

Mercury distribution and speciation in waters of the coastal lagoons of Rio de Janeiro, SE Brazil

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Abstract

The distribution and speciation of Hg in surface waters from the coastal lagoons of Rio de Janeiro State, Brazil, sampled in 1997–1998, showed highest concentrations of all Hg species (reactive, total dissolved and particulate) in lagoons affected by metropolitan areas, where total suspended solids (TSS) were, in general, very high. Total dissolved Hg varied from 18.2 to 55.2 pM, one to two orders of magnitude higher than open ocean concentrations. Highest values were found in lagoons located at the metropolitan area of Rio de Janeiro city, and the lowest values in the hypersaline Araruama lagoon. Reactive Hg (Hg⁰ + HgII) concentrations varied from 0.18 to 0.43 pM, comprising less than 2% of the total dissolved Hg, a fraction much lower than frequently reported for the open ocean or coastal plain estuaries. The fraction of reactive Hg was negatively correlated with total dissolved Hg. Particulate and total Hg concentrations (dissolved plus particulate) ranged from 18 to 230 pM and 37 to 285 pM, respectively, with lowest values in lagoons with the lowest TSS concentrations. Mercury concentrations in TSS and bottom sediments, on a weight basis, varied from 0.7 to 2.9 $\mu\text{g g}^{-1}$ and 0.12 to 0.44 $\mu\text{g g}^{-1}$, respectively. However, Hg concentrations in the water column did not correlate significantly with the Hg concentrations in TSS or in bottom sediments. The results clearly show that most dissolved Hg in these lagoons is in strongly bound forms. Also, high TSS due to resuspension of bottom sediments maintains large amounts of both dissolved and particulate Hg in the water column. Relatively low water–particle distribution coefficients ($K_D = 0.6\text{--}5.5 \times 10^5$) suggest sorption/desorption processes as responsible for this. These results suggest that the behavior of Hg in the coastal lagoons is similar to that described previously for the turbidity maximum zone of coastal plain estuaries. Therefore, a survey of Hg concentrations in key biological components of these ecosystems is recommended. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Mercury; Dissolved species; Suspended solids; Coastal lagoons; Brazil

1. Introduction

Increasing concern with diffuse anthropogenic sources of Hg to lakes and lagoons has led to

extensive surveys of Hg concentrations and speciation in water since Hg from this type of sources, which includes atmospheric deposition and surface runoff, reaches these environments mostly as dissolved Hg species which are readily available for methylation and/or biological uptake (Mason et al., 1994; Porcella et al., 1995; Lacerda, 1998). Among these potentially threatened areas, coastal lagoons are of key environmental significance since they serve as

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nursery areas for many marine species of high economic importance, and presently support large fisheries. Also, with the recent boom of tourism in coastal lagoons world wide, high environmental quality standards are necessary for coping with economic growth (Kjerfve, 1994).

Coastal lagoons are unstable environments due to their relative shallowness, which maximizes the effect of physical forces, such as winds, tides, storm events and relative sea level changes upon the biogeochemistry of these ecosystems. A major result is rapid variation of physical and chemical conditions in the water column, which are also influenced by tidal regime, freshwater inputs, season and degree of anthropogenic influence. Eutrophication may also be a key factor controlling water and sediment chemistry in most lagoons, particularly in the tropics and sub-tropics. The residence time of water and sediments in coastal lagoons, and consequently of chemical substances are, in general, much longer than in typical coastal plain estuaries or other restricted coastal features (Kjerfve, 1994). This can allow long-term accumulation and complex biogeochemical processes to occur. When water column stability is broken, however, remobilization of accumulated substances takes place and unexpected and sudden response to concentration increases affect both the water column chemistry and the availability of chemicals to the lagoon biota. The resultant changes on the distribution, speciation and bioavailability of chemical substances in coastal lagoon ecosystems will result in variable accumulation by the lagoon biota (Lacerda, 1994; Lacerda et al., 1992).

Coastal lagoons of the Rio de Janeiro State are a typical example of the importance of diffuse sources as the major pathway of Hg contamination of key coastal environments. There is no significant point source of Hg to these lagoons. However, preliminary results obtained for the region showed large atmospheric Hg deposition rates and relatively high Hg concentrations in the biota. Marins et al. (1996) estimated atmospheric Hg deposition over Sepetiba Bay lagoon, south of Rio de Janeiro, to reach $76 \mu\text{g m}^{-2} \text{ year}^{-1}$, resulting in a direct annual Hg input from the atmosphere to Sepetiba Bay basin of about 90 kg year^{-1} . Annual runoff input from Sepetiba lagoon basin is also significant, reaching about 350 kg year^{-1} (Marins et al., 1999). As a result, fish Hg

content from this lagoon is relatively high, notwithstanding the lack of direct Hg sources (Kherig, 1995). Monitoring of bulk atmospheric deposition over the northeastern coastal zone of Rio de Janeiro showed Hg concentrations varying from one to four times higher than the expected background for the region, also suggesting important atmospheric inputs to this part of the coast (Marins et al., 1998).

A survey on Hg concentrations in sediments of the lagoons of this region of Rio de Janeiro (Gonçalves, 1999) showed higher concentrations in lagoons with larger basins and closer proximity to metropolitan areas, suggesting the importance of non-point sources as the major pathway of contamination. Therefore, it is reasonable to expect that diffuse sources of Hg may also be affecting Hg distribution in the water column and its availability to coastal lagoon biota.

Partitioning of Hg in the water column of coastal lagoons may be of high environmental significance since it will not only control the eventual export of Hg to coastal waters but also the capacity of these water bodies to accumulate large amounts of Hg in their sediments. Previous studies in estuarine areas showed that most dissolved Hg is strongly bound to refractory organic colloids and, in general, shows an inverse relationship with salinity along the estuarine gradient (Guentzel et al., 1996; Stordal et al., 1996). Also, total dissolved Hg concentrations are generally much higher at maximum turbidity zones, creating sharp spatial gradients (Coquery, 1994; Coquery et al., 1995, 1997; Vandal and Fitzgerald, 1995; Leermakers et al., 1995). Since coastal lagoons, similar to coastal plain estuaries, are particularly rich in dissolved organic matter, a larger fraction of the dissolved Hg would probably be bound to organic complexes compared to the open ocean where dissolved gaseous Hg (DGM) dominates dissolved Hg species (Mason and Sullivan, 1999; Mason et al., 1998). However, different from coastal plain estuaries, the frequent resuspension of bottom sediments remobilizes refractory organic matter formed in bottom sediments (Bernardes et al., 1998; Knoppers et al., 1999), which although maintains large amounts of Hg dissolved in the water column may decrease its reactivity.

In this paper, we present the distribution and speciation of Hg in waters of 11 tropical coastal

lagoons, of different environmental characteristics, along the northeastern coast of Rio de Janeiro State, SE Brazil. The goal is to evaluate the importance of complexation and of suspended matter concentration on the availability of Hg to potential sedimentation or biological uptake. Also, by comparing with typical coastal plain estuaries and the open ocean, it is possible to test whether permanent mixing, due to physical forcing, shallow depths and resultant resuspension of sediments, may increase total and dissolved Hg concentrations and speciation in the water column, even when no Hg point sources are present in these lagoons.

2. Study site

The NE quaternary coastal plain of Rio de Janeiro includes a group of lagoons formed between 2500

and 5000 years BP (Fig. 1). They range from nearly freshwater to hypersalinity and from oligotrophy to hyper-eutrophy, due to nutrient inputs from a population of about 12 million. These lagoons are still a significant spawning ground for fisheries and are key pieces in the recent urban and tourism development of the region. We selected 11 of the most typical of these lagoons which represent a gradient of physical, chemical and environmental conditions found in the coastal region (Table 1). Among them, the Itaipu, Piratininga, Marapendi, Jacarepagua and Rodrigo de Freitas lagoons are located in the metropolitan area of Niteroi-Rio de Janeiro, receiving mostly contaminated surface runoff and untreated sewage from their highly populated basins. On the other extreme are the lagoons of Saquarema, Urussanga, Marica, Guarapina and Jacone, which are relatively pristine, particularly the latter, which is very isolated from

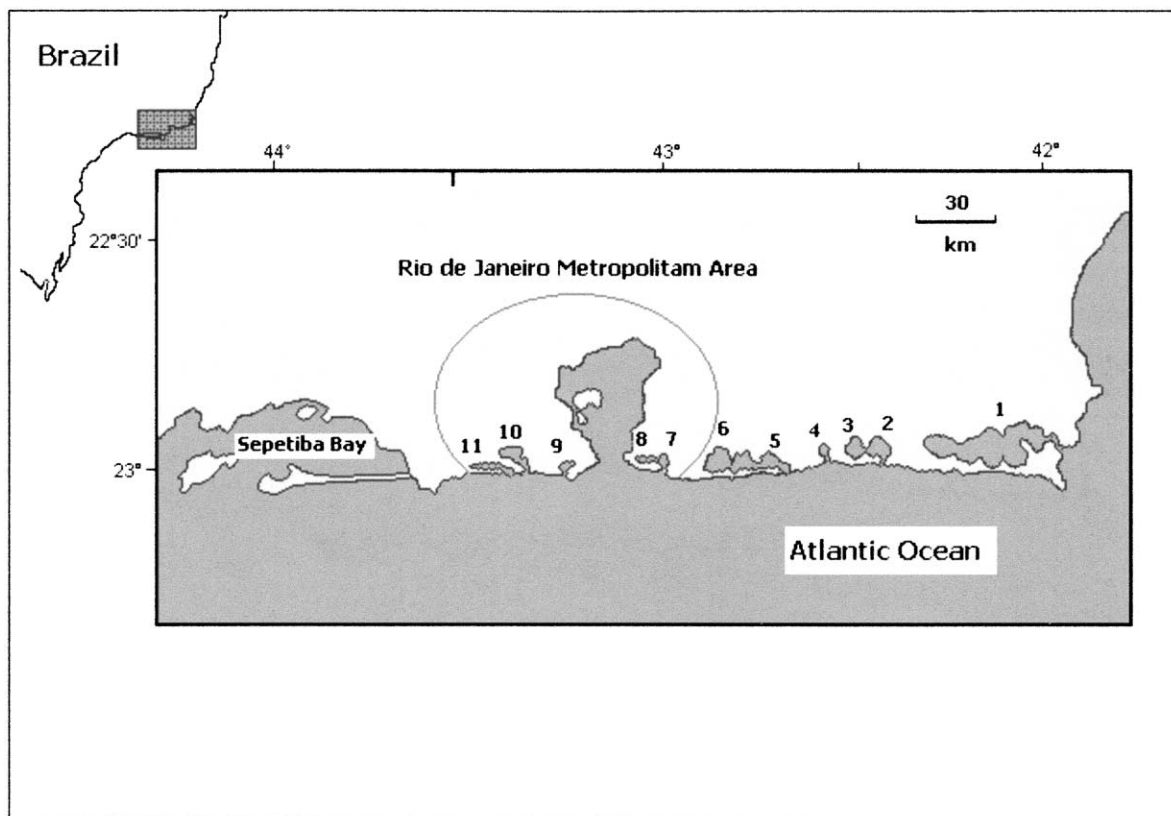


Fig. 1. Map showing the location of the studied coastal lagoons in Rio de Janeiro, SE Brazil. 1—L. Araruama, 2—L. Saquarema, 3—L. Urussanga, 4—L. Jacone, 5—L. Guarapina, 6—L. Maricá, 7—L. Itaipu, 8—L. Piratininga, 9—L. Rodrigo de Freitas, 10—L. Jacarepaguá, 11—L. Marapendi.

Table 1
Major environmental aspects of the coastal lagoons of Rio de Janeiro State, SE Brazil

Lagoon	Area (km ²)	Mean depth (m)	Salinity range	Dissolved oxygen (mg l ⁻¹)	pH	TSS (mg l ⁻¹)	Eh (mV)	DOC (mg l ⁻¹)	Trophic state
Araruama	215	2.0	52–56	7.9–8.3	8.2–8.3	4.2–4.5	120–240	2.2	oligotrophic
Saquarema	6.5	0.6	17–25	3.4–7.6	7.2–7.6	9.0–15.0	130–220	6.9	mesotrophic
Urussanga	12.5	0.6	7–22	6.9–8.3	7.1–7.4	14.2–15.6	150–200	8.5	mesotrophic
Jacone	1.5	1.2	4–28	5.5–6.6	7.4–7.6	11.0–12.0	220–370	8.7	eutrophic
Guarapina	6.5	0.6	9–34	5.9–7.7	7.9–8.0	23.0–30.0	220–310	6.2	mesotrophic
Marica	19.5	1.2	3–18	5.1–8.3	7.2–7.9	13.5–15.0	220–370	7.2	mesotrophic
Itaipu	2.0	1.0	25–31	7.0–8.5	8.1–8.3	16.0–21.0	190–300	8.8	mesotrophic
Piratininga	2.9	0.6	3–12	6.8–7.9	7.9–8.0	21.0–41.0	80–310	6.8	hyper-eutrophic
Marapendi	2.5	0.8	16–32	7.3–7.6	7.2–7.3	6.7–18.0	220–310	–	eutrophic
Jacarepagua	12	0.6	2–11	7.4–7.9	7.0–7.2	8.7–13.0	190–240	–	mesotrophic
Rodrigo de Freitas	2.5	1.4	9–15	6.8–7.0	7.9–8.1	13.0–15.0	200–340	–	mesotrophic

anthropogenic activities. Lastly, in the Araruama lagoon, the largest hypersaline lagoon in Brazil, fresh water input is nearly restricted to atmospheric deposition.

All of the lagoons studied, except the hypersaline Araruama lagoon, have high dissolved organic carbon (DOC) concentrations (> 1.0 mg l⁻¹) due to high primary productivity (1.0–11.1 g C m⁻² day⁻¹) and terrigenous input of organic matter (Machado and Knoppers, 1988; Carmouze et al., 1991, 1994; Knoppers, 1994; Knoppers et al., 1999; Bernardes et al., 1998). Araruama lagoon has lower productivity (0.20–0.65 g C m⁻² day⁻¹) and very small inputs of materials from its basin (Kjerfve et al., 1996). For a detailed description of the lagoons system of the Rio de Janeiro coast, one is referred to Lacerda et al. (1984) and Knoppers (1994).

3. Material and methods

Four samples in each lagoon, two in summer and two in winter of 1997–1998, were collected with 0.5-l pre-cleaned Teflon bottles and Teflon gloved hands, following careful procedures to avoid sampling contamination (Ferrara and Maserti, 1992). The sampling bottles were rinsed three times with the lagoon water before being filled. The bottles were capped while immersed in the water to prevent contact with the atmosphere between sampling and han-

dling. Bottles were double bagged in acid-washed plastic bags and transported in an ice box to the laboratory. All samples were analyzed immediately after collection and filtration (within 6 h maximum). Filtration was done using 0.45- μ m pore size cellulose acetate Millipore filters (pre-cleaned with 50% HNO₃) by pressure filtration using Teflon apparatus (Krabbenhoft et al., 1998; Leermakers et al., 1995). Filters with the collected total suspended solids (TSS), were kept frozen until analysis, performed between 48 and 72 h after filtration.

Unacidified filtered sub-samples (250 ml) were analyzed for reactive Hg (we use here the terminology of Mason et al. (1993), i.e. considering reactive Hg as the fraction that is reduced and therefore volatilized from solution after the addition of 0.5 ml of 10% SnCl₂ solution in 2.6 M HCl. This fraction includes mostly ionic (Hg²⁺) plus dissolved gaseous Hg (DGM), but also the Hg fraction weakly bound to inorganic and organic dissolved complexes. 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 literature which use acidified samples (e.g. Dalziel, 1992, 1995).

Total dissolved Hg was determined in other sub-samples after oxidation with bromide monochloride (BrCl). After oxidation, NH₂OH · HCl was used to reduce the excess BrCl (Bloom and Crecelius, 1983). This was followed by a reduction with the same

SnCl_2 solution used for reducing reactive Hg. This fraction includes all dissolved Hg species strongly bound to soluble complexes.

Particulate Hg was analyzed on the weighed filters, after total digestion with 50% aqua regia for 1.0 h at 70 °C in a closed Pirex[®] system, followed by the same reduction procedure described above. All samples were analyzed in duplicate. Five blank filters were digested and analyzed using the same procedure for the calculation of the detection limit for the particulate Hg analysis.

The Hg^0 resultant from the reduction reaction for water and TSS samples was purged from the sample with Hg-free Argon, at a flow rate of 40 ml min^{-1} , for 3 min, and collected on a Au wool trap connected to the outlet of the reaction vessel. Two Au traps in the gas line stripped any Hg from the carrier gas. All connecting tubing was made of Teflon with glass–Teflon connections made with clean silicone tubing. Mercury determination was done using a Tekran Model 2500 Cold Vapor Atomic Fluorescence Spectrophotometer (Mason and Fitzgerald, 1991, 1993; Chan and Sadana, 1993). Under the operational conditions described, the analytical detection limit of the method, based on three standard deviations of the reagents blank measurements was 0.1 pM for dissolved Hg and 1.5 ng g^{-1} for suspended particulate Hg. An inter-calibration exercise using these lagoon waters performed with Frontier Geosciences, Seattle gave differences between the two laboratories ranging from 7% to 20% (N. Bloom, personal communication).

Dissolved organic carbon (DOC) was measured in samples from eight lagoons (Rodrigo de Freitas, Jacarepaguá and Marapendi were not analyzed for this parameter) using a TOC5000 Shimadzu Carbon auto analyzer, after acid spike and oxygen bubbling for inorganic carbon (IC) removal. Samples were oxidized on a platinum catalytic surface, a non-dispersive detector measured the produced carbon dioxide. Calibration curves were constructed with phthalate acid standards (Eyroll and Benaim, 1999).

Surface sediments (0–5.0 cm) were collected by hand at two stations in each lagoon. Samples were stored in plastic bags and frozen for transport. Surface sediments were thawed and wet sieved to separate the fraction < 63 μm for Hg analysis, to allow comparison among the different lagoons and with the

Hg distribution in suspended particles (Gonçalves, 1999).

Sediment samples were dried at 50 °C to constant weight and 1.0 g sub-samples were digested in duplicate with 50% aqua regia for 1.0 h at 70 °C in a closed system (Marins et al., 1998). Mercury was analyzed electrochemically by CVAAS, in a Bacharach MAS-50D Hg analyzer system. Differences between duplicates were always smaller than 5%. Simultaneous determination of Hg in reference standards (NIST-USA no. 2704, “Buffalo River sediments”; with 60 ng g^{-1} of Hg) were performed using the same analytical procedure, and the results gave 58 ± 6 ng g^{-1} ($n = 15$). Detection limit of the method based on three times the value of reagent blanks was 5.0 ng g^{-1} .

During the sampling, some major physical and chemical parameters were also measured in situ. Salinity was determined using a SHIBUYA refractometer. Dissolved oxygen was determined using a DIGIMED portable oxygen meter, whereas pH 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. Unfortunately, no dissolved carbon determinations were performed on the samples.

4. Results and discussion

The concentrations of Hg species measured in the coastal lagoons of Rio de Janeiro are presented in Table 2. Differences between sampling periods were in the same range of within period sampling, therefore, all four samples were included in a single statistics, making up four samples at each lagoon. Lack of systematic seasonal variation is due to the large environmental impact of meteorological events upon these shallow lagoons. Meteorological events result in frequent resuspension of bottom sediments, changing water chemistry (Carmouze et al., 1994; Knoppers et al., 1999) and trace metal partitioning between solid and aqueous phases (Lacerda et al., 1992).

Reactive Hg concentrations varied little among the lagoons, with average concentrations varying from 0.18 to 0.43 pM. Total dissolved Hg concentrations were much higher, but also showed a relatively

Table 2

Mercury species concentrations (pM) in waters of the coastal lagoons of Rio de Janeiro State, SE Brazil
Means of four seasonal samplings in parentheses.

Lagoon	Reactive Hg ^a	Total dissolved Hg	Particulate Hg ^b	Total Hg ^b
Araruama	0.15–0.20 (0.18)	18.0–19.5 (18.5)	16–19 (18)	36–38 (37)
Saquarema	0.30–0.40 (0.36)	19.1–22.2 (21.5)	13–43 (28)	35–60 (50)
Urussanga	0.30–0.45 (0.38)	24.4–29.6 (26.4)	22–29 (26)	50–55 (52)
Jacone	0.30–0.35 (0.32)	29.0–37.5 (33.6)	27–36 (31)	65–70 (65)
Guarapina	0.25–0.30 (0.29)	29.8–37.2 (33.0)	135–160 (150)	160–195 (183)
Marica	0.15–0.20 (0.19)	44.5–55.0 (51.0)	85–90 (88)	135–140 (139)
Itaipu	0.10–0.20 (0.19)	54.2–56.5 (55.2)	55–65 (62)	105–120 (117)
Piratininga	0.30–0.35 (0.34)	54.5–56.4 (55.0)	175–285 (230)	230–340 (285)
Marapendi	0.20–0.25 (0.24)	24.2–37.3 (32.8)	25–110 (70)	65–135 (103)
Jacarepagua	0.15–0.20 (0.19)	12.5–19.2 (18.2)	30–32 (31)	45–50 (49)
Rodrigo de Freitas	0.34–0.45 (0.43)	27.4–30.6 (28.5)	80–115 (100)	110–145 (129)

^aReactive Hg includes DGM, as samples were not purged of Hg⁰ before analysis.

^bThese results are rounded to unity.

limited variability, varying from 18.2 to 55.2 pM. Particulate Hg showed the largest variability among lagoons, varying from 18 to 230 pM. Concentrations of all Hg species were lowest in more isolated lagoons that receive small fluvial inputs and have basin soils formed mostly by sands, particularly the hypersaline Araruama lagoon. Highest concentrations of all Hg species were measured in lagoons receiving runoff from urban areas and with basins extending out of the quaternary plain. This trend is most pronounced for particulate Hg with concentrations > 100 pM in all lagoons with such characteristics, in particular, the hyper-eutrophic Piratininga lagoon. The distribution of Hg in the water column is similar to the Hg distribution pattern found in bottom sediments reported by Gonçalves (1999).

Reactive Hg concentrations were very small relative to total dissolved Hg in all lagoons, varying from 0.4% to 1.7% of total dissolved Hg. This suggests that over 98% of the total dissolved Hg in these lagoons is strongly bound to dissolved complexes, probably refractory organic colloids. Stordal et al. (1996) found 12% to 93% of the filter-passing (< 0.45 µm) Hg concentrations associated with organic colloids in the water column of several coastal lagoons of the Gulf of Mexico coast. We lack DOC concentrations for all our studied lagoons. However, in the eight lagoons where DOC was measured, high concentrations were found (6.2–8.8 mg l⁻¹) but no significant correlation was found between DOC and

the total dissolved Hg concentrations. The lack of correlation is probably due to the small range of DOC values found and the small number of data available. Therefore, the suggestion that most dissolved Hg concentrations are associated with organic colloids is only circumstantial, but since only 2% of the dissolved concentration is reactive Hg and DOC is very high in the lagoons, this conclusion is quite probable. On the other hand, a significant negative correlation ($P < 0.01$) was found between the percentage of reactive Hg and the total dissolved Hg concentrations (Fig. 2).

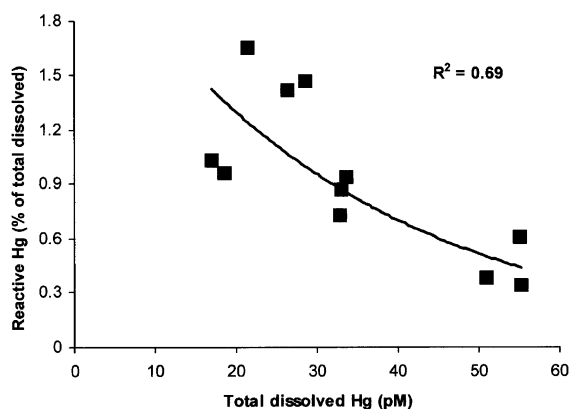


Fig. 2. Relationship between the percentage of reactive Hg and the total dissolved Hg concentrations in the coastal lagoons of Rio de Janeiro, SE Brazil.

In a recent comparable study of the North Atlantic, Mason et al. (1998) found mean concentrations of reactive Hg of 0.8 ± 0.44 pM, whereas in the South and Equatorial Atlantic, reactive Hg is somewhat higher (1.7 ± 1.2 pM) (Mason and Sullivan, 1999). In the Strait of Gibraltar and the Alboran Sea, reactive Hg ranged from < 0.2 to 0.5 pM (Cossa et al., 1994). Along the Scheldt estuary, reactive Hg varied from 0.05 to 0.3 pM, representing 20–80% of the total dissolved Hg (Leermakers et al., 1995). The lower reactive Hg concentrations found in Rio de Janeiro coastal lagoons, compared to the Atlantic open ocean values, results from the large complexation capacity of lagoon waters, compared to the open ocean. This is due to the elevated values of DOC (6.2 – 8.8 mg l⁻¹), the relatively large input of terrestrial organic matter, and the resuspension of organic-rich bottom sediments (Carmouze et al., 1991, 1994; Knoppers, 1994). High complexation capacity, in general, increases the dissolved concentrations of trace metals in coastal lagoons (George, 1988; Mackey and Szymczak, 1988; Lacerda, 1998; Lacerda et al., 1992). The effect of complexing substances on Hg concentrations results in the extremely small percentages of reactive Hg relative to total dissolved Hg ($< 2.0\%$) and the negative correlation between the two variables (Fig. 2). Reactive Hg concentrations observed in this study, however, are similar to other coastal waters studied by Cossa et al. (1994), for example, at the mouth of the Mediterranean. Total dissolved Hg concentrations in this enclosed sea, contrary to open ocean waters, are highly influenced by particulate Hg (Ferrara and Maserti, 1992), which may explain the similar concentrations of reactive Hg. Reactive Hg concentrations in the coastal lagoons of Rio de Janeiro are similar to those found in the upper region of coastal plain estuaries. However, the percentage relative to the total dissolved Hg, which in coastal plain estuaries typically range from 20% to 90%, is at least 10 times lower (Leermakers et al., 1995; Coquery et al., 1997; Cossa and Gobeil, 2000).

Total dissolved Hg concentrations are comparable to most data in the literature. These, contrary to reactive Hg, are from one to two orders of magnitude higher than total dissolved Hg concentrations reported for open ocean waters, which typically vary from 0.5 to 5.0 pM (Gill and Fitzgerald, 1987;

Dalziel, 1992, 1995; Guentzel et al., 1996; Baeyens and Leermakers, 1998; Mason and Sullivan, 1999; Mason et al., 1998). Most values, however, fall into the range reported for brackish estuarine waters. Total dissolved Hg in the low salinity region of the Ochlockonee River estuary, for example, ranged from 25 to 30 pM, with 35–87% strongly bound to colloidal complexes (Guentzel et al., 1996). At the upper St. Lawrence estuary, Canada, total dissolved Hg reaches 12 pM, with 50–80% strongly bound to organic matter (Cossa et al., 1988). At the Scheldt estuary, The Netherlands, total dissolved Hg concentrations reached 25 pM, mostly as strongly bound Hg, particularly at the upper estuary, where it accounts for over 80% of the total dissolved Hg (Leermakers et al., 1995; Baeyens and Leermakers, 1998). In areas of the Adriatic Sea affected by terrigenous inputs, total dissolved Hg are even higher than those reported here, reaching up to 75 pM (Ferrara and Maserti, 1992).

The relatively higher dissolved Hg concentrations in these lagoons are probably linked to anthropogenic inputs of Hg since lagoons closer to metropolitan areas showed highest Hg concentrations. However, even considering the more isolated lagoons, such as Jacone, and Guarapina, total dissolved Hg concentrations are still higher relative to reported values for coastal and estuarine areas, in general. These lagoons are located in rural areas without significant direct anthropogenic input but with atmospheric deposition. Internal processes of these shallow lagoons are also very important in keeping relatively high Hg concentrations in the water column. One key process is the remobilization of sediments and pore waters due to the shallow depths of these lagoons (Kjerfve, 1994; Kjerfve and Magill, 1989). Coastal lagoon sediments from resuspension are enriched with trace metals relative to stabilized bottom sediments (Calvo et al., 1991). Pore waters, in particular, are also enriched in Hg relative to surface waters (Gagnon et al., 1997). In Sepetiba Bay lagoon, south of Rio de Janeiro city, remobilization of sediments and pore waters, is responsible for most Hg cycling in this lagoon (Marins et al., 1997, 1998). In Piratininga and Itaipu lagoons, mobilization of bottom sediments due to tidal forces correlates with increasing trace metal uptake by aquatic biota, suggesting increasing concentration of

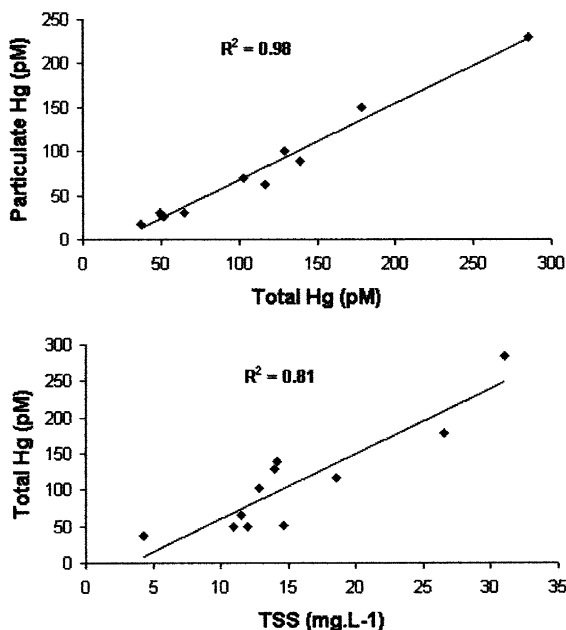


Fig. 3. Relationships between particulate Hg and total Hg concentrations, and between total Hg concentrations and TSS, in the coastal lagoons of Rio de Janeiro, SE Brazil.

dissolved species (Lacerda et al., 1992). In the coastal lagoons studied here, other trace metals and nutrients have been reported to remobilize to the water column through sediment resuspension (Machado and Knoppers, 1988; Lacerda, 1994; Knoppers, 1994; Knoppers et al., 1990, 1999).

Such remobilization processes are highly important, given the high TSS and particulate Hg concentrations found in most of the studied lagoons. Fig. 3 shows the significant positive ($P < 0.01$) correlation between TSS and total Hg concentrations and between total Hg and particulate Hg concentrations. Clearly, the particulate fraction dominates total Hg in our study area as a whole. The effect of high suspended matter and sediment resuspension have been reported as responsible for the higher concentrations of total Hg in other coastal sites, such as in different portions of the Adriatic Sea (Ferrara and Maserti, 1992), and in Sepetiba Bay, Brazil (Marins et al., 1998). In the semi-closed, shallow environment of the coastal lagoons of Rio de Janeiro, the effect of TSS on total Hg concentration is maximized. No significant correlation, however, was found between

the total dissolved Hg concentrations and the TSS, but in general, those were also higher in the lagoons with higher TSS. Also, no significant correlation ($P > 0.05$) was found between the concentrations of the different Hg species in the water column and the physical and chemical properties determined in each lagoon.

Mercury concentrations, on a weight basis, measured in the TSS and bottom sediments of the studied lagoons are presented in Table 3. Concentrations of Hg in the TSS ranged from 0.7 to 2.9 $\mu\text{g g}^{-1}$, being higher in Urussanga and Saquarema lagoons and lower in Piratininga lagoon. This range of concentrations compares well with those measured in the maximum turbidity zone of coastal plain estuaries. Coquery et al. (1995) found Hg concentrations in the TSS at the low salinity zone of three arctic estuaries to range from 0.03 to 0.4 $\mu\text{g g}^{-1}$, increasing to higher values, of up to 1.88 $\mu\text{g g}^{-1}$ at the mixing zone of the same estuaries. At the Scheldt estuary, The Netherlands, Hg concentrations in the TSS from the maximum turbidity zone reach up to 1.5 $\mu\text{g g}^{-1}$, decreasing to about 0.6 $\mu\text{g g}^{-1}$ outside this zone (Leermakers et al., 1995). Thus, similarly to the dissolved fraction, the concentrations found in the TSS are typical of high turbidity regions of coastal plain estuaries.

Table 3

Average Hg concentrations ($\mu\text{g g}^{-1}$), in total suspended solids (TSS) and the fine fraction ($< 0.63 \mu\text{m}$) ($n = 4$) of surface bottom sediments (BS), in the coastal lagoons of Rio de Janeiro State, SE Brazil, and the water-particle coefficient of distribution (K_D) and the ratio between the concentrations of Hg in the TSS and in bottom sediments

Lagoon	Hg in TSS ($\mu\text{g g}^{-1}$)	K_D ($\text{kg l}^{-1} \times 10^5$)	Hg in BS ($\mu\text{g g}^{-1}$)	Hg (TSS/BS)
Araruama	1.2	3.2	0.21	5.7
Saquarema	2.1	4.8	0.40	5.3
Urussanga	2.9	5.5	0.13	23.2
Jacone	1.8	2.7	0.12	15.6
Guarapina	0.9	1.4	0.14	6.5
Marica	0.8	0.8	0.17	4.6
Itaipu	1.6	1.2	0.13	12.8
Piratininga	0.7	0.6	0.21	3.3
Marapendi	0.9	1.4	0.36	2.6
Jacarepagua	1.7	4.7	0.35	4.8
Rodrigo de Freitas	0.7	1.2	0.44	1.6

Average Hg concentrations in the silt and clay fraction ($< 63 \mu\text{m}$) of surface bottom sediments ranged from 115 ng g^{-1} in L. Jacone, the most isolated of the lagoons studied, with no significant fluvial input, to 440 ng g^{-1} in L. Rodrigo de Freitas, located in downtown Rio de Janeiro city. Higher Hg concentrations, in general, occurred in the lagoons located in metropolitan areas, resulting in an east–west gradient in Hg concentrations, with higher concentrations occurring at the western end, at the Niteroi-Rio de Janeiro metropolitan area.

Surface sediment Hg concentrations compare well with other moderately contaminated tropical coastal areas. For example, at the Paraíba do Sul River estuary, at the north coast of Rio de Janeiro, concentrations ranged from 80 to 220 ng g^{-1} (Lacerda et al., 1993). In Sepetiba Bay lagoon, south of Rio de Janeiro city, Hg concentrations ranged from 17 to 160 ng g^{-1} (Marins et al., 1998), whereas in the Todos os Santos estuarine complex, NE Brazil, Hg concentrations ranged from 50 to 300 ng g^{-1} (Queiroz et al., 1993). On the other hand, the concentrations found in the Rio de Janeiro coastal lagoons are well below those reported for heavy contaminated coastal sites, which typically reach concentrations 10–20 times higher (Ferrara and Maserti, 1992; Bonnevie et al., 1994; Gagnon et al., 1997; Pereira et al., 1999; Mason et al., 1999; among others).

The ratios between Hg concentrations in the TSS and in bottom sediments ranged from 1.6 at Rodrigo de Freitas Lagoon to 23.2 at Urussanga. This suggests that not only resuspension promotes a relative enrichment in Hg, probably by affecting preferably the very fine fraction (clay and organic matter) present in sediments. Unfortunately it was not possible to measure POC in the suspended matter, but other studies have suggested that increasing total concentrations of Hg in the water column of coastal areas are largely due to POC (Mason et al., 1999).

The particle–water partition coefficient (K_D , 1 kg^{-1}) ranged over one order of magnitude, from low values ($0.6\text{--}1.5 \times 10^5$) in Piratininga, Marica, Rodrigo de Freitas, Guarapina, Marapendi and Itaipu lagoons, to intermediate values ($2.7\text{--}3.2 \times 10^5$) in Jacone and Araruama lagoons, to relatively high values ($4.7\text{--}5.5 \times 10^5$) in Jacarepagua, Saquarema and Urussanga lagoons. This range of K_D values is

similar to those reported for moderately contaminated estuaries, e.g. the Patuxent, USA, of $6 \times 10^4\text{--}5 \times 10^5$ (Benoit et al., 1998), the Thames, England, of $2 \times 10^4\text{--}2 \times 10^5$ (Nelson, 1981), the Loire, France, of 2.4×10^5 (Coquery, 1994), the Elbe, Germany, of $2.5\text{--}3.0 \times 10^5$ (Imrer et al., 1988), and the Scheldt, The Netherlands, of $2 \times 10^5\text{--}1 \times 10^6$ (Leermakers et al., 1995). The K_D values found for the Rio de Janeiro lagoons, on the other hand, are higher than those reported for pristine arctic estuaries, of $0.8\text{--}1.7 \times 10^5$ (Coquery et al., 1995).

The $\log K_d$ distribution in the lagoons is a function of the TSS concentration, following an inverse correlation ($r = -0.602$; $P < 0.05$). However, the changes are relatively small over the TSS range measured in the lagoons ($4\text{--}41 \text{ mg l}^{-1}$). In general, the $\log K_d$ s were lower in lagoons with higher TSS (Fig. 4). Mason et al. (1999) found a similar behavior in Chesapeake Bay, with a TSS varying from 4 to 30 mg l^{-1} . Other studies, e.g. Benoit et al. (1998) in the Patuxent River, Mason and Sullivan (1998) in the Anacostia River and Coquery et al. (1997) at the Loire and the Seine estuaries, also found this inverse relationship between $\log K_d$ and TSS.

Leermakers et al. (1995) suggested that K_D values of about 2.0×10^5 are a result of physical sorption/desorption processes, while higher values, of about 1.0×10^6 may also result from precipitation/dissolution of minerals, in particular of sulfides. The range of K_D values $0.6\text{--}5.5 \times 10^5$ found in this study therefore suggests that physical sorption/desorption processes dominate the Hg particle–water interaction. Also, although higher Hg concentrations, both dissolved and in the TSS and bottom sediments, tend to occur in lagoons located at metropolitan

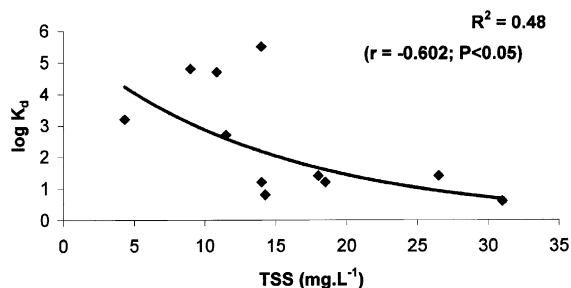


Fig. 4. Relationship between total suspended solids concentrations and $\log K_D$ in the coastal lagoons of Rio de Janeiro, SE Brazil.

Table 4

Mercury concentrations and percent distribution of the reactive (Hg_R), total dissolved (Hg_{TD}) and particulate (Hg_{Part}) fractions in the open ocean, coastal plain estuaries and the coastal lagoons of Rio de Janeiro

Site	Hg_R (pM)	Hg_R (% of Hg_{TD})	Hg_{TD} (pM)	Hg_{Part} (pM)	Hg_{Part} (% of total Hg)	Author
South Atlantic Ocean	1.7 ± 1.2	58 ^a	2.9 ± 1.7	0.1 ± 0.05	3 ^a	Mason and Sullivan (1999)
North Atlantic Ocean	0.8 ± 0.44	33 ^a	2.4 ± 1.6	0.045	2 ^a	Mason et al. (1988)
Lower St. Lawrence Estuary	< 0.2–1.1	20 ^b	1.8–7.8	–	–	Cossa and Gobeil (2000)
Scheldt Estuary	0.05–0.3	20–80 ^b	2.5–26	–	–	Leermakers et al. (1995)
Loire Estuary	< 0.4–1.1	5–24 ^b	4.1 ± 2.1	27.4 ^a	87 ^b	Coquery et al. (1997)
Seine Estuary	< 0.4–2.1	5–24 ^b	11.5 ± 9.7	219 ^a	95 ^b	Coquery et al. (1997)
Rio de Janeiro Lagoons	0.18–0.43	1–2	18.5–55.2	18–230	24–97	This study

^aEstimated from author's results.

^bAs appearing in the original paper.

areas, no significant correlation ($P > 0.05$) was found between the reactive, total dissolved and total Hg concentrations in the water column and the concentration of Hg in the TSS or the bottom sediments on a weight basis.

A comparison between the Hg concentrations and speciation obtained in the coastal lagoons of Rio de Janeiro and those of open ocean waters and coastal plain estuaries is presented in Table 4. As expected, the total Hg concentrations in open ocean waters are dominated by the dissolved fraction, which is constituted mostly by reactive Hg. On the other hand, total Hg concentrations in coastal lagoons, similarly to coastal plain estuaries, are high and dominated by particulate Hg. However, when comparing the dissolved fraction, reactive Hg is much less important in coastal lagoons than in coastal plain estuaries. Such low reactive Hg concentrations are normally found only in the turbidity maximum zone of estuaries.

In conclusion, the results reported here suggest that even lacking point sources of Hg, the coastal lagoons of Rio de Janeiro are characterized by relatively high Hg concentrations. This is not only due to the importance of non-point sources of Hg to the lagoons, but also due to the biogeochemical characteristics of these ecosystems, which maintain relatively high Hg concentrations in the water column. Sediment resuspension and the high TSS content of these waters is responsible for keeping high total Hg concentrations in these lagoons. Our results confirm previous investigations on the importance of strongly

bound forms on the total dissolved Hg concentrations under estuarine conditions. Notwithstanding the high total dissolved Hg concentrations, coastal lagoon waters show very low reactive Hg concentrations relative to the open ocean or even to coastal plain estuaries. In fact, coastal lagoons seem to be the extreme case relative to coastal plain estuaries, with strongly bound forms composing over 98% of the total dissolved Hg.

Increasing trace metal availability to coastal lagoon biota due to resuspension of bottom sediments has been already demonstrated for aquatic macrophytes, but not yet for animals. The exposure of these animals to trace metals, in particular filter feeding organisms, should be even larger than aquatic plants and in particular for Hg, which may accumulate through food chains. Therefore, the relatively high Hg concentrations found in the coastal lagoons of Rio de Janeiro, coupled with the high environmental significance of these ecosystems, make urgent the establishment of a monitoring program to evaluate the potential contamination of lagoon biota.

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