μm (silt and clay particles). Sieved sediments were used for Mn analysis to minimize errors due to presence of roots and sand grains.

Duplicates of 1.0 g of dried sediment (< 63 μm fraction) were leached with a weak-acid solution (20 mL of 0.5 M HCl), after shaking for 12 h at room temperature, and filtered (GUEIROS, 1997; LACERDA *et al.,* 1999); the Mn concentrations in the extracts are considered as the 'weakly-bound fraction'. The weakly-bound concentration is considered as the potentially bioavailable Mn. Although it might be expected a high variability between the sediment geochemical composition in different environments, weakly-bound phases are probably composed of geochemically reactive carbonates, amorphous oxihydroxides, amorphous sulfides, and labile organic compounds at different proportions with sediment depth and between different environments. Concentrations in residual sediments retained by the filters are considered as 'strongly-bound fraction', including all Mn occluded in lattice positions, refractory oxihydroxides, refractory sulfides, and Mn bound to refractory organic matter. Strongly-bound concentrations were determined after an acid digestion in a mixture of concentrated HNO_3, HF, and HCl (3:2:2 v/v/v) at 100 °C until dryness (FISZMAN *et al.,* 1984; GUEIROS, 1997). The residue was re-dissolved in 30 mL of 0.5 M HCl. Solid-phase Mn concentrations were analyzed by AAS, and the detection limit was 0.01 $\mu g\ g^{-1}$. Reproducibility between duplicate analysis of sediment subsamples was better than 15%. Results of sediment analysis of the two cores from each station were averaged per depth to represent and describe the general concentration trends of Mn vertical distribution within a station (*e.g.* DONAHOE and LIU, 1998). Total Mn concentrations were obtained by the sum of the weakly-bound and the strongly-bound fractions.

RESULTS AND DISCUSSION

Sediment Description

Major characteristics of sediments are shown in Table 1. Changes in the sediment color from brown hues to gray or black hues have been attributed to the transition from oxidized to reduced (sulfidic) conditions (SUNDBY *et al.,* 1981; HARBISON, 1984; PAYNE *et al.,* 1997; CLARK *et al.,* 1998). Sand flat sediments showed consistently lighter hues with depth than muddy sediments (mud flat and mangrove forest sediments). Brown to light gray colors were observed in sand flat sediments, with highly oxidized layers (light brown colored) up to nearly 3–4 cm depth. While mud flat surface oxidized layers (brown colored) extended to nearly 4–6 cm depth, in the mangrove forest the oxidized layers extended to nearly 6–8 cm depth. The brown to dark gray colors observed in mud flat and mangrove forest sediment profiles probably reflect a more reduced and organic-rich environment than sand flat

Table 1. *Major descriptive features of sediment cores from Coroa Grande, Sepetiba Bay. Values of the organic matter (OM) content in surface sediments and the silt-clay content of top and bottom sediments are ranges of results from the analysis of duplicate cores.*

	Sand Flat	Mud Flat	Mangrove Forest
Core description	Coarse-grained, sandy sediments; light brown color layer to a depth of 3–4 cm; brown to light gray color below this depth.	Fine-grained, muddy sediments; brown color to a depth of 4–6 cm; gray to black color below this depth; cyanophycea film covering core surface.	Fine-grained, muddy sediments; brown color to a depth of 6–8 cm; gray to black color below this depth; dense rhizosphere between about 2–12 cm.
OM (%)	1.6–2.7	18.1–19.2	15.9–17.6
Silt-clay (%)			
Core top	5.5–16.6	33.1–72.8	33.3–61.4
Core bottom	0.35–2.22	14.4–19.6	13.3–26.4

sediments. These observations are in agreement with gravimetric measurements of the organic matter content in surface (0–10 cm depth) sediments (Table 1), where organic matter contents were comparable to the muddy environments, whereas much lower organic contents were present in sand flat sediments.

Distinctive grainsize distributions were observed between the coarse-grained (sand flat) cores and the fine-grained (mangrove forest and mud flat) cores (Table 1). No consistent grainsize differences between the muddy environments were observed, however a consistent decrease in the content of fine particles (< 63 μm) was observed with depth in the sandy and the muddy environments. These changes in fine contents suggest recent changes in the sedimentation regime in Coroa Grande coast. Because pore water circulation and the flux of pore water constituents across the sediment-water interface will be affected by sediment permeability (*e.g.* SHUM and SUNDBY, 1996), the highly contrasting sediments observed between the sandy and muddy environments will tend to reflect different sedimentationary processes. Therefore, a substantial effect from the physical characteristics of the sediment may be expected on redox conditions (*e.g.* PAYNE *et al.,* 1997) and on Mn distribution in different depositional environments (HARBISON, 1984; BADARUDEEN *et al.,* 1996).

Mangrove forest sediments contained roots below 1–3 cm depth, with a root mat horizon (rhizosphere) reaching more than 20 cm depth; and highest root density occurred generally at a subsurface layer (Table 1). Rhizospheres may substantially affect the sediment chemistry, particularly the organic matter content (NEDWELL *et al.,* 1994; ALONGI, 1996; CAÇADOR *et al.,* 1996), the microbial activity (ALONGI *et al.,* 1993; NEDWELL *et al.,* 1994; SPRATT and HODSON, 1994), and the pore water physicochemical conditions (*e.g.* redox and acidity; LACERDA *et al.,* 1993; CLARK *et al.,* 1998; ARAGON *et al.,* 1999).

Pore Water Physicochemical Characterization

Generally a moderate variability in pore water salinity and low or moderate variability in pore water acidity are observed within the environments and between sampling seasons (Table 2). A consistent trend of increase in salinity from November to June has been observed in all the environments, particularly in subsurface and deep sediment layers of the mangrove forest (Table 2). These results appear to be related to variations in rainfall intensity in the study area; nearly 3-times higher in November than in June (DENAEE, 1997). Rainfall intensity may induce changes in the water table level, affecting the pore water salt dilution, acidity and redox conditions (CLARK *et al.,* 1997, 1998). However, circumneutral pH values were observed in pore water samples, and slightly higher pH values were recorded in June than in November, except for subsurface layers of mud flat sediments (Table 2). The seasonal pH variability in sand flat pore water agrees with the greater acidity expected under more oxidizing con-

Table 2. *Physicochemical characteristics and dissolved Mn concentrations of pore water profiles in inter-tidal sediments in Coroa Grande, Sepetiba Bay, in rain season (November 1995) and in dry season (June 1996). Values are averages of duplicate samples.*

	Salinity		pH		Eh (mV)		Mn (mg L^{-1})	
Station	Nov	Jun	Nov	Jun	Nov	Jun	Nov	Jun
Sand flat								
0–5 cm depth	20.0	22.5	6.6	7.4	+70.5	+7.0	0.35	—
10–15 cm depth	21.0	25.0	7.1	7.3	+27.0	+14.5	0.08	0.66
25–30 cm depth	20.0	24.5	6.6	7.2	+85.0	+8.0	ND	0.74
Mud flat								
0–5 cm depth	22.5	26.5	6.9	7.4	+11.5	+127	0.15	2.47
10–15 cm depth	22.0	25.0	7.7	5.9	−257	−92	1.00	1.20
25–30 cm depth	—	22.5	—	7.5	—	−142	—	0.80
Mangrove forest								
0–5 cm depth	21.5	25.0	6.4	7.0	−148	−104	0.81	3.80
10–15 cm depth	18.0	24.5	6.8	7.2	−135	−152	1.80	1.97
25–30 cm depth	18.0	24.0	6.6	7.2	−202	−143	1.50	1.64

Note. —, not available. ND, not detectable.

ditions (CAÇADOR *et al.*, 1996; CLARK *et al.*, 1998; DONAHOE and LIU, 1998). These observations do not occur consistently in the other environments. Consistent pH differences between sampling stations within a season were not found. The release of organic acids by organic matter decomposition processes (*e.g.* TAM *et al.*, 1995), and probable differences in microbial composition and activity within the sediment types will probably affect the studied environments differently, and masks trends within the sediment profile and between sampling seasons in the organic-rich muddy sediments.

Pore water redox potentials have large differences between sampling stations (Table 2). The coarse-grained sand flat sediments allow a better percolation of pore waters, resulting in more oxidized conditions in the entire profile. A smaller diffusion of water and atmospheric O_2 penetration in the fine-grained mud flat and mangrove forest sediments, as well as their higher organic matter content, allow the development of more reduced conditions of depth. Although mud flat pore water experiences oxidizing conditions in the surface layers and reducing in subsurface layers, the mangrove forest sediments maintained reducing conditions throughout their profile.

Considerable care is required to interpret the Eh data, and because sampling was conducted during low tides, only a general indicator of the redox conditions at the time of sampling is obtained. It may be assumed that the Eh values, particularly in surface sediment layers, are the extreme high of the Eh oscillation range expected because of tidal water flooding and the water table heights change (see HARBISON, 1986; CLARK *et al.*, 1998; LACERDA *et al.*, 1999). Moreover, at the resolution level utilized here, it is not possible to observe an oxidized surface layer in the mangrove forest sediments by Eh measurement. These results indicate that the redox boundary of mangrove forest sediments occur at depths less than 5 cm during both seasons, but oxidized layers are seen in other environments.

Sand flat sediments have consistently higher Eh values in November than in June (Table 2), whereas mud flat sediments showed the reverse trend with higher Eh values in June. Mangrove forest Eh values have less variation within a season, although there is the same trend in the mud flat sediments. These trends may be explained by the different levels of water retention by the sediments, with a large difference in freshwater input between the sampling seasons (see CLARK *et al.*, 1997, 1998). Furthermore, different microbial activity levels (*e.g.* sulfate reduction prevailing below the redox boundary and photosynthetic O_2 release in the sediment surface) within sediments may account for the different redox gradients observed between the environments.

The oxidizing activity of mangrove rhizospheres has been largely demonstrated (ANDERSEN and KRISTENSEN, 1988; MCKEE *et al.*, 1988; NEDWELL *et al.*, 1994). CLARK *et al.* (1998) showed that the concentration and chemical speciation of many trace metals in mangrove forest sediments may be affected by the distribution of geochemically distinct horizons, with an observable oxidation from root activity. As for many mangrove areas (ALONGI *et al.*, 1993; ALONGI, 1996; ARAGON *et al.*, 1999), the Eh measurements in the mangrove forest pore water do not indicate an uniform subsurface oxidizing layer. An observable root oxidizing effect is probably associated more to higher root densities than to sampled sediments. Alternatively, the lack of a consistent seasonal pattern in redox conditions of the mangrove forest sediments is attributable to a higher trap and stabilization of sediments by root systems than in bare sand flat and mud flat environments, because mangrove roots and stems may reduce the hydrodynamic energy and physical disturbance of intertidal sediments (WOLANSKI, 1995; WASSERMAN *et al.*, 2000).

Dissolved Mn Distribution

Dissolved Mn behavior is substantially different between the muddy and the sandy environments (Table 2). Higher Mn concentrations were observed in the surface pore water than in the subsurface and deeper pore water of sand flat sediments in November. Mangrove forest and mud flat samples had a reverse trend compared to the sand flat in November, but a similar trend in June. Sand flat pore water at higher depths have much lower dissolved Mn values in November than in June (Table 2). In contrast, pore water in muddy environments tended to show very similar dissolved Mn concentrations between November and June. Muddy sediment pore water tended to have higher dissolved Mn concentrations than sand flat pore water, and mangrove forest had higher concentrations than the mud flat environment (Table 2).

Differences in the redox conditions along the vertical profiles and between the different sampling stations may explain the observed Mn behavior. Redox conditions determine the intensity of Mn dissolution from solid phase, as well as the diffusion and precipitation of dissolved Mn (BRYANT *et al.*, 1997; GAGNON *et al.*, 1997; GOBEIL *et al.*, 1997; DONAHOE and LIU, 1998). Predicted models of the Mn redox behavior indicate that the Mn dissolution and enrichment in reduced pore water of deeper sediments, and the dissolved Mn precipitation and depletion in oxidized pore water of surface sediments occur, resulting in dissolved Mn diffusion from reduced pore water to oxidized pore water (SHAW *et al.*, 1990; SHIMMIELD and PEDERSEN, 1990; GOBEIL *et al.*, 1997). A surface enrichment in dissolved pore water Mn concentrations has been observed in some sedimentary environments (BRYANT *et al.*, 1997; GAGNON *et al.*, 1997). BRYANT *et al.* (1997) suggest that after the diagenetic enrichment of solid-phase Mn at the sediment surface, Mn dissolution back to pore water (under more reducing conditions) can induce simultaneous solid phase and pore water surface peaks. This process may explain the high pore water surface concentrations observed in muddy sediments during June, and in sand flat sediments during November, relative to subsurface and deep layers (Table 2).

In the relatively low-energy Coroa Grande intertidal area, the sand flat appears to be the environment most susceptible to physical influences of coastal hydrodynamic (*e.g.* sediment resuspension and erosion). As overlying water turbulence may affect pore water solute transport (SHUM and SUNDBY, 1996; LAIMA *et al.*, 1998), it can contribute to the Mn concentration gradients observed in sand flat pore water, and can partly explain the strong surface enrichment in November. Muddy environments may also be substantially affected by

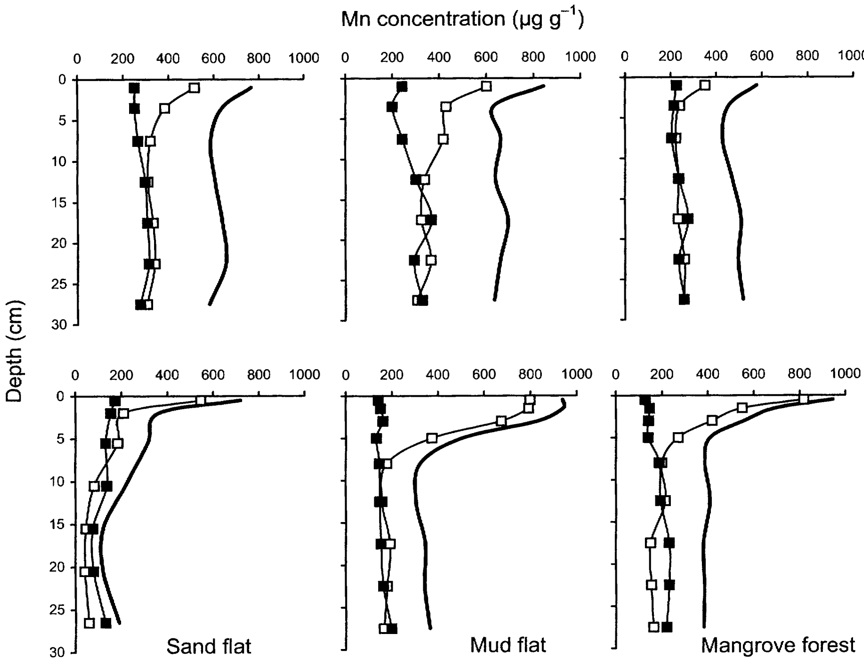

Figure 2. Strongly-bound Mn (closed symbols), weakly-bound Mn (open symbols), and total Mn (heavy line) concentrations in sediment profiles in intertidal sediments of Coroa Grande, Sepetiba Bay. Symbols indicate the average concentrations of duplicate cores for each depth. The upper row shows the rain season data (November 1995) and the lower row shows the dry season data (June 1996).

tidal currents influencing pore water transport in the sediment surface layers (SUNDBY *et al.*, 1981; ARAGON *et al.*, 1999; LACERDA *et al.*, 1999); this effect will be probably lower than for coarse-grained sediments. These non-diffusional processes may explain differences observed between sand flat pore water sampling seasons, rather than dissolved Mn migration by diffusion.

The decrease in dissolved Mn concentrations from subsurface to surface layers of muddy sediments observed in November may indicate a precipitation of Mn in solid (oxidized) phases at the sediment surface (SHAW *et al.*, 1990; THAMDRUP *et al.*, 1994; GOBEIL *et al.*, 1997; DONAHOE and LIU, 1998). Moreover, the release of dissolved Mn from sediments to the overlying water may occur (by diffusion or non-diffusional processes) when the rate of Mn oxidation in the sediment is outpaced by the rate of dissolved Mn supply from deeper layers (SUNDBY *et al.*, 1981; HUNT, 1993; THAMDRUP *et al.*, 1994). The decrease in dissolved Mn concentrations within surface layers relative to subsurface layers in muddy sediments (where reduced conditions prevail), is most likely a Mn transfer from pore water to tidal water, possibly resulting in Mn exportation to adjacent environments (*e.g.* HARBISON, 1986).

Total Solid Phase Mn Distribution

Vertical profiles of solid-phase Mn distribution in the sediments are presented in Figure 2. Maximum total Mn concentration peaks occur closely (with few centimeters depth) to sediment surface in all profiles. In June, sediment profiles of muddy environments presented higher total Mn concentrations in surface sediment layers, with a progressive depletion in the subsurface layers and a relatively constant and lower concentration in the deeper layers. In the same sampling period, sand flat sediments showed a very sharp decrease from the surface total Mn peak to a very low and relatively constant subsurface total Mn levels. These general profile shapes are in excellent agreement with predicted models of Mn behavior in a redox boundary (see SHAW *et al.*, 1990; SHIMMIELD and PEDERSEN, 1990; GOBEIL *et al.*, 1997). We observed a much lower increase of surface total Mn in relation to subsurface in November (25% for sand flat, 29% for mud flat and 20% for mangrove forest), than in June (by a factor of 2.5 for muddy sediments and by a factor of 3.8 for sandy sediments).

Assuming that total Mn concentrations are mainly composed by oxidized phases, it is not expected that all Mn buried below the redox boundary will be dissolved if its concentration exceeds the organic carbon content in terms of reduction equivalents (GOBEIL *et al.*, 1997). This may support the relatively low and constant subsurface Mn background concentrations observed here (Figure 2). Our results demonstrate that strongly-bound Mn phases are buried at approximately similar levels within the sediments, except by a relatively high Mn levels observed with higher depths in mud flat sediments in November (Figure 2). The vertical variability of weakly-bound Mn trapped within the sediments seems to control both the surface peak concentrations and the subsurface background concentrations.

Particulate matter sedimentation is the more reliable Mn source to Coroa Grande intertidal sediments (BARCELLOS *et al.*, 1997). Our data indicates that different Mn levels are stored within the sediments sampled in November and within the sediments sampled in June from sand flat and mud flat environments (Figure 2), for example, due to spatial differences in detrital Mn input and preservation between sampled sediments within a station. These environments presented consistently higher Mn background values in November than in June, while mangrove forest profiles present relatively similar Mn background concentrations between the sampling periods (Figure 2).

Although mangrove trees roots are able to oxidize their rhizospheres and its effect on trace metal biogeochemistry in mangrove sediments have been demonstrated (see CLARK *et al.,* 1998; LACERDA, 1998), our results seem to indicate that the Mn cycling and redistribution within the sediments may present faster rates than typical mechanisms which affect the mangrove sediment chemistry (*e.g.* root O_2 release and bioturbation). This possibly prevents a higher influence of such mechanisms over the Mn vertical distribution in sediments of the Coroa Grande mangrove forest. Processes as bioturbation may be unlike to remove surface Mn peaks within the rate of Mn oxihydroxides accumulation at the sediment surface (GOBEIL *et al.,* 1997). Although these assumptions may be valid for the environments studied here, they do not exclude the possibility of a substantial effect of such processes on the Mn vertical distribution within sediments with more developed rhizosphere zones (*e.g.* CLARK *et al.,* 1998) or more heavily bioirrigated. ALLER and ALLER (1997) demonstrated experimentally that high densities of benthic animal burrows may increase the net production of dissolved Mn in marine anoxic sediments, which possibly may affect the Mn fluxes and distribution near the sediment-water interface.

Partitioning of Solid Phase Mn

The Mn geochemical partitioning in intertidal sediments indicates that the total solid-phase Mn variability within sediments is dominated by weak-acid extractable phases (Figure 2), and suggests that these reliably correspond to most remobilizable Mn phases. Weakly-bound Mn composed most of the solid-phase Mn in the sediment surface, and generally half of the solid-phase Mn in the subsurface sediment layers in all the environments. These results are in agreement with previous studies on coastal sediments, where the total Mn concentrations in sediments are substantially or mostly composed by geochemically reactive phases (SUNDBY *et al.,* 1981; HARBISON, 1986; TAM *et al.,* 1995; LACERDA *et al.,* 1999). The ratio between weakly-bound and total Mn concentrations (weakly:total ratio) was remarkably similar for surface Mn-enriched sediment layers of the three environments in November (0.61–0.7) and in June (0.73–0.83), as well as for the subsurface Mn-depleted layers in November (0.46–0.55). In June, the weakly:total ratios tended to be slightly lower for sand flat Mn-depleted subsurface layers (0.31–0.38) than for muddy environments (0.40–0.55).

Despite several environmental contrasts (*e.g.* sediment texture and physicochemical conditions), these results suggest that the Mn remobilizable fraction, generally, do not vary substantially in relation to the total Mn concentration among the studied intertidal sediments, in both sampling seasons. Where comparable solid-phase Mn concentrations occur, the weakly:total ratios were approximately constant within the Mn-enriched uppermost few centimeters and in Mn-depleted subsurface layers, in all sediment profiles. In June, the lower values of weakly:total ratios in sand flat subsurface were associated to a lower solid phase Mn content than observed in the sand flat in November, and in other environments (Figure 2). These observations and the elevated pore water dissolved Mn concentrations in subsurface layers in June (with a consistently lower Eh; Table 2), in comparison to November, suggest that the lower Mn content in sediments may be partly due to a relatively higher dissolution and redistribution of weakly-bound Mn phases. This relatively high remobilization of weakly-bound Mn, possibly explains the maintenance of a surface solid-phase peak concentration comparable to the other profiles, supported by Mn-richer subsurface sediments.

The observation of solid-phase Mn partitioning with depth suggests that a remobilization of geochemically reactive phases, following the substantial seasonal variability in the pore water O_2 concentration and penetration depth, is a consistent explanation to the vertical variability in the Mn concentration, between seasons. Weakly-bound phases may be mainly composed by Mn oxihydroxides (previously precipitated near the sediment-water interface), Mn carbonate phases (due to detrital deposition in sediment surface or authigenic formation with sediment depth), and Mn bound to organic compounds (*e.g.* organic acid complexes; PATCHINEELAM and SOUZA, 1987). Adsorbed Mn bound to particle surfaces (*e.g.* with Mn and Fe oxides in oxidized sediments, and with FeS in reduced sediments) may potentially form a substantial reactive Mn fraction in sediments (SHIMMIELD and PEDERSEN, 1990; ARAKAKI and MORSE, 1993). PATCHINEELAM and SOUZA (1987) demonstrated that organic acid-Mn complexes are mostly fulvic acid complexes, and that their Mn contents may reach less than 10% of total Mn concentration in sediments from Coroa Grande mangrove forest. Mangrove sediments tend to present a consistent increase in both alkalinity (NEDWELL *et al.,* 1994; ARAGON *et al.,* 1999) and dissolved Mn with depth (Table 2), in their pore water reducing subsurface layers. These characteristics suggest that authigenic manganous carbonates (*e.g.* $MnCO_3$ and mixed carbonate phases, as $MnCaCO_3$ compounds) may be a solid-phase Mn form commonly present in mangrove sediments. Under alkaline conditions, the manganous carbonate sink may have a considerable contribution to the Mn weakly-bound phases with sediment depth (see SHIMMIELD and PEDERSEN, 1990). Because the high Mn oxihydroxides accumulation at the sediment surface, and their burial, probably these compounds mostly contribute to the weakly-bound Mn concentrations of studied sediments.

Many studies in sedimentary environments have demonstrated the relationship between Mn geochemistry and the geochemistry of other trace metals, mainly by scavenging, coprecipitation and redissolution with Mn oxides (HARBISON, 1984, 1986; BADARUDEEN *et al.,* 1996; CORNWELL, 1987; SHAW *et al.,* 1990; GAGNON *et al.,* 1997; DONAHOE and LIU, 1998). Thus, an elevated environmental significance of the sedimentary Mn cycling is expected due to its coupling with the behavior of harmful metal pollutants. Remarkably, these processes may be essentially associated to the relationship between geochemically reactive phases of these pollutants (*e.g.* anthropogenic Hg) and geochemically reactive Mn phases (*e.g.* GAGNON *et al.,* 1997).

Bioavailability of Mn in Sediments

All studied environments present an elevated Mn accumulation in potentially bioavailable solid-phases (as authigenic amorphous oxides, carbonates, organo-complexes, and adsorbed Mn forms). This characterizes the intertidal sediments as a substantial potential Mn source to living organisms inhabiting the sediments (*e.g.* microbial populations, burrowing fauna and rooting macrophytes). Moreover, dissolved and particulate Mn transport to overlying water may allow the Mn uptake by filter-feeding organisms and plankton communities. Benthic organisms may ingest particulate metal forms in coastal environments, particularly in shallow turbid water (*e.g.* PARK and PRESLEY, 1997), and a substantial contribution of sediments to Al, Fe, Mn and Pb burdens in mollusc species has been observed (KENNEDY, 1986). Thus, it is expected that the sediment metal concentrations may be reflected in tissue concentrations of, for example, filter-feeding oysters and mussels (PARK and PRESLEY, 1997) and deposit-feeder worms (MASON *et al.,* 1988).

The Mn uptake by mangrove tree species seems to have a particular ecological significance, due to differences between the patterns of Mn accumulation by mangrove plants compared to other trace elements. In opposition to the general trends observed for most trace metals, a positive correlation between the sediment solid-phase Mn concentrations and the leaf Mn concentrations of mangrove trees has been reported (LACERDA *et al.,* 1986; SADIQ and ZAIDI, 1994), and leaf Mn concentrations may exceed the root concentrations (RAGSDALE and THORHAUGH, 1980; SILVA *et al.,* 1990). The trend of mangrove tree species present a higher Mn transport to leaves than most other trace metals is possibly associated to the relatively elevated natural levels and to the generally high bioavailability of Mn in sediments (LACERDA, 1998). These findings may explain the similar (RAGSDALE and THORHAUGH, 1980; SADIQ and ZAIDI, 1994) or higher (SILVA *et al.,* 1990; TAM *et al.,* 1995) Mn concentrations observed in mangrove tree leaves than those observed in their substrate.

Sediment-water Mn Exchange

In coastal sedimentary environments, it must be expected that the amounts of dissolved Mn which escape from sediments will be negligible in comparison to solid-phase Mn resuspension (*e.g.* SUNDBY *et al.,* 1981). In the sediment-water interface, sediment resuspension probably mainly involve the finest Mn-rich sediment particles, which would be expected to escape from immediate resedimentation, and may be available to overlying water transport (SUNDBY *et al.,* 1981). However, tidal pumping effects on pore water solute flux from the sediment surface may result in a highly frequent Mn output from the intertidal sediments, which may be largely increased by sediment resuspension events (SHUM and SUNDBY, 1996; LAIMA *et al.,* 1998). As dissolved Mn concentrations in tidal waters over mud flat sediments in Sepetiba Bay present magnitudes of about 0.02 mg L^{-1} (LACERDA *et al.,* 1999), the formation of a concentration gradient throughout the sediment-water interface can support a Mn diffusion from sediment pore waters, with concentrations (see Table 2) one or two orders of magnitude higher than in overlying waters. LACERDA *et al.* (1999) demonstrated that, with the advance of Sepetiba Bay waters (showing Mn levels of about 0.005 mg L^{-1}) over a mud tidal flat, the dissolved Mn concentrations may increase to 0.065 mg L^{-1}, simultaneously to an increase in the mass of solids in suspension by several orders of magnitude, which imply in an increase in tidal water dissolved Mn related to mud flat sediment resuspension.

CONCLUSIONS

Our results indicate a highly dynamic nature of Mn species under the studied environmental conditions and the balance between the Mn post-depositional remobilization and transference from subsurface and deep (reducing) sediment layers to surface (oxidizing) sediment layers, as previous studies have suggested, may compose the major process affecting Mn biogeochemistry in the studied environments. Sediment resuspension and dissolved Mn transport to overlying waters may promote the Mn transference between intertidal environments or expose it to Sepetiba Bay currents transport.

Diverse conditions observed in mangrove forest, mud flat and sand flat environments seem to affect the Mn vertical distribution in sediments (*e.g.* rhizosphere presence in mangrove forest sediments and the high sediment permeability of sand flat sediments), and may contribute to the high seasonal variability presented by solid phase Mn concentrations. A general apparent decrease in the intensity of the Mn diagenetic remobilization from mangrove forest to mud flat to sand flat sediments was observed, which confirms that the degree of redox conditions seem to dominate the Mn mobility in these intertidal environments. Non-diffusional transport (due to physical entrainment) may largely contribute to the dissolved Mn behavior in sand flat pore waters and also may contribute, at a lower extent, to dissolved Mn behavior in the pore water of the muddy environments.

As geochemically reactive Mn phases are maintained in elevated levels at a wide range of sedimentary conditions (*e.g.* pore water redox variability and organic matter content), research on the factors regulating the diagenetic behavior of Mn is essential to understand the modes of accumulation and the transfer of this element within each particular condition, its transport to the overlying waters and bioavailability, as well as its possible relationship with the behavior and the bioavailability of other elements, especially in polluted sedimentary environments.

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☐ RESUMO ☐

Nós investigamos o comportamento do Mn em ambientes entre marés de uma área dominada por manguezais, na Baía de Sepetiba, sudeste do Brasil, para caracterizar a contribuição da remobilização diagenética para a ciclagem e biodisponibilidade do Mn, próximo à interface sedimento-água. Testemunhos de sedimento e águas intersticiais foram coletados em uma floresta de manguezal mista e em planícies de lama e de areia adjacentes, sem cobertura vegetal, durante as estações úmida (novembro de 1995) e seca (junho de 1996). As condições redox controlaram a distribuição das fases sólidas do Mn nos sedimentos, associada ao transporte de Mn dissolvido nas águas intersticiais, por processos de difusão e não-difusionais. Diferentes condições observadas nos ambientes estudados (por exemplo, rizosferas em florestas de manguezal e a alta permeabilidade de sedimentos de planície de areia) podem afetar a distribuição do Mn nos sedimentos e contribuir para a sazonalidade desta distribuição. A variabilidade da distribuição das fases sólidas do Mn foi fortemente associada às fases fracamente ligadas (extraídas em HCl 0,5 N), que compõem a maior parte das fases sólidas do Mn nas camadas superficiais, enriquecidas em Mn, e cerca de metade das fases sólidas do Mn nas camadas subsuperficiais, empobrecidas em Mn, em todos os ambientes. A natureza dinâmica das espécies de Mn, nas condições ambientais estudadas, particularmente nos ambientes de sedimentos finos, sugere que: (i) ocorre uma transferência de Mn dissolvido das águas intersticiais para as superficiais e o seu transporte para ambientes adjacentes; (ii) o Mn é presente em formas biodisponíveis nos sedimentos; e (iii) o Mn pode ter uma forte influência sobre o comportamento de outros elementos (como poluentes metálicos) nos sedimentos entre marés.