



Manganese dynamics in a mangrove mud flat tidal creek in SE Brazil

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Abstract

This study investigated the behavior of soluble and particulate manganese, during tidal cycles in a mangrove tidal creek and adjacent mud flats in SE Brazil. We identify the major processes affecting manganese transport to mangroves. The results showed that manganese variability occurs both seasonally, and over the tidal cycle, in response to changing redox potentials. Tidal water flooding mud flats are enriched in manganese, originating from upward migration of reduced species and further adsorption onto suspended particles under oxic conditions. During the tidal cycle, particulate manganese concentrations are higher during flood periods, whilst dissolved concentrations are higher during ebb periods. Although quantitatively different, this pattern occurs both in winter and summer. The dynamics of manganese characterized in this study suggest that this metal may play a significant role as a conveyor of trace metals to mangrove ecosystems, as suggested by earlier studies.

Introduction

The cycling of trace metals in mangrove ecosystems has been the subject of recent studies, due to the potential role of mangroves in the abatement of trace metal pollution (Lacerda, 1998). Trace metals enter mangrove ecosystems with the incoming tide associated with suspended particles, iron and manganese oxo-hydroxides (Lacerda et al., 1988). When reaching the reducing conditions, dominant in most mangrove environments, these oxo-hydroxides are reduced and dissolved, and can release their trace metal load to the water column. Since mangrove waters can have as much as 10 mg l^{-1} of dissolved sulfide, due to the predominant sulfate reduction metabolism of mangrove sediments, many trace metals are efficiently precipitated as insoluble sulfides (Harbinson, 1986; Lacerda et al., 1997; Clark et al., 1997). Due to permanent anaerobic conditions of mangrove sediments and high sedimentation rates in mangrove environments, trace metals suffer rapid accumulation and burial in the sedimentary column. Thus, mangroves can act as biogeochemical barriers to trace metal transport in

coastal waters (Lacerda, 1998). The mechanisms described above may also hamper trace metal uptake by mangrove plants. However, trace metals which do not form stable sulfides, will not be affected by this precipitation process (Lacerda, 1997).

Many studies on trace metals in mangrove plants have shown concentration factors (leaf concentration to sediment concentration ratio) lower than 1.0 for most trace metals, the only exception being Mn, which always has concentration factors higher than 1.0. Of all trace elements studied, Mn generally, shows a significant correlation between sediment and leaf concentrations (Lacerda, 1997). Manganese sulfides are very unstable ($K_{sp}(\text{MnS}) = 9.6$ and 12.6) (Förstner and Wittman, 1979), and are only formed when total dissolved sulfur exceeds total carbonates by a factor of at least 100 (Krauskopf, 1979). Therefore, MnS has never been detected in mangrove environments (Lacerda, 1998). Under the prevailing anoxic conditions, many bacteria that can oxidize organic matter with the reduction of Fe(III) can also dissimilatory reduce Mn(IV), using it as an electron acceptor. Also, under anoxic conditions, Mn(IV) is easily reduced through

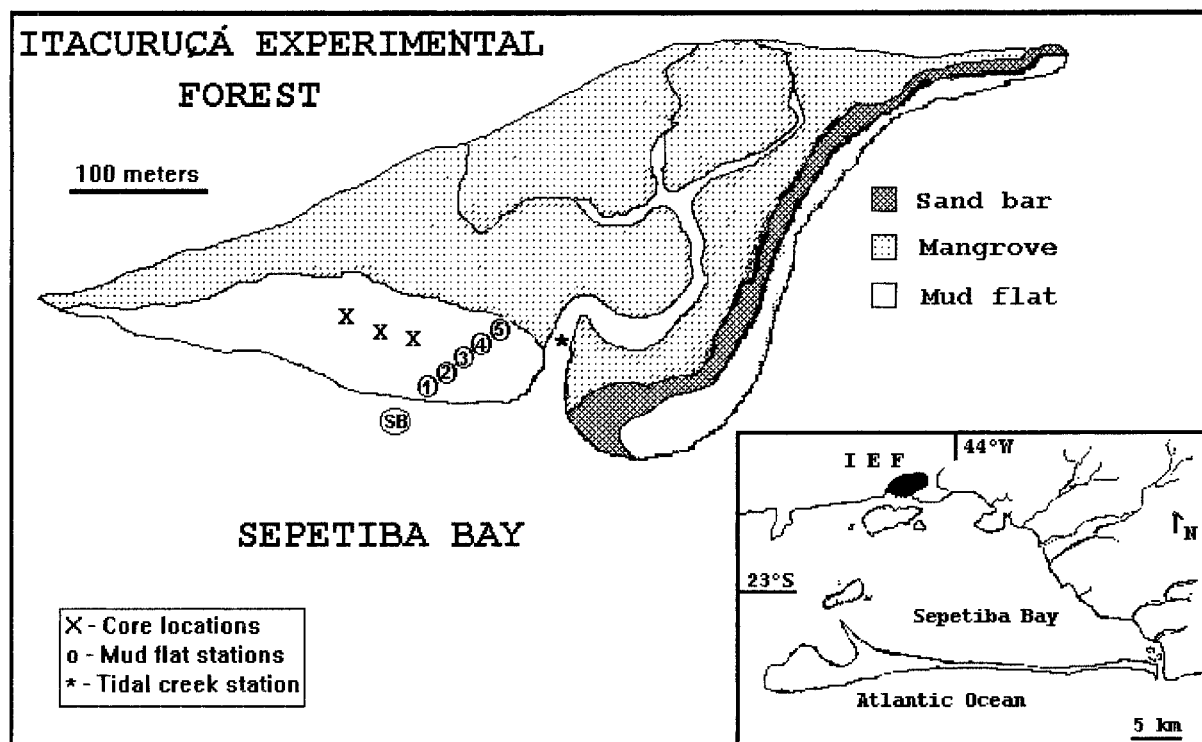


Figure 1. Map showing the different features of the Itacuruçá Experimental Forest, Rio de Janeiro, SE Brazil: (*) Location of sampling station at the creek mouth; (o) Location of sampling stations for tidal waters at the mud flat surface; (X) Location of sediment cores.

non-enzymatic mechanisms to soluble Mn(II) (Gratton et al., 1990; Lovley, 1993; Sprat et al., 1994; Luther III et al., 1998). Thus, Mn would not behave like most other trace metals as described above and a significant fraction of this element would be available for plant uptake. However, these mechanisms would also make Mn available for exportation to adjacent coastal waters. Since changes in the Mn(II) \leftrightarrow Mn(IV) equilibrium will result in the changes in trace metal availability, due to the significant scavenging capacity of Mn oxi-hydroxides, understanding Mn dynamics in mangrove ecosystems is of key importance to understand the geochemistry and bioavailability of most trace metals of environmental significance in this environment.

Most transfer of water and materials between mangroves and coastal waters, occurs through tidal creeks, which characteristically change hydrochemistry during tidal cycles, and are also affected by adjacent mud flats (Kjerfve, 1990). Mud flats, frequently occurring along the seaward margin of most mangroves, are exposed during low tide and present oxidized surfaces but extremely reducing conditions in their pore waters, due to high organic matter content and very fine grain

size sediments. When tidal waters flood these flats, dissolved substances accumulated in the reducing pore waters are washed out and may enter the adjacent mangroves (Harbinson, 1986). This process contributes significantly to the nutrient budget of mangrove forests (Ovalle et al., 1991) and can also affect the transport of redox sensitive metals such as Fe and Mn.

In the present study, we investigated the behavior of the soluble and particulate forms of Mn, during seasonal tidal cycles in a mangrove creek and adjacent mud flats in SE Brazil, in order to more fully characterize the Mn cycle in this complex environment, and to assess the causes of its relatively higher availability for plant uptake.

Study area

The study was done at the Itacuruçá Experimental Forest (IEF), located along the North shore of Sepetiba Bay, approximately 100 km from Rio de Janeiro (23° S, 44° W) (Figure 1). Sepetiba Bay is a 447 km² coastal lagoon, with an average depth of 6.0 m and tidal range of less than 2.0 m. Sepetiba basin harbors,

an industrial park, with over 400 industries, and a population of about 1.2 million. Effluents containing trace metals have been an increasing environmental threat to aquatic biota, including important fisheries (Barcellos and Lacerda, 1994).

Mangroves cover about 38 km², mostly as fringe forests along the Bay's north and northeastern coasts. The Bay's mangroves are important barriers to the spread of trace metal contamination in the region, by accumulating relatively large amounts of trace metals in a non-bioavailable form. However, the mechanisms involved are still far from fully understood (Lacerda, 1998).

The IEF is a typical fringe mangrove forest with *Rhizophora mangle* L., as dominant species, although isolated trees of the black mangrove (*Avicennia schaueriana* Stapf and Leech.) and of the white mangrove (*Laguncularia racemosa* Gaertn.) occur throughout the forest. The IEF has an area of approximately 10 ha. At the seaward edge, the forest is lined by an approximately 70 m wide strip of mud flats, frequently exposed during low tide. At the landward edge, the forest is bordered by saline sands with stunted *L. racemosa* trees and the fern *Achrosticum aureum* L. The IEF is drained by a tidal creek (10 × 300 m) running almost perpendicular to the shore and land. This creek is responsible for over 90% of the water exchange at the IEF (Ovalle et al., 1991). Creek depth depends on tides and ranges from 0.6 to 2.6 m. Average air temperatures range between 18 °C in winter and 23 °C in summer. Annual rainfall is c.a. 2300 mm, with a typical rainy season in December and a dry season in July. The IEF forest structure has been studied by Silva et al. (1991). In summary, average tree density is 4510 ha⁻¹, with an average height of 6 m and an average diameter of 8 cm. Basal area is 22 m² ha⁻¹ and the total biomass is 82 t ha⁻¹, distributed between aboveground (65.4 t ha⁻¹) and below ground (16.3 t ha⁻¹) biomass. Freshwater to the IEF is from groundwater and rainwater, and the inundation pattern is controlled by tidal amplitude.

Methods

Tidal creek sampling

In the two field campaigns (winter and summer), the hydrochemistry and Mn dynamics of the tidal creek waters were monitored through complete tidal cycles, at a central point at the mouth of the creek draining the

IEF (Figure 1). Creek depth was monitored by a fixed ruler. Most hydrochemical variables (water temperature, pH, Eh, salinity, and dissolved oxygen (O₂) were determined *in situ* by a diver, with portable electrodes, see Ovalle et al. (1991), for a detailed description of methods and equipment.

Samples for the determination of dissolved Mn, were collected using 5-l acid-clean Van Dorn bottles, operated by hand at the monitoring station, at about 10 cm below the water surface. A 500 ml aliquot, from this sample was filtered through 0.45 μm pore diameter cellulose acetate membranes, in the field. Two 100-ml replicates of the filtrate were collected and acidified with 2 ml of 6N HCl and frozen. Filters were used for the determination of the total suspended solids (TSS) after drying during 24 h at 50 °C. For the determination of particulate Mn, 5 l of water were collected in polyethylene bottles and transported to the laboratory. Bottles were left overnight to settle suspended particles and samples were filtered using 0.45 μm pore diameter cellulose acetate filters.

Sampling of mud flat waters

Changes in Mn concentrations in tidal waters due to flooding of adjacent mud flats, were investigated by placing a pair of 250 ml polyethylene bottles attached to a fixed sticks at the surface of the sediment. Bottle pairs were fixed at five points, 10 m apart, in a 50-m transect from the fringe of the mangrove forest. The last pair of bottles were placed at the mangrove fringe close to the creek margin (Figure 1). As a pair of bottles were filled by the incoming tide, they were removed and filtered in the field, as described for creek waters. Filters and filtrate were frozen upon collection. Simultaneously, approximately 20 g of surface sediments (0.0–1.0 cm of depth), were collected at each site.

In selected areas of the central part of the tidal flat, three sediment cores were collected by inserting acrylic tubes (9.0 cm of internal diameter) into the sediment. Sediment cores were sliced in 2.0 cm layers in the field and packed in acid-cleaned plastic bags for transport.

Manganese analysis

For the determination of dissolved Mn in creek and mud flat tidal waters, we needed to pre-concentrate the water samples. In this work, we extract dissolved Mn from the aqueous matrix with 20 ml of a 8-hydroxyquinoline solution (0.06%) in chloroform,

at a pH range of 9.0–9.5, followed by a re-extraction with 6 ml of 7M HNO₃ (Landing and Bruland, 1980, Resing and Mottl, 1992). After the complete evaporation of the acid, the residue was totally dissolved in 10 ml of 0.5N HCl. The final extracts were analyzed by the conventional flame atomic absorption spectrophotometry against known standards. Calibration curves showed correlation coefficients higher than 0.999, and the detection limit of this method, based on three times the reagent blanks was $0.1 \pm 0.05 \mu\text{g l}^{-1}$.

Determination of particulate Mn was carried on in duplicate, in suspended matter captured on filters, in surface bottom sediments and core slices, after oven-drying (60 °C for 24 h). Filters from the tidal creek samples were digested with 10 ml of a strong acid mixture (2 ml HF_{conc.} + 2 ml HNO_{3 conc.} + 3 ml HCl_{conc.}) and re-dissolved in 30 ml of 0.5N HCl. Filters and surface bottom sediments from the mud flat cores were first leached with a 0.5N HCl solution for 12 h, to extract the weakly bound fraction of Mn. Sequentially, they were totally digested, as described above, for the determination of the strongly bound Mn. The sum of these two fractions compares with the total Mn concentrations measured in the TSS tidal creek samples. However, the different grain size between surface sediments and core sediments do not allow comparison between the two samples. For details of these extraction procedures see Fiszman et al. (1984). The final extracts were also analyzed by conventional flame atomic absorption spectrophotometry. Simultaneous analyses of reference sediment standards (NIST-USA, estuarine sediments) gave results always within 10% difference from certified values. Detection limit for this method was $0.1 \pm 0.05 \mu\text{g g}^{-1}$, on a dry weight basis.

Results and discussion

Tidal creek water chemistry

Hydrochemical characteristics of the tidal creek in winter and summer are presented in Figures 2 and 3, respectively, for the tidal cycles monitored. The range of values observed for all variables during a tidal cycle, with the exception of Mn concentrations, was similar or even larger than the range observed between the two different seasons. This confirms previous hydrochemical studies at IEF, which showed the greater importance of tidal variations compared to seasonal (Ovalle et al., 1991).

Water temperature ranged from 21 °C to 28 °C in winter and 27 °C to 31 °C in summer. In general, flood waters were colder than ebb waters. Water pH was also slightly lower in winter (7.3–7.8, mean = 7.7), than in summer (7.2–9.1, mean = 8.0), and presented a steady increase with the incoming tide, with highest pH observed at the maximum flood period. Total suspended solids (TSS) were higher in winter (22–90 mg l⁻¹, mean = 48 mg l⁻¹) and lower in summer (10–40 mg l⁻¹, mean = 28 mg l⁻¹). Previous studies at the IEF related this behavior to the largest frequency of cold fronts in winter, causing stronger erosion of mangrove and mud flat sediments and larger litter fall and transport (Rezende et al., 1990). Peak concentrations of TSS occurred in winter, when the maximum concentrations were achieved (90 mg l⁻¹). In summer, maximum TSS values reached only half of maximum winter values (40 mg l⁻¹).

Average salinity varied little in summer (30–32). In winter higher and more variable values were observed, ranging from 26 to 38, along the tidal cycles. Higher salinity was observed in ebb waters and, most probably, resulted from the washing out of more concentrated mangrove pore waters (Ovalle et al., 1991). Dissolved oxygen concentrations showed large variability, both between seasons, and during the tidal cycles. In winter, creek waters contained lower oxygen levels (2.3–3.1 mg l⁻¹, mean = 2.8 mg l⁻¹), whereas in summer, the levels were much higher (3.2–6.0 mg l⁻¹, mean = 5.3 mg l⁻¹). Dissolved oxygen concentrations were higher during flood periods than during ebb periods. Notwithstanding the large variability in dissolved oxygen, redox potentials varied little between seasons (+60 to +130 mV and +40 to +180 mV in summer and winter, respectively), but varied up to 4.5-fold within the tidal cycle, generally following the dissolved oxygen concentrations.

The range of redox potentials found in this study affects oxidation–reduction reactions of Mn. These reactions will not be affected by the small variability found in salinity (Sprat and Hodson, 1994). The higher dissolved oxygen concentrations and higher pH observed in summer, may be a result of the higher temperatures and primary production in creek waters in summer observed in the area (Ovalle et al., 1991). These variables will strongly affect Mn redox reactions, which are mostly mediated by bacterial activity (Sprat et al., 1994).

The variability of Mn species in winter and summer during the tidal cycles studied was also large. Particulate Mn concentrations were much higher in

WINTER

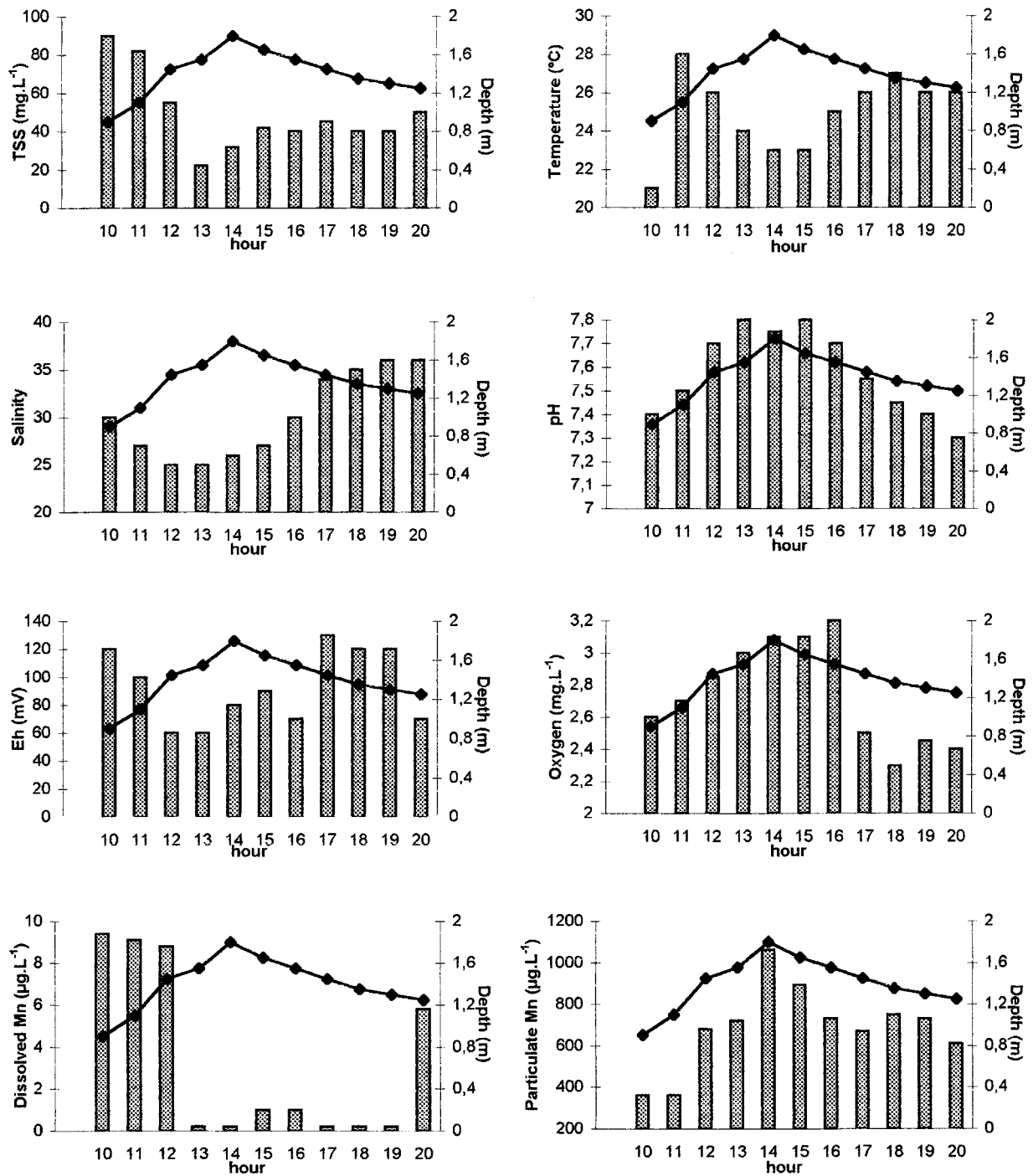


Figure 2. Major hydrochemical parameters and Mn concentrations in tidal creek waters during a tidal cycle, at the Itacuruça Experimental Forest in winter. Continuous line represents depth in meters, bars represent the different variables measured.

SUMMER

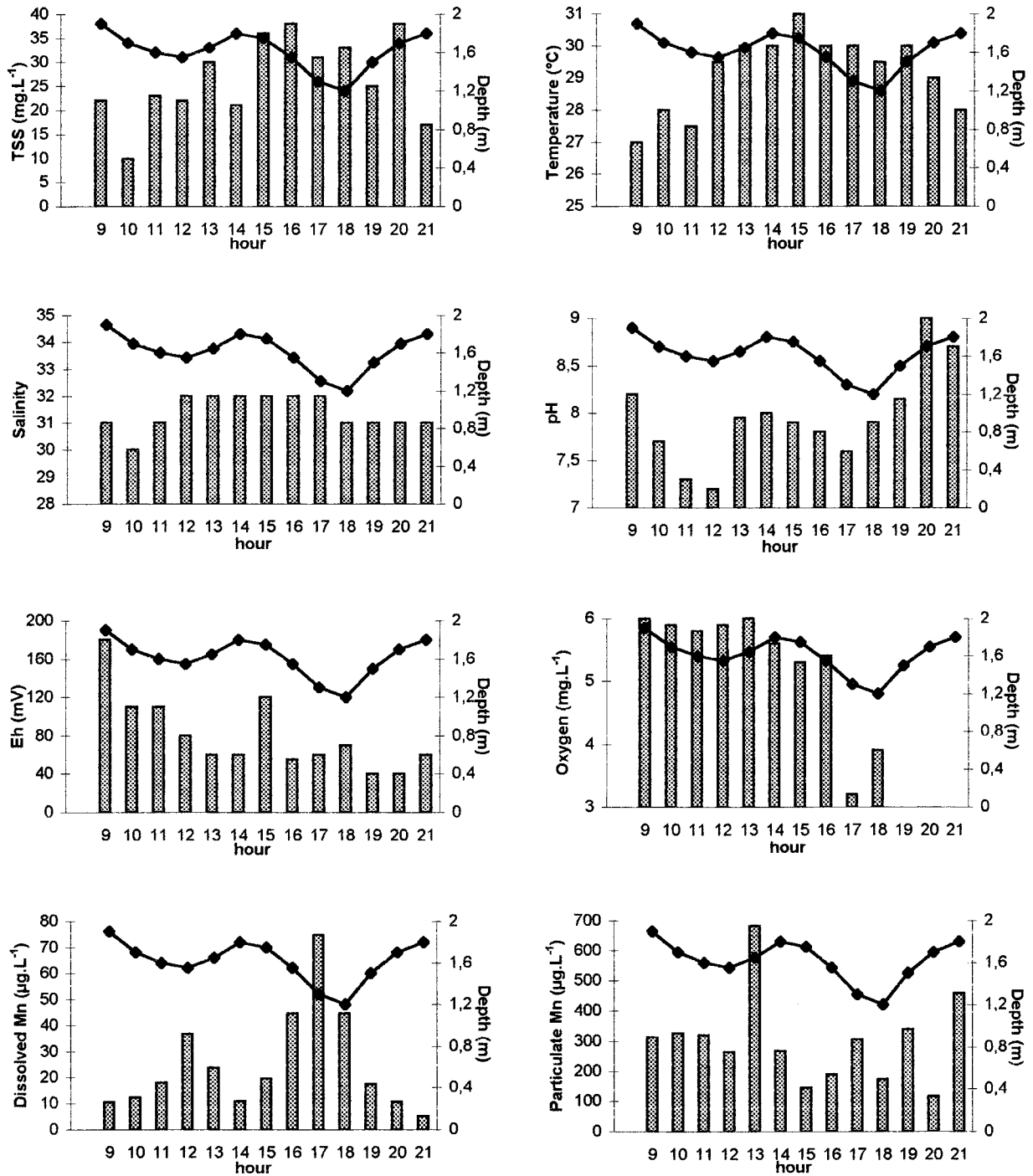


Figure 3. Major hydrochemical parameters and Mn concentrations in tidal creek waters during a tidal cycle, at the Itacuruça Experimental Forest in summer. Continuous line represents depth in meters, bars represent the different variables measured.

winter ($357\text{--}1055\ \mu\text{g l}^{-1}$, mean = $700\ \mu\text{g l}^{-1}$) than in summer ($68\text{--}680\ \mu\text{g l}^{-1}$, mean = $280\ \mu\text{g l}^{-1}$), whereas dissolved Mn concentrations showed an inverse pattern with lower concentrations in winter (< 1.0 to $9.4\ \mu\text{g l}^{-1}$, mean = $2.8\ \mu\text{g l}^{-1}$) and much higher in summer ($5.2\text{--}74.8\ \mu\text{g l}^{-1}$, mean = $26.1\ \mu\text{g l}^{-1}$). The higher concentrations of particulate Mn and lower concentrations of dissolved Mn in winter, are probably associated with the higher amount of suspended matter in creek water at this time, as reported for some other estuarine areas (Morris et al., 1982; Ackroyd et al., 1986), or slower bacterial reduction of oxidized Mn species to reduced Mn species in winter, as suggested by the lower temperatures (Gratton et al., 1990). A negative correlation ($r = 0.992$, $P < 0.01$) between dissolved Mn concentrations and temperature was observed.

The variation of Mn species during the tidal cycles were very clear, with generally higher concentrations of particulate Mn at flood periods and lower levels during ebb periods. Concentrations of dissolved Mn showed a symmetrical behavior, with highest concentrations during ebb periods and lower during flood periods. This pattern is more strikingly in winter, with ebb tide concentrations of dissolved Mn, more than one order of magnitude higher than the flood tide concentrations, and with particulate Mn peaking at the flood tide, at least six times higher in concentration than at the ebb tide. In summer, although the same pattern was observed, concentration differences between tidal periods were smaller.

Previous work in the IEF showed that TSS flowing into the forest through the tidal creek is of marine origin (Rezende et al., 1991). Heavy metals associated with this marine TSS are mostly oxo-hydroxides of Fe and Mn (Lacerda et al., 1988; Lacerda, 1998), and occur at high concentrations, due to industrial inputs to Sepetiba Bay (Barcellos and Lacerda, 1994). However, the concentrations of dissolved and particulate Mn, in open bay waters, do not explain the high concentrations found in creek waters. In general, Sepetiba Bay waters contain dissolved Mn concentrations 1–2 orders of magnitude lower than the average creek waters (Lacerda et al., 1988). Thus, the influence of other sources of Mn to creek waters is suggested, such as inputs of Mn from the mud flat-tidal water interactions during flooding.

Mud flat chemistry

Figure 4 shows the variation of Eh, dissolved Oxygen, pH and TSS in rising tidal waters passing over the mud

flat surface adjacent to the IEF, prior to reaching the tidal creek. When reaching the mud flat area, Sepetiba bay waters (SB) changed significantly. There is a sharp reduction in redox potential and dissolved oxygen (Figure 4a) and a significant increase in pH and TSS (Figure 4b). These changes suggest re-suspension of bottom sediments, and the flushing out of mud flat pore waters. Pore waters typically contain low oxygen and Eh values and an increase in alkalinity as a result of sulfate reduction (Marins et al., 1997, Lacerda et al., 1997). These characteristics are generally maintained throughout the surface of the tidal flat up to the edge of the tidal creek at station 5. This suggests that intrusion of pore water continues, at least from station 1 to station 4. However, sediment re-suspension seems to occur only at the edge of the mud flat (station 1), and to a lesser extent in stations 2 and 3. From station 4 onward, hydrochemistry is similar to that observed in creek waters at high tide (Figures 2 and 3). Ovalle et al. (1991) and Ovalle (1992) proposed a piston-like mechanism to explain the nutrient enrichment observed in incoming tidal waters at the IEF. Through this mechanism, reducing pore waters, enriched in nutrients, are pushed up from mud flat sediments by tidal forcing, enriching oxidized tidal creek waters with dissolved nutrients.

Figure 5 shows the variation of dissolved Mn concentrations in incoming tidal waters passing over the mud flat surface, and the weakly and strongly bound Mn concentrations in the TSS and surface sediments along the mud flat. Care is necessary in comparing absolute concentrations and the geochemical partitioning of Mn from these surface samples with the top layers of sediment cores. Surface sediments (0–1.0 cm of depth) contained fine sands, which contain relatively lower Mn concentrations, whereas sediment cores, which were collected below 1.0 cm, were composed of fine and uniform grain size, with relatively higher Mn concentrations. There is a clear increase in dissolved and particulate Mn concentrations as the water advances over the mud flat to the adjacent tidal creek and to the mangrove forest (Figure 5a,b). This enrichment may be explained by re-suspension, followed by desorption of Mn-enriched sediments or, alternatively, by tidal flushing of dissolved Mn-enriched pore waters, followed by adsorption onto the TSS, from Sepetiba Bay water to station 2. Although re-suspension of bottom sediment does occur at the mud flat, as confirmed by the increase in TSS (Figure 4b), there is no significant variation either in weakly or strongly bound Mn concentrations in surface sediments (Figure 5c),

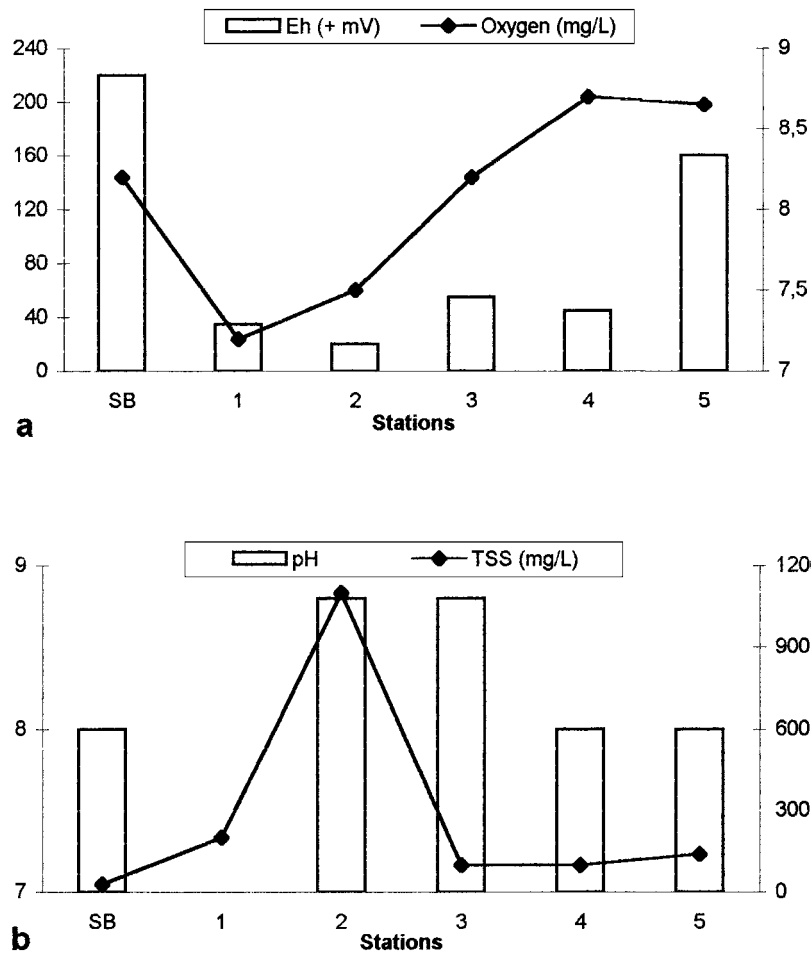


Figure 4. Average values of Eh, dissolved oxygen, pH and TSS, along the mud flat gradient during flooding at the Itacuruça Experimental Forest. SB represents Sepetiba Bay Station.

as well as strongly bound Mn concentrations in the TSS (Figure 5b). This suggests that re-suspension of bottom sediments has no significant effect on the Mn concentrations of tidal waters. However, a 20-times increase of dissolved Mn and a six-times increase in the weakly bound concentrations of Mn in the TSS, are observed in tidal water as it floods the mud flat (station 1). This strongly suggests that flushing of Mn enriched pore waters, followed by adsorption onto the TSS is occurring. When dissolved Mn reaches oxidized surface waters, enriched in TSS at station 1, the dominant oxidizing conditions of the flood waters result in the oxidation of Mn II to Mn IV and adsorption onto suspended particles, forming coatings. As a result, tidal waters reaching the tidal creek are enriched in dissolved Mn by at least four times relative to the original bay water. Also, it shows a 10-times enrichment in particulate Mn adsorbed to TSS.

Some support of the described mechanism is obtained through the analysis of Mn distribution and partitioning in sediment cores in the mud flat. Figure 6 shows the Mn distribution in sediment cores from the studied mud flat. Strongly bound Mn concentrations were nearly constant throughout the sediment profile, with values of about $200 \mu\text{g g}^{-1}$. However, weakly bound concentrations were up to five times higher in the top portion of the cores compared to deeper layers. This increase in the weakly bound fraction of Mn at the top of the core, is well documented in literature, as a result of the upward migration of reduced Mn II from deeper, reducing, sediment layers, followed by adsorption to sediment particles upon reaching oxidized layers (Giblin et al., 1986; Sprat and Hodson, 1994; Lacerda et al., 1997). The results obtained on sediment cores, support the upward migration of Mn II and further oxidation and adsorption onto sediments,

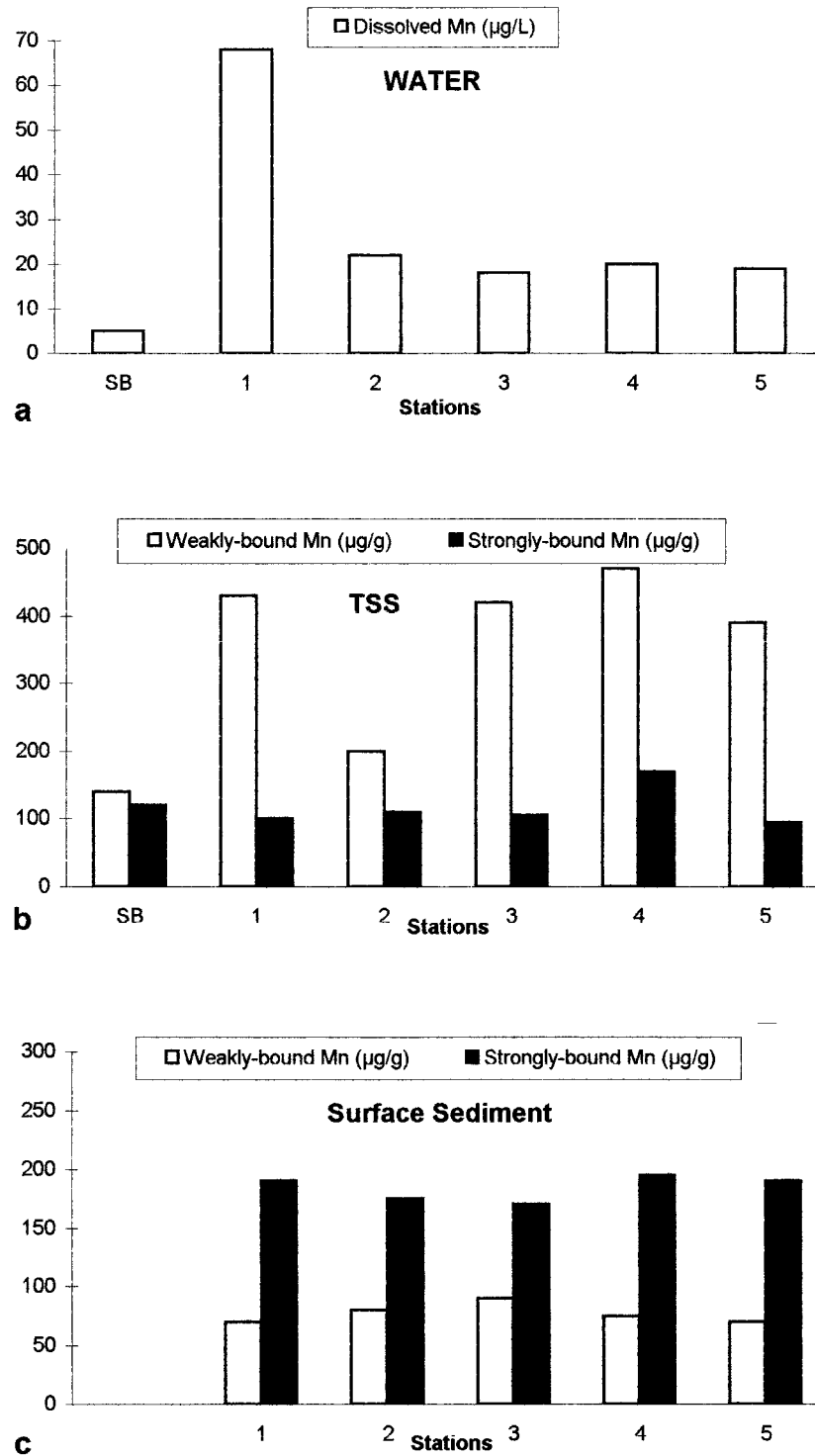


Figure 5. Average Mn concentrations in water, in total suspended solids (TSS) and surface bottom sediments, along the mud flat gradient during flooding at the Itacuruça Experimental Forest.

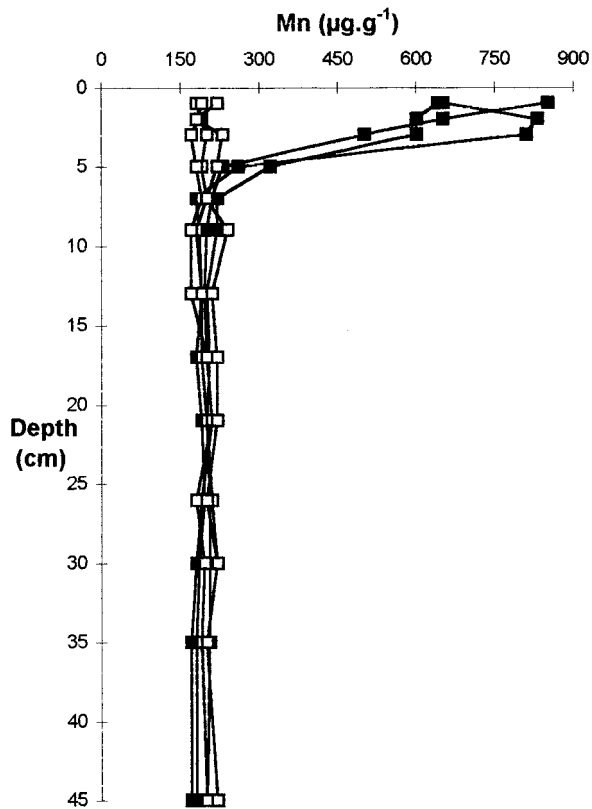


Figure 6. Depth distribution of weakly bound Mn (■) and strongly bound Mn (□) concentrations along sediment cores from the Itacuruça Experimental Forest mud flat. Each line represents average Mn concentrations from a duplicate sample of a single core.

as the major mechanism responsible for the Mn enrichment of tidal waters and TSS entering the IEF tidal creek.

In conclusion, dissolved Mn concentrations result from a dynamic balance between the rate of production of dissolved Mn (through reduction of oxidized species) and the rate of production of particulate Mn (through oxidation of reduced forms) (Gratton et al., 1990; Luther III et al., 1998). Manganese is highly reactive particle and dissolved Mn concentrations are low in oxic waters as a result of oxidative scavenging onto suspended particles. Reduced Mn species oxidize to insoluble Mn oxy-hydroxides and amorphous coatings, frequently associated with Fe (Giblin et al., 1986; Saager et al., 1997). The freshly formed Mn coatings are very efficient in scavenging additional Mn and Fe, as well as other trace metals, from the water column. When reaching the reducing conditions during ebb tide periods inside the mangrove, Mn coatings dissolve, releasing soluble Mn. Manganese is kept in solution and able to be incorporated by mangrove

plants, explaining the relatively high Mn concentrations in mangrove leaves and their correlation with Mn concentrations in sediments. A larger proportion of the dissolved Mn may be exported to adjacent coastal waters, able to start its biogeochemical cycle at the mud flat–mangrove interface.

Acknowledgments

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References

- Ackroyd, D.R., Bale, A.J., Howland, R.J.M., Knox, G.E., Millward, G.E. and Morris, A.W. 1986. Distribution and behavior of dissolved Cu, Zn and Mn in the Tamar Estuary. *Estuarine, Coastal and Shelf Science* 23: 621–640.
- Barcellos, C. and Lacerda, L.D. 1994. Cadmium and zinc source assessment in Sepetiba Bay and basin region. *Environmental Monitoring and Assessment* 29: 183–199.
- Clark, M.W., McConchie, D., Saenger, P. and Pillsworth, M. 1997. Hydrological controls on copper, cadmium, lead and zinc concentrations in an anthropogenically polluted mangrove ecosystem, Wynnnum, Brisbane, Australia. *Journal of Coastal Research* 13: 1150–1158.
- Fizszman, M., Pfeiffer, W.C. and Lacerda, L.D. 1984. Comparison of methods for analyses and geochemical partitioning of heavy metals in sediments from Sepetiba Bay, Rio de Janeiro, Brazil. *Environmental Technology Letters* 5: 567–575.
- Förstner, U. and Wittmann, G.T.W. 1979. *Metal Pollution in the Aquatic Environment*. Springer-Verlag, Berlin.
- Giblin, A.E., Luther III, G.N. and Valiela, I. 1986. Trace metals solubility in salt marsh sediments contaminated with sewage sludge. *Estuarine, Coastal and Shelf Science* 23: 477–498.
- Gratton, Y., Edenborn, H.M., Silverberg, N. and Sundby, B. 1990. A mathematical model for manganese diagenesis in biodisturbed sediments. *American Journal of Science*. 290: 246–262.
- Harbinson, P. 1986. Diurnal variations in the chemical environment of a shallow tidal inlet, Gulf of St Vincent, South Australia: implications for water quality and trace metal migration. *Marine Environmental Research* 20: 161–195.
- Kjerfve, B. 1990. *Mangrove Hydrology*. UNESCO, Paris.
- Krauskopf, K.B. 1979. *Introduction to Geochemistry*. 2nd edition. McGraw-Hill Kogakusha, Tokyo.
- Lacerda, L.D. 1997. Trace metals in mangrove plants, why such low concentrations? pp. 71–78. In: Kjerfve, B., Lacerda, L.D. and Diop, E.S. (eds), *Mangrove Ecological Studies in Latin America and Africa*. UNESCO, Paris.

- Lacerda, L.D. 1998. Biogeochemistry of trace metals and diffuse pollution in mangrove ecosystems. ISME occasional papers 2. International Society for Mangrove Ecosystems, Okinawa.
- Lacerda, L.D., Martinelli, L.A., Rezende, C.E., Mozetto, A.A., Victoria, R.L., Silva, C.A.R. and Nogueira, F.B. 1988. The fate of trace metals in suspended matter in a mangrove creek during a tidal cycle. *Science of the Total Environment* 75: 249–259.
- Lacerda, L.D., Freixo, J.L. and Coelho, S.M. 1997. The effect of *Spartina alterniflora* Loisel on trace metals accumulation in inter-tidal sediments. *Mangroves and Salt Marshes* 1: 201–209.
- Landing, W.M. and Bruland, K.W. 1980. Manganese in the North Pacific. *Earth & Planetary Sciences Letters* 49: 45–56.
- Lovley, D.R. 1993. Anaerobes and heavy metals: Dissimilatory metal reduction in anoxic environments. *Trends in Ecology and Evolution* 8: 241–245.
- Luther III, G.W., Brendel, P.J., Lewis, B.L., Sundby, B., Lefrançois, L., Silverberg, N. and Nuzzio, D. 1998. Simultaneous measurements of O₂, Mn, Fe, S⁻ and S(-II) in marine pore waters with a solid-state voltametric microelectrode. *Limnology & Oceanography* 43: 325–333.
- Marins, R.V., Lacerda, L.D., Gonçalves, G.O. and Paiva, E.C. 1997. Effect of root metabolism on the post-depositional mobilization of mercury in salt marsh soils. *Bulletin of Environmental Contamination and Toxicology* 58: 733–738.
- Morris, A.W., Boile, A.J. and Holwstuarins, M. 1982. The dynamics of manganese cycling. *Estuarine, Coastal and Shelf Science* 14: 175–192.
- Ovalle, A.R.C. 1992. Hidroquímica de um canal de mare do manguezal de Itacuruça, Baía de Sepetiba, RJ. PhD dissertation, Universidade Federal de São Carlos, São Carlos.
- Ovalle, A.R.C., Rezende, C.E., Lacerda, L.D. and Silva, C.A.R. 1991. Hydrochemistry of a mangrove tidal creek in Sepetiba Bay, Rio de Janeiro, Brazil. *Estuarine, Coastal and Shelf Science* 31: 639–650.
- Resing, J.A. and Mottl, M.J. 1992. Determination of manganese in sea water using flow injection analysis with on-line pre-concentration and spectrophotometric detection. *Analytical Chemistry* 64: 2682–2687.
- Rezende, C.E., Lacerda, L.D., Ovalle, A.R.C., Silva, C.A.R. and Martinelli, L.A. 1990. Nature of POC transport in a mangrove ecosystem: a carbon isotopic study. *Estuarine, Coastal and Shelf Science* 30: 641–645.
- Saager, P.M., de Baar, H.J.W., de Jong, J.T.M., Nolting, R.F. and Schijf, J. 1997. Hydrography and local sources of dissolved trace metals Mn, Ni, Cu and Cd in the northeast Atlantic Ocean. *Marine Chemistry* 57: 195–216.
- Silva, C.A.R., Lacerda, L.D. and Rezende, C.E. 1991. Forest structure and biomass distribution in a red mangrove stand in Sepetiba bay, RJ. *Revista Brasileira de Botânica* 14: 23–28.
- Sprat, H.G. and Hodson, G. 1994. The effect of changing water chemistry on rates of manganese oxidation in surface sediments of a temperate salt marsh and a tropical mangrove estuary. *Estuarine, Coastal and Shelf Science* 38: 119–135.
- Sprat, H.G., Siekman, B.C. and Hodson, G. 1994. Microbial manganese oxidation in salt marsh surface sediments using a leuco crystal manganese detection technique. *Estuarine, Coastal and Shelf Science* 38: 91–112.