Mercury distribution, speciation and flux in the Sepetiba Bay tributaries, SE Brazil

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Abstract

Dissolved gaseous Hg, reactive Hg, total dissolved Hg and particulate Hg concentrations were measured in samples of majors tributaries of the Sepetiba Bay, SE Brazil (Itimirim, Itinguçu, Guarda, Guandu, São Francisco and Ita rivers), in dry and rainy seasons. The average Hg concentrations found varied from 0.02 to 0.18 ng L^{-1} for dissolved gaseous Hg, from 0.1 to 18.1 ng L^{-1} for reactive Hg, from 0.1 to 66.6 ng L^{-1} for total dissolved Hg and from 0.3 to 250 ng L^{-1} for particulate Hg. During the rainy season, a decrease in the dissolved Hg concentrations and an increase in the particulate Hg concentrations was observed. Positive correlations were found between the reactive Hg and the total dissolved Hg concentrations ($r = 0.99$), between the particulate Hg and TSS concentrations ($r = 0.82$) and between total Hg and particulate Hg concentrations ($r = 0.95$). The instantaneous Hg fluxes varied among rivers from 0.02 to 412 µg s^{-1} for total dissolved Hg and from 0.03 to 12,572 µg s^{-1} for particulate Hg. The log K_d varied from 3.76 to 6.43 and showed a significant increase in rainy season following an increase in particulate Hg and a decrease in dissolved Hg concentrations. These results suggest that erosion and runoff are the major pathways of Hg transport to rivers and eventually to Sepetiba Bay.
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Keywords: Mercury; Speciation; Fluxes; Distribution coefficients; Sepetiba Bay Tributaries

1. Introduction

The processes occurring at the land–sea interface play a significant role in regulating the input of trace metals and suspended matter to coastal areas and oceans. The biogeochemical cycling of trace metals in the coastal zone has been altered by man's activities, especially with respect to man's encroachment of rivers and estuaries, and the resultant enhanced input of trace metals to these locations from point and non-point sources. Among the

various trace metals of environmental significance, Hg is the one which cycle is most affected by anthropogenic activities [1–5].

Mercury is considered extremely toxic to human and marine life. This element can be present as diverse dissolved chemical species in natural waters as well as adsorbed to sedimentary phases in the bottom sediments of rivers, lakes and oceans. The main toxicity of mercury to humans is related to methylmercury rather than to inorganic mercury or metallic mercury. Symptoms of methylmercury poisoning include mental disturbance, ataxia and impairment of speech, hearing, vision and movement [6]. Mercury becomes available to food chains through the transformation of inorganic mercury to organic methylmercury by microorganisms present in sediment and water. This process is controlled by redox

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potential, temperature, bacterial activity, pH, metal availability, organic matter and sulfide 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 [7,8].

In the aquatic environment, inorganic mercury is associated in solution and in suspension by various geochemical ligands: organic acids, salts, Fe and Mn oxihydroxides, clay minerals, dissolved organic matter, among others. The residence time of Hg in the water column is dependent on many processes, particularly the physical–chemical conditions, the hydrodynamics of the waterbody and the form of discharge, which affect Hg species in the water column and their form of occurrence.

The Sepetiba Bay Basin is located in a heavily industrialized and urbanized area in southeast Brazil. Its basin receives freshwater inputs from many rivers, with larger tributaries crossing an industrialized area of the basin. Marins et al. [9] estimated that the total Hg emission from the industrial park and urban sources 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 ($< 1 \, kg \, yr^{-1}$), the large atmospheric and soil loads may contaminate fluvial systems through atmospheric deposition, surface runoff and groundwater flow. Also, diversion of waters from an adjacent river basin, the Paraíba do Sul River Basin, brings an additional Hg load of about $200 \, kg \, yr^{-1}$ to Sepetiba Bay Rivers. The total fluvial Hg discharge into Sepetiba Bay is estimated to be 400–$650 \, kg \, yr^{-1}$ [10,11].

The aims of this study are to characterize the Hg distribution and speciation in major fluvial systems reaching Sepetiba Bay, to determine the fluxes of different Hg species to the bay and to evaluate the relationship between particulate and dissolved Hg along the fluvial transport.

2. Study site

The Sepetiba Bay is located approximately at latitude $23°S$ and longitude $44°W$, about 60 km south of the Rio de Janeiro city (Fig. 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 h. The mean water volume is $2.56 \times 10^9 \, m^3$, ranging between 3.06×10^9 and $2.38 \times 10^9 \, m^3$. The region is under a hot-humid tropical climate, with the mean annual precipitation ranging from 1400 mm to 2500 mm, depending on the location along the coast. The annual atmospheric precipitation over Sepetiba Bay (0.5 to $10 \times 10^7 \, m^3 \, yr^{-1}$) equals and may even surpass
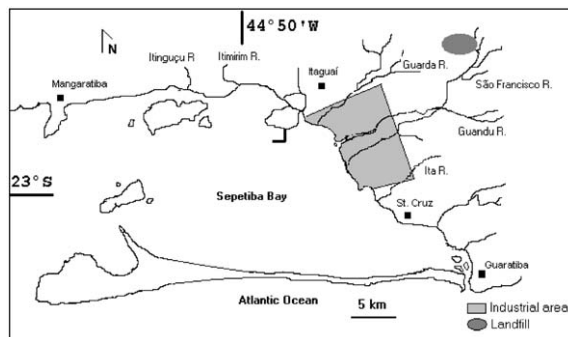

Fig. 1. Map of Sepetiba Bay showing the rivers sampled.

the fluvial inputs, increasing the importance of atmospheric derived pollutants from local smelters [12–14].

The lowlands of the eastern coast of Sepetiba Bay, with good transport facilities, cheap and ample land, good fresh water supply and low population density, became interesting in terms of industrial development, further facilitated by the building in the late 1970s of large harbor facilities. The population of the basin has increased from 600,000 people in 1978 to 1.2 million, mostly concentrated along the northeastern shore as a result of the industrial growth. This fact and the unplanned development resulted in high contamination of the bay in direct conflict with the necessity of environmental conservation and the sustainable utilization of the bay's natural resources [12]. Sepetiba Basin harbors nearly 400 industries and important fisheries and tourist activities are also present.

Nine rivers draining the quaternary plain at the northeastern coast of the Bay are responsible for almost the totality of freshwater inputs, reaching an annual flow of 5.7–$7.6 \times 10^9 \, m^3$. The São Francisco River with an annual flow of $5.7 \times 10^9 \, m^3$ is responsible for over 86% of the total freshwater flow and 73% of the total suspended solid (TSS) inputs to the bay [13]. There is no substantial seasonal variation in fluvial discharge to the bay. This is due to the nearly constant flow of the two major rivers (São Francisco e Guandu Rivers), which are artificially controlled by a water treatment plant located upstream from the major industrial area [13,15]. The Sepetiba Bay basin receives a large volume of water through water transposition to the São Francisco e Guandu Rivers from the adjacent basin, the Paraíba do Sul River system, a heavily industrialized region north of Sepetiba Bay.

Mercury is a ubiquitous contaminant present in the urban and industrial effluents reaching Sepetiba Bay. Mercury emissions to soils, waters and the atmosphere at Sepetiba Bay basin are mostly from diffuse sources, particularly from an oil-fired electric power plant, steel and iron production, waste incineration and leaching from a large landfill. A significant fraction of the total

anthropogenic Hg input reaches Sepetiba Bay through atmospheric deposition; however, fluvial inputs dominate the total Hg load to the bay. Once reaching the bay, Hg, as well as other trace metals transported by rivers, which are mostly adsorbed to suspended particles, are distributed following tidal currents within the bay, creating accumulation areas along its northeastern coast [14,16,17].

3. Sampling and analysis

All sampling and analytical materials were pre-cleaned according to accepted protocols [18]. Three samplings were conducted, two during the autumn–winter (April 2000 and June 2001, in the dry season) in the six major tributaries of the Sepetiba Bay, Itinguçu, Itimirim, Guarda, Guandu, São Francisco and Ita Rivers, and one during the summer (February 2001 in the rainy season) only in the Guandu and São Francisco Rivers. Samples were collected from the bridges of the highway BR-101, using 0.5 L pre-cleaned Teflon bottles, and stored in 0.5 L pre-cleaned PET bottles [19]. Sampling bottles were rinsed three times with the local water before being filled. Storage bottles were double bagged in acid-washed plastic bags and transported in an icebox to the laboratory. Three samples from each of river were collected to determine Hg species, including dissolved gaseous Hg, reactive Hg, total dissolved Hg, total Hg (dissolved + particulate) and particulate Hg.

All samples were immediately analyzed, in duplicate, after collection (within 4–48 h maximum) [20,21]. During the period between sampling and analysis samples were kept in an icebox.

Dissolved gaseous Hg fraction (DGM) was analyzed in unfiltered, non-acidified, sub-samples (200 mL) purged 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.

Unfiltered, non-acidified, sub-samples (20 mL) were analyzed for reactive Hg considered here as the fraction of the total Hg concentration that is reduced and

therefore released from solution after the addition of 1.0 mL of an acidic (1% v/v distillated HCl) 10% SnCl$_2$ solution. This fraction includes mostly ionic (Hg^{2+}) plus DGM, and also the Hg fraction weakly bound to inorganic and organic complexes [22–24]. However, it does not include Hg leachable from particulate matter [25]. Since we did not acidify the samples prior to analysis, our reactive Hg fraction does not compare with the reactive Hg fractions typically reported in the literature that used acidified samples [25,26].

The total dissolved Hg fraction was determined in unfiltered, non-acidified, sub-samples (50 mL) after oxidation with 0.2 mL of a bromine monochloride solution (0.1 mL KBrO$_3$ 1% m/v + 0.1 mL HCl 20% v/v) at room temperature. After oxidation, 0.1 mL of 1% m/v ascorbic acid solution was used to reduce the excess BrCl. This was followed by a reduction with the same SnCl$_2$ solution used for reducing the reactive Hg fraction [21,27]. Dissolved total Hg includes all dissolved Hg species strongly bound to soluble inorganic and organic complexes, and Hg weakly bound to suspended particles.

The total Hg (dissolved + particulate) fraction was determined in unfiltered, non-acidified, sub-samples (40 mL) after oxidation with 10 mL of 50% v/v aqua regia solution (4H$_2$O:3HCl:1HNO$_3$), at 70–80°C for 1 h [28] followed by a reduction with the same SnCl$_2$ solution used for reducing the reactive Hg fraction. Total Hg (D + P) includes all dissolved and particulate Hg species present in the sample. Particulate Hg fraction can be obtained by the difference between total Hg (D + P) and total dissolved Hg.

The validation of the sequential method used for the determination of particulate Hg concentration is presented in Table 1. The samples were collected in the Guandu River during the dry season. The particulate Hg concentrations, obtained by the difference between the total Hg concentration and total dissolved Hg concentrations measured using the sequential methodology used in this paper, presented an average of 80.5 ± 11.0 ng L^{-1} whereas the particulate Hg concentrations obtained by the analysis of filters containing

Table 1
Validation of the sequential method used for the determination of particulate Hg concentration

	DGM (ng L^{-1})	Reactive Hg (ng L^{-1})	Total dissolved Hg (ng L^{-1})	Total Hg (D + P) (ng L^{-1})	Particulate Hg[a] (ng L^{-1})	Particulate Hg[b] (ng L^{-1})
Average	0.11	2.4	3.2	83.7	80.5	88.8
SD	0.02	0.2	0.7	11.4	11.0	11.1
Min	0.08	2.2	2.1	68.8	66.8	69.0
Max	0.14	2.7	4.2	95.7	92.8	106
N	8	8	8	8	8	15

[a] Total Hg (D + P)−Total dissolved Hg.
[b] Filters analysis.

suspended solids presented an average concentration of $88.8 \pm 11.1 \, \mathrm{ng \, L^{-1}}$. Both results presented relatively low variability ($<15\%$) and an analysis of variance showed no statistically significant difference between the two averages ($P \geqslant 0.05$), therefore validating the sequential method used in this paper.

The Hg^0 resultant from the reduction reaction was purged from the sample with Hg-free Argon, at a flow rate of $760 \, \mathrm{mL \, min^{-1}}$, 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 [27]. 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 $S_{y/x}$ ($S_{y/x} = \{\Sigma(y_i - y)^2(n - 2)^{-1}\}^{1/2}$) and the slope of the regression line of the calibration curve [29]. All samples were analyzed in duplicate. Differences between duplicates remained below 15% for all samples.

From each river, 500 mL sub-samples were collected for total suspended solids (TSS) analysis, which was determined after filtration through a 0.70 μm Whatman Glass Microfiber GF/F filter.

During the sampling, some major physical and chemical parameters were also measured in situ. Conductivity was measured with a DIGIMED Conductivity-meter. Dissolved oxygen (DO) was determined using a DIGIMED portable oxygen meter, whereas pH, temperature and redox potential (Eh) were measured with a DIGIMED pH-meter, with a combined glass electrode, and a platinum electrode, for pH and Eh determinations, respectively. The precision of such filed determinations was 0.1 U.

4. Results and discussion

The major physical and chemical parameters and the concentrations of Hg species measured in the tributaries that flow into Sepetiba Bay are presented in Tables 2 and 3, respectively. The physical chemical parameters (Table 2) characterize the freshwater input as neutral to basic due pH values variation from 6.6 to 7.8. The lower conductivity ($37-98 \, \mathrm{\mu S \, cm^{-1}}$) and higher DO values ($6.2-8.3 \, \mathrm{mg \, L^{-1}}$) observed in Itimirim, Itinguçu and São Francisco Rivers typify these environments as lesser impacted whereas the Guarda, Guandu and Ita Rivers showed an opposite trend with higher conductivity ($320-1370 \, \mathrm{\mu S \, cm^{-1}}$) and lower DO values ($1.3-3.1 \, \mathrm{mg \, L^{-1}}$), suggesting these rivers as the most impacted along the basin. This impact is mostly attributable to untreated sewage inputs, particularly the Guandu and Ita Rivers. The Guarda River also receives runoff waters leaching saline soils from converted mangroves. Similar results have been reported by other authors working in these rivers [13,15].

The DGM concentrations in rivers had an average concentration varying from 0.02 to $0.18 \, \mathrm{ng \, L^{-1}}$ (Table 3). In dry season, the Itinguçu River presented the higher DGM concentration among all rivers. The temporal distribution showed lower DGM values during the rainy season in the São Francisco and Guandu Rivers compared with samples collected during the dry season. In the dry season, reactive Hg was lowest in the Itimirim, Guarda and São Francisco Rivers, with average concentrations of $0.3 \, \mathrm{ng \, L^{-1}}$. Intermediate values were found in the Itinguçu and Ita Rivers, varying from 1.0 to $1.3 \, \mathrm{ng \, L^{-1}}$, followed by the highest average concentration measured in the Guandu River ($18.1 \, \mathrm{ng \, L^{-1}}$). In the rainy season sampling, reactive Hg concentrations observed in São Francisco and Guandu Rivers were 0.1 and $3.8 \, \mathrm{ng \, L^{-1}}$, a decrease of three and five times, respectively, in relation to the dry season. These values, with the exception of the Guandu River data, are similar to those found in moderate impacted rivers worldwide, e.g. the Loire and Siene Rivers, France, with concentrations ranging from 0.08 to $0.22 \, \mathrm{ng \, L^{-1}}$ and 0.08 to $0.42 \, \mathrm{ng \, L^{-1}}$, respectively [4], and in the Narragansett Bay tributaries, USA, with concentrations varying from 1.6 to $5.8 \, \mathrm{ng \, L^{-1}}$ [5] (Table 4).

Table 2
Average values ($n = 3$) of major physical chemical parameters measured in Sepetiba Bay tributaries, SE Brazil

	pH	Temperature (°C)	Conductivity (μS cm⁻¹)	Dissolved oxygen (mg L⁻¹)	Redox potential (mV)	TSS (mg L⁻¹)
Itinguçu River	7.0	23	43	6.2	159	1.7
Itimirim River	7.6	23	37	8.3	171	4.4
Guarda River	6.8	25	1370	3.1	210	15.5
São Francisco River	7.8	25	98	7.6	214	15.1
Guandu River	7.1	24	320	1.3	74	189.2
Ita River	6.6	25	470	1.8	−22	34.3

Table 3
Mercury species concentrations measured in Sepetiba Bay tributaries, SE Brazil

	Dissolved gaseous Hg (ng L^{-1})	Reactive Hg (ng L^{-1})	Total dissolved Hg (ng L^{-1})	Reactive Hg (%)	Total (D + P) Hg (ng L^{-1})	Particulate Hg (ng L^{-1})	Particulate Hg (%)
Itinguçu River	0.16–0.19	0.9–1.1	1.1–1.3	82.7–85.3	2.3–2.5	1.0–1.4	42.9–56.4
(n = 4); av.	0.18	1.0	1.2	84.0	2.4	1.2	49.7
Itimirim River	0.08–0.09	0.1–0.4	0.2–0.5	59.1–83.0	0.9–1.0	0.4–0.5	44.4–46.5
(n = 6); av.	0.09	0.3	0.4	71.1	1.0	0.4	45.5
Guarda River	0.09–0.10	0.1–0.6	0.2–0.8	20.0–85.7	1.0–38.3	0.2–38.0	15.2–99.3
(n = 6); av.	0.09	0.3	0.5	52.1	19.7	19.2	72.7
São Francisco River	0.09–0.11[d]	0.1–0.6	0.2–0.7	37.5–85.7	1.4–8.3	0.7–8.1	50.0–97.8
	0.10[d]	0.3	0.4	61.5	4.9	4.5	84.9
(n = 6); av.	0.02[r]	0.1	0.1	84.6	69.1	68.9	99.8
Guandu River	0.09–0.11[d]	3.7–48.9	4.9–167	19.6–82.5	102–323	96.4–156	48.3–95.5
(n = 6); av.	0.10[d]	18.1	66.6	56.0	188	121	76.5
	0.03[r]	3.8	3.9	99.2	254	251	98.5
Ita River	0.08–0.09	1.10–1.43	1.20–1.51	91.7–94.7	1.44–1.80	0.24–0.29	16.1–16.7
(n = 4); av.	0.08	1.27	1.36	93.2	1.62	0.27	16.4

av. = average value; [d]dry season; [r]rainy season. All values are rounded to one decimal except for dissolved gaseous mercury.

Table 4
Comparison of mercury species concentrations from the Sepetiba Bay tributaries with others rivers, coastal plain estuaries and coastal lagoons

Site	DGM (ng L^{-1})	Reactive Hg (ng L^{-1})	Total dissolved Hg (ng L^{-1})	Particulate Hg (µg g^{-1})	Author
Loire R.	<0.01	0.08–0.22	0.42–2.02	0.08–0.50	[4]
Siene R.	<0.01	0.08–0.42	0.50–8.00	0.43–2.66	
Patuxent R.	0.02 ± 0.01	—	1.32 ± 1.29	—	
Susquehanna R.	0.01 ± 0.01	—	1.78 ± 1.58	0.59 ± 0.66	[1]
Baltimore Harbor	0.02 ± 0.01	—	5.4 ± 4.7	—	
Scheldt Estuary	0.05–0.70	0.01–4.7	0.42–2.02	—	[34]
Coastal Lagoons, SE Brazil	—	0.02–0.1	2.5–11.3	2.6–57.0	[22]
Itinguçu R.	0.18	1.0	1.2	0.7	
Itimirim R.	0.09	0.3	0.4	0.1	
Guarda R.	0.09	0.3	0.5	1.2	
São Francisco R.	0.10[d]/0.02[r]	0.3[d]/0.1[r]	0.4[d]/0.1[r]	0.3[d]/0.4[r]	This study
Guandu R.	0.10[d]/0.03[r]	18.1[d]/3.8[r]	66.[d]/3.9[r]	0.6[d]/1.0[r]	
Ita R.	0.08	1.3	1.4	<0.1	

[d] dry season ; [r]rainy season. All values from Sepetiba bay tributaries are rounded to one decimal except for DGM.

DGM production in natural waters is a result of different competitive and additive reactions favored or inhibited depending on the water chemistry of a given system. In general, Hg reduction competes with Hg methylation and adsorption onto particles for the available reactive Hg. DGM production is generally higher in low oxygen, well-illuminated waters with low suspended matter concentrations and higher reactive Hg [30–32]. Our results, although not very clearly, seem to fit into this general pattern. The highest DGM concentrations were found during the dry season in the low conductivity (43 µS cm^{-1}) and moderate dissolved oxygen (6.2 mg L^{-1}) and redox potential values (+159 mV) in the Itinguçu River, which also presented

Table 5
Mercury species and TSS fluxes to Sepetiba Bay from its major tributaries, SE Brazil

	Water flux[a] $(m^3 s^{-1})$	Total suspended solid $(mg L^{-1})$	Total dissolved Hg Flux $(\mu g s^{-1})$	Particulate Hg flux $(\mu g s^{-1})$	TSS flux $(kg s^{-1})$
Itinguçu River	0.04	1.5–1.7	0.41–0.51	0.38–0.54	$5.7–6.5 \times 10^{-4}$
($n = 4$); av.		1.7	0.46	0.46	6.5×10^{-4}
Itimirim River	0.06	2.1–9.1	0.01–0.03	0.02–0.03	$1.3–5.8 \times 10^{-4}$
($n = 6$); av.		4.4	0.02	0.03	2.8×10^{-4}
Guarda River	12.2	11.3–18.2	2.4–10.2	1.8–463.9	0.14–0.22
($n = 6$); av.		15.5	6.0	234.4	0.19
São Francisco River	182.2	13.2–16.4[(d)]	29.2–131.3	131.3–1480.5	2.4–3.0
($n = 6$); av.		15.1[(d)]	72.9	816.8	2.7
		197[(r)]	23.7	12571.7	35.9
Guandu River	6.2	90.0–340.7[(d)]	30.1–1032.4	596.2–964.0	0.56–2.1
($n = 6$); av.		189.2[(d)]	411.9	749.4	1.2
		261[(r)]	23.8	1549.3	1.6
Ita River	2.5	32.5–36.1	3.0–3.8	0.60–0.73	0.08–0.09
($n = 4$); av.		34.3	3.4	0.68	0.09

av. = average value;
[a] Ref. [13]. [(d)]dry season; [(r)]rainy season.

the highest reactive Hg concentrations $(1.0 \, ng \, L^{-1})$, compared to the other rivers with the exception of the Guandu and Ita rivers. These two rivers, although presenting low DO and redox potential, present very high TSS concentrations, which could compete for the reactive Hg. The sharp decrease in DGM concentrations in the São Francisco and Guandu Rivers in the rainy season compared to the dry season also corroborates this hypothesis, since during the rainy season there is an increase in TSS (see Tables 3 and 5) and a decrease in reactive Hg concentrations of about three and five times in the São Francisco and Guandu Rivers, respectively.

The total dissolved Hg concentrations during the dry season showed the highest values in the Guandu River, with an average of $66.6 \, ng \, L^{-1}$ whereas the lowest concentration was measured in the Itimirim River, with an average of $0.4 \, ng \, L^{-1}$ (Table 3). In the Itinguçu, Guarda, São Francisco and Ita Rivers intermediate values were found, with averages varying from 0.4 to $1.4 \, ng \, L^{-1}$. In the rainy season, the total dissolved Hg measured in the São Francisco and Guandu Rivers showed a decrease of three and 17 times, respectively, compared to the dry season concentrations, similar to the reactive Hg decreases. In fact, a significant positive correlation ($r = 0.99$, $P < 0.01$) was found between the reactive Hg concentrations and the total dissolved Hg concentrations (Fig. 2).

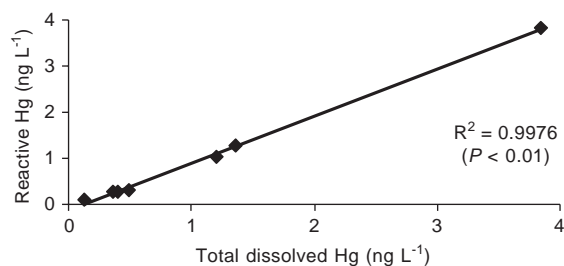The high total dissolved Hg values found in the Guandu river are similar to those reported in other

Fig. 2. Relationship between total dissolved Hg and reactive Hg concentrations in Sepetiba Bay tributaries, SE Brazil.

heavily impacted and industrialized areas, as in the Narragansett Bay tributaries, USA, with a range from 7.2 to $30 \, ng \, L^{-1}$ [5], and in Lake Michigan tributaries, USA, with a range from 0.6 to $182 \, ng \, L^{-1}$ [33]. On the other hand, the other rivers in Sepetiba Bay basin had Hg values similar to those of slightly impacted areas, such as the Patuxent River, USA, that showed <0.5– $6 \, ng \, L^{-1}$ [3], and the Loire and Siene Rivers, France, with averages of 0.82 ± 0.42 and $2.3 \pm 1.94 \, ng \, L^{-1}$, respectively [4] (Table 4). Values are also similar to those found in the St. Lawrence, Canada, where the concentrations varied from 0.08 to $2.64 \, ng \, L^{-1}$ [2], in Chesapeake Bay tributaries, USA, with average concentrations ranging from 1.32 ± 1.29 to $5.4 \pm 4.7 \, ng \, L^{-1}$ [1] and in the Scheldt Estuary 0.42 to $2.0 \, ng \, L^{-1}$ [34] (Table 4).

The percent of reactive Hg relative to the total dissolved Hg concentrations observed during the dry season were smaller in the Guarda River, with an average of 52.1%, followed by the São Francisco River, with an average of 61.5%. Itimirim River showed an average of 71.1% and the Itinguçu River presented an average of 84%. The higher percentage was found in Ita River, with an average of 93.2%. In the rainy season, the percentages increased to 84.5 and 99.2% in the São Francisco and Guandu Rivers, respectively.

During the dry season, the highest particulate Hg concentrations were found in the Guandu River, with an average of $121 \, ng \, L^{-1}$, followed by the Guarda River, with an average of $19.2 \, ng \, L^{-1}$, while the lowest concentrations were found in the Ita River, with an

average of $0.3 \, ng \, L^{-1}$. In the Itimirim, Itinguçu, and São Francisco Rivers the average values ranged from 0.4 to $4.5 \, ng \, L^{-1}$. The sampling performed in the rainy season showed an increase of 15 and two times in the São Francisco and Guandu Rivers, respectively.

During the dry season, the percent of particulate Hg relative to the total $(D + P)$ Hg concentrations was higher in the São Francisco River, with an average of 84.9%; in the Guandu river, with an average of 76.5%; and in the Guarda River, with an average of 72.7%. The lower percentages were found in the Ita River, with an average of 16.4%; in the Itimirim River, with an average of 45.5%; and in the Itinguçu River, with an average of 49.7%. In the rainy season, the percentages increased to 99.8% and 98.5% in the São Francisco and Guandu Rivers, respectively.

The highest values found in the Guandu River reflect the activities observed in the basin, as an important industrial park and the most important water treatment plant that discharge all refuses in this water body.

The samples collected in the São Francisco and Guandu River during the rainy season showed a decrease of all dissolved Hg fractions, while the particulate Hg fraction showed a large increase. This temporal variability suggests a dilution effect onto the dissolved phases associated with the increase of total suspended solids (TSS) that supply binding sites for dissolved Hg sorption, which also results in a decrease in DGM concentrations in these two rivers as mentioned. The increase of the particulate Hg fraction was proportional to the increase of the TSS, as observed in Fig. 3, which shows a significant positive correlation between particulate Hg concentrations and TSS ($r = 0.82$, $P < 0.01$) as well as between the total Hg and particulate Hg concentrations ($r = 0.95$, $P < 0.01$).

Fig. 4 summarizes the Hg partitioning between different Hg species in the rivers. The São Francisco and Guandu Rivers, in both dry and rainy season, and the Guarda River showed the predominance of particulate Hg fraction whereas in the Ita River the dissolved
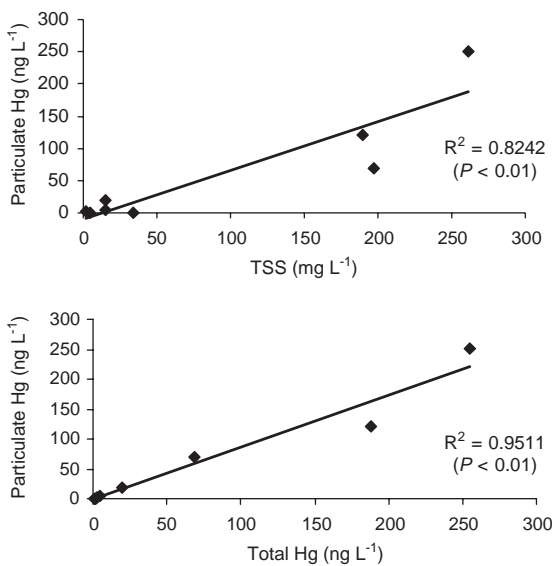

Fig. 3. Relationship between TSS and particulate Hg concentrations, and between total Hg and particulate Hg concentrations, in the Sepetiba Bay tributaries, SE Brazil.
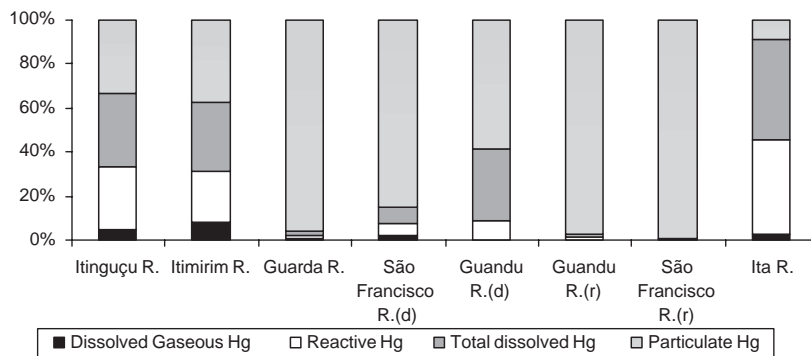

Fig. 4. The partitioning between Hg species measured in the Sepetiba Bay tributaries, SE Brazil (d = dry season sampling, r = rainy season sampling).

Hg fraction is greater. In the Itinguçu and Itimirim Rivers the dissolved and particulate Hg fraction had an equal contribution.

The total dissolved and particulate Hg and TSS fluxes were calculated for the Sepetiba Bay tributaries and are given in Table 5. The higher dissolved and particulate Hg and TSS fluxes were found in the Guandu and São Francisco Rivers, which are responsible for over 86% of the total freshwater input to the bay [13]. On the other hand, the Itinguçu and Itimirin Rivers showed lower Hg and TSS fluxes, while the Ita and Guarda showed intermediate values. The results showed that most of the Hg transported by rivers is associated with suspended particle. This is in agreement with the Hg distribution in Sepetiba Bay bottom sediments previously reported by Marins et al. [16], showing higher Hg concentrations in sediments closer to the major two rivers and following the deposition pattern of suspended particles into the Bay.

The present study showed a significant increase in the particulate Hg and TSS fluxes during the rainy season in the Guandu and São Francisco Rivers. In the rainy season, in the São Francisco River particulate Hg and TSS fluxes increased by a factor of 13 and in the Guandu River particulate Hg flux increased over two times in comparison to the dry season. In these rivers, the total dissolved Hg fluxes decreased by over three times and 17 times in the São Francisco and Guandu Rivers, respectively, between the dry and rainy seasons. These results suggest the importance of the surface runoff promoted by the heavy summer rains as the major

mobilizer of Hg in the Sepetiba Basin-Bay system and are in agreement with the highest inputs of Hg from anthropogenic sources being to soils [9], where deposited Hg is carried into rivers by erosion and runoff.

The total dissolved Hg flux was estimated as $11 \, kg \, yr^{-1}$ whereas the particulate Hg flux was estimated as $190 \, kg \, yr^{-1}$. The TSS flux was estimated as $4.8 \times 10^8 \, kg \, yr^{-1}$. The Guandu River was responsible for 81% of the total dissolved Hg flux whereas the São Francisco River was responsible for 80% of the particulate Hg flux and 90% of the TSS flux.

The relative affinity of Hg for dissolved and particulate phases was measured by the particle–water partition coefficient (K_d, $L \, kg^{-1}$). An elevated K_d value indicates high affinity for the particulate phases. The K_d values ranged over three orders of magnitude, from low values (0.06–0.65×10^5) in the Guandu River, during the dry season, and in the Ita River, to intermediate values (1.90–6.02×10^5) in the Itimirim, Guandu Rivers, during the rainy season, and in the Itinguçu River, to high values (13.32–44.25×10^5) in the São Francisco and Guarda Rivers (Table 6). The relative increase in K_d from the dry to the rainy season, in the São Francisco and Guandu Rivers, parallel with the increase of the TSS in this period, also suggest erosion and leaching of soils as the major source of Hg to rivers, since the major inputs of the Hg are to the soils ($143 \, kg \, yr^{-1}$), in agreement with the total Hg emission to Sepetiba Bay estimated by Marins et al. [9]. Although the water flux shows no significant increase during the rainy season, due to the artificially controlled nature of major rivers,

Table 6
The particle–water distribution coefficient (K_d) in Sepetiba Bay tributaries, SE Brazil

	Particulate Hg ($\mu g \, g^{-1}$)	Total dissolved Hg ($ng \, L^{-1}$)	Kd ($L \, kg^{-1} \times 10^5$)	$\log K_d$
Itinguçu River	0.59–0.83	1.1–1.3	4.42–7.61	5.65–5.88
($n = 4$); av.	0.71	1.2	6.02	5.76
Itimirim River	0.09–0.11	0.5–0.5	1.82–1.97	5.26–5.30
($n = 6$); av.	0.10	0.5	1.90	5.28
Guarda River	0.01–2.45	0.2–0.8	0.12–93.23	4.06–6.97
($n = 6$); av.	1.24	0.5	44.25	5.89
São Francisco River	0.05–0.54[d]	0.2–0.7	0.66–29.87	4.82–6.48
($n = 6$); av.	0.30[d]	0.4	13.32	5.86
	0.35[r]	0.1	26.9	6.43
Guandu River	0.51–0.82[d]	4.9–167	0.05–1.13	3.69–5.05
($n = 6$); av.	0.64[d]	66.6	0.65	4.49
	0.96[r]	3.9	2.50	5.40
Ita River	0.007–0.009	1.2–1.5	0.05–0.06	3.75–3.77
($n = 4$); av.	0.008	1.4	0.06	3.76

av. = average value; [d]dry season; [r]rainy season. Total dissolved Hg values are rounded to one decimal.

the surface runoff from soils to the rivers is enlarged. The log K_d values found are similar to those reported for other rivers, e.g. The Loire and the Siene Rivers, France, of 5.3 ± 0.2 and 6.0 ± 0.2, respectively [4], the Rhône River, France, ranging from 5.6 to 5.8 [35], the Lena, Ob and Yenisei Rivers, Russia, of 5.2 ± 0.2, 4.9 ± 0.1 and 5.3 ± 0.2, respectively [36], Wisconsin Rivers, USA, of 4.8 ± 0.7 [37] and Chesapeake Bay tributaries, USA, ranging from 5.06 to 5.52 [1]. Only the Ita River showed lower values than the above reported ones.

The K_d values of about 2.0×10^5 are related to physical sorption/desorption processes whereas the K_d values of about 10.0×10^5 or higher are related to precipitation/dissolution of minerals, in particular of sulfides [34] thus, the K_d values found suggest that in the Itinguçu, Itimirim, Guandu e Ita Rivers the physical sorption/desorption processes control the Hg particle–water interaction whereas in the Guarda and São Francisco Rivers this interaction may also be partially controlled by the precipitation/dissolution of minerals. A better knowledge of the nature of the TSS in these rivers is necessary to explain the high K_d values found. Our results suggest that since the TSS load to Sepetiba tributaries controls Hg distribution and speciation, intensive studies are necessary, in particular on the nature of the effluents from the water treatment plant and its immediate effect on Hg distribution and speciation in the two major rivers draining into Sepetiba Bay.

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