



## Dissolved mercury concentrations and reactivity in mangrove waters from the Itacurussa Experimental Forest, Sepetiba Bay, SE Brazil

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### Abstract

Mangrove waters from the Itacurussa Experimental Forest (IEF), SE Brazil are enriched in reactive-Hg ( $15 \pm 2.0$  pM) and total-Hg ( $28 \pm 2.5$  pM) relative to open bay waters ( $4.5 \pm 3.0$  pM and  $19 \pm 8.5$  pM, for reactive-Hg and total-Hg respectively). Mercury concentrations and reactivity varied according to tidal flux in mangrove creek waters. Reactive-Hg concentrations were higher in ebb tide waters ranging from 4.5 to 8.5 pM, than in flood water (<1.0 to 3.5 pM), whereas total-Hg concentrations were higher in flood waters, from 40 to 360 pM, than in ebb water (30 to 250 pM). Low-Hg, open bay waters are enriched in Hg when flowing over mud flats prior to entering the IEF, where it mixes with pore waters containing extremely high Hg concentrations (up to 2,500 pM). Similar distributions of Hg and DOC in pore waters, suggests that DOC may facilitate Hg migration through the sedimentary column, as shown for other estuarine areas. Mud flat pore waters are the more likely source of total Hg to mangrove waters, but not for reactive Hg. These results suggest that mangroves act as a sink to total Hg, as has been shown for other trace metals at the IEF and other mangrove forests. On the other hand mangroves act as a source of reactive Hg to adjacent coastal waters. The mechanisms involved in this processes have not been studied in this paper. However, the similar distribution of DOC and Hg among the different water masses of the IEF, suggest that the dynamics of Hg-DOC complexes may play a dominant role.

### Introduction

Mercury behavior in coastal areas is somewhat unusual compared to other trace metals because of the diversity of dissolved Hg species present in the water column, the major component of the Hg biogeochemistry in coastal areas (Mason et al., 1995). Mercury also presents a non-conservative behavior during estuarine mixing due to its particularly high reactivity, undergoing strong speciation changes which may result in different bioavailability along estuarine gradients (Coquery et al., 1997; Stordal et al., 1996). Studies on the Hg budget of coastal areas and estuaries have confirmed this assumption. For example, Krom et al. (1994) reported that only 10% of the total Hg entering Haifa Bay, Israel, was retained within the bay's bottom sediments. Vandal and Fitzgerald (1995) in a

preliminary budget for Narragansett Bay, USA, reported a relative retention of about 50% of the total Hg input to that Bay. Whereas Marins et al. (1999) concluded, based on a preliminary mass balance study, that only about 15% of the total Hg entering the Sepetiba Bay, SE Brazil, is retained within the Bay sediments, the remaining being available for export and/or biological uptake. In the same Bay, much larger fractions (>60%) of other heavy metal's loads are retained within the sediments (Barcellos, 1995; Pedlowski et al., 1991). This result suggests that the Sepetiba Bay estuarine 'filter' is much less able to retain Hg than the other heavy metals of environmental significance for the region. Therefore, contamination of adjacent areas by Hg is very likely.

Part of the explanation for a larger Hg dissolved fraction relative to sediment burial, is due to the ability of Hg to form stable soluble Hg-organic complexes. Thiol groups (Boulegue et al., 1982), by-products of the organic matter diagenesis through sulfate reduction (Marins et al., 1997), which are the dominant metabolism of most intertidal ecosystems, such as mangroves, play an important role in enhancing Hg solubility. Mangroves in particular, are important generators of dissolved organic carbon (DOC) to coastal waters. DOC is the major form of carbon exported by mangroves to Sepetiba Bay (Rezende et al., in press), where they occupy 35% of the shore perimeter. Also, changing redox conditions in a sub-oxic environment, which typically occurs in mangrove waters during a tidal cycle (Lacerda et al., 1999), may significantly affect Hg concentrations and speciation in the water column.

To evaluate the importance of mangroves in the distribution of Hg in the water column of Sepetiba Bay, we characterized the distribution and speciation of dissolved Hg in tidal waters entering and leaving a mangrove forest during a tidal cycle, at the Itacurussa Experimental Forest, Sepetiba Bay, SE Brazil. To understand dissolved Hg concentrations changes during the tidal cycle, Hg distribution in mangrove surface and pore waters, and in open Bay waters was also determined.

## Material and methods

### Study area

The study was done at the Itacurussa Experimental Forest (IEF), located along the North shore of Sepetiba Bay, approximately 100 km from Rio de Janeiro (23°S latitude and 44°W longitude) (Figure 1). Sepetiba Bay is a 447 km<sup>2</sup> coastal lagoon, with 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, particularly of Cd, Zn and Hg, have been increasing the environmental threat to the Bay's aquatic biota, including important fisheries (Barcellos and Lacerda, 1994; Marins et al., 1999). A recent survey on Hg content in the snapper *Micropogonias furnieri* (Kherig et al., 1998) from Sepetiba Bay, showed highest Hg concentrations in fish collected far from major rivers, which are the principal source of Hg to the Bay (Marins et al., 1999). The explanation for this apparent paradox may be the increase in

Hg reactivity along the estuarine gradient, where Hg faces different physico-chemical environments from different water masses, including from mangroves.

Mangroves cover about 38 km<sup>2</sup>, mostly as fringe forests along the Bay's north and northeastern coasts. The Bay's mangroves are important steps in the biogeochemical cycle of trace metals in the region, by accumulating relatively large amounts of trace metals in a non-bioavailable form, but also affecting their speciation in the water column. However, the mechanisms involved are still far from fully understood (Lacerda, 1998).

The IEF (Figure 1) 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 a 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). Tidal water entering the IEF strongly interacts with extensive mud flats adjacent to the forest prior to reaching the creek. During this period tidal waters are enriched in nutrients and Mn from the fluxing out of mud flat pore waters (Ovalle et al., 1991; Lacerda et al., 1988, 1999). Creek depth depends on tides and ranges from 0.6 m to 2.6 m. Average air temperature ranges between 18 °C in winter and 23 °C in summer. Annual rainfall is c.a. 2,300 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 4,510 trees.ha<sup>-1</sup>, with an average height of 6 m and an average diameter of 8 cm. Basal area is 22 m<sup>2</sup>.ha<sup>-1</sup> and the total biomass is 82 t.ha<sup>-1</sup>, distributed between aboveground (65.4 t.ha<sup>-1</sup>) and below ground (16.3 t.ha<sup>-1</sup>) biomass. Freshwater to the IEF is from groundwater and rainwater, and the inundation pattern is controlled by tidal amplitude.

### Tidal creek sampling

Samples were collected in three campaigns during the summer and fall 1999. During the first campaign, surface water samples were collected in small creeks

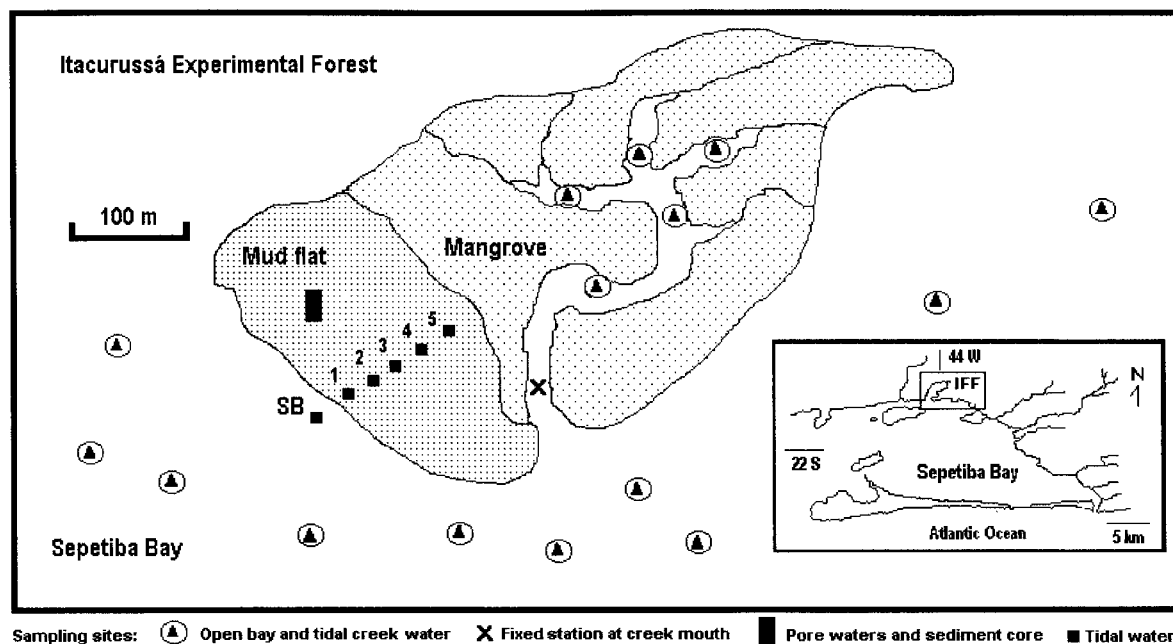


Figure 1. Map showing the location of the Itacurussa Experimental Forest (IEF) and sampling sites.

Table 1. Mean, standard deviation and range of major physical and chemical parameters and of Hg concentrations in water from the mangrove of the IEF and from adjacent Sepetiba Bay waters. (n = number of samples).

Variable	Open bay waters	Mangrove waters
pH	7.9 ± 0.3 (n = 8)	7.3 ± 0.1 (n = 4)
Salinity	33.9 ± 1.5 (n = 8)	34.5 ± 0.7 (n = 4)
Temperature	24 (n = 8)	24 (n = 4)
POC (mg.L <sup>-1</sup> )	0.9 ± 0.5 (n = 4)	3.2 ± 0.4 (n = 4)
DOC (mg.L <sup>-1</sup> )	1.8 ± 0.2 (n = 4)	4.7 ± 1.2 (n = 4)
Reactive Hg (pM)	4.5 ± 3.0 (n = 10)	15.0 ± 2.0 (n = 5)
Total Hg (pM)	19.0 ± 8.5 (n = 10)	28.0 ± 2.5 (n = 5)
Reactive Hg as % of the total	24	53

inside the mangrove forest during low tide, and in open bay waters adjacent to the IEF. Number of samples for each variable analyzed is shown in Table 1.

During a second campaign, 10 surface water samples were collected at 30 minutes intervals, in a fixed station at the mouth of the tidal creek draining the IEF (Figure 1), during a tidal cycle. Previous studies in this section of the creek showed that incoming tidal waters are strongly affected by the flushing out of pore waters from adjacent mud flats in front of the IEF, which mix with tidal waters before entering the tidal creek (Ovalle et al., 1991; Lacerda et al., 1988, 1999).

All sampling and analytical ware were pre-cleaned according to accepted protocols (Guentzel et al., 1996). Surface water samples from Sepetiba Bay and the mangrove creek draining the IEF were collected with 0.5 L pre-cleaned Teflon bottles and Teflon gloved hands below the surface micro-layer, following careful procedures to avoid sampling contamination (Ferrara and Maserti, 1992). The sampling bottles were rinsed three times with local water before being filled. The bottles were capped while immersed in the water to prevent contact with the atmosphere between sampling and handling. Bottles were double bagged in acid-washed plastic bags and transported in an icebox

to the laboratory. All samples were immediately analyzed after collection (within 4 to 8 hours maximum). During the period between sampling and analysis, samples were kept in an icebox. A sub-sample from each collection was used for the determination of temperature, salinity, pH and Eh, *in situ*, with portable electrodes. A 500 mL sub-sample from each collection was also used for the determination of total suspended solids (TSS), after filtration in Millipore 0.45  $\mu$ .

From samples of mangrove creek and open bay waters, a 250 mL sub-samples were collected for Dissolved Organic Carbon (DOC) and particulate organic carbon (POC) analysis. Particulate organic carbon (POC) was determined after filtration in Watman GF/C glass fiber filters (1.2 $\mu$  in diameter) in a high temperature catalytic oven under oxygen (boat sampler 183 Dohrmann). For DOC analyses, an aliquot of 4.0 mL was sampled from the 250 mL bottle, acidified and purged immediately prior to the injection with CO<sub>2</sub>-free nitrogen for inorganic carbon removal. Total oxidation was performed by high temperature catalytic oxidation with a TOC 5000 Shimadzu analyzer. Standards were done with phtalate solution.

During the sampling, some major physical and chemical parameters were also measured *in situ*. Salinity was determined using a SHIBUYA refractometer whereas pH and temperature, were measured with a DIGIMED pH-meter, with a combined glass electrode. Detailed description of methods and procedures for these parameters can be found in Ovalle et al. (1991).

#### *Mud flat sampling*

During a third campaign, at low tide, pore waters from the mud flat adjacent to the IEF, were collected at different sediment depths using five (5) porous ceramic capped acrylic tubes inserted into the sediments, at 5.0 cm intervals to 35 cm of depth. After placing of the collectors into the sediment, vacuum was created by means of a hand pump. From 30 to 60 minutes were necessary to collect up to 200 mL of pore waters. Pore waters were collected from the tubes using syringes attached to tygon tube, avoiding contact with the atmosphere. Samples were discharged directly into Teflon 125 mL bottles, treated similarly as those used for the tidal creek sampling. A sub-sample from each depth was used for the determination of temperature, salinity, pH and Eh, *in situ*, with portable electrodes, and of DOC at the laboratory, as described above. Simultaneously, two sediment cores with 50 cm in length

and 9 cm diameter, were also collected in the same site, using acrylic tubes operated by hand. Cores were capped and later sliced in 5 cm layers in the laboratory.

Changes in Hg concentrations in tidal waters due to flooding of adjacent mud flats, were investigated by placing a pair of 250 mL Teflon bottles, and a 500 mL plastic bottle, attached to fixed sticks at the surface of the sediment. Bottles 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 group of bottles were filled by incoming tide, they were removed and placed in an ice box for transport. Samples collected in Teflon bottles were used for Hg determination, whereas the plastic bottle was used for the determination of temperature, salinity, pH, Eh and total suspended solids (TSS). This last parameter was obtained after filtration in Millipore 0.45  $\mu$ .

#### *Hg analysis*

Unfiltered, non-acidified, sub-samples (20 mL) of open bay and creek waters, were analyzed in duplicate for reactive Hg, considered here as the fraction of the total Hg concentration that is reduced and therefore volatilized from solution after the addition of 1.0 mL of acidic (2.6 N HCl) 1.0% SnCl<sub>2</sub> solution (Mason et al., 1993; 1994). This fraction includes mostly ionic (Hg<sup>2+</sup>) plus dissolved gaseous Hg<sup>0</sup> (DGM), but also the Hg fraction weakly bound to inorganic and organic complexes. However, it does not include Hg leacheable from particulate matter (Mason et al., 1993, 1998). Since we did not acidified the samples prior to analysis, our reactive Hg fraction does not compare with the reactive Hg fractions typically reported in literature which used acidified samples (Mason et al., 1993, 1998). For mud flat waters, however, only the total dissolved Hg concentrations were analysed, due to the small amount of sample.

Total Hg was determined after oxidation with bromide monochloride (BrCl). After oxidation, 0.1 mL of a 1% ascorbic acid solution was used to reduce the excess BrCl, this was followed by a reduction with the same SnCl<sub>2</sub> solution used for reducing the reactive Hg fraction (Bloom and Crecelius, 1983). Total Hg includes all dissolved Hg species and those bound to soluble inorganic and organic complexes and Hg weakly bound to suspended particles. Typically, the difference between total Hg and reactive Hg concentrations corresponds mostly to dissolved Hg-organic

complexes, in particular of methyl-Hg (Mason et al., 1993; Benoit et al., 1999; Gill et al., 1999).

The Hg<sup>0</sup> resultant from the reduction reaction, was purged from the sample with Hg-free Argon, at a flow rate of 40 mL min<sup>-1</sup>, for 3 min, and collected on a Au wool trap connected to the outlet of the reaction vessel. Two Au traps in the gas line stripped any Hg from the carrier gas. All connecting tubing was made of Teflon with glass-Teflon connections made with clean silicone tubing. Mercury determination was done, in a Tekran Model 2500 Cold Vapor Atomic Fluorescence Spectrophotometer, which has the necessary wide range of measurable Hg concentrations to be used either in surface and pore waters. Under the operational conditions described, the analytical detection limit of the method, based on three standard deviations of the reagents blank measurements was 1.0 pM. All samples were analyzed in duplicate. Differences between duplicates remained below 15% for all samples.

## Results and discussion

### Surface waters

Mercury, organic carbon concentrations and major physical and chemical parameters from mangrove and open bay surface waters collected during the first campaign are presented in Table 1. The two water masses were similar regarding major physical and chemical parameters. Since no significant fresh water input enters the IEF, mangrove and bay waters are virtually of the same origin (Lacerda et al., 1988; Ovalle et al., 1991). As expected however, mangrove waters were enriched in POC and DOC by a factor of ~3 relative to open bay waters (POC: 0.9 vs 3.2 mg.L<sup>-1</sup>; DOC: 1.8 vs 4.7 mg.L<sup>-1</sup>; for open bay and mangrove waters respectively). POC and DOC concentrations are in the same range reported for the IEF and Sepetiba Bay by Rezende et al. (in press), and also compare well with mangrove waters from similar latitudes world wide (Alongi et al., 1998; Dittmar, 1999).

Reactive Hg concentrations were lowest in open bay waters, ranging from 2.0 to 11.0 pM (average 4.5 ± 3.0 pM), whereas in mangrove waters reactive Hg concentrations were significantly ( $p < 0.01$ ) higher, ranging from 14.0 to 15.5 pM (average 15.0 ± 2.0 pM). Total Hg concentrations in open bay waters were also significantly ( $p < 0.01$ ) lower (4.0 to 33.0 pM; average 19.0 ± 8.5 pM), than in mangrove waters (25.0

Table 2. Range of reactive and total Hg concentrations in ebb and flood waters collected in the Itacurussa Experimental Forest tidal creek during one tidal cycle.

Hg concentrations (pM)	Ebb water	Flood water
Reactive	4.5–8.6	<1.0–3.5
Total	30–250	40–360

to 30.0 pM; average 28.0 ± 2.5 pM). The percentage of reactive Hg relative to the total Hg concentrations was on an average about 2 times higher in mangrove waters (53%) compared to open bay waters (24%) (Table 1).

Mercury concentrations measured in Sepetiba Bay open waters and in the IEF, are higher than those reported for open ocean waters (Guentzel et al., 1996), but compare well with other results from shallow coastal areas. Mason et al. (1999) reported similar values, up to 15 pM, of total Hg concentrations in Chesapeake Bay, with higher concentrations, of up to 31 pM, in the inner reaches of its estuary. Vandal and Fitzgerald (1995) found reactive Hg concentrations ranging from 2 to 17 pM in Narragansett Bay, also with higher values in the inner reaches of the Bay. Similarly, Leermakers et al. (1995), found total Hg concentrations ranging from 2.5 to 25 pM, in the Scheldt river Estuary.

Mangrove waters were particularly enriched in reactive Hg compared to open Bay waters. Many studies have reported the strong relationship between reactive Hg and DOC of estuarine and coastal waters (Mason et al., 1993, 1999; Stordal et al., 1996; Guentzel et al., 1996), particularly in mangrove influenced areas, such as Sepetiba Bay (Andren and Harris, 1975; Lacerda et al., in press). In coastal lagoon waters of Rio de Janeiro, including in Sepetiba Bay, Lacerda and Gonçalves (in press) and Lacerda et al. (2001), found a strong correlation between reactive Hg and DOC concentrations, confirming the importance of this parameter in increasing Hg reactivity in this area.

### Tidal waters

Figure 2a,b,c shows the variation of Hg concentrations during a tidal cycle at the mouth of the tidal creek at IEF. Samples 1, 2, 9 and 10 comprise mangrove waters coming out of IEF, here on called ebb-water, whereas samples 3, 4, 5, 6, 7 and 8, comprise incoming bay waters entering IEF after flooding the adjacent mud flats, here on called flood-water. Table 2 summarizes

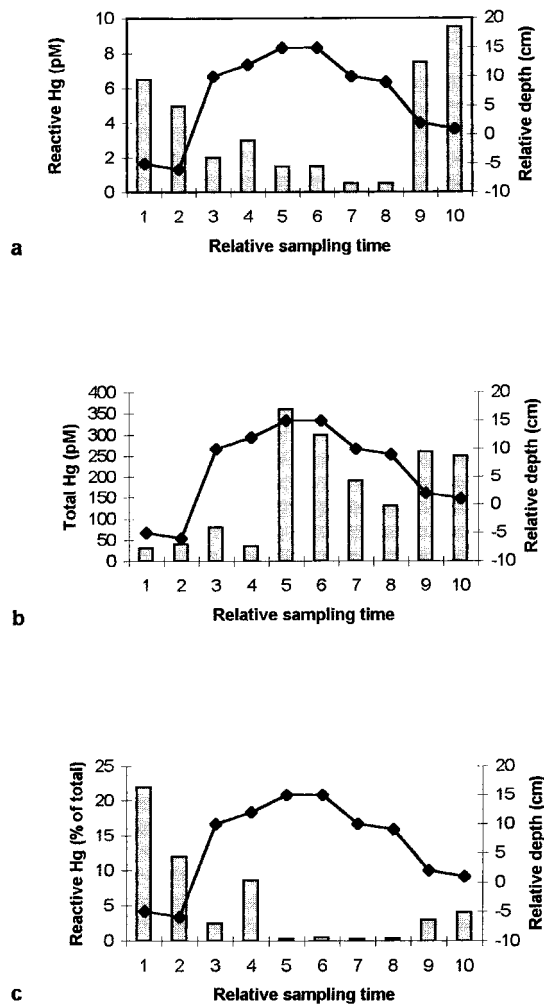


Figure 2. Variation of reactive Hg (a), total Hg (b) and percent of reactive Hg to total Hg (c) (vertical bars), and water depth (-◆-), at the mouth of the IEF tidal creek during a tidal cycle.

the concentrations measured in these samples. During high tide Sepetiba Bay waters interact with the adjacent mud flat prior to entering the creek. During low tide, mangrove surface and pore waters drain into the creek before reaching Sepetiba Bay. Therefore, creek water fluxing out of IEF integrates the products of all biogeochemical reactions occurring inside the forest (Ovalle et al., 1991; Lacerda et al., 1999). Major physical and chemical changes have been reported at the IEF tidal creek waters during the tidal cycle, in particular changes in redox potential and oxygen concentrations (Ovalle et al., 1991; Rezende et al., 1990; Lacerda et al., 1999). The behavior of the major physical and chemical parameters observed in this study

was similar to those reported by those authors to the IEF. During the studied cycle however, these changes were of minor importance, since their variability never reached extremes capable of affecting Hg behavior. Dissolved oxygen was high during the entire sampling period ranging from a minimum value of  $7 \text{ mg.L}^{-1}$  in ebb-water to a maximum of  $9.4 \text{ mg.L}^{-1}$  in flood-water. pH followed the same trend with minimum values in ebb-water of about 7.0 and maximum values in flood-water (8.4). Salinity (25 to 30) and temperature ( $26$  to  $29^\circ\text{C}$ ) remained nearly constant throughout the tidal cycle.

Reactive and total Hg concentrations presented a completely different behavior during the tidal cycle sampled. Reactive Hg concentrations (Figure 2a) were higher in ebb-waters compared to flood-waters. Ebb-water reactive Hg concentrations ranged from 4.5 to 8.5 pM. Highest values were measured at the second part of the cycle, which sampling, due to logistic difficulties, had to be stopped before reaching the same creek water depth of the first part of the cycle. Reactive Hg concentrations were much lower in flood-waters with values ranging from the detection limit of the method (1.0 pM) to 3.5 pM.

Total Hg concentrations (Figure 2b) variability along the tidal cycle was not as clear as reactive concentrations. Total Hg concentrations were up to two orders of magnitude higher than reactive Hg concentrations. Total Hg levels were lower in ebb-water, ranging from 30 to 250 pM. Also showing higher values at the second half of the tidal cycle. However, values were much higher during flood-water, ranging from 40 to 360 pM.

Reactive Hg concentrations, both in ebb and flood-waters, were in the same order of magnitude of the values measured in open waters of Sepetiba Bay. However, total Hg concentrations measured in ebb and flood-waters were 2 to 10 times higher than the values measured in open Bay waters. In fact, these values are similar to total Hg concentrations measured in waters of shallow coastal lagoon along the Rio de Janeiro coast, typically influenced by strong resuspension of bottom sediments (Lacerda and Gonçalves, in press). This strongly suggests that interaction with the adjacent mud flats may be responsible for the Hg enrichment found in flood-water.

#### *Mud flat waters*

Changes in total Hg concentrations in tidal waters passing over the mud flats prior to reaching the IEF

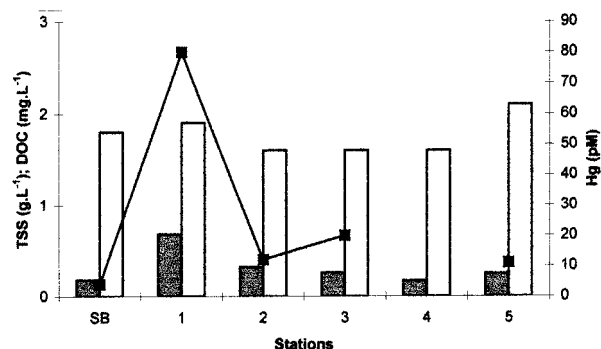


Figure 3. Variation of total Hg concentrations (—■—), total suspended solids (TSS, ■) and DOC concentrations (□), in tidal waters along the mud flat transect. SB is the background Sepetiba Bay station.

tidal creek are shown in Figure 3. Concentrations at the SB station at the Bay in front of the IEF, showed Hg concentrations in the same range of typical Sepetiba Bay open waters, of about 4 pM. Upon reaching the mud flat, Hg concentration increases to 81 pM at the first station. Further on to station 5 at the mangrove-mud flat interface, total Hg concentrations presented an erratic behavior, with values ranging from a minimum of 9 pM to a maximum of 20 pM. Similarly to the tidal cycle sampling, hydrochemistry of surface waters has not shown major differences along the mud flat. Temperature (31 °C), salinity (32 to 34), pH (7.2 to 8.4) and Eh (+200 to +250 mV), were nearly constant along the mud flat transect. The only parameter that changed significantly was the total suspended solids. TSS showed a similar behavior to Hg, with higher values at station one (0.6 to 0.8 g.L<sup>-1</sup>) and lower values (0.2 to 0.4 g.L<sup>-1</sup>) along the remaining stations. This suggests that upward diffusion of Hg from pore waters and resuspension of fine bottom sediments, may significantly increase Hg concentrations in tidal waters prior to reaching the IEF tidal creek.

Figure 4 shows Hg concentrations in pore waters and in sediments, as well as DOC content measured in pore waters at the mud flats adjacent to the IEF. Concentrations of both parameters increase continuously from deep sediment layers to the sediment-water interface, suggesting an upward migration of DOC and Hg concentrations along the sedimentary column. DOC concentrations ranged from about 5 mg.L<sup>-1</sup> at deeper layers to 120 mg.L<sup>-1</sup>. Mercury presented very high concentrations relative to the surface Bay waters, ranging from 1,100 pM in deeper layers to 2,400 pM at the sediment-water interface. This represents from

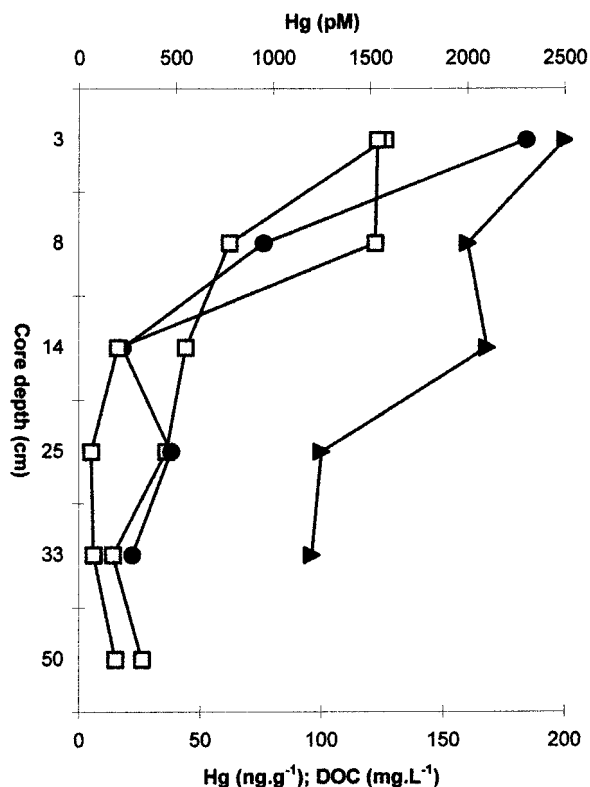


Figure 4. Total Hg (pM, —●—) and DOC (—□—) concentrations in pore waters, and Hg concentrations in sediments (ng.g<sup>-1</sup>, —▲—), in sediment cores from the mud flats of the IEF.

100 to 400 times higher compared to open bay water concentrations. These high concentrations can easily explain the high Hg content measured in the incoming tidal water after interacting with the mud flat surface. Also, since sediment Hg also increases from bottom (14–26 ng.g<sup>-1</sup>) to surface sediment layers (62–126 ng.g<sup>-1</sup>), resuspension of enriched surface layers may contribute to high total Hg concentrations found in the tidal creek waters.

Flux chamber experiments (Gill et al., 1999) and field evidence from some coastal areas under sub-oxic conditions, showed elevated concentrations of Hg in close proximity of the sedimentary source (Mason et al., 1999; Bloom et al., 1998). Diffusion of Hg from pore waters of the IEF mud flats have been suggested to explain Hg distribution in sediment cores by Martins et al. (1997). Also, the enrichment of incoming tidal waters with Mn migration from pore waters at the IEF was recently demonstrated (Lacerda et al., 1999). Apart from diffusion from pore waters, some degree of resuspension of surface bottom sediments of the mud flats also occur during the tidal flooding. This

have been proved of small importance in the enrichment process of Mn (Lacerda et al., 1999), but not for other trace metals (Lacerda et al., 1988, 1991), and can not be ruled out as an enrichment mechanism in the case of Hg, since we worked with unfiltered, total Hg concentrations.

Although we have analyzed only total Hg concentrations in pore waters, Hg incorporated into the incoming tidal water from upward diffusion of pore waters, is probably mostly constituted of refractory organic-Hg complexes, since DOC concentrations varied similarly to Hg, with very high concentrations of about 120 mg.L<sup>-1</sup> at the surface layers and 4–16 mg.L<sup>-1</sup> in deeper layers. Gill et al. (1999), found methyl-Hg as the dominant Hg species in pore waters of Lavaca Bay, Texas. Stordal et al. (1996) estimated that about 60% of pore water Hg constitute of refractory Hg-organic compounds. Since methyl-Hg is essentially produced by sulfate reducing bacteria in saline environments at the sediment-water interface (Gill et al., 1999; Benoit et al., 1999), and since sulfate reduction is the principal metabolism of the IEF (Aragon et al., 1999), it is highly possible that the large enrichment in Hg concentrations observed in pore waters is of methyl-Hg, although other refractory Hg-organic complexes can not be ruled out at this stage of our research. Preliminary results on the speciation of Hg in pore waters from the studied mud flats confirm the importance of the organic-Hg fraction in pore waters of the IEF mud flats (Marins et al., 2000). This is further confirmed by the increase in total Hg concentrations, but not of reactive Hg concentrations, in flood waters in the IEF tidal creek.

In conclusion, lower total Hg concentrations in ebb-water relative to flood-water, implies that mangroves at IEF efficiently traps Hg from the incoming tide. This trapping mechanisms have been described in detail for many other trace metals at the IEF. The processes involved the deposition and trapping of suspended particles in the entangled root mat of mangroves, and eventual precipitation as sulfides and/or refractory organic-metal complexes and rapid burial due to fast sedimentation rates (details can be found in Lacerda et al., 1988, 1991, 1999; Lacerda, 1998). Since Hg forms stable sulfide compounds, these mechanisms should also act upon this metal. However, since a large proportion of the Hg entering the IEF mangroves may be composed of methyl-Hg and/or other organic-Hg complexes, these forms may also be accumulated in the mangrove environment, where major environmental conditions will not favor their total oxidation (Lacerda,

1998). Part of the trapped organic-Hg complexes can be broken and re-exported to Sepetiba Bay. This would result in increasing of Hg reactive forms, as shown by the higher reactive Hg concentrations in ebb-water, and in particular, by the higher percentage of reactive Hg to total Hg concentrations in ebb-water relative to flood-water and in relation to open bay waters. However, the characterization of the processes involved in the Hg cycle in mangroves are still far from being concluded.

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