MERCURY SPECIATION AND DISSOLVED ORGANIC CARBON CHARACTERIZATION IN THE SURFACE WATERS OF SEPETIBA BAY, SE BRAZIL

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ABSTRACT

Mercury speciation and dissolved organic carbon (DOC) were measured during a flood tide event in surface waters of Sepetiba Bay, SE Brazil. Average concentrations were 0.08 ± 0.01 ng L^{-1} for elemental Hg, 1.0 ± 0.2 ng L^{-1} for reactive Hg, 2.3 ± 1.2 ng L^{-1} for total Hg, 5.9 ± 5.5 ng L^{-1} for particulate Hg and 1.2 ± 1.0 ng L^{-1} for organic Hg. Hg species concentrations showed no significant correlations between them, but total Hg concentrations were negatively correlated with the percent of reactive Hg relative to the total Hg concentrations ($r = -0.92$). Molecular fluorescence spectroscopy of DOC showed excitation/emission matrices, Ia/Ic and EM$_{450}$/EM$_{500}$ ratios typical of relatively young marine DOC rich in microbially derived fulvic acids, which may explain the observed relative increase of reactive Hg concentrations with increasing tidal height and favor Hg transport through the bay.

RESUMO

A especiação do Hg e o conteúdo de carbono orgânico dissolvido (COD), num evento de entrada de maré nas águas da Baía de Sepetiba, SE Brasil, mostraram concentrações médias de: $0,08 \pm 0,01$ ng L^{-1} para Hg elementar; $1,0 \pm 0,2$ ng L^{-1} para Hg reativo; $2,3 \pm 1,2$ ng L^{-1} para Hg total; $5,9 \pm 5,5$ ng L^{-1} para Hg particulado e $1,2 \pm 1,0$ ng L^{-1} para Hg orgânico. Não foi observada correlação significativa entre as concentrações das espécies de Hg, porém o Hg total foi correlacionado negativamente com a porcentagem de Hg reativo em relação ao Hg total ($r = -0,92$). A espectrofotometria de fluorescência molecular, através das matrizes de excitação/emissão e das razões Ia/Ic e EM$_{450}$/EM$_{500}$, caracterizou um COD relativamente jovem, marinho e rico em ácidos fúlvicos de origem microbiológica, explicando o aumento relativo do Hg reativo com o aumento da maré favorecendo seu o transporte na Baía.

INTRODUCTION

Coastal environments are complex systems submitted to tidal conditions, involving the intense exchange and mixing of fresh water and seawater. The biogeochemical cycling of trace metals in the coastal zone has been altered by human activities through the input of trace metals to these regions from point and diffuses sources. Among the various trace metals of environmental significance, Hg is one which cycle is most affected by anthropogenic activities (Vandal & Fitzgerald, 1995; Coquery *et al.*, 1997; Benoit *et al.*, 1998; Cossa & Gobeil, 2000; Lawson *et al.*, 2001).

Mercury is considered extremely toxic to human and marine life even at low concentrations. This element can be present as dissolved ionic complexes or adsorbed onto particulate matter, as dissolved or particulate organic species and as dissolved or gaseous species in natural waters, as well as adsorbed to sedimentary phases in bottom sediments of rivers and oceans. Methylmercury is the Hg form more toxic to humans and aquatic life and is formed through the transformation of inorganic mercury by microorganisms present in sediment and water. This process is influenced by redox potential, temperature, bacterial activity, pH, metal availability, organic matter and sulphide contents and most important the availability of

Hg^{2+}. Therefore, knowing the chemical speciation of Hg in aquatic environments is a key step in assessing the environment's methylation capacity (Quevauviller *et al.*, 1992; Morel *et al.*, 1998).

It is known that both particulate and dissolved organic carbon play a significant role in the biogeochemical cycling of Hg in aquatic environments. In coastal waters, more than 60 % of the total dissolved mercury is associated to organic matter or suspended particles (Fitzgerald & Lyons, 1973). Whereas dissolved organic carbon (DOC) appears to control the bioavailability of mercury due to its high Hg-binding capacity (Barkay *et al.*, 1997; Cai *et al.*, 1999).

The study of the fluorescent dissolved organic carbon has often been used to distinguish between water masses from various sources (marine, coastal or terrestrial) (Coble, 1996) or to study the mixing processes in coastal and estuarine environments. It has contributed to the understanding of the biogeochemical processes affecting fluorescence of dissolved organic matter during transport through estuaries and in the ocean (Sierra *et al.*, 1994, 1997; Parlanti *et al.*, 2000). The fluorescence in natural waters is predominantly generated by organic acids (humic and fulvic) and the amino-acid groups within proteins. This fluorescent organic matter may be derived from decomposed plant material and from both floral and faunal organic material present in water or they may be leached into the aquatic environment from terrestrial plants, leaf litter, soil or subsurface deposits (Senesi *et al.*, 1991). McKnight *et al.* (2001) showed that the chemical differences between the microbially derived fulvic acids and the terrestrially derived fulvic acids influence the ecological role of fulvic acids due the difference of aromaticity of these compounds.

Several studies have investigated the fluorescent organic matter in marine and coastal waters (Coble, 1996; Parlanti *et al.*, 2000) and have revealed the presence of several fluorescence intensity peaks at excitation and emission wavelength pairs. Many factors may influence the fluorescence intensity and wavelength of dissolved organic matter in natural waters, such as pH, metal–ion interactions and temperature (Senesi *et al.*, 1991; Patel *et al.*, 2002). However, keeping these parameters controlled during analysis, fluorescence intensity peaks and wavelength can be used as consistent proxies of organic carbon origin and reactivity in aquatic ecosystems.

Recent studies in Sepetiba Bay suggested important changes to occur in Hg reactivity (Lacerda *et al.*, 2001) and eventually bioavailability (Khering, 1995) during its transport through the estuarine gradient, but failed to describe under what conditions or which parameters influence these changes. Therefore, the aim of the present work is to study changes in Hg reactivity in Sepetiba Bay through the characterization of the Hg speciation in the surface water of the external area of bay, to characterize the dissolved organic matter through fluorescence technique and to investigate their relationship.

STUDY SITE

Sepetiba Bay is located approximately at latitude 23º S and longitude 44º W, about 60 km south of the Rio de Janeiro city (Figure 1). The Bay is a semi-enclosed water body with 447 km^2 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. The region is under a hot-humid tropical climate, with mean annual precipitation from 1,400 mm to 2,500 mm, depending on the location along the coast. High annual atmospheric precipitation over Sepetiba Bay increases the importance of atmospheric derived pollutants from the local industrial park, particularly of smelters (Lacerda *et al.*, 1987; Barcellos & Lacerda, 1994; Rodrigues, 1990). Sepetiba Basin harbors an industrial park with over 400 industries, a population of about 1.2 million and important fisheries and tourist activities.

Mercury is an ubiquitous contaminant present in the urban and industrial effluents reaching Sepetiba Bay. Mercury emissions to soils, waters and the atmosphere at Sepetiba Bay basin are mostly from diffuse sources, particularly from leaching of a large landfill, an oil-fired electric power plant, steel and iron
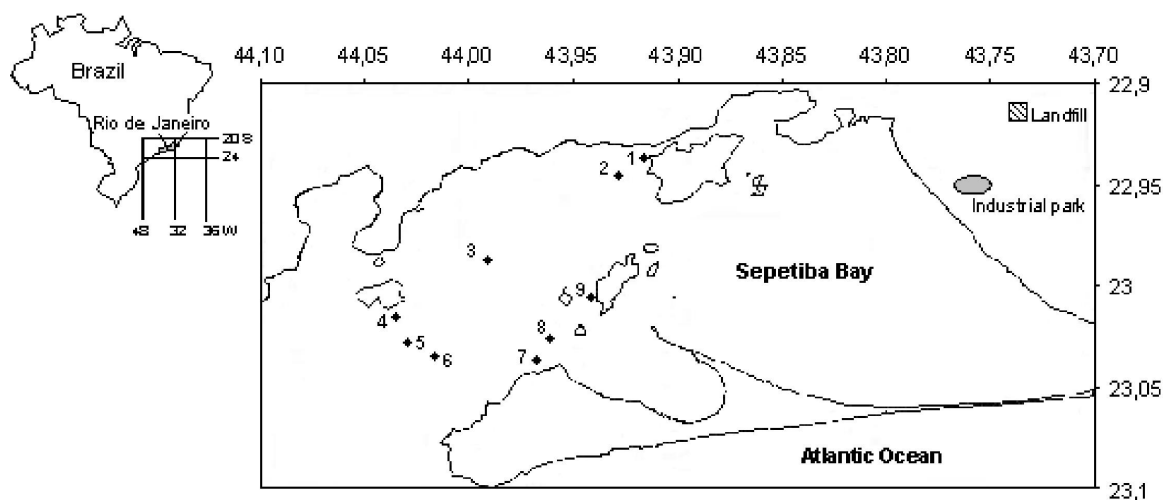
Figure 1 – Sampling sites location in Sepetiba Bay SE, Brazil.

production and waste incineration. Marins *et al.* (1998a) estimated that the total Hg emission to Sepetiba Bay basin ranges from 251 to 417 kg yr^{-1}. Major emissions are to the atmosphere (167 - 201 kg yr^{-1}) and to soils (84 – 216 kg yr^{-1}). Although direct emissions to waterways from the industrial park are very small (less than 1 kg yr^{-1}), the large atmospheric and soil loads may contaminate fluvial systems through atmospheric deposition, surface runoff and groundwater flow.

Recent studies showed that 16 to 85 % total Hg inputs through the majors tributaries of Sepetiba Bay are associated with total suspended solid (TSS) (Paraquetti *et al.*, 2004). Once reaching the bay, Hg, as well as other trace metals associated with TSS and transported by rivers, is distributed following tidal currents within the bay (Lacerda *et al.*, 1987; Barcellos *et al.*, 1997; Marins *et al.*, 1998b). However, only 15% of the total Hg inputs to Sepetiba Bay accumulate in near shore sediments and 85 % this inputs is exported to the external bay area, cycling within the water column and becoming bioavailable for methylation processes and eventually be exported to the adjacent continental shelf waters (Marins *et al.*, 1996; Marins *et al.*, 1999).

SAMPLING AND ANALYSIS

All sampling and analytical materials were pre-cleaned according to accepted protocols (Guentzel *et al.*, 1996). The sampling was conducted during a flood tide event in autumn (April, 2001) in surface waters of the external area of Sepetiba Bay, avoiding the influence of major river inputs. Nine stations were sampled consecutively with station 1 at the beginning of the tide event and station 9 sampled at the end of the flood period (Table 1). Samples were collected near the surface and stored using 0.5 L pre-cleaned Teflon bottles for mercury 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.

Table 1 – Average values (n=3) of major physical chemical parameters measured in surface waters of the Sepetiba Bay, SE Brazil.

Station	Sampling Hour	Tidal Height (cm)	Temperature (°C)	Salinity ‰	Dissolved oxygen (mg L^{-1})	pH
1	10:00 h	48	20	31	4.5	8.2
2	10:20 h	44	22	31	4.8	8.3
3	11:20 h	32	20	32	4.5	8.3
4	12:40 h	53.5	20	32	5.1	8.2
5	13:00 h	60	21	30	5.2	8.2
6	13:20 h	66.5	21	31	5.0	8.2
7	14:40 h	93.5	22	32	5.2	8.2
8	15:00 h	100	20	32	5.5	8.2
9	15:40 h	113.5	20	35	6.5	8.3

All samples were immediately analyzed, in duplicate, after collection (within 4 to 48 h maximum) to preserve the studied species (Bloom & Crecelius, 1983; Bloom, 1994). During the period between sampling and analysis samples were kept in an icebox.

Two samples from each of sampling sites were collected to determinate Hg species, including elemental Hg, reactive Hg, total Hg,

particulate Hg and organic Hg fraction estimated by difference between total Hg and the reactive Hg.

Elemental Hg fraction was analyzed in non-acidified, sub-samples (200 mL) purged with Hg-free argon, at a flow rate of 760 mL min^{-1}, 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 results more satisfactory than the use of 4 min of purge in this analytical systems (Marins *et al.*, 2002).

Reactive Hg was analyzed in non-acidified, sub-samples (20 mL) after the addition of an acidic (1 % v/v distillated HCl + 1% m/v ascorbic acid) 10% SnCl$_2$ solution. This fraction includes mostly ionic (Hg^{2+}) plus elemental Hg, but also the Hg fraction weakly bound to inorganic and organic complexes (Mason *et al.*, 1993; Mason & Sullivan 1999; Cossa & Gobeil, 2000; Lacerda & Gonçalves, 2001; Rolfhus and Fitzgerald, 2001; Horvat *et al.*, 2003).

Total Hg fraction was determined directly in non-acidified, sub-samples (50 mL) after oxidation with a bromine monochloride solution (KBrO$_3$ 1 % m/v + HCl 20 % v/v) at room temperature. This was followed by a reduction with the same SnCl$_2$ solution used for reducing the reactive Hg fraction. 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 (Bloom & Crecelius, 1983; Marins *et al.*, 2002; EPA, 2002). The difference between reactive Hg and total Hg fraction correspond to non-reactive Hg fraction and could be related to organic Hg complexes.

Particulate Hg fraction was obtained by the difference between the total Hg determined with BrCl and the total Hg content in the sample. The total Hg content was determined in unfiltered, non-acidified, sub-samples (40 mL) after oxidation with a 50 % v/v aqua-regia solution (4H$_2$O:3HCl:1HNO$_3$), at 70 to 80 °C for 1 hour followed by a reduction with the same SnCl$_2$ solution used for reducing the reactive Hg fraction. This Hg fraction includes all Hg

dissolved species present in the sample as well as the Hg strongly bound to particulate matter and humic substances. This methodology of determination of particulate Hg was tested and confirmed in a recent work in the same region (Paraquetti *et al.*, 2004). The error found between the determination of particulate Hg by this method and the analysis of filters containing suspended solids presented relatively low variability (< 15 %), and statistical analysis showed no difference between the two methods, therefore validating this methodology. The methodology used in this study provides higher analytical speed and minimize the contamination during the filtration.

The final detection of Hg^0 resultant from the reduction reaction was purged from the sample with Hg-free Argon, at a flow rate of 760 mL min^{-1}, 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 (Mason & Sullivan, 1999; Lacerda & Gonçalves, 2001; Marins *et al.*, 2002; Conaway *et al.*, 2003). 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 $S_{y/x}$ ($S_{y/x} = \{(y_i - y)^2 . (n-2)^{-1}\}^{1/2}$), 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 (Miller & Miller, 1993). All samples were analyzed in duplicate. Differences between duplicates remained below 15 % for all samples.

From each sampling site, 0.5 L samples were collected for total suspended solid (TSS), dissolved organic carbon (DOC) and particulate organic carbon (POC) analysis. The sub-samples were filtered through a glass micro fiber filter (0.7 µm, Whatman GF/F), directly after sampling. The filters had been pre-treated by heating at 450 °C for 12 hours in order to destroy traces of organic carbon. The filtrates were preserved with 100 mL of 1 M sodium azide

solution and were kept in 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 mim. The sample was analyzed by high temperature catalytic combustion (650 ºC). The obtained detection limit for this procedure was 0.15 mg L^{-1}. The POC concentration was measured using the same analytical system but with other furnace (SSM 5000A) at 900 ºC. Each analysis was made in triplicate to determine the average concentrations.

The DOC present in the samples was characterized using molecular fluorescence spectroscopy. Fluorescence measurements were undertaken using a HITACHI F 4500 fluorescence spectrophotometer. The spectrophotometer used a xenon excitation source and slits were set to 10 nm for excitation and 5 nm for emission. To obtain fluorescence excitation emission matrixes (EEM), excitation wavelengths were incremented from 200 to 500 nm at 5 nm steps; for each excitation wavelength the emission was detected from 250 to 600 nm at 5 nm steps. Scan speed was set at 30,000 nm mim^{-1}. The excitation fluorescence spectra were collected from 200 to 420 nm at a fixed emission wavelength of 435 nm, and emission fluorescence spectra were collected from 350 to 600 nm at a fixed excitation wavelength of 340 nm. Scan speed was set at 240 nm mim^{-1}.

During the sampling, some major physical and chemical parameters were also measured in situ. Salinity was determined using a SHIBUYA refratometer. Dissolved oxygen (DO) was determined using a DIGIMED portable oxygen meter, whereas pH, and temperature were measured with a DIGIMED pH-meter, with a combined glass electrode for pH determinations. Precision of such field determinations was 0.1 unit.

RESULTS AND DISCUSSION

Mercury speciation

The major physical and chemical parameters and the concentrations of Hg species measured in the surface waters of Sepetiba Bay are presented in Tables 1 and 2, respectively. There was no substantial variation in pH and temperature in the surface waters of Sepetiba Bay during the sampling. Between the beginning and the end of the tidal event, the temperature varied from 20 to 22 ºC and pH varied from 8.2 to 8.3. Dissolved oxygen values increased from 4.5 to 6.5 mg L^{-1} whereas salinity increased from 30 to 35. More oxygenated and saline waters compared to estuarine waters of Sepetiba Bay characterize the influence of ocean waters.

The elemental Hg concentrations in the surface waters of the external area of Sepetiba Bay varied little (0.07 to 0.10 ng L^{-1}), with an average concentration of 0.08 ± 0.01 ng L^{-1}. There was no clear trend between different periods of the tidal event. The reactive Hg concentrations varied from 0.8 to 1.6 ng L^{-1}, with an average concentration of 1.0 ± 0.2 ng L^{-1}

Table 2 – Average values (n=4) of mercury species concentrations measured in surface waters of the Sepetiba Bay, SE Brazil.

Station	Elemental Hg (ng L^{-1})	Reactive Hg (ng L^{-1})	Total Hg (ng L^{-1})	Organic Hg (ng L^{-1})	Reactive Hg (%)	Organic Hg (%)	Particulate Hg (ng L^{-1})	Particulate Hg (%)
1	0.09	1.0	1.7	0.7	58.3	41.7	7.5	81.7
2	0.08	1.1	3.6	2.5	30.1	69.9	4.5	55.5
3	0.08	1.0	1.2	0.2	87.5	12.5	19.2	94.1
4	0.08	0.8	2.5	1.7	32.3	67.7	7.8	75.4
5	0.07	0.9	2.5	1.5	37.9	62.1	2.2	47.1
6	0.08	0.9	1.9	0.9	50.0	50.0	1.7	48.1
7	0.09	0.9	1.1	0.2	78.9	21.1	5.0	82.1
8	0.10	1.6	4.8	3.2	33.8	66.2	4.3	47.2
9	0.09	1.0	1.3	0.3	75.0	25.0	1.1	46.1

whereas the total Hg concentrations varied from 1.1 to 4.8 ng L^{-1}, with an average concentration of 2.3 ± 1.2 ng L^{-1}. Again, there was no clear temporal trend. However, higher concentrations of these species were generally found at the end of the peak of high tide.

The organic Hg concentrations, obtained by the difference between reactive Hg and total Hg, varied from 0.2 to 3.2 ng L^{-1}, with an average concentration of 1.2 ± 1.0 ng L^{-1}. The percentage of reactive Hg relative to the total Hg concentrations varied from 30.1 to 87.5%, with an average concentration of 53.8 ± 22.2 % whereas the percent of organic Hg relative to the total Hg concentrations varied from 12.5 to 69.9%, with an average of 46.2 ± 22.2 % (Table 2).

Particulate Hg concentrations varied from 1.1 to 19.2 ng L^{-1}, with an average concentration of 5.9 ± 5.5 ng L^{-1} and the percentage of particulate Hg relative to the total (D+P) Hg concentrations varied from 46.1 to 94.1 %, with an average of 64.1 ± 19.0 % (Table 2). Particulate Hg and its relative importance to the total Hg concentrations were, in general, lower at the end of the flood event.

The total Hg concentrations showed a significant negative correlation with the percent of reactive Hg relative to the total Hg concentrations (r = - 0.92, *P* < 0.01). The relationship between these parameters followed a potential equation (Figure 2) with highest percentages of reactive Hg, up to 80 %, occurring when lowest total Hg content was measured (1.1 ng L^{-1}). A recent study (Lacerda *et al.*, 2001) in surface waters of Sepetiba Bay showed the same tendency.
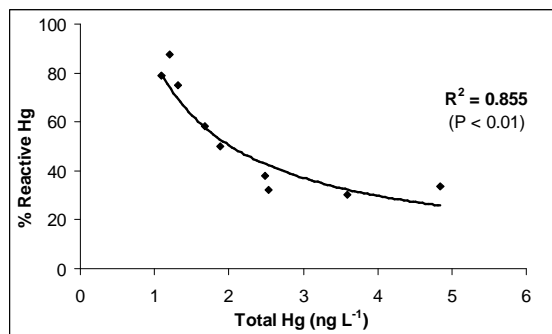
Figure 2 – Relationship between total Hg and reactive Hg as percentage of the total Hg concentrations in the surface waters of Sepetiba Bay, SE Brazil.

Figure 3 summarizes the Hg partitioning between the major species in the surface waters of the external area of Sepetiba Bay. The results show a tendency of increase of reactive Hg and a decrease of particulate Hg during the flood tide period. The elemental Hg fraction was practically constant whereas the organic Hg fraction did not follow a clear tendency. Although the major Hg input to Sepetiba Bay is associated with suspended particulate material (SPM) (Paraquetti *et al.*, 2004), this fraction is retained at the inner reaches of the bay, close to river mouths (Marins *et al.*, 1999).
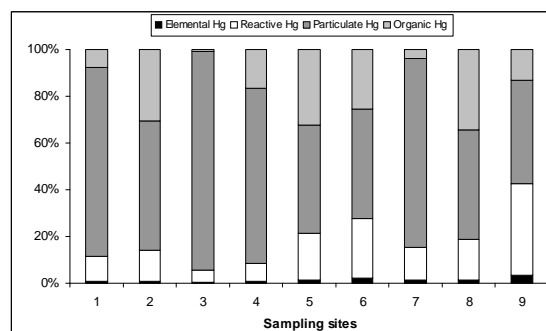
Figure 3 – The partitioning between the majors Hg species measured in the surface waters of Sepetiba Bay, SE Brazil.

No relationship was found between DOC or POC concentrations and Hg species, suggesting that the organic matter do not regulate Hg behavior despite its proved complexing capacity for mercury (Mounier *et al.*, 2001; Lu & Jaffe, 2001).

The elemental Hg concentrations found in this work are similar to those reported for others moderate contaminated estuaries, e.g. the Scheldt Estuary, with concentrations varying from 0.02 to 0.13 ng L^{-1} (Baeyens *et al.*, 1998); the St. Lawrence Estuary, varying from 0.04 to 0.07 ng L^{-1} (Cossa & Gobeil, 2000); the North Atlantic, with an average concentration of 0.09 $\pm$ 0.06 ng L^{-1} (Mason *et al.*, 1998) and the North Sea, varying from 0.02 to 0.90 ng L^{-1} (Coquery & Cossa, 1995). Mason & Sullivan (1999) reported higher values in the South and Equatorial Atlantic, with an average concentration of 0.24 ± 0.16 ng L^{-1}. The values found by Coquery & Cossa (1995) are related to the dissolved gaseous mercury (DGM) but include only the elemental Hg because the measure was analyzed after 6h of sampling and this time is sufficient for the loss of the dimetil mercury present in the sample, according to

Bloom & Crecelius (1993)

The reactive Hg concentrations found in this work were always in the upper range of values reported in the literature considering the same analytical methodology. Reactive Hg concentrations reported in the literature typically vary from 0.16 to 0.90 ng L^{-1} (Mason *et al.*, 1998; Mason & Sullivan, 1999; Cossa & Gobeil, 2000; Rolfhus and Fitzgerald, 2001; Horvat *et al.*, 2003).

Conaway *et al.* (2003) reported total Hg concentrations varying from 0.15 to 88.2 ng L^{-1} in San Francisco Bay. Similar values were reported by Lacerda & Gonçalves (2001) in the coastal lagoons of SE Brazil, varying from 2.5 to 11.3 ng L^{-1}. However, the values measured in Sepetiba Bay were higher than those reported in open ocean areas, such as the North Atlantic (Mason *et al.*, 1998) and the South and Equatorial Atlantic (Mason & Sullivan, 1999).

The particulate Hg concentrations found are similar to those reported for coastal plain estuaries in literature, e.g. in the Scheldt estuary, varying from 0.35 to 1.6 µg g^{-1} (Baeyens *et al.*, 1998); the Loire and Siene estuaries, varying from 0.1 to 1.0 µg g^{-1} and from 0.5 to 2.0 µg g^{-1} respectively (Coquery *et al.*, 1997); the Costal Lagoons of SE Brazil, varying from 0.7 to 2.9 µg g^{-1} (Lacerda & Gonçalves, 2001); the San Francisco Bay estuary, with an average concentration of 0.36 ± 0.10 ng L^{-1} (Conaway *et al.*, 2003) and in the North Sea, varying from 0.12 to 0.48 ng L^{-1} (Coquery & Cossa, 1995).

### *Characterization of the dissolved organic carbon*

Figure 4 presents peaks position of the excitation emission matrix (EMM) of the Sepetiba Bay´s surface waters. The locations of fluorescence intensity peaks in the EEM can be ascribed to the different fluorophores (protein-like, fulvic-like and humic-like) characterizing three different regions. The first region is a region of protein-like fluorophores with peaks at 225-230:300-345 nm. The second region is characteristic of the fulvic-like fluorophores region with peaks at 250-265:400-440 nm whereas the third region characterizes the humic-
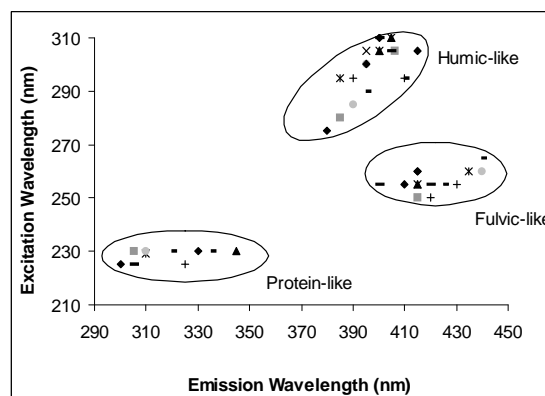
Figure 4 – Excitation and emission wavelengths for the three main fluorescence peaks (protein-like, fulvic -like and humic-like) observed in the surface waters of Sepetiba Bay, SE Brazil.

like fluorophores region with peaks at 275-310:380-415nm.

The locations of fluorescence intensity peaks found in the EEM for the surface waters of the external area of Sepetiba Bay are comparable to the values reported in literature for marine waters (Coble, 1996) but are not comparable to the values reported for coastal waters (**Figure** 5). It shows that the dissolved organic matter of the external area of Sepetiba Bay receives little influence of the internal area, richer in terrestrial organic matter.
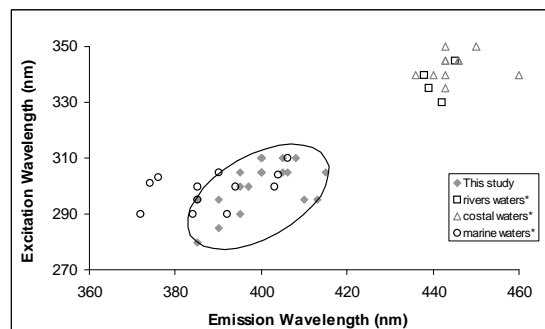
Figure 5 – Comparison between the excitation and emission wavelengths for humic-like peaks found in the surface waters of Sepetiba Bay and the values reported in literature (Coble, 1996).

The intensity ratio between two fluorescence maxima can be used to define the quality of the fluorescent organic matter in natural waters (Coble, 1996). We will use the fluorophores type A (fulvic-like) and type C (humic-like) present in the water samples to calculate the fulvic-like:humic-like fluorescence intensity ratio (Ia/Ic). Small Ia/Ic ratios are characteristic of more aromatic organic matter (polycondensed), higher molecular weight and

lesser complexation sites, therefore less reactive. Whereas larger Ia/Ic ratios are characteristic of a less aromatic organic matter, rich in lesser-conjugated, younger, fluorescent compounds, and with elevated complexation and oxidation capacity, therefore more reactive (Patel *et al.*, 2002). The results obtained are presented in Table 3. The Ia/Ic ratio values are practically constant throughout the sampling period, varying from 1.3 to 1.5. Hence it was not possible to point out any significant changes in the Ia/Ic ratio during the flood tide event. Similar values were reported by Coble (1996) in the Dabob Bay, USA (Ia/Ic = 1.60).

Table 3 – Total Suspended Solid (TSS), Dissolved Organic Carbon (DOC) and Particulate Organic Carbon (POC) concentrations and Ia/Ic and E_{450}/E_{500} ratios measured in surface waters of the Sepetiba Bay, SE Brazil.

Station	TSS (mg L^{-1})	DOC (mg L^{-1})	POC (µg L^{-1})	Ia/Ic *	E_{450}/E_{500} **
1	17.9	2.4	171.9	1.4	2.3
2	13.4	2.4	64.4	1.4	2.3
3	18.8	2.4	67.6	1.3	2.4
4	14.7	2.2	103.0	1.3	2.5
5	17.3	2.2	168.9	1.4	2.3
6	14.8	3.5	112.9	1.4	2.3
7	17.9	2.1	508.8	1.4	2.3
8	16.6	2.2	329.3	1.5	2.4
9	15.1	3.9	77.6	1.3	2.3
* Fulvic-like : humic-like fluorescence intensity ratio (Ia/Ic)					
** Fluorescence index is the ratio of emission intensity at 450 nm and at 500 nm (excitation wavelength at 340nm)					

McKnight *et al.* (2001) recently proposed to use a fluorescence index to distinguish the microbially derived fulvic acids from the terrestrially derived fulvic acids. The index is defined as the ratio of fluorescence emission intensity at wavelength of 450 nm to 500 nm (E_{450}/E_{500}). The microbially derived fulvic acids generally contain low fluorophores and low aromaticity with a fluorescence index value of ~1.9. However, terrestrially derived fulvic acids contain a relatively higher aromaticity and fluorophores with a fluorescence index value of

~1.4. The calculated values of the fluorescence indices are presented in Table 3. Fluorescence index varied from 2.3 to 2.5, showing that the fulvic acids in the surface waters of the external area of Sepetiba Bay are mostly formed by microbial processes. Dissolved organic carbon (DOC), particulate organic carbon (POC) and total suspended solid (TSS) concentrations measured in the surface waters of the external area of Sepetiba Bay are also presented in Table 3. The DOC concentrations varied from 2.1 to 3.9 mg L^{-1}; the POC concentrations varied from 64.4 to 508.8 ¼g L^{-1} and the TSS concentrations varied from 13.4 to 18.8 mg L^{-1}.

CONCLUSIONS

The results suggest the importance of the flood tide event in the Hg speciation of the surface waters of external area of Sepetiba Bay showing that Hg fractions are modified during the flood tide with an increase of the reactive Hg fraction and a decrease of the particulate one. The locations of fluorescence intensity peaks in the EEM as well as the Ia/Ic and E_{450}/E_{500} ratios showed that the dissolved organic matter in the surface waters of the external area of Sepetiba Bay is essentially of marine origin and relatively young and rich in microbially derived fulvic acids. This more reactive organic matter is probably enhancing Hg reactivity in the dissolved phase. The increase in the reactive Hg concentrations during the flood event is negatively correlated to the total Hg concentrations. This suggests Hg reactivity to be enhanced by way of oxidation or by association with the fresh marine organic matter detected by fluorescence spectroscopy, and/or desorption from the particulate phase.

ACKNOWLEDGEMENTS

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