

## Mercury Speciation Changes in Waters of the Sepetiba Bay, SE Brazil during Tidal Events and Different Seasons

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Este estudo descreve as mudanças na especiação de Hg nas águas da Baía de Sepetiba, SE, Brasil, ao longo do gradiente estuarino, durante eventos de maré em diferentes estações. A avaliação química das águas da baía indicou uma exportação de material particulado em suspensão (MPS) pobre em carbono orgânico para a plataforma continental adjacente, principalmente durante a estação chuvosa e uma importação de MPS oceânico rico em carbono orgânico, provavelmente de origem fitoplanctônica, durante a estação seca. A especiação química do Hg demonstrou que a produção de Hg<sup>0</sup> na Baía de Sepetiba pode ser controlada pela produtividade primária, e que a baía atua como produtora e exportadora de formas orgânicas de Hg para as áreas adjacentes, já que as maiores concentrações de Hg não-reativo foram encontradas durante a maré vazante. Não foram observadas correlações significantes entre as concentrações de Hg não-reativo e carbono orgânico dissolvido ou particulado. Em geral, as frações de Hg particulado, Hg não-reativo e Hg reativo representam 55%, 35% e 9,5% do conteúdo total de Hg nas águas da Baía de Sepetiba, respectivamente.

This work describes changes in Hg speciation in water along the transport from Sepetiba Bay, SE Brazil, to the adjacent continental platform during tide events and in different seasons. The chemical evaluation of Sepetiba Bay waters showed that the bay exports suspended particulate material (SPM) impoverished in organic carbon to adjacent continental platform areas, mainly during the wet season and imports SPM enriched in organic carbon from the ocean, probably of phytoplanktonic origin, during the dry season. The chemical speciation of Hg during the study period showed that Hg<sup>0</sup> production can be controlled by primary productivity and that the bay acts as a producer and exporter of organic species of Hg to adjacent areas, since the highest non-reactive Hg concentrations were observed during the ebb tide. No significant correlations were found between non-reactive Hg and dissolved or particulate organic matter concentrations. In general the particulate Hg, non-reactive Hg and reactive Hg fractions represents 55%, 35.5% and 9.5% of the total Hg content in Sepetiba Bay waters, respectively.

**Keywords:** mercury speciation, coastal area, organic carbon, Sepetiba Bay

### Introduction

Coastal environments are complex and very dynamic systems showing a strong salinity gradient, high variation of suspended matter concentration and complex hydrodynamic processes. They act as links between the

terrestrial and oceanic environments, present a large capacity to accumulate materials of continental and marine origin and are strongly affected by tidal events and continental hydrology. These environments are also characterized by land-sea gradients of physicochemical processes such as oxidation/reduction, sorption/desorption and precipitation/dissolution, which result in gradients of dissolved chemical species concentration, ionic force, pH

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and redox potential, which are responsible for the precipitation of the major part of the particulate material that enters the marine environment through rivers and for the physicochemical changes in trace metals speciation before reaching the open ocean.<sup>1</sup>

The biogeochemical cycle of trace metals in the coastal zone has been altered by human activities mostly due to changes in land-use at the coastal zone and through inputs from point and diffuse anthropogenic sources. Among the various trace metals of environmental significance, Hg is one which cycle is most affected by anthropogenic activities and which speciation changes strikingly along physicochemical gradients in coastal waters.<sup>2-6</sup> The residence time of Hg in the water column of coastal waters depends on many processes, particularly the physicochemistry and hydrodynamics. Dissolved Hg species occur in coastal waters mostly as complexes of  $\text{Hg}^{2+}$  with various organic and inorganic ligands and organic Hg compounds, among them highly toxic methylmercury ( $\text{CH}_3\text{Hg}^+$ ) and dimethylmercury ( $(\text{CH}_3)_2\text{Hg}$ ). Dissolved elemental mercury ( $\text{Hg}^0$ ) is another dissolved Hg species present in coastal waters.<sup>7,8</sup> Depending on the redox potential, this species can be oxidized and complexed with inorganic ligands, consequently increasing its solubility.<sup>9,10</sup> In addition, to the dissolved Hg species can be adsorbed onto suspended particles or to sedimentary phases in bottom sediments. In oxygenated freshwaters, the main inorganic Hg species found are  $\text{HgCl}_2$  and  $\text{Hg}(\text{OH})_2$  whereas in saline, oxygen-rich waters Hg forms strong inorganic complexes with chloride ( $\text{HgCl}_4^{2-}$  and  $\text{HgCl}_3^-$ ), but also binds strongly to DOC.<sup>11,12</sup> MethylHg the most toxic Hg form to humans and aquatic organisms, originates by methylation processes transforming  $\text{Hg}^{2+}$  to  $\text{CH}_3\text{Hg}^+$  by microorganisms present in sediment and water, although photomethylation has been also reported as a possible methylation process.<sup>13</sup> The methylation process is influenced by redox potential, temperature, bacterial activity, pH, organic matter and sulphide contents and most important the availability of  $\text{Hg}^{2+}$ .<sup>9,14-17</sup> Therefore, the diversity of physicochemical environments in coastal waters may result in high rates of Hg methylation. Recent study using microcosms showed that under biotic conditions, the  $\text{Hg}^0$  is transformed to organic mercury in both aerobic and anaerobic conditions, but this process occurs mainly in anaerobic condition.<sup>18</sup> In Amazon region, this process can be the way for the transformation of metallic mercury used in the gold mining in organic mercury forms more toxic.

It has been widely reported that the suspended particulate matter and dissolved organic matter play an

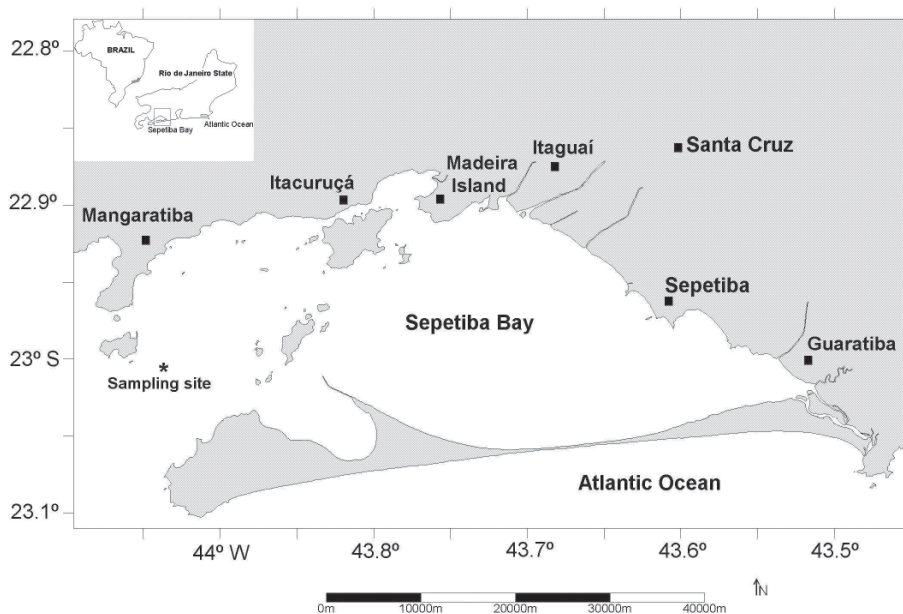
important role in the biogeochemical cycling of Hg in aquatic environments due to its high Hg complexation and/or adsorption capacity.<sup>12,19-27</sup> In Sepetiba Bay, SE Brazil, these constituents as well as physicochemical conditions, change significantly with season and tides and may result in the maintenance of relatively high Hg concentrations in the water column, as has been suggested by Marins *et al.*<sup>28</sup> Therefore, some Hg species can be exported to adjacent coastal waters, potentially affecting productive fisheries. Therefore, the aim of this work is to evaluate the Hg speciation changes during tidal events, in the dry and wet seasons, at the interface between Sepetiba Bay waters and the adjacent coastal waters and characterize the transport of the different Hg species to the open ocean.

## Experimental

### Site description

Sepetiba Bay is located approximately at latitude 23° S and longitude 44° W, about 60 km south of the Rio de Janeiro city (Figure 1).

The Bay is a semi-enclosed water body with 447 km<sup>2</sup> of area, average depth of 6.0 m, tidal range of less than 2.0 m and a water turnover time of about 100 hours. Mean water volume is  $2.56 \times 10^9$  m<sup>3</sup>, varying between  $2.38 \times 10^9$  m<sup>3</sup> and  $3.06 \times 10^9$  m<sup>3</sup>. Nine rivers draining the Sepetiba Bay Basin are responsible for freshwater inputs, reaching an annual flow of 5.7 to  $7.6 \times 10^9$  m<sup>3</sup>.<sup>29</sup> There is no substantial seasonal variation in fluvial water discharge to the bay. This is due to the nearly constant flow of the two major rivers (São Francisco and Guandu Rivers), which are artificially controlled by a water treatment plant located upstream from the major industrial area.<sup>30,31</sup> However, a significant increase in suspended matter load to the bay occurs during the rainy season due to erosion of this mostly deforested watershed. The Sepetiba Bay basin receives a large volume of water (about  $2.8 \times 10^9$  m<sup>3</sup> year<sup>-1</sup>) through water transposition of the adjacent Paraíba do Sul River system basin, a heavily industrialized region north of Sepetiba Bay to the São Francisco and Guandu Rivers.<sup>32</sup> The region is under a hot-humid tropical climate, with mean annual precipitation varying from 1,400 mm to 2,500 mm, depending on the location along the coast, being highest between December and March and lowest between June and August. Total annual rainfall over Sepetiba Bay reaches ( $0.5$  to  $1.0 \times 10^9$  m<sup>3</sup> year<sup>-1</sup>), increasing the importance of atmospheric derived pollutants from the local industrial park, particularly of



**Figure 1.** Map of Sepetiba Bay, Rio de Janeiro State, SE Brazil.

smelters.<sup>30,33,34</sup> Sepetiba Basin harbors an industrial park with over 400 industries, a population of about 1.2 million and important fisheries and tourist activities.

The water circulation in the bay is dominated by the winds and tides. Dominant regional winds (SW 25°) add seawater from the Atlantic Ocean through the western channel, creating a clockwise current pattern, which drives freshwater and fluvial sediments to Guaratiba region and keeps water salinity around 30. However, during strong NE 70° winds this clockwise pattern is inverted, and most of the fluvial sediments are transported to the coast between Madeira Island and Itacuruçá (Figure 1), lowering surface salinities to about 20.<sup>35</sup>

Mercury is an ubiquitous contaminant of urban and industrial effluents reaching Sepetiba Bay. Hg emissions to soils, waters and the atmosphere in Sepetiba Bay basin are mostly from diffuse sources, particularly from leaching of a large landfill, an oil-fired electric power plant, steel and iron production and waste incineration. Total Hg emission from the industrial park and urban sources to Sepetiba Bay was estimated<sup>36</sup> in 0.56 t year<sup>-1</sup> with the major inputs to soils (59%) and to the atmosphere (27%). Although direct inputs to waterways are small (14%), the large atmospheric and soil loads may contaminate fluvial systems through atmospheric deposition, surface runoff and groundwater flow.<sup>28</sup> Marins *et al.*<sup>28</sup> showed that the direct atmospheric deposition contributes with only 5% of the total Hg input to the Sepetiba Bay while the fluvial systems contribute with 95%, between 15% to 30% of the total Hg input to the bay accumulate in bottom sediments and 70% to 85% stay cycling within the water

column becoming bioavailable for methylation processes and export to the adjacent continental shelf waters.<sup>28,36</sup>

In the last years, many studies had been made about the Hg in the sediment,<sup>37,38</sup> in the atmospheric deposition,<sup>39,40</sup> in the fresh and coastal waters<sup>41-46</sup> and in the biota<sup>37,47,48</sup> of the Sepetiba Bay, showing the Hg distribution and geochemical in different end-members.

Recent studies showed that 16 to 85% of total Hg inputs through the major tributaries of Sepetiba Bay are associated with suspended particulate material (SPM).<sup>44</sup> Annual fluxes of total dissolved and particulate Hg and sediment from major Sepetiba Bay tributaries were estimated by Paraquetti *et al.*<sup>44</sup> as 11 kg year<sup>-1</sup>, 190 kg year<sup>-1</sup> and 4.8 × 10<sup>8</sup> kg year<sup>-1</sup>, respectively. Once reaching the bay, Hg, as well as other trace metals associated with suspended particulate matter and transported by rivers, are distributed following tidal currents within the bay.<sup>33,37,49</sup>

#### Sample collection

Four field campaigns (F<sub>1</sub>, F<sub>2</sub>, F<sub>3</sub> and F<sub>4</sub>) were conducted in the water column at the mouth of Sepetiba Bay, in a fixed point at the main canal of the Bay, during the flood and ebb periods and in the dry and wet seasons (Figure 1). In each campaign, vertical profiles in the water column were sampled hourly during a half tidal cycle in three different depths: surface, mid water and bottom with water depths of 1, 6 and 12 meters, respectively. The campaigns F<sub>1</sub> and F<sub>2</sub> were performed in the dry season (September and October of 2002, respectively) and the campaigns F<sub>3</sub> and F<sub>4</sub> in the wet season (both in March of 2003). In the

F<sub>1</sub> sampling campaign four profiles were collected during the flood tide in the dry season (FT/DS) whereas in the F<sub>2</sub> seven profiles were collected during the ebb tide in the dry season (ET/DS). In the F<sub>3</sub> four profiles were collected during the ebb tide in the wet season (ET/WS) whereas in the F<sub>4</sub> four profiles were collected during the flood tide in the wet season (FT/WS). The water column profiles were sampled using a Teflon van Dorn bottle and stored in 0.5 L pre-cleaned Teflon bottles for Hg analysis and in 0.5 L pre-cleaned Polyethylene bottles for carbon analysis. Sampling bottles were rinsed three times with the local water before being filled, double-bagged in clean plastic bags and transported in an icebox to the laboratory. All sampling and analytical materials were pre-cleaned according to accepted protocols.<sup>50</sup> All samples were analyzed in duplicate.

During the sampling, some major physical and chemical parameters were also measured in situ. Salinity, dissolved oxygen (DO) and temperature were determined using a YSI 85 probe, whereas pH was measured with a DIGIMED MD-2 pH-meter, with a combined glass electrode. Precision of such filed determinations was 0.1 units.

#### Mercury analysis

All samples were immediately analyzed, in duplicate, after collection (within 4 to 48 h maximum) to preserve the studied species.<sup>51,52</sup> During the period between sampling and analysis samples were kept in an icebox.

To avoid contamination during the filtration and taking into consideration the relatively low SPM concentrations, we analyze all samples without filtration. Therefore, the Hg speciation followed the operational definitions by EPA<sup>53</sup> and was obtained through the determination of the main Hg species, including elemental Hg, reactive Hg, total Hg and non-reactive Hg fraction estimated by difference between total Hg and reactive Hg. The particulate Hg fraction was obtained by sub-samples filtration.

Elemental Hg (Hg<sup>0</sup>) was analyzed in non-acidified sub-samples (200 mL) purged with Hg-free argon, at a flow rate of 760 mL min<sup>-1</sup>, for two cycles of 2 min, and collected on a gold wool trap connected to the outlet of the reaction vessel. The use of purge in two cycles of 2 min to elemental Hg determinations present more satisfactory results than the use of 4 min of purge in this analytical systems.<sup>54</sup>

Reactive Hg was analyzed in non-acidified sub-samples (20 mL) after the addition of an acidic (1% (v/v) distilled HCl + 1% (m/v) ascorbic acid) 10% SnCl<sub>2</sub>

solution. This fraction includes mostly ionic (Hg<sup>2+</sup>) plus elemental Hg, but also the Hg fraction weakly bound to inorganic and organic complexes.<sup>5,42,55-58</sup>

Total Hg was determined directly in non-acidified sub-samples (50 mL) after oxidation with a bromine monochloride solution (KBrO<sub>3</sub> 1% (m/v) + HCl 20% (v/v)) at room temperature. This was followed by a reduction with the same SnCl<sub>2</sub> solution used for reducing the reactive Hg fraction.<sup>51,53,54</sup> Total Hg includes all dissolved Hg species strongly bound to soluble inorganic and organic complexes, and probably some of the Hg weakly bound to suspended particles according to Bloom and Crecelius,<sup>51</sup> Marins *et al.*<sup>54</sup> and EPA.<sup>53</sup> A recent study in Sepetiba Bay<sup>44</sup> shows that the total Hg extracted with bromine monochloride solution roughly correspond the dissolved Hg fraction due to low SPM concentrations.

The difference between reactive Hg and total Hg corresponds to non-reactive Hg fraction constituted mostly by stable organic Hg complexes.<sup>54,59-61</sup> Since the sample oxidation with bromine monochloride solution (BrCl) is sufficient to cleave C-Hg covalent bonds of the very stable organic-Hg complexes and liberate Hg<sup>+2</sup> for reduction as part of the sparging step.<sup>51,54,59-63</sup>

Particulate Hg fraction was determined after the filtration of the non-acidified sub-samples through a glass micro fiber filter (0.70 μm, Whatman GF/F) pre-treated by heating at 450 °C for 12 h, directly after sampling. The filters were analyzed by oxidation with a 50% (v/v) aqua-regia solution (4H<sub>2</sub>O:3HCl:1HNO<sub>3</sub>), at 70 to 80 °C for 1 h followed by a reduction with the same SnCl<sub>2</sub> solution used for reducing the reactive Hg fraction.

Elemental Hg resultant from the reduction reaction was purged from the sample with Hg-free Argon at a flow rate of 760 mL min<sup>-1</sup>, for 2 min and collected on a gold 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 of clean silicone tubing. Mercury determination was performed at a wavelength of 253.7 nm, in a Tekran Model 2500 Cold Vapor Atomic Fluorescence Spectrophotometer.<sup>42,54,56,64</sup> Under the operational conditions described, the analytical detection limit of the method was 1.0 pg, based on the ratio between three standard deviation estimated by S<sub>y/x</sub> (S<sub>y/x</sub> = {(y<sub>i</sub> - y)<sup>2</sup> (n-2)<sup>-1</sup>}<sup>1/2</sup>), where the axis x and y were done in mass (ng Hg) and fluorescence intensity, respectively and the slope of the regression line of the calibration curve.<sup>65</sup> All samples were analyzed in duplicate. Differences between duplicates remained below 15% for all samples.

### Carbon analysis

Samples were collected in polyethylene bottles for suspended particulate matter (SPM), dissolved organic carbon (DOC) and particulate organic carbon (POC) analysis. The sub-samples were filtered through a glass micro fiber filter (0.70  $\mu\text{m}$ , Whatman GF/F), directly after sampling. The filters were pre-treated by heating at 450  $^{\circ}\text{C}$  for 12 h in order to destroy traces of organic carbon. The filtrates were preserved with 100  $\mu\text{L}$  of 1mol  $\text{L}^{-1}$  sodium azide solution and were kept under refrigeration.

The DOC concentration was measured using a SHIMADZU TOC 5000 equipped with an auto sampler. To eliminate dissolved carbonates 50 mL of HCl was added followed by oxygen bubbling for 10 min. The sample was analyzed by high temperature catalytic combustion (650  $^{\circ}\text{C}$ ). The obtained detection limit was 0.15  $\text{mg L}^{-1}$ . The POC concentration was measured using the same analytical system but with a different furnace (SSM 5000A) at 900  $^{\circ}\text{C}$ . Each analysis was made in triplicate to determine the average concentrations. Differences among triplicates remained below 10% and 15% for DOC and POC analysis, respectively.

## Results and Discussion

The results of major physical and chemical parameters analyzed showed no statistical differences among the three depths sampled, characterizing a non-stratified, well mixed water column. Differences in Hg speciation between the different depths and profiles in a given fields campaign were also not found. Therefore, we used the samples collected from the three depths and different profiles to obtain the mean and standard deviation for each variable.

Outlier values of each variable were excluded from distribution of data through box-and-whisker plot (outside the  $\pm 1.5$  quartiles). Differences in parameters among the four groups analyzed were quantified using the t-student test with significance set at  $P < 0.01$ . Thus, all the discussions to follow with regard to significant differences between the parameters are based in this statistical test.

### Water chemistry

Figure 2 represents graphically the mean and standard deviation of the concentrations measured in waters of Sepetiba Bay.

Water salinity showed no significant difference ( $P < 0.01$ ) between the different seasons (Figure 2a), being higher during ebb tide (33.1  $\pm 0.2$ ,  $n = 36$  and 33.4  $\pm 0.3$ ,  $n = 21$  in the dry and wet season respectively) than during

flood tide (32.9  $\pm 0.3$ ,  $n = 24$  and 32.4  $\pm 0.9$ ,  $n = 23$  in the dry and wet season respectively). The pH values found during the dry season (7.9  $\pm 0.2$ ,  $n = 24$  and 8.0  $\pm 0.1$ ,  $n = 38$  in flood and ebb tide, respectively) were similar to the values found during the wet season (7.9  $\pm 0.1$ ,  $n = 21$  and 8.0  $\pm 0.1$ ,  $n = 21$  in flood and ebb tide respectively). This results show that this system is predominantly marine. Water temperature in the dry seasons was higher in the ebb tide (23.7  $\pm 0.4$   $^{\circ}\text{C}$ ,  $n = 38$ ) than in the flood tide (21.6  $\pm 0.3$   $^{\circ}\text{C}$ ,  $n = 24$ ). During the wet season, however, due to rapid changes of temperature typical of the summer period, higher values were observed during the flood tide (26.7  $\pm 0.4$   $^{\circ}\text{C}$ ,  $n = 23$ ) than in the ebb tide (25.8  $\pm 0.4$   $^{\circ}\text{C}$ ,  $n = 21$ ). This result demonstrates that temperature variation was principally a function of sampling time (Figure 2b).

Average dissolved oxygen (DO) concentration during the dry season (6.8  $\pm 0.6$   $\text{mg L}^{-1}$ ,  $n = 64$ ) was higher than in the wet season (5.5  $\pm 0.9$   $\text{mg L}^{-1}$ ,  $n = 44$ ) (Figure 2c) and always higher in flood tide (7.5  $\pm 0.3$   $\text{mg L}^{-1}$ ,  $n = 24$  and 6.0  $\pm 0.9$   $\text{mg L}^{-1}$ ,  $n = 23$  during the dry and the wet season respectively) than in ebb tide (6.4  $\pm 0.2$   $\text{mg L}^{-1}$ ,  $n = 40$  and 5.0  $\pm 0.3$   $\text{mg L}^{-1}$ ,  $n = 21$  in the dry and wet season respectively). Average percent saturation of dissolved oxygen obtained was higher during the dry season (105.8  $\pm 4.0\%$  and 93.4  $\pm 3.4\%$  in the flood and ebb tide respectively) than during the wet season (92.1  $\pm 14.2\%$  and 75.4  $\pm 5.0\%$  in flood and ebb tide respectively).

There was no statistical difference ( $P < 0.01$ ) between suspended particulate matter (SPM) concentrations in ebb (11.0  $\pm 1.2$   $\text{mg L}^{-1}$ ,  $n = 40$ ) and flood (11.4  $\pm 1.3$   $\text{mg L}^{-1}$ ,  $n = 24$ ) periods during the dry season. However, during the wet season SPM concentrations were significantly higher ( $P < 0.01$ ) in the ebb tide (17.4  $\pm 1.1$   $\text{mg L}^{-1}$ ,  $n = 18$ ) than in the flood tide (15.8  $\pm 1.4$   $\text{mg L}^{-1}$ ,  $n = 22$ ). These results demonstrate that Sepetiba Bay is a net exporter of SPM to the ocean and adjacent coastal waters at least during the rain period. The average SPM concentration during the wet season (16.5  $\pm 1.5$   $\text{mg L}^{-1}$ ,  $n = 40$ ) was higher than during the dry season (11.2  $\pm 1.2$   $\text{mg L}^{-1}$ ,  $n = 64$ ) (Figure 2d) due to the increase of SPM inputs resultant from the intensive runoff to the Bay through the majors Sepetiba Bay tributaries during the heavy rain periods.<sup>44</sup>

The DOC concentrations were similar during the wet season at ebb (1.6  $\pm 0.0$   $\text{mg L}^{-1}$ ,  $n = 17$ ) and flood (1.7  $\pm 0.1$   $\text{mg L}^{-1}$ ,  $n = 23$ ) tide. However, during the dry season the DOC concentrations were higher ( $P < 0.01$ ) in the ebb tide (1.9  $\pm 0.1$   $\text{mg L}^{-1}$ ,  $n = 38$ ) than in the flood tide (1.7  $\pm 0.1$   $\text{mg L}^{-1}$ ,  $n = 24$ ). The average DOC concentration was higher during the dry season (1.8  $\pm 0.1$   $\text{mg L}^{-1}$ ,

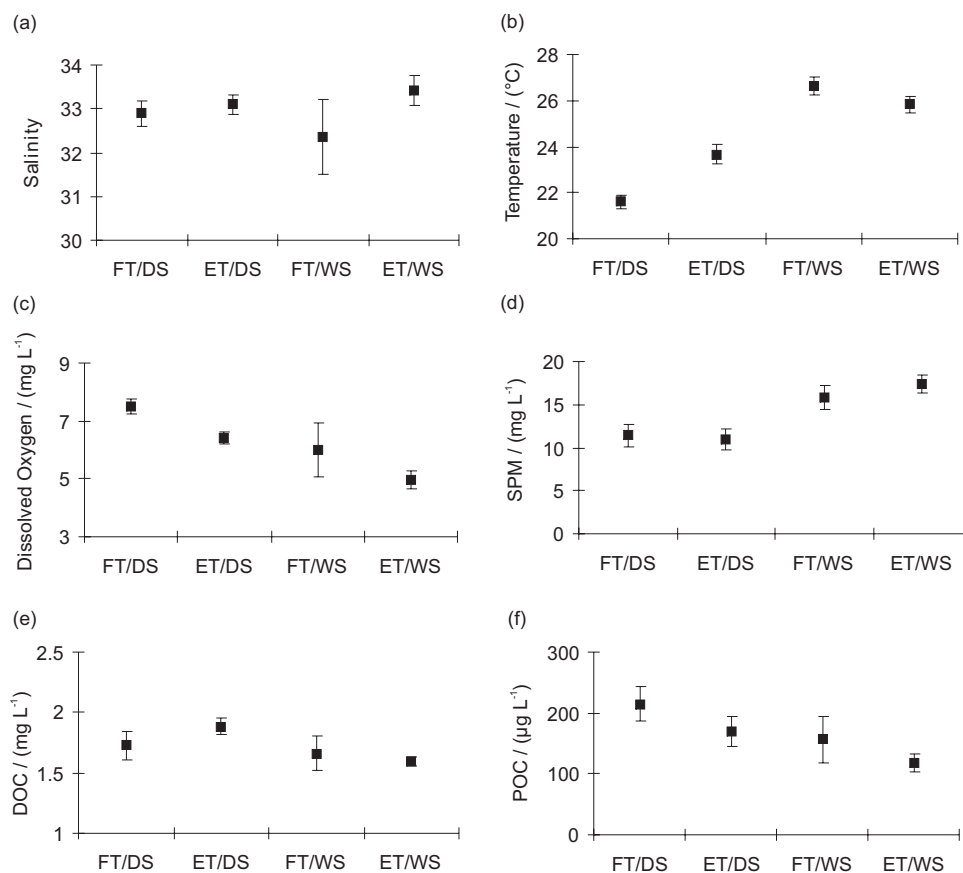
$n = 62$ ) than during the wet season ( $1.6 \pm 0.1 \text{ mg L}^{-1}$ ,  $n = 40$ ) (Figure 2e). The POC concentrations were always much higher during the flood tide ( $214.8 \pm 28.2 \mu\text{g L}^{-1}$ ,  $n = 24$  and  $156.3 \pm 37.2 \mu\text{g L}^{-1}$ ,  $n = 23$  in the dry and in wet season respectively) than during the ebb tide ( $170.2 \pm 24.6 \mu\text{g L}^{-1}$ ,  $n = 37$  and  $118.5 \pm 15.3 \mu\text{g L}^{-1}$ ,  $n = 20$  in the dry and in wet season respectively). The average POC concentration was also higher in the dry season ( $187.7 \pm 34.0 \mu\text{g L}^{-1}$ ,  $n = 61$ ) than in the wet season ( $138.7 \pm 34.6 \mu\text{g L}^{-1}$ ,  $n = 43$ ) (Figure 2f). The average percent of organic carbon in the SPM was always higher in flood tide ( $1.9 \pm 0.2\%$  and  $1.0 \pm 0.3\%$  during the dry and wet season respectively) than in ebb tide ( $1.5 \pm 0.2\%$  and  $0.7 \pm 0.1\%$  during the dry and wet season respectively). These results showed the SPM from Sepetiba Bay is essentially clastic and is brought by Sepetiba Bay tributaries. However, marine waters bring particulate organic carbon to the bay. The POC concentration shows a significant positive correlation ( $r = 0.80$ ,  $n = 55$ ,  $P < 0.01$ ) with the dissolved oxygen concentration. The highest POC values, the highest percent saturation of dissolved oxygen and the lowest SPM concentrations measured in the flood tide during the dry

season strongly suggest an elevated primary productivity, and therefore POC from phytoplanktonic origin.<sup>45</sup> On the other hand, the lowest POC values found in the ebb tide during the wet season, when the lowest percent saturation of dissolved oxygen and the highest SPM values also occurred, suggest low primary productivity. The increase in SPM concentration decreases the transparency and limiting primary productivity rates.

### Mercury speciation

Figure 3 represents graphically the mean and standard deviation of the Hg species concentrations measured in the waters of Sepetiba Bay.

Elemental Hg concentrations were statistically similar ( $P < 0.01$ ) during the dry season in flood ( $0.04 \pm 0.01 \text{ ng L}^{-1}$ ,  $n = 24$ ) and ebb ( $0.04 \pm 0.02 \text{ ng L}^{-1}$ ,  $n = 37$ ) periods, whereas during the wet season higher elemental Hg concentrations were found in flood tide ( $0.03 \pm 0.01 \text{ ng L}^{-1}$ ,  $n = 19$ ) than in ebb tide ( $0.02 \pm 0.01 \text{ ng L}^{-1}$ ,  $n = 17$ ) (Figure 3a). The average  $\text{Hg}^0$  concentration during the dry season ( $0.04 \pm 0.01 \text{ ng L}^{-1}$ ,  $n = 61$ ) was significantly



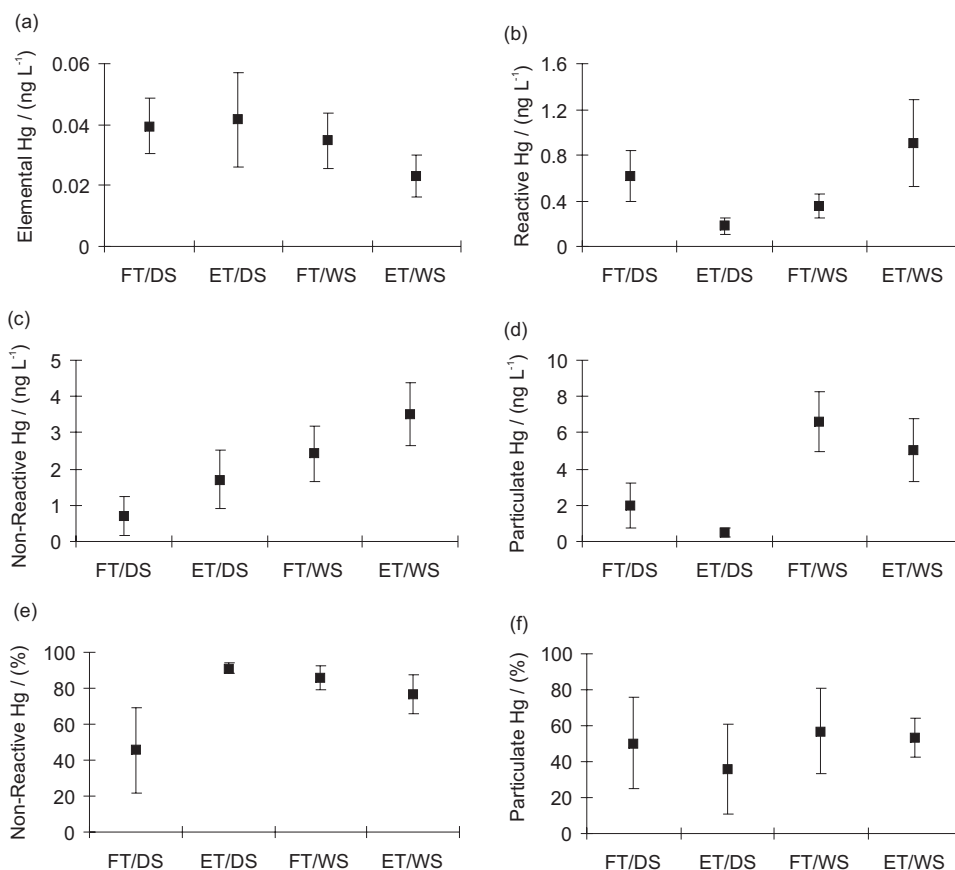
**Figure 2.** Mean and standard deviation of the physicochemical parameters and carbon content measured in Sepetiba Bay waters in flood and ebb periods during the dry and wet seasons. (a) Salinity; (b) Temperature; (c) DO; (d) SPM; (e) DOC and (f) POC. FT/DS = flood tide in dry season; ET/DS = ebb tide in dry season; FT/WS = flood tide in wet season; ET/WS = ebb tide in wet season.

higher ( $P < 0.01$ ) than during the wet season ( $0.03 \pm 0.01$  ng L<sup>-1</sup>,  $n = 36$ ). These values are consistent with those measured in other coastal areas, as in the St. Lawrence Estuary, Canada ( $0.04 \pm 0.02$  ng L<sup>-1</sup>),<sup>5</sup> in the Seine Estuary, France ( $0.03$  to  $0.09$  ng L<sup>-1</sup>),<sup>3</sup> in the Loire Estuary, France ( $0.01$  to  $0.02$  ng L<sup>-1</sup>),<sup>3</sup> in the North Sea ( $0.05 \pm 0.02$  ng L<sup>-1</sup>),<sup>66</sup> in the Scheldt Estuary ( $0.02$  to  $0.13$  ng L<sup>-1</sup>)<sup>67</sup> and in the Mediterranean Sea ( $0.01$  to  $0.10$  ng L<sup>-1</sup>).<sup>58</sup> Mason and Sullivan,<sup>56</sup> however, reported higher values in the South and Equatorial Atlantic, with an average concentration of  $0.24 \pm 0.16$  ng L<sup>-1</sup>.

The average fraction the total Hg as Hg<sup>0</sup> found during the dry season varied from  $3.2 \pm 1.8\%$  to  $2.5 \pm 1.3\%$ , in flood and ebb tide respectively. However, during the wet season this fraction varied from  $1.3 \pm 0.6\%$  to  $0.5 \pm 0.2\%$ , in flood and ebb tide respectively. These values are slightly lower than those reported by Cossa and Gobeil<sup>5</sup> and Mason *et al.*,<sup>68</sup> who observed ratios of about 5%.

Formation of Hg<sup>0</sup> in waters can occur by both biotic and abiotic mechanisms. Studies in marine waters suggest that biotic processes are most important and it is associated

with phytoplankton activity.<sup>16,69-71</sup> A positive potential correlation was found between percent saturation of dissolved oxygen and the percent of Hg<sup>0</sup> relative to the total Hg concentrations ( $r = 0.60$ ,  $n = 94$ ,  $P < 0.01$ ). This result suggests that the Hg<sup>0</sup> production depends on primary production and is in agreement with other authors<sup>3,69,70</sup> who also showed relationships between primary productivity and Hg<sup>0</sup> concentrations in marine waters. The abiotic mechanisms (photochemical reduction) increases its relative importance in coastal and estuaries areas due to larger loads of dissolved organic matter (humic and/or fulvic acids) which is essential to abiotic reduction.<sup>7,72-76</sup> Positive correlation was also found between DOC and percent of Hg<sup>0</sup> relative to the total Hg concentrations ( $r = 0.45$ ,  $n = 94$ ,  $P < 0.01$ ). This increase in DOC concentrations can increase the abiotic reduction rates and consequently increase the Hg<sup>0</sup> formation. Studies in temperate environments<sup>77</sup> have shown that the Hg photoreduction occurs in a wide range of aquatic systems, from pH 5.7 to 8.3 and DOC from 1.0 to 9.0 mg L<sup>-1</sup> but tropical waters have not been so extensively studied so far.



**Figure 3.** Mean and standard deviation of the major Hg species concentrations measured in Sepetiba Bay waters in flood and ebb periods during the dry and wet seasons. (a) Elemental Hg; (b) Reactive Hg; (c) Non-Reactive Hg; (d) Particulate Hg; (e) % Non-Reactive Hg relative to the total Hg concentrations and (f) % Particulate Hg relative to the Hg in Sepetiba Bay waters (total + particulate Hg). FD/TS = flood tide in dry season; ET/DS = ebb tide in dry season; FT/WS = flood tide in wet season; ET/WS = ebb tide in wet season.

The reactive Hg concentrations found in the dry season were higher in flood tide ( $0.6 \pm 0.2 \text{ ng L}^{-1}$ ,  $n = 24$ ) than in ebb tide ( $0.2 \pm 0.1 \text{ ng L}^{-1}$ ,  $n = 34$ ) while during the wet season, the highest values were found in ebb tide ( $1.1 \pm 0.5 \text{ ng L}^{-1}$ ,  $n = 21$ ). Flood tide waters presented reactive Hg concentrations of  $0.4 \pm 0.1 \text{ ng L}^{-1}$ ,  $n = 22$  (Figure 3b). The average reactive Hg concentration during the dry season ( $0.4 \pm 0.3 \text{ ng L}^{-1}$ ,  $n = 58$ ) was lower than during the wet season ( $0.7 \pm 0.5 \text{ ng L}^{-1}$ ,  $n = 43$ ). These values are in agreement with those reported in literature, as in the Mediterranean Sea ( $0.09$  to  $0.38 \text{ ng L}^{-1}$ ),<sup>58</sup> in Long Island Sound, USA ( $0.26$  to  $0.90 \text{ ng L}^{-1}$ ),<sup>57</sup> in the South and Equatorial Atlantic ( $0.10$  to  $1.4 \text{ ng L}^{-1}$ ),<sup>56</sup> in the St. Lawrence Estuary, Canada ( $< 0.04$  to  $0.22 \text{ ng L}^{-1}$ )<sup>5</sup> and in the North Atlantic ( $0.16 \pm 0.09 \text{ ng L}^{-1}$ ).<sup>78</sup> During the dry season, the percent of reactive Hg relative to the total Hg concentrations presented an average of  $54.8 \pm 24.2\%$  in flood and  $9.0 \pm 3.0\%$  in ebb tide, whereas during the wet season averages of  $14.2 \pm 6.3\%$  in flood and  $23.4 \pm 11.2\%$  in ebb tide were observed. These values are also similar to those reported in the St. Lawrence Estuary, Canada ( $8$  to  $59\%$ , with an average of  $20\%$ )<sup>5</sup> but lower than in other regions, as in the Mediterranean Sea ( $15$  to  $98\%$ , with an average of  $57\%$ )<sup>58</sup> and in the Long Island Sound, USA ( $14$  to  $71\%$ ).<sup>57</sup>

The reactive Hg concentrations showed a significant positive non-linear correlation with the total Hg concentrations ( $r = 0.60$ ,  $n = 101$ ,  $P < 0.01$ ) indicating that until a given concentration ( $\sim 2.5 \text{ ng L}^{-1}$ ) there is no relationship between reactive Hg and total Hg concentrations, however under higher reactive Hg concentration ( $< 2.5 \text{ ng L}^{-1}$ ) the same linear increase found in the Sepetiba Bay tributaries<sup>44</sup> is observed. This increase of the reactive Hg concentrations can also be associated with some saturation mechanisms or complexation limit of the DOC.<sup>25</sup>

A negative correlation was also found between reactive Hg and DOC concentrations ( $r = -0.44$ ,  $n = 101$ ,  $P < 0.01$ ) showing that increasing DOC can decrease Hg reactivity and thus influence Hg availability and reactivity in the dissolved phase, such as methylation processes. These results are in disagreement which previously results found in the internal waters of the Sepetiba Bay by Lacerda *et al.*<sup>41</sup> which showed a positive correlation between these parameters, suggesting that the DOC did not control the Hg reactivity in the internal area of the bay or that this DOC was sufficiently labile to keep the Hg under reactive forms, even after complexation.

The non-reactive Hg fraction that represents mostly the organic Hg fraction was estimated by the difference between reactive and total Hg concentrations.<sup>51,54,59-63</sup>

This fraction was always higher during the ebb tide ( $1.7 \pm 0.8 \text{ ng L}^{-1}$ ,  $n = 40$  and  $3.5 \pm 0.9 \text{ ng L}^{-1}$ ,  $n = 21$  in dry and wet season respectively) than during the flood tide ( $0.7 \pm 0.5 \text{ ng L}^{-1}$ ,  $n = 24$  and  $2.4 \pm 0.8 \text{ ng L}^{-1}$ ,  $n = 23$  in dry and wet season respectively) (Figure 3c). The average non-reactive Hg fraction during the dry season ( $1.3 \pm 0.9 \text{ ng L}^{-1}$ ,  $n = 64$ ) was lower than during the wet season ( $3.0 \pm 1.0 \text{ ng L}^{-1}$ ,  $n = 44$ ). The percent of non-reactive Hg relative to the total Hg concentrations presented an average of  $45.5 \pm 24.1\%$  in flood and  $91.0 \pm 3.0\%$  in ebb periods during the dry season. However, during the wet season this fraction presented an average of  $85.8 \pm 6.3\%$  in flood and  $76.6 \pm 11.2\%$  in ebb periods (Figure 3e). The non-reactive Hg concentration shows a significant positive correlation with the temperature ( $r = 0.70$ ,  $n = 55$ ,  $P < 0.01$ ) and a negative correlation with the DO ( $r = -0.76$ ,  $n = 55$ ,  $P < 0.01$ ) but no relationship was found between non-reactive Hg and DOC or POC concentrations, suggesting that the organic carbon content present in Sepetiba Bay waters is not a limiting factor for the organic Hg formation but that temperature and DO concentrations appear to control this process. Similar results were reported by Mason *et al.*<sup>68</sup> in Chesapeake Bay. Thus, the results demonstrate that Sepetiba Bay functions as a producer and exporter of non-reactive Hg species (organic Hg) to the adjacent continental shelf. Certainly, the highest methylation rates are found in the anoxic deeper waters or in bottom sediments, from where it be transported by diffusion and advection to the superficial layers.<sup>79</sup> As Sepetiba Bay is a shallow water body, winds and waves avoid stratification, as confirmed by the similarity of all parameters concentrations measured throughout the depth profiles.

Mercury concentrations in suspended particles during the dry season varied from  $0.2 \pm 0.1 \mu\text{g g}^{-1}$ ,  $n = 22$  in flood and  $0.04 \pm 0.02 \mu\text{g g}^{-1}$ ,  $n = 26$  in ebb periods, whereas during the wet season the Hg concentrations in suspended particles varied from  $0.4 \pm 0.2 \mu\text{g g}^{-1}$ ,  $n = 23$  in flood and  $0.3 \pm 0.1 \mu\text{g g}^{-1}$ ,  $n = 17$  in ebb periods. The particulate Hg concentrations, derived from the SPM concentrations, were statistically similar ( $P < 0.01$ ) during the wet season ( $6.6 \pm 1.6 \text{ ng L}^{-1}$ ,  $n = 22$  and  $5.0 \pm 1.7 \text{ ng L}^{-1}$ ,  $n = 16$  in flood and ebb tide respectively) but during the dry season, the concentrations were higher in flood tide ( $2.0 \pm 1.3 \text{ ng L}^{-1}$ ,  $n = 22$ ) than in the ebb tide ( $0.5 \pm 0.2 \text{ ng L}^{-1}$ ,  $n = 26$ ) (Figure 3d). These values are consistent with those observed in other coastal areas, as in the Loire and Seine Estuaries, France ( $0.1$  to  $1 \mu\text{g g}^{-1}$  and  $0.5$  to  $2.0 \mu\text{g g}^{-1}$ , respectively),<sup>3</sup> in San Francisco Bay, USA ( $0.02$  to  $2.0 \mu\text{g g}^{-1}$ ),<sup>64</sup> in the Elbe Estuary, Germany ( $0.3$  to  $1.4 \mu\text{g g}^{-1}$ )<sup>66</sup>

and in the Scheldt Estuary, The Netherlands ( $0.35$  to  $1.6 \mu\text{g g}^{-1}$ ).<sup>67</sup> The percent of particulate Hg relative to the Hg in Sepetiba Bay waters (total Hg fraction + particulate Hg fraction) presented an average of  $50.3 \pm 25.7\%$  and  $35.7 \pm 25.2\%$  in flood and ebb tide respectively during the dry season and of  $56.9 \pm 23.6\%$  and  $53.4 \pm 11.0\%$  in flood and ebb tide respectively during the wet season (Figure 3f). These percentages are lower than those found in the Elbe and Scheldt Estuary which presented percentages above  $90\%$ .<sup>66,67</sup>

A significant positive correlation was found between total Hg and non-reactive Hg concentrations ( $r = 0.96$ ,  $n = 55$ ,  $P < 0.01$ ) as well as between the Hg in Sepetiba Bay water (total Hg + particulate Hg) and particulate Hg concentrations ( $r = 0.98$ ,  $n = 55$ ,  $P < 0.01$ ). Since total Hg concentration mainly represents the dissolved Hg fraction in waters with low content of SPM, the results found demonstrate that the non-reactive Hg fraction (organic Hg) governs the dissolved Hg phase in Sepetiba Bay waters whereas the particulate Hg dominates the total Hg content present in the Sepetiba Bay waters, mainly during the wet season.

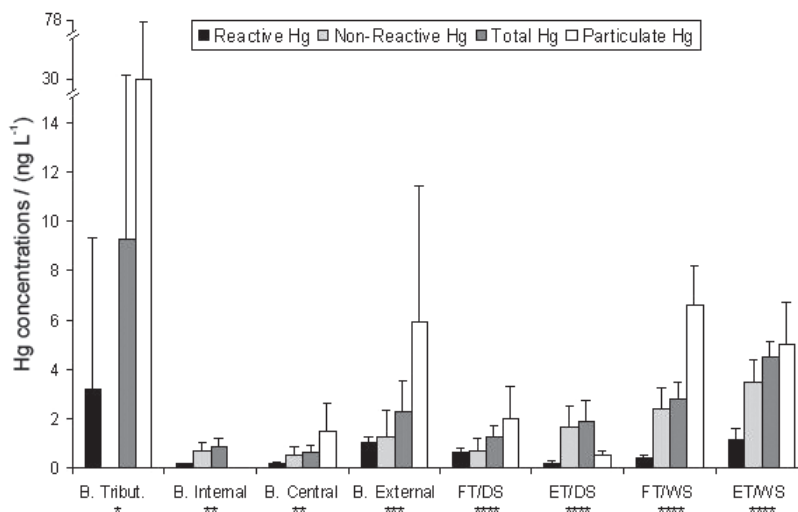
Recent studies showed that Sepetiba Bay tributaries are the main Hg source to the bay, although not receiving emissions from Hg point sources, and are responsible for an annual Hg flux of about  $200 \text{ kg year}^{-1}$ , with  $95\%$  in the particulate form.<sup>44</sup> In the bay internal portion, close to rivers mouths, highest Hg concentrations in sediments are observed, due to the highest sedimentation rates in this region of the bay.<sup>37</sup> In the bay's central and external portions, there is a decrease of the influence of its tributaries and a gradual dilution of Hg concentrations in sediments<sup>37</sup> and in waters occurs.<sup>41,45</sup>

Figure 4 presents the non-reactive, reactive, total and particulate Hg distribution along the estuarine gradient in Sepetiba Bay, including results from earlier works<sup>41,44,45</sup> and those obtained in the present study.

Despite the main Hg fraction in the rivers being associated with suspended particles, the dissolved Hg fraction concentrations in rivers are, in general, one order of magnitude higher than those measured in the bay. In the bay internal portion an intensive changes in the mercury partition and a large dilution of the Hg concentrations is observed.

This spatial distribution showed a strong increase of the dissolved fractions in the external area of the bay. If the non-linear positive tendency found between reactive Hg and total Hg concentrations in the bay's external area represents a saturation mechanisms or complexation limit of DOC, this could explain the highest reactive Hg concentrations in the external area of the Sepetiba Bay. These results show the necessity of more specific studies on Hg complexation with the dissolved organic phase for a better interpretation of the observed variations.

Based on the Hg concentrations in function of tide and season it was possible to observe an exportation of Hg organic fractions to adjacent areas during the ebb tide in both the seasons. This transport seems to be intensified during the wet season. The confirmation of the Hg exportation to adjacent continental platform can explain the higher Hg values found in fish from adjacent coastal water outside Sepetiba Bay,<sup>47</sup> which does not receive direct anthropogenic inputs such as in Sepetiba Bay.



**Figure 4.** Reactive, non-reactive, total and particulate Hg concentrations distribution along the estuarine gradient in Sepetiba Bay, SE Brazil. \* Sepetiba Bay tributaries;<sup>44</sup> \*\* Sepetiba Bay internal and central areas,<sup>41</sup> the particulate Hg concentration in Bay internal was not measured in this work; \*\*\* Sepetiba Bay external area;<sup>45</sup> \*\*\*\* FT/DS = flood tide in dry season; ET/DS = ebb tide in dry season; FT/WS = flood tide in wet season; ET/WS = ebb tide in wet season (This study).

## Conclusions

In this work all the values of Hg concentrations found are similar those reported in the literature for moderately impacted coastal area. The results obtained here suggest that the Sepetiba Bay exports suspended particulate material (SPM) impoverished in organic carbon to adjacent continental platform areas, mainly during the wet season and imports SPM enriched in organic carbon from the ocean, probably of phytoplanktonic origin, during the dry season. The chemical speciation of Hg in the Sepetiba Bay waters showed that Hg<sup>0</sup> production can be controlled by primary productivity and that the bay acts as a producer and exporter of organic species of Hg to adjacent areas, since the highest non-reactive Hg concentrations were observed during the ebb tide. This exportation of the organic species can explain the higher Hg values found in the biota from adjacent coastal water outside Sepetiba Bay.

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