

## Geochemistry of Mercury in Sediments of a Sub-Tropical Coastal Lagoon, Sepetiba Bay, Southeastern Brazil

R. V. Marins,<sup>1</sup>L. D. Lacerda,<sup>1</sup>H. H. M. Paraquetti,<sup>2</sup>E. C. de Paiva,<sup>2</sup>  
R. C. Villas Boas

<sup>1</sup>Department of Geochemistry, Fluminense Federal University, Niterói,  
24020-007, RJ, Brazil

<sup>2</sup>Mineral Technology Center, Rio de Janeiro, 21941-100, RJ, Brazil

Received: 8 December 1997/Accepted: 1 May 1998

Sheltered coastal areas have been acting as final receptors of industrial and urban effluents in most developing countries. The capacity of such water bodies to act as sinks of pollutants, in particular, of heavy metals, is related to the anaerobic conditions generally found in their bottom sediments. However, this capacity is mostly unknown and remobilization processes may eventually release deposited heavy metals to the water column (Nixon, 1980; Rasmussen, 1994; Barcellos *et al.*, 1997). Therefore, knowing the total concentration of heavy metals in coastal sediments is not sufficient to determine the potential contamination of a given area. Rather, the potential availability of heavy metals in such environments is dependent on the strength of the binding with sedimentary phases.

Sepetiba Bay is a coastal lagoon located approximately 60 km south of Rio de Janeiro city, SE Brazil. The Bay has an area of 440 km<sup>2</sup>, an average depth of 6.0 m and a water turnover time of 100 hours. It receives a fluvial input of *circa* 7.6 million m<sup>3</sup> per year, mostly from an artificial canal with nearly constant flow due to the controlled discharge of a water treatment plant, the Canal de São Francisco (figure 1). This canal is responsible for over 86% of the total freshwater flow to the Bay (Watts, 1990). Sepetiba Bay basin harbors nearly 400 industries and approximately 1.1 million inhabitants, and important fisheries and tourist activities are also present.

Mercury is an ubiquitous contaminant present in the urban and industrial effluents reaching Sepetiba Bay. Mercury emissions to soils, waters and the atmosphere at Sepetiba Bay basin are mostly from diffuse sources, particularly from an oil-fired electric power plant, steel and iron production, waste incineration and leaching from a large land fill. Total anthropogenic Hg input to Sepetiba Bay ranges from 500 to 750 kg.yr<sup>-1</sup> (Marins *et al.*, 1998). A significant fraction of the total input reaches the bay through atmospheric deposition at a rate of 76 µg.m<sup>-2</sup>.y<sup>-1</sup>. Total accumulation from atmospheric deposition ranges from 115 to 150 kg.yr<sup>-1</sup> (Marins *et al.*, 1996). Fluvial inputs, however, dominates the total Hg load to the Bay, ranging from 300 to 650 kg.yr<sup>-1</sup>. Once reaching the Bay, Hg, as well as other trace metals transported by rivers, which are mostly adsorbed with suspended particles, are distributed following tidal currents within the bay, which create accumulation areas along its northeastern coast (Lacerda *et al.*, 1987; Barcellos *et al.*, 1997).

The accumulation of Hg in the Bay's bottom sediments will depend not only on the physical distribution of fluvial inputs, but also on the geochemical interaction between Hg and sedimentary phases. The strength of the binding between Hg and

sedimentary phases will eventually control its bioavailability. There is no survey on the fate of Hg in Sepetiba Bay sediments and its availability (FEEMA, 1989) and the very fate of Hg in tropical coastal areas is still poorly known. The primary objective of this study is to examine the spatial distribution of Hg in bottom sediments and its geochemical associations with the major carriers of Hg in coastal environments (Salomons & Förstner, 1984; Meyer, 1996) namely, Fe and Mn hydro-oxides, organic matter, and sulfides. The presence of Hg in fish is a good indicator of its bioavailability in aquatic systems and represents the main Hg contamination pathway for humans (Porcella, 1994; Kehrig, 1995; Meyer, 1996). A secondary objective of this study is to determine the Hg content of selected fish species to determine the potential bioavailability of Hg in Sepetiba Bay waters.

## MATERIALS AND METHODS

Bottom sediment samples were collected in the major rivers and the bay area from a boat using a Van Veen grab sampler (Figure 1). A homogenized sampling from the central part of the grab was taken, to avoid the sediment in contact with grab walls. Samples were put in plastic bags and frozen immediately upon collection. This avoided any major oxidation of sediments during the period of collection. Samples were kept frozen until analysis, which took place no longer than 2 days after sampling.

Selected top carnivorous fish species; flounder (*Paralichthys brasiliensis*, Bothidae), snook (*Centropomus undecimalis*, Centropomidae), and croaker (*Micropogonias furnieri*, Scianidae), were obtained from local fisherman. Two fillets, each weighing approximately 200 g, were cut from each individual and immediately frozen. Three individuals of each species were analyzed.

At the laboratory, sub-samples of the sediment were analyzed for organic matter content, after combustion at 450 °C for 24 hours. The ashen sediment samples were analyzed for total Fe and Mn concentrations through conventional flame atomic absorption spectrophotometry. Total sulfur concentrations were analyzed in a Leco-SC-232 auto analyzer. National Institute of Standards and Technology, USA, Estuarine Sediments were analyzed simultaneously for these constituents. The results were always within 10% of the refereed concentration.

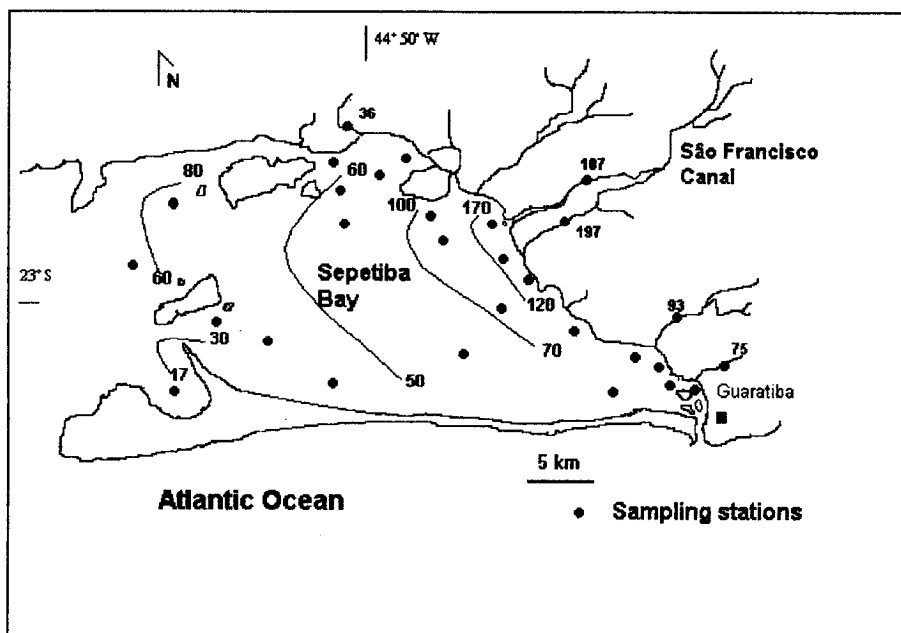
Total mercury concentrations in sediment samples (dried at 60 °C until constant weight) were determined after acid extraction and stannous chloride reduction by cold vapor atomic absorption spectrophotometry, following standard procedures described in Gonçalves (1993). Reagent blanks and intercalibrated sediment samples (National Institute of Standards and Technology, USA), were run simultaneously for precision determination of the methods used. All blanks gave Hg concentrations smaller than 30% of the lowest Hg concentrations found in samples. Intercalibration with reference samples gave values of  $58 \pm 3.0 \text{ ng.g}^{-1}$  (n=15) for a refereed value of  $60 \text{ ng.g}^{-1}$ .

In addition from the total Hg determinations, sediment samples were also submitted to a sequential extraction procedure to remove Hg associated with exchangeable phases (leaching with cold 0.5 N HCl, after 34 hours contact) (Fiszman *et al.*, 1984), with amorphous Fe and Mn hydro-oxides (leaching with  $\text{NH}_2\text{OH.HCl}$  0.1M +  $\text{CH}_3\text{COOH}$  25% v/v after 4 hours of contact) (Souza *et al.*, 1986), with refractory Fe and Mn hydro-oxides (leaching with a Na ditionite-citrate solution, after 4 hours of contact), and with organic matter (leaching with NaOH 0.2N, after 2 hours of

shaking (Lechler *et al.*, 1997). Analysis of Hg in these extracts were run following the same procedures as the total Hg analysis. The remaining Hg is considered residual, either encapsulated in silica or as Hg sulfides (Lechler *et al.*, 1997). Mercury content of fish were analyzed according to methods described in Malm *et al.* (1989). Standard reference material was analyzed simultaneously and results were always within 10% of the certified value).

## RESULTS AND DISCUSSION

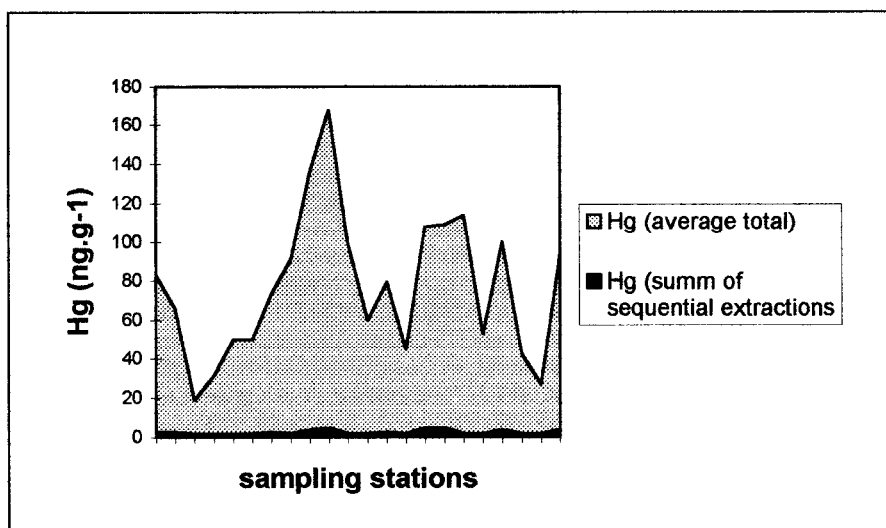
Mercury concentrations in bottom sediments of the major rivers reaching Sepetiba Bay ranged from 36 to 197  $\text{ng.g}^{-1}$ , with higher concentrations found in rivers draining the industrial area of the basin. Bottom sediments from the bay showed Hg concentrations ranging from 17 to 163  $\text{ng.g}^{-1}$ , with the highest concentrations being found close to major river discharges, confirming the strong influence of fluvial loads on Hg distribution in the Bay (Figure 1). From the stations with high sediment concentration close to river mouths, Hg content in bottom sediments decreases consistent with the dispersion and dilution of fluvial sediments by currents into the bay, in a manner similar to other trace metals from anthropogenic sources previously studied in Sepetiba bay (Lacerda *et al.*, 1987; Barcellos, 1995).



**Figure 1.** Mercury concentrations in bottom sediments from major rivers (average values from three samples in each river) and from Sepetiba Bay, SE Brazil ( $\text{ng.g}^{-1}$ ).

The previous investigation of Mar-ins *et al.* (1997) found pm-industrial Hg concentrations ranging from 20 to 30  $\text{ng.g}^{-1}$  in sediment cores from Sepetiba Bay. These concentrations are similar those found in this study in surface sediments at the outer sampling stations of Sepetiba Bay. Therefore, we can consider these concentrations to reflect the regional background. The concentrations of Hg in Sepetiba Bay sediments show a ten-fold increase at the inner sampling stations due to anthropogenic inputs.

Mercury distribution in potentially mobile geochemical phases (as the sum of the fractions obtained using the selective extractions, i.e. exchangeable, associated with Fe and Mn hydro-oxides, and with organic matter) and of total Hg, is shown in figure 2. Over 95% of the total Hg content of sediments was highly refractory to the extractors used, and could not be removed by any of the sequential treatments affecting, exchange sites, Fe and Mn hydro-oxides or organic matter. This suggests that the only possible form of Hg in such sediments would be either Hg present in detrital geological silicate material or Hg sulfides (Lechler *et al.*, 1997). Since there is no Hg-bearing detrital silicate or sulfide phases in the Sepetiba Bay source areas geology (Bidone, 1988) and that Hg is emitted to Sepetiba Bay from diffuse sources, therefore expected to be mostly as  $Hg^{2+}$ , it is unlikely that any resistant Hg species is a component of the anthropogenic emissions reaching the Bay (Marins *et al.*, 1998). Therefore the refractory Hg must be formed *in situ* (or by sediment diagenetic processes), within the sediments themselves, after deposition. Thus Hg sulfides associated with other metal sulfides, formed after deposition, are probably the major geochemical substrates for Hg in the Bay's bottom sediments.

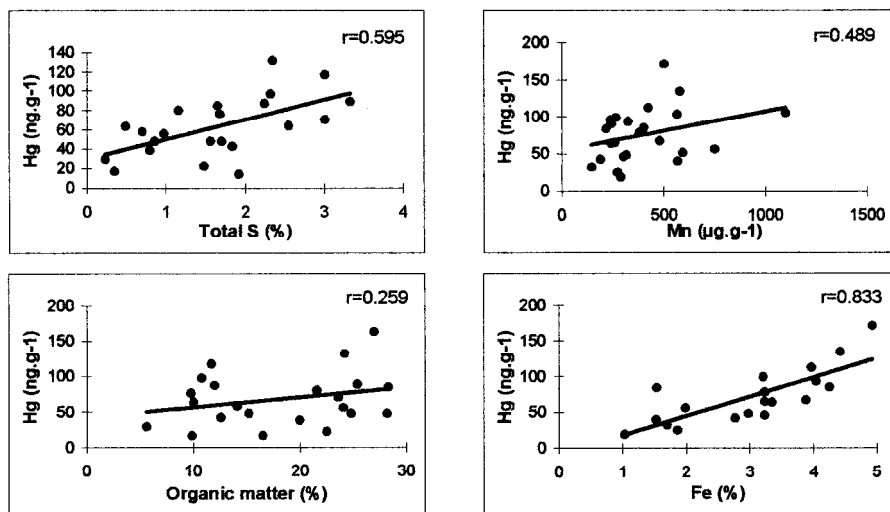


**Figure 2.** Mercury distribution in selected geochemical phases in bottom sediments of Sepetiba Bay, SE, Brazil.

The relationships between Hg concentrations and those of Fe, Mn, organic matter and total sulfur, are presented in figure 3. Mercury is significantly correlated with Fe ( $r=0.833$ ,  $P<0.01$ ,  $n=22$ ) and sulfur ( $r=0.595$ ,  $P<0.01$ ,  $n=22$ ) concentrations, but not with organic matter content ( $r=0.259$ , ns,  $n=22$ ), and Mn ( $r=0.489$ , ns,  $n=22$ ) concentrations.

The absence of a significant correlation between Hg and the organic matter and Mn content of sediments, and the strong correlation with Fe and S, confirm the sequential extraction done, strongly suggesting that Hg- and/or Fe-sulfides are the major geochemical substrates for Hg in Sepetiba Bay bottom sediments. In sub-oxic and anoxic sediments, Hg concentrations are sulfide dependent and, at pH 7 and 1 mM to 10 mM sulfide, Hg may precipitate as  $HgHS_2$  and  $HgS_2$  (Dyrssen, 1985) or coprecipitate with FeS and polysulfides (Boulegue *et al.*, 1982) starting to

accumulate in sediments (Gaillard *et al.*, 1988; Feijtel *et al.*, 1988; Lacerda *et al.*, 1993). These conditions are permanently found in most bottom sediments of Sepetiba Bay (Barcellos, 1995; Marins *et al.*, 1997). Upon oxidation however, Hg sulfides present in bottom sediments dissociate (Engler & Patrick, 1975). This has been shown to occur in sediments at the margins Sepetiba Bay due the bioturbation caused by the root metabolism of salt marsh plants (Marins *et al.*, 1997) which can also transfer the absorbed Hg to leaves (Kraus *et al.*, 1986). Wave action and tidal currents can also oxidize sediments from shallow (< 1.0 m) areas of Sepetiba Bay, which represents *circa* 35% of the total bay area (Barcellos, 1995).

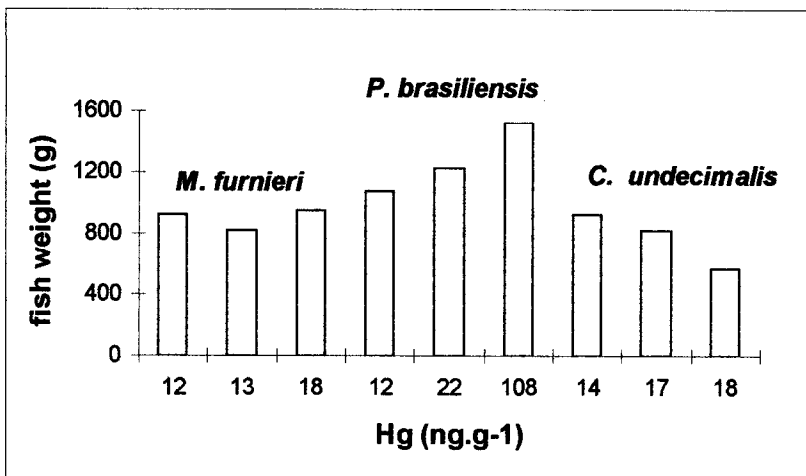


**Figure 3.** Correlation between Hg concentrations and the concentrations of Fe, Mn, organic matter and total S in bottom sediments from Sepetiba Bay, SE Brazil.

Once in pore water, metals may complex with water soluble organic substances and migrate through the sediment column (Sikora & Keeney, 1983). Organo-sulfur molecules, which are particularly resistant to oxidation and are enriched in coastal bottom sediments, may play an important role in the complexation, solubilization and diffusion of metals, in particular Hg (Boulegue *et al.*, 1982; Rasmussen, 1994). Also these Organic-Hg complexes can facilitate Hg methylation by bacterial activities, enhancing the bioavailability of Hg to aquatic food chains and environmental transport (Krishnamurthy, 1992). Mercury methylation is linked to the sulfur cycling in aquatic sediments, probably via sulfate reduction (Campeau & Bartha, 1985; Gilmour & Henry, 1991).

Methyl-Hg is the dominant Hg species in fish flesh and, in general, correlates positively with fish size (Huckabee *et al.*, 1979; Porcella, 1994). Although methyl-Hg was not analyzed in this study, the evaluation of total Hg concentrations in fish may be a good indication of the occurrence of the methylation process.

Figure 4 shows Hg distribution in the three fish species analyzed from Sepetiba Bay according to their body weight Mercury concentrations were low ranging from 12 - 18 ng.kg<sup>-1</sup> in *Micropogonias furnieri* and *Centropomus undecimalis*, to 108 ng.kg<sup>-1</sup> in the largest individuals of *Palalichthys brasiliensis*. This latter species is a top carnivore abundant in the bay and intensively consumed by the local population.



**Figure 4.** Mercury concentrations in fish species from Sepetiba Bay, SE Brazil. Bar height is the average Hg concentration from a duplicate sample of a single individual.

It was not the objective of the present study to analyze the Hg distribution in fish from Sepetiba Bay, but to use fish Hg concentrations as an indicator of Hg remobilization and possibly methylation in the Bay.

A previous large survey done in the same area by Kehrig (1995) with *Micropogonias furnieri*, found Hg concentrations ranging from 19.5 in smaller individuals (close to the size used in this study) to 252.2 in larger individuals, and Hg concentrations did correlate significantly with body weight. Notwithstanding the preliminary nature of the fish analysis and the low concentrations found in this study, probably due to the utilization of relatively small individual fish, Hg distribution presented a significant correlation with fish weight, when all fish species were considered together ( $r=0.757$ ,  $P<0.01$ ,  $n=9$ ). For a single species however, only the top predator, *Paralichthys brasiliensis*, showed this relationship (figure 4). These results are sufficient, however, to strongly suggest that methyl-Hg is being formed in Sepetiba Bay, probably after the remobilization and oxidation of Hg associated with sulfides in bottom sediments (Marins *et al.*, 1997) via sulfate reduction (Compeau & Bartha, 1995).

In conclusion, Hg in Sepetiba Bay bottom sediments shows an enrichment by a factor of 10 relative to local background. Concentrations are distributed according to the deposition of fluvial sediments. After deposition, Hg is associated with sulfides formed, *in situ*, within the sediments. However, although these geochemical substrates are an efficient sink for Hg, oxidation of bottom sediments due to various processes may remobilize the associated Hg. Fish Hg concentration distributions suggest that part of the sediment Hg can be transformed to methyl-Hg and incorporate in the local biota. Therefore, knowing the total concentration of Hg in coastal sediments is not sufficient to determine the potential contamination of a given area. Rather, the potential availability of Hg in such environments is dependent on the biogeochemical processes affecting Hg after deposition.

*Acknowledgments.* This work was supported by Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação de Amparo a Pesquisa do Estado do Rio de Janeiro (FAPERJ) and the Ministry of Education (CAPES), Brazil, for grants to the authors. Thanks are also due to the support and Rural Federal University of Rio de Janeiro for logistics in Sepetiba bay.

## REFERENCES

- Barcellos C (1995) Biogeodinamica de Cd e Zn na Baía de Sepetiba. Tese de Doutorado, Universidade Federal Fluminense, Niterói, p 212
- Barcellos C, Lacerda LD, Serrini C (1997) Sediment and trace metals balance in a sub-tropical coastal area, Sepetiba Bay, SE Brazil. *Environ Geol* 32:203-209
- Bidone ED (1986) Estudos integrados do sistema de drenagem das bacias das lagoas de maria e guarapina. Projeto FINEP. Final Report Univ Fed Fluminense, Niteroi, p 356
- Boulegue J, Lord III CJ, Church TM (1982) Sulfur speciation and associated trace metals (Fe, Cu) in the pore waters of Great Marsh, Delaware. *Geochim Cosmochim Acta* 46:453-464
- Campeau GC, Bartha R (1985) Sulfate-reducing bacteria: principal methylators of mercury in anoxic estuarine sediments. *Appl Environ Microbiol* 50:498-502
- Dyrssen D (1985) Metal complex formation in sulfidic seawater. *Mar Chem* 15:285-293
- Engler RM, Patrick Jr. WH (1975) Stability of sulfides of manganese, iron, zinc, copper and mercury in flooded and non-flooded soils. *Soil Sci* 119:217-221
- FEEMA (1989) Qualidade das Águas do Estado do Rio de Janeiro 1987-1989, vol. IV - Baía de Guanabara e Sepetiba. Fundação Estadual de Engenharia do Meio Ambiente, Rio de Janeiro, p 180
- Fejtel TC, DeLaune RD, Patrick Jr WH (1988) Biogeochemical control on metal distribution and accumulation in Louisiana sediments. *J Environ Qual* 17:88-94
- Fizman M, Pfeiffer WC, Lacerda LD (1984) Comparison of methods used for extraction and geochemical distribution of heavy metals in bottom sediments from Sepetiba Bay, RJ. *Environ Technol Lett* 5:567-575
- Gaillard JF, Jeandel C, Michard G, Nicolas E, Renard D (1986) Interstitial water chemistry of Villefranche Bay sediments: Trace metal diagenesis. *Mar Chem* 18:233-247
- Gilmour CC & Henry EA (1991) Mercury methylation in aquatic systems affected by acid deposition. *Environ Pollut* 71:131-169
- Gonçalves GO (1993) Instrução Técnica, IT 003, Biblioteca CETEM, Rio de Janeiro, p 6
- Huckabee JW, Elwood JW, Hildebrand SG (1979) Accumulation of mercury in freshwater biota. In: JO Nriagu (ed) *the Biogeochemistry of mercury in the Environment*, Elsevier North/Holland, New York, p 277-302
- Kehrig HA (1995) *Estudo da contaminação por Hg em corvinas (Micropogonias furnierii) em quatro áreas costeiras do Brasil*. Tese de Mestrado, Pontifícia Universidade Católica, Rio de Janeiro, p 132
- Kraus ML, Weis P, Crow JH (1986) The excretion of heavy metals by salt marsh cord grass *Spartina alterniflora*, and *Spartina's* role in mercury cycling. *Mar Environm Res* 20:207-216
- Krishnamurthy S (1992) Biomethylation and environmental transport of metals. *J Chem Education* 69:347-350
- Lacerda LD, Pfeiffer WC, Fizman M (1987) Heavy metal distribution, availability and fate in Sepetiba Bay (SE-Brazil). *Sci Tot Environ* 65:163-173

- Lacerda LD, Carvalho CEV, Tanizaki KF, Ovalle AR, Rezende CE (1993) The biogeochemistry and trace metals distribution of mangrove rhizospheres. *Biotropica* 25:252-257
- Lechler J, Miller JR, Hsu LC, Desilets MO (1997) Mercury mobility at the Carson River Superfund Site, west-central Nevada, USA: interpretation of mercury speciation data in mill tailings, soils and sediments. *J Geochem Exploration* 58: 259-267.
- Malm O, Pfeiffer WC, Bastos WR, Souza CMM (1989) Utilização do acessório de geração de vapor frio para análise de mercúrio em investigações ambientais por espectrometria de absorção atômica. *Ciência Cultura* 41: 88-92
- Marins RV, Silva Filho EV, Lacerda LD (1996) Atmospheric deposition of mercury over Sepetiba bay. *J Braz Chem Soc* 7: 177-180
- Marins RV, Lacerda LD, Gonçalves GO, Paiva EC (1997). Effect of root metabolism on the post-depositional mobilization of mercury in salt marsh soils *Bull Environ Contamin Toxicol.* 58:733-738
- Marins RV, Lacerda LD, Villas Boas RC (1998) Relative importance of non-point sources of mercury to an industrialized coastal system, Sepetiba Bay, SE Brazil. In: Ebinhaus R, Turner RR, Lacerda LD, Vasiliev O, Salomons W (eds), *Mercury Contaminated Sites: Assessment and Remediation*. Springer Verlag, Berlin, (in press)
- Meyer U (1996) On the fate of mercury in the Northeastern Brazilian mangrove system, Canal de Santa Cruz, Pernambuco. *Zentrum für Marine Tropenökologie, Bremen*, p 105
- Porcella DB (1994) Mercury in the environment: Biogeochemistry. In: *Mercury Pollution: Integration and Synthesis*. Watras CJ & Huckabee JW (eds), p 3-19
- Nixon SW (1980) Between coastal marshes and coastal waters - A review of twenty years of speculation and research on the role of salt marshes in estuarine productivity and water chemistry. In: Hamilton P, Macdonald KB (ed.), *Estuarine & Wetland Process with Emphasis on Modeling*. Plenum Publ. Corp., New York. p 437
- Rasmussen PE (1994) Current methods of estimating atmospheric mercury fluxes in remote areas. *Environ Sci Technol* 28:2233-2241
- Salomons W, Förstner U (1984) *Metals in the Hydrocycle*. Springer Verlag, Berlin, p 349
- Sikora LJ, Keeney DR (1983) Further aspects of soil chemistry under anaerobic conditions. In: Gore APJ (ed.), *Mires, Swamp, Bog, Fen and Moor. General Studies*. Elsevier Sci. Publ. Amsterdam, p 247
- Souza CMM, Pestana MHD, Lacerda LD (1986) Heavy metal geochemical partitioning in sediments of three estuaries along the Rio de Janeiro coast. *Sci Tot Environ* 58:63-72
- Watts PPR (1990) Entradas fluviais de metais pesados para a baía de Sepetiba e seu comportamento na região estuarina. MSc. T., Dept. Geoquímica, Univ. Fed. Fluminense, Niterói, p 151