



## **MERCURY DISTRIBUTION IN SEDIMENTS OF A SUB-TROPICAL COASTAL LAGOON, SEPETIBA BAY, SE BRAZIL**

L. Veeck<sup>1,2</sup>, E. V. Silva-Filho<sup>1\*</sup>, J.C. Wasserman<sup>3</sup>, S. M. Sella<sup>4</sup>, I.R. Santos<sup>2</sup>, L.D. Lacerda<sup>1,5,\*</sup>

<sup>1</sup>Universidade Federal Fluminense, Depto de Geoquímica  
Niterói, RJ, Brasil, 24020-007.

<sup>2</sup>Southampton Oceanography Centre, SOES.  
European Way Southampton, UK, SO14 3ZH.

<sup>3</sup>Universidade Federal Fluminense, Depto de Análise Geoambiental  
Niterói – RJ, 24.210-340, Brazil

<sup>4</sup>Universidade Federal Fluminense, Depto de Química Analítica  
Niterói - RJ, 24020-007, Brazil.

<sup>5</sup>Instituto de Ciências do Mar, Universidade Federal do CearáFortaleza, CE, Brasil 60165-081.

\*E-mail: pgcmt@labomar.ufc.br

Recebido em janeiro de 2006, aprovado para publicação em novembro de 06

### **ABSTRACT**

The distribution of Hg accumulated in sediments of Sepetiba Bay (Rio de Janeiro, Brazil) and its possible associations with sediment geochemical properties (iron, organic carbon, nitrogen, sulphur concentrations and organic matter content) were investigated. The spatial distribution of the variables considered in this study is predominantly determined by the pattern of water circulation, sediment transport along the eastern shore as well as natural and anthropogenic sources. The most important mercury source for the bay is the input from the main rivers, and their mouths are the most favourable sites for mercury accumulation. Sediment composition in this bay is strongly influenced by fluvial inputs of mercury, organic matter and fine-grained sediments, suggesting the partitioning of the bay into two regions; one receiving a strong influence from the rivers and the other mainly influenced by the sea.

### **RESUMO**

É apresentada a distribuição de Hg em sedimentos de fundo da Baía de Sepetiba (Rio de Janeiro, Brasil) e discutida suas associações com parâmetros geoquímicos (concentração de ferro, carbono orgânico, nitrogênio, enxofre e conteúdo de matéria orgânica). A distribuição especial das variáveis consideradas é predominantemente determinada pelo padrão de circulação de águas na Baía, pelo transporte de sedimentos ao longo do litoral este e pelas entradas naturais e antrópicas de Hg. A principal fonte de Hg para a baía é a entrada fluvial e a foz dos principais rios a área de deposição preferencial do metal. A composição dos sedimentos na Baía também é fortemente influenciada pelas entradas fluviais de Hg, material orgânica e sedimentos finos, sugerindo duas regiões distintas na Baía, uma influenciada fortemente pelas entradas fluviais e uma segunda sob influência marinha.

### **INTRODUCTION**

The strategic importance of the coastal regions has been a relevant factor

to the increasing vulnerability of these environments. The development of industrial and urban activities, both with massive utilization of natural resources have caused

alterations in the balance of these ecosystems and in the natural cycling of its components. In some cases, sediments accumulation in areas that receives domestic and industrial wastes were identified as a point source of trace metals to surrounding aquatic systems (Andersson et al., 1990; Burton Jr & Scott, 1992).

The Sepetiba Bay, located in the metropolitan region Rio de Janeiro (Brazil), is a typical example of this. It is connected with the Atlantic Ocean through two channels and the largest channel provides ship access to Sepetiba harbour, which is an important export pathway for industrial production in this region. An industrial park comprising about 400 industries (mostly pyrometalurgic) is responsible for trace metals input, which reach the bay via the main rivers and atmospheric deposition (Marins et al., 1996; Molisani et al., 2004; Pedlowski et al., 1991). As a result of the high number of industries in the region, the population has increased quickly and disorderly, and consequently Sepetiba Bay has been a site of industrial and domestic waste discharge, which constituents are accumulated within the bay due to the reduced current dynamics.

Previous studies on the contamination of Sepetiba Bay with heavy metals have highlighted cadmium (Cd) and zinc (Zn) as the main contaminants, with mercury (Hg) and other metals also showing significant concentrations (Barcellos and Lacerda, 1994; Magalhaes, 1996; Wasserman et al., 2001). Studies were also published on the geochemistry, mobility and sources of mercury in Sepetiba Bay. These studies have dealt mainly with water column chemistry (Paraquetti et al., 2004), mercury biogeochemistry in mangroves (Marins et al., 1998; Quevauviller et al., 1992; Silva et al., 2003) and atmospheric deposition (Marins et al., 1996), but further approaches are needed in order to establish the spatial distribution of mercury and of the factors controlling its distribution in bottom sediments. The aim of this paper is to determine mercury distribution in sediments from Sepetiba Bay and to identify possible geochemical carriers

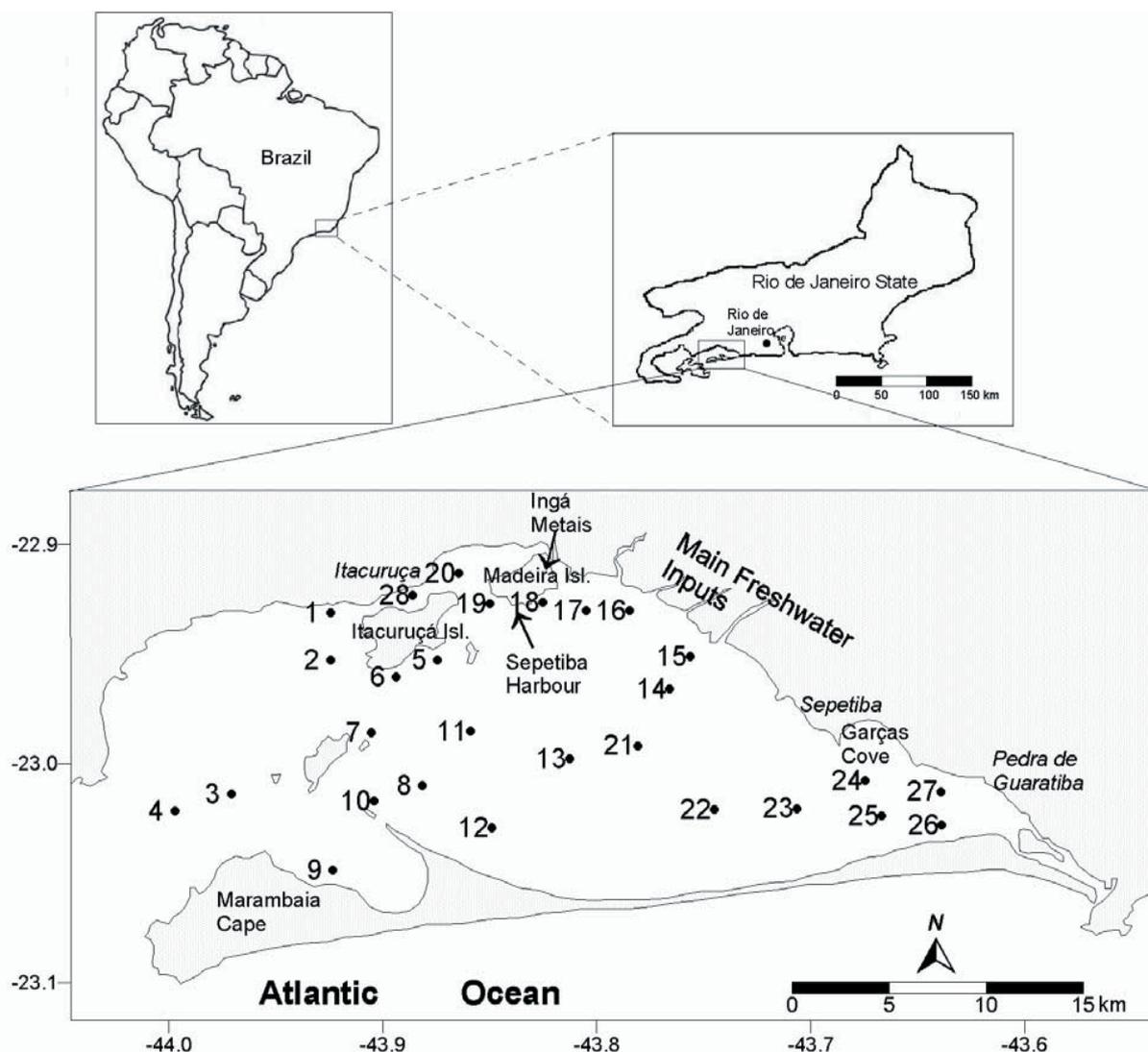
in bottom sediments.

## MATERIALS AND METHODS

Sepetiba Bay (Figure 1) is a partially mixed estuarine system located at latitude 23° S and longitude 44° W. It has a total area of 447 Km<sup>2</sup> (high tide) and a volume of 3.06 x 10<sup>9</sup> m<sup>3</sup>. The annual freshwater input of 7.6 x 10<sup>9</sup> m<sup>3</sup> reaches the bay through the main rivers in the north-eastern shore, causing a gradient of density which, together with both tide and wind has a strong influence on the pattern of water circulation. Dominant winds are SW, adding seawater from the Atlantic Ocean through the main channel. This water heats up in the inner part of the Bay close to river mouths, creating a clockwise current pattern, which drives fresh water and fluvial sediments southwards (Molisani et al., 2004; Signorini, 1980a; Signorini, 1980b). The present sedimentation is essentially clastic, and silt is the most representative granulometric fraction followed by sand and clay (Suguio et al., 1979).

Sediments were collected in 28 stations using a Van Veen grab (Figure 1). Samples from the central part of the grab were taken avoiding the sediment in contact with the grab walls. Interstitial water redox potential was measured *in situ* using a combined glass electrode, just after sample collection. Samples were stored in plastic bags and immediately frozen. In the laboratory, a sub-sample was taken to determine grain-size and the remaining was lyophilised and grounded for analysis of mercury (Hg), carbon (C), nitrogen (N), sulphur (S), iron (Fe) and organic matter (OM).

Total Hg concentrations were determined after acid digestion of the freeze-dried sediment samples (Lacerda et al., 2004; Malm et al., 1989; Marins et al., 1998). Acid digestion was performed by using a cold finger condensation system, adding 10 ml of HCl + HNO<sub>3</sub> (3:1) and 10 ml of bi-distilled water to 2 g of sediment. After digestion, mercury in the extract was reduced to Hg<sup>0</sup> by using SnCl<sub>2</sub>. Hg<sup>0</sup> was determined by Cold Vapor Atomic Absorption Spectrophotometry



**Figure 1** - Location of Sepetiba Bay, SE Brazil and of sediment sampling stations.

(CV-AAS). The detection limit of the method was  $0.045 \text{ ng.g}^{-1}$  and quality assurance of the method was determined with CRMs, United States Department of Commerce - Bureau of Standards (certified value of  $60 \text{ ng.g}^{-1}$ ; measured value of  $58 \pm 3 \text{ ng.g}^{-1}$ ,  $n=5$ ).

Total C and N were determined by high temperature combustion ( $1020 \text{ }^\circ\text{C}$ ), using an CHN analyser (Verardo et al., 1990), and total S using a LECO CS244 analyser, by combustion at  $1,370^\circ\text{C}$  converting sulphur to sulphate which is measured with an infra-red detector. To determine total Fe, lyophilised samples were placed in Teflon containers with concentrated  $\text{HNO}_3$  for wet oxidation (Loring and Rantala, 1977) and then analysed by Atomic Absorption Spectrophotometry (AAS) using an air-acetylene flame. Organic

matter (OM) content was determined by loss on ignition in dried sediment samples after combustion at  $450 \text{ }^\circ\text{C}$  for 16 hours. Granulometric analyses were performed by wet sieving.

## RESULTS AND DISCUSSION

Total Hg concentrations in Sepetiba Bay sediments ranged from 18 to  $109 \text{ ng.g}^{-1}$  (Table 1) with the higher values found in the region close to rivers mouths which drain the industrial area of the basin. This suggests a strong influence of these rivers on Hg concentrations in sediments. Higher concentrations occurred in the NE portion of the bay, making a gradient of concentration to the West, which follows the general pattern

**Table 1:** Geochemical parameters (average, standard deviation and range, n=28) of sediments from Sepetiba Bay sediments.

	Hg (ng.g <sup>-1</sup> )	Eh (mV)	OM	Fe	C	N (%)	S	Silt/Clay
Average	57	-262	15.8	6.34	1.81	0.35	0.94	65.7
St. Dev.	26	193	7.3	2.96	0.76	0.17	0.71	12.7
Max	108	160	24.6	11.50	3.16	0.76	2.15	81.4
Min	18	-510	1.0	0.04	0.22	0.06	0.04	32.6

of water circulation (Figure 2) (Signorini, 1980a). This distribution suggests that Hg is associated with particulate matter from the rivers. When mixed with the bay water, these river waters follow the circulation pattern and particles are partially and selectively deposited in sediments. This is in accordance with flux data from Paraquetti et al. (2004) showing the dominance of particulate-Hg input to the total Hg reaching Sepetiba bay from rivers. Fine grain sediments were also found in higher concentrations in the NE portion of the bay.

As known, Hg tends to bound to fine grain sediments (Moore and Ramamoorthy, 1984). Therefore, a normalisation procedure was applied, in order to compensate granulometric variations across the studied area, by assuming that all Hg was bound to the fine grain fraction of sediments. Besides of a new concentration value being calculated, no significant effect on the total Hg spatial distribution was found, and higher

concentrations were still observed in the NE portion of the bay.

Significant positive correlations were found between Hg concentrations and organic matter content ( $r = 0.81$ ,  $P < 0.01$ ), N concentrations ( $r = 0.72$ ,  $p < 0.01$ ), S concentrations ( $r = 0.67$ ,  $p < 0.01$ ), total C ( $r = 0.54$ ,  $p < 0.01$ ) and the fine grain fraction of sediments ( $r = 0.52$ ,  $p < 0.01$ ). Significant negative correlation was obtained between total Hg and Eh ( $r = -0.79$ ,  $p < 0.01$ ).

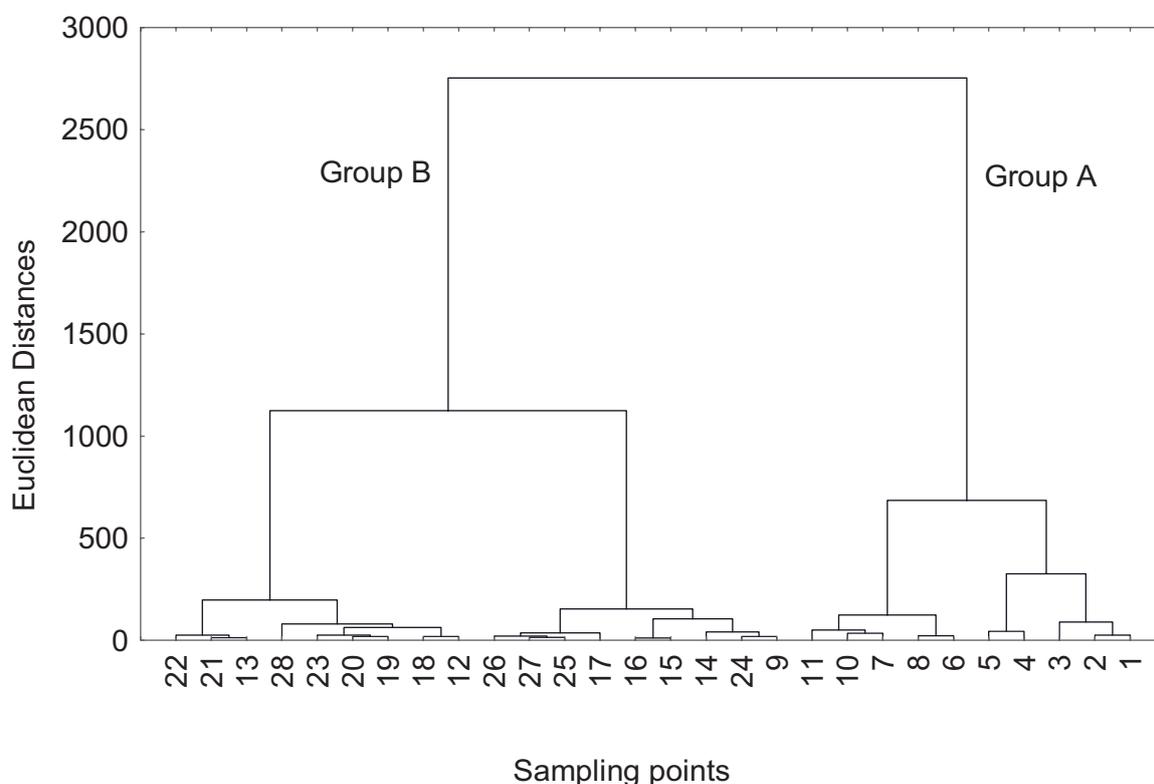
The high significant correlation between total Hg, organic matter and nitrogen suggest that Hg is mainly bound with organic fraction of the sediments. mercury usually forms stables complexes with a variety of organic compounds (Moore and Ramamoorthy, 1984), which can explain these high correlations. The observed correlation between Hg and total sulphur suggests not only the formation of organic complexes containing sulphur, but also the probable formation of mercury

**Figure 2** - Mercury distribution in superficial bottom sediments of Sepetiba Bay, SE Brazil.

sulphides, also enriched in organic richer sediments. However, a recent work on Hg speciation in Sepetiba Bay showed that most of the mercury was present under quite available forms (Wasserman et al., 2002). The authors suggest that although it is a reducing environment with a large provision of total sulphur, little Hg sulphide is being formed. Rather, Mounier et al, 2001) suggested that organo-sulphur compounds play a major role in Hg cycling in Sepetiba Bay sediments. This point is further confirmed by a work carried out in the neighbouring Guanabara Bay, a very reducing environment, where results from sequential extractions showed that Hg was not associated preferably to sulphides in surface sediments (Barrocas and Wasserman, 1998).

No significant correlation was found between iron and sulphur, but iron shows a significant correlation with total Hg ( $r = 0.60$ ,  $p < 0.01$ ), suggesting a possible association between total Hg and iron oxides and hydroxides. Iron oxides and hydroxides in bottom sediments of aquatic systems could adsorb Hg, decreasing its mobility

(Rasmussen et al., 1998). The existence of Hg associations with sulphur and oxidised species (like iron oxides and hydroxides) seems unusual, but it is possible in an oxidising anaerobic zone, where oxygen and sulphides are not present at equilibrium (Wollast, 1986), as has been demonstrated by the distribution of Hg in mud flats pore waters of Sepetiba Bay (marins et al., 1995; Mounier et al., 2001). Redox potential measurements have shown negative values confirming that Sepetiba Bay is a reducing environment, but the inner part of the bay has an intense flushing with oceanic water, which can cause an oxidising anaerobic condition in the superficial sediments, similar to the effects of tides on mud flats sediments (Lacerda et al., 1999; Mounier et al 2001). Once this condition has been established, mercury sulphides are not stable and organically complexed oxidised species of mercury can be present (Mounier et al., 2001). However, as this discussion has been based on redox potential values, it is very important that we consider the operational difficulties associated with these measurements in natural environments.



**Figure 3** - Cluster distribution of Hg concentrations in superficial bottom sediments of Sepetiba Bay, SE Brazil showing the two major group of samples: A – Oceanic influence and B – Fluvial influence.

Figure 3 shows the result of a hierarchical cluster analysis. As it can be seen two large groups (A and B) are evident. Group A, consisting of station 1 to station 8 plus stations 10 and 11 and group B, which is composed of station 12 to 28 plus station 9. The stations included in Group A are located in the westernmost part of the bay, closest to the ocean. The stations in Group B are located in the most landward inner region.

Therefore, differences between groups A and B are possibly related to the relative importance of marine or fluvial influences as well as to the main sources of Hg and organic matter located in the Northeast side. Moreover, it is probable that only a small fraction of the Hg transported by the rivers is exported to the ocean due to the high retention of Hg in the most landward region. Other studies have highlighted similar behaviour of Hg in estuaries (Benoit *et al.*, 1998; Muhaya *et al.*, 1997).

In addition, similar distributions of Mn, Cu, Cr, Cd, Zn and Pb also takes place in Sepetiba Bay sediments (Lacerda *et al.*, 1987). It suggests that these metals, as well as Hg, are entering the bay mainly through rivers, and are associated with suspended particles (Paraquetti *et al.*, 2004). This behaviour should seem obvious but as Hg is a volatile element, atmospheric inputs could also be important. In this study, atmospheric inputs do not obviously appear to be a source of mercury to Sepetiba Bay sediments.

## CONCLUSIONS

Results of this study show that the major source of mercury to Sepetiba Bay is the fluvial input from the rivers. Mercury is accumulated in the north-eastern margin of the bay, where there high sediment resuspension occurs as well as high organic matter production and accumulation, which improves adsorption process. Sediment transport intensity along the east margin of the bay is associated with the clockwise pattern of water circulation and contributes to the Hg concentration gradient in the sediments, as seen from the intermediate Hg concentrations distributed along the Marambaia sand spit.

The Hg distribution in sediments of the bay is highly influenced by Hg fluvial input and is slightly influenced by sediment grain size. This suggests the formation of two different regions regarding to Hg distribution in the bay; one receiving a strong influence from the rivers and another principally influenced by the water exchange with the Atlantic Ocean.

## ACKNOWLEDGEMENTS

We thank Dr. A.R. Ovalle for carbon, nitrogen and sulphur analyses. This study was partly supported by CNPq through the Instituto do Milênio Project 420.050/2005-1 and FAPERJ through PRONEX Project E-26-171.175/2003-1. CNPq also provided a scholarship to L. Veeck.

## REFERENCE

- ANDERSSON, I.; PARKMAN, H.; JERNELOV, A. (1990) The role of sediments as sink or source for environmental contaminants - a case of mercury and chlorinated organic compounds. *Limnologica*, 20: 347-359.
- BARCELLOS, C. & LACERDA, L.D. (1994) Cadmium and Zinc source assessment in the Sepetiba Bay and basin region. *Environmental Monitoring and Assessment*, 29: 183-199.
- BARROCAS, P.R. & WASSERMAN, J.C. (1998) Mercury behaviour in sediments from a sub-tropical coastal environment in SE Brazil. in J.C. Wasserman, Silva-Filho E.V., Vilas-Boas A.C. (ed.), *Environmental Geochemistry in the Tropics*, Springer-Verlag, Berlin, 171-184.

- BENOIT, J.M.; GILMOUR, C.C.; MASON, R.P.; REIDEL, G.S.; REIDEL, G.F. (1998) Sources and cycling of mercury in the Patuxent estuary. *Biogeochemistry*, 40: 249-265.
- BURTON JR, G.A. & SCOTT, K.J. (1992) Sediment toxicity evaluation, their niche in ecological assessment. *Environmental Science & Technology*, 26: 2068-2075.
- LACERDA, L.D.; PFEIFFER, W.C.; FISZMAN, M. (1987) Heavy metal distribution, availability and fate in Sepetiba Bay, SE Brazil. *The Science of The Total Environment*, 65: 163-173.
- LACERDA, L.D.; RIBEIRO, M.G.R.; GUEIROS, B.S. (1999) Manganese dynamics in a mangrove- mud flat tidal creek in SE Brazil. *Mangroves & Salt Marshes*, 3: 105-111.
- LACERDA, L.D.; REZENDE, C.E.; OVALLE, A.R.C.; CARVALHO, C.E.V. (2004) Mercury distribution in continental shelf sediments from two offshore oil fields in southeastern Brazil. *Bulletin of Environmental Contamination and Toxicology*, 72: 172-185.
- LORING, D.H. & RANTALA, R.T.T. (1977) Geochemical analysis of marine sediments and suspended particulate matter 1977. In *Canadian Technical Report of Fisheries and Aquatic Sciences*, Montreal, 58p.
- MAGALHAES V.F. (1996) Contaminação ambiental por arsênio: o caso da Baía de Sepetiba, RJ. Dissertação de Mestrado, Universidade Federal do Rio de Janeiro.
- MALM, O.; PFEIFFER, W.C.; BASTOS, W.R.; SOUZA, C.M.M. (1989) Utilização do acessório de geração de vapor a frio para análise de mercúrio em investigações ambientais por espectrofotometria de absorção atômica. *Ciência e Cultura*, 41: 88-92.
- MARINS, R.V.; SILVA-FILHO, E.V.; LACERDA, L.D. (1996) Atmospheric deposition of mercury over Sepetiba Bay, SE Brazil. *Journal of Brazilian Chemistry Society*, 7: 177-180.
- MARINS, R.V.; LACERDA, L.D.; GONÇALVES, G.O.; PAIVA, E.C. (1997) Effects of root metabolism on the post-depositional mobilization of mercury in salt marsh soils. *Bulletin of Environmental Contamination & Toxicology* 58: 733-738.
- MARINS, R.V.; LACERDA, L.D.; PARAQUETTI, H.H.M.; PAIVA, E.C.; VILLAS-BOAS, R.C. (1998) Geochemistry of mercury in sediments of a sub-tropical coastal lagoon, Sepetiba Bay, Southeastern Brazil. *Bulletin of Environmental Contamination and Toxicology*, 61: 57-64.
- MOLISANI, M.M.; MARINS, R.V.; MACHADO, W.; PARAQUETTI, H.H.M.; BIDONE, E.D.; LACERDA, L.D. (2004) Environmental changes in Sepetiba Bay, SE Brazil, *Regional Environmental Change*, 4: 17-27.
- MOORE, J.W. & RAMAMOORTHY, S. (1984) Heavy metals in natural waters - Applied monitoring and impact assessment, Springer-Verlag, New-York, 268 pp.
- MOUNIER, S.; LACERDA, L.D.; MARINS, R.V.; BENAÏM, J. (2001) Copper and mercury complexing capacity of organic matter from a mangrove mud flat environment (Sepetiba Bay, Brazil). *Bulletin of Environmental Contamination and Toxicology*, 67: 519-525.
- MUHAYA, B.B.M.; LEERMAKERS, M.; BAEYENS, W. (1997) Total mercury and methyl mercury in sediments and in the polychaete *Nereis diversicolor* at Groot Buitenschoor (Scheldt Estuary, Belgium). *Water, Air and Soil Pollution*, 94: 109-123.
- PARAQUETTI, H.H.M.; AYRES, G.A.; ALMEIDA, M.D.; MOLISANI, M.M.; LACERDA, L.D. (2004) Mercury distribution, speciation and flux in the Sepetiba Bay tributaries, SE Brazil. *Water Research*, 38: 1439-1448.

- PEDLOWSKI, M.A.; LACERDA, L.D.; OVALLE, A.R.C.; WATTS, P.P.R.; SILVA-FILHO, E.V. (1991) Atmospheric inputs of Zn, Fe and Mn into the Sepetiba Bay, Rio de Janeiro. *Ciência e Cultura*, 43: 380-382.
- QUEVAUVILLER, P.; DONARD, O.F.X.; WASSERMAN, J.C.; MARTIN, F.M.; SCHNEIDER, J. (1992) Occurrence of methylated tin and dimethyl mercury compounds in a mangrove core from Sepetiba Bay. *Applied Organometallic Chemistry*, 6: 221-228.
- RASMUSSEN, P.E.; VILLARD, D.J.; GARDNER, H.D.; FORTESCUE, J.A.C.; SCHIFF, S.L.; SHILTS, W.W. (1998) Mercury in lake sediments of the precambrian shield near Huntsville, Ontario, Canada. *Environmental Geology*, 33: 170-182.
- SIGNORINI, S.R. (1980a) A study of the circulation in bay of Ilha Grande and bay of Sepetiba - Part I. A survey of the circulation based on experimental field data. *Boletim do Instituto Oceanografico*, 29: 41-55.
- SIGNORINI, S.R. (1980b) A study of the circulation in bay of Ilha Grande and bay of Sepetiba - Part II. An assessment to the tidally and wind-driven circulation using a finite element numerical model. *Boletim do Instituto Oceanografico*, 29: 57-68.
- SILVA, L.F.F.; MACHADO, W.; LISBOA FILHO, S.D.; LACERDA, L.D. (2003) Mercury accumulation in sediments of a mangrove ecosystem in SE Brazil. *Water, Air and Soil Pollution*, 145: 67-77.
- SUGUIO, K.; VIEIRA, E.M.; BARCELOS, J.H.; SILVA, M.S. (1979) Interpretação ecológica dos foraminíferos de sedimentos modernos da Baía de Sepetiba e adjacências, Rio de Janeiro. *Revista Brasileira de Geociências*, 9: 233-247.
- VERARDO, D.J.; FROELICH, P.N.; MCINTIRE, A. (1990) Determination of organic carbon and nitrogen in marine sediments using the Carlo Erba NA-1500 analyser. *Deep-Sea Research*, 37: 157-165.
- WASSERMAN, J.C.; FIGUEIREDO, A.M.G.; PELLEGATTI, F.; SILVA-FILHO, E.V. (2001) Elemental composition of sediment cores from a mangrove environment using neutron activation analysis. *Journal of Geochemical Exploration*, 72: 129-146.
- WASSERMAN, J.C.; AMOUROUX, D.; WASSERMAN, M.A.V.; DONARD, O.F.X. (2002) Mercury speciation in sediments of a tropical coastal environment. *Environmental Technology*, 23: 899-910.
- WOLLAST, R. (1986) Basic concepts in geochemical modelling. in P. Buat-Ménard (ed.), *The role of air-sea exchange in geochemical cycling*. D. Reidel Publishing Company, Dordrecht, p: 1-34.

(Footnotes)

<sup>1</sup>To whom the correspondence should be sent: [pgcmt@labomar.ufc.br](mailto:pgcmt@labomar.ufc.br)