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Land–sea mercury transport through a modified watershed, SE Brazil

Mauricio Mussi Molisani[a,], Björn Kjerfve[b], Renata Barreto[c], Luiz Drude de Lacerda[a,c]*

[a]*Instituto de Ciências do Mar, Universidade Federal do Ceará, Av. Abolição 3207, CEP: 60165-081, Fortaleza (CE), Brazil*
[b]*College of Geosciences, Texas A & M University, College Station, TX 77843-3148, USA*
[c]*Departamento de Geoquímica, Universidade Federal Fluminense, Outeiro de São João Batista s/n, CEP: 24020-007, Niterói (RJ), Brazil*

ABSTRACT

River management has altered the land–sea transport of water, sediments, and chemical compounds with profound impacts on the structure of continental and costal ecosystems. Understanding riverine transport across modified watersheds allow for better assessment of the influence of river management on material fluxes to coastal waters. Here, we assess the quantitative and qualitative aspects of mercury (Hg) transport across a modified watershed by diversion of Paraíba do Sul River waters into Sepetiba Bay, Brazil. We measured concentrations and speciation of Hg in water samples collected at sites within the modified watershed. These data, together with water discharge and sediment load from numerical models and measurements were used to estimate mass balances. In the Sepetiba watershed, mercury is mainly associated with suspended sediments (90%) and therefore Hg flux displayed the characteristic trend of downstream reduction due to trapping efficiency of particulate load by successive reservoirs. The mass balance suggests that the major source of mercury to Sepetiba Bay is the erosion of soil-derived particles from the drainage basin rather than mercury diverted from Paraíba do Sul River watershed.

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1. Introduction

Coastal zones worldwide suffer from human-induced changes due to intense occupation. Apart from anthropogenic modifications within coastal water bodies, coastal environments are also impacted by activities within the drainage basin. Water diversion, river regulation, and damming have become important driving forces for coastal change, even when occurring far from the coast. Alteration of river discharge often modifies significantly discharge and sediment load to the coast, which in turn affect salinity regimes, coastal erosion/sedimentation, and pollution (Kjerfve, 1976; Carriquiry and Sanchez, 1999). Likewise, alteration of river discharge may play a significant role in regulating the input of inorganic and organic chemical species, since water and sediment are the main carriers of chemical species (Hostettler et al., 1999; Tomaszek and Koszelnik, 2003). Thus, land–ocean material fluxes may be severely affected by human-induced regulation of river discharge.

Considering alterations imposed by river management, Marins et al. (1999) suggested that water diversion could act as an additional source of mercury (Hg) to the coast after establishing a mass-balance budget of Hg for Sepetiba Bay in southeastern Brazil. According to her calculations, urban and industrial emission of Hg from the Sepetiba basin was estimated to range between 251 and 417 kg yr^{-1} (Marins et al., 1998a) with 53% to the atmosphere, 47% to the soil, and less than 1% to the rivers flowing into the bay. Although direct input of Hg to the rivers is small, Hg may reach the rivers

through atmospheric deposition, superficial runoff, and groundwater recharge. Thus, the total Hg emissions from fluvial sources in the river basin were assumed to be the main Hg input to Sepetiba Bay. The major river channels into the bay were monitored and indicated that the fluvial input of total Hg to be 560–740 kg yr^{-1} (Marins et al., 1999). The resulting mass balance (Marins et al., 1998a) suggests twice the expected Hg emission from sources within the basin. The imbalance indicates Hg sources from outside the river Bay basin, since the emission scenario was validated by other trace metal inventories (Barcellos and Lacerda, 1994; Lacerda et al., 2002). The explanation is simple. Sepetiba Bay receives water discharge from the adjacent Paraíba do Sul River basin to the north by means of a complex water diversion project

(Fig. 1) (Molisani et al., 2006a). Thus, we hypothesized that Paraíba do Sul River is the source of additional Hg to Sepetiba Bay, considering that the Paraíba do Sul River flows across one of most industrialized regions of Brazil. Mello (1999) found Hg concentration in Paraíba do Sul River, upstream of the diversion, to be twice the concentration permissible by the Brazilian Law.

The objectives of this study are to improve on the understanding of Hg transported through the modified drainage basin into Sepetiba Bay, evaluate the importance of Paraíba do Sul River on the Hg emission into Sepetiba Bay, characterize the chemical speciation of the Hg fluxes, and apply mass-balance calculations to estimate sources, sinks, and Hg fluxes to Sepetiba Bay.
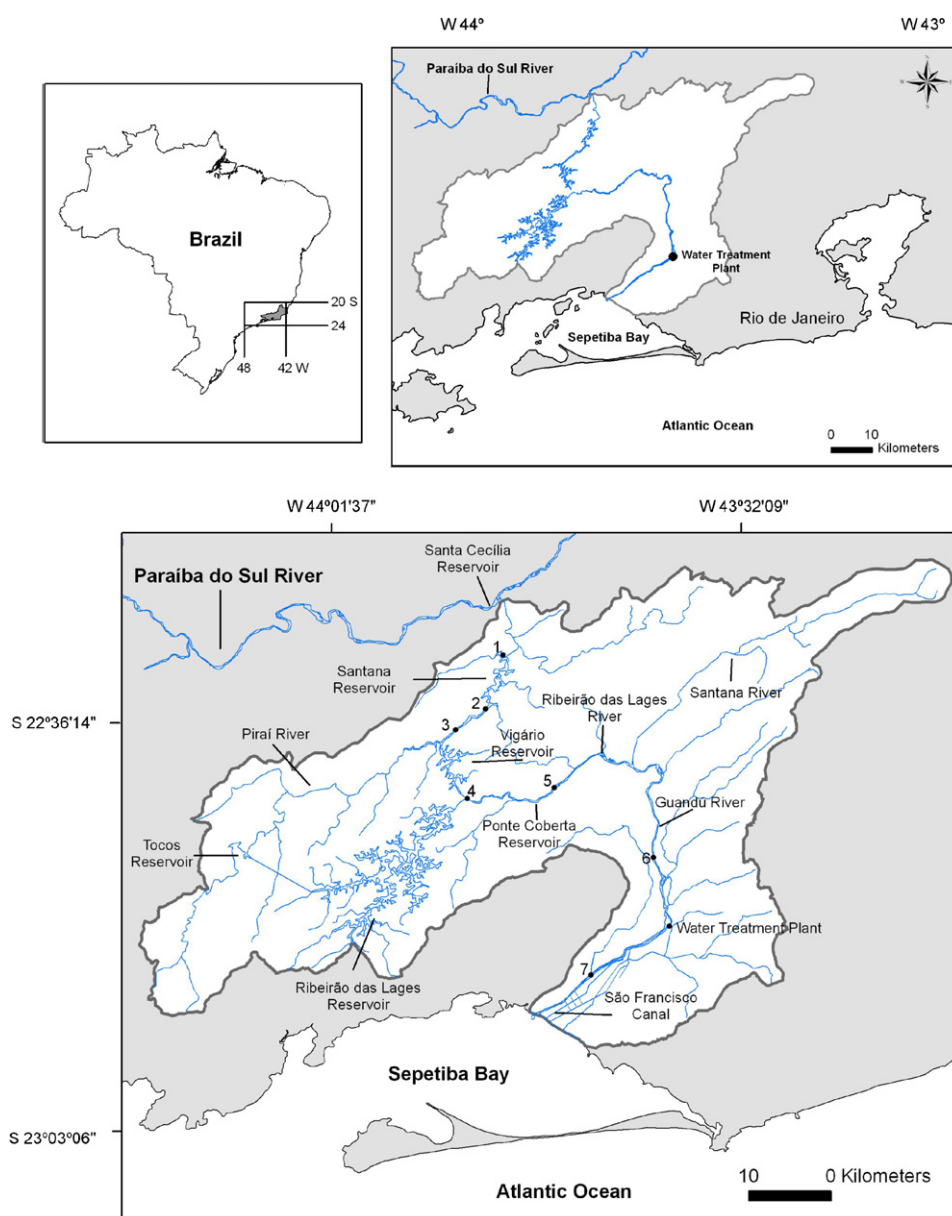

Fig. 1 – Map of the water diversion scheme and sampling sites: 1, water from the Paraíba do Sul River; 2, outflow of Santana reservoir; 3, Inflow of Vigário reservoir; 4, outflow of Vigário reservoir; 5, outflow of Ponte Coberta reservoir; 6, Middle Guandú river basin, 7, discharge to Sepetiba Bay.

2. Material and methods

2.1. Study site

The Paraíba do Sul River is one of the most important and impacted rivers of Brazil (Fig. 1). The subtropical/tropical drainage basin measures $56,600 \, km^2$ and the river flows west to east for 1145 km and discharges in the Atlantic Ocean at latitude 22°S. The mean discharge at the diversion site is currently $244 \, m^3 \, s^{-1}$, with average flow varying from 180 to $437 \, m^3 \, s^{-1}$. Construction of dams for irrigation and industries took place at the same time that a major a diversion scheme was implemented in response to increased water demand. Numerous industrial complexes were located along the Paraíba do Sul River valley, including the major Brazilian metallurgical plant, steel, paper, plastic, rubber, and chemical manufacturing plants, in all numbering 600 industries (Governo do Estado do Rio de Janeiro, 1999).

The major hydrological modification of the Paraíba do Sul River is the diversion of river water into the Guandú River to supply potable water to the metropolitan area of Rio de Janeiro (Fig. 1), which has experienced an explosive growth during the past 60 years with an increase in population from 2.23 to 10.80 million. Because of limited freshwater resources within the basins of the metropolitan area, $160 \, m^3 \, s^{-1}$ is currently diverted from the Paraíba do Sul River into the Guandú River basin. A portion of this diverted water is treated and distributed to the city of Rio de Janeiro at a rate of $47 \, m^3 \, s^{-1}$. The remaining water is allowed to discharge into Sepetiba Bay and is a significant source of dissolved and particulate materials to the bay, including sediments and pollutants (Molisani et al., 2006a).

The Paraíba do Sul River was first dammed in 1950. Four pumps were installed to deliver water 10 m uphill into the Piraí River basin (Figs. 1 and 2) to fill the Santana Reservoir (Fig. 1) until the Piraí River dam. The discharge from the Santana Reservoir and the Piraí River is pumped an additional 33 m upwards into the Vigário Reservoir. From Vigário Reservoir, the subsequent fall to the coast at Sepetiba Bay is 390 m. The total distance between Paraíba do Sul River and Sepetiba Bay is 94 km. Three hydroelectric power generating stations have been constructed along this fall and have a combined generating capacity of 612 MW. The Guandú River receives an additional $9 \, m^3 \, s^{-1}$ from Ribeirão das Lages Reservoir, which constitutes the dammed upper river basin, and eventually discharges into Sepetiba Bay via forested and agricultural lands and several small cities (Molisani et al., 2006a).

Sepetiba Bay is the receiving basin of the residual water and sediment discharges from the local basins and the additional water pumped from Paraíba do Sul River. Sepetiba Bay is a $443 \, km^2$ tidal estuarine system, supporting extensive mangrove wetlands and a rich and productive fishery. Nine small rivers drain the Quaternary plain along the northeastern shores and provide some freshwater input to the bay, still a minor amount compared to Guandú River. Industrial and urban activities were recently accelerated by the construction of large commercial harbor on Sepetiba Bay in the late 1970s. During the past three decades, new industries in the Sepetiba Bay basin include metallurgical and petrochemical plants, pyrometallurgical smelters, plastic and rubber plants, and food and beverage industries (Molisani et al., 2004).

2.2. Sampling and analytical procedures

Water samples were collected at seven sites judged to be the most critical locations between Paraíba do Sul River and Sepetiba Bay (Figs. 1 and 2). Each site was sampled 7 times during 2 years (2001 and 2002), twice in the dry season (August) and 5 times in the rainy season (November, December, and February).

All sampling and analytical materials were pre-cleaned according to accepted protocols for trace metal analysis (Guentzel et al., 1996). The water samples were collected with
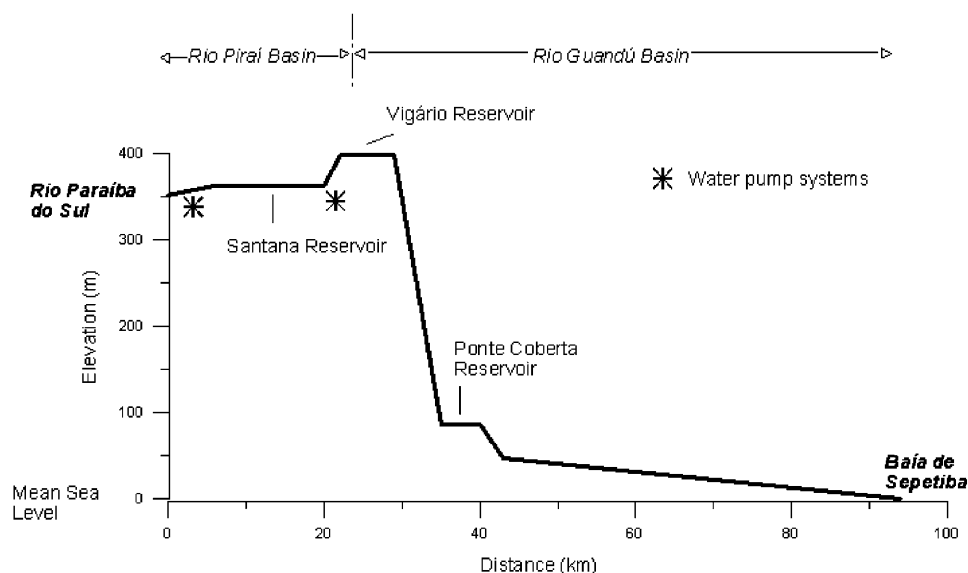

Fig. 2 – Basin transect from the Paraíba do Sul River to Sepetiba Bay.

pre-cleaned (HCl 1%) Teflon bottles and stored in 0.5 L PET bottles (Copeland et al., 1996), which were rinsed with the local water before filled. Bottles were double-bagged in acid-washed plastic bags and transported on ice to the laboratory. Filtration was conducted in laboratory within 4 h maximum after collection. Duplicate samples from each site were subjected to Hg speciation, included dissolved gaseous Hg (DGM), reactive Hg, total dissolved Hg, and Hg bound to suspended sediments (particulate Hg). All samples were analyzed 4–48 h after collection. During the period between sampling and analysis, the samples were kept frozen.

Dissolved gaseous Hg (DGM) was analyzed in sub-samples purged with Hg-free argon and collected on a gold (Au) wool trap connected to the outlet of the reaction vessel. Unfiltered, non-acidified, sub-samples were analyzed for reactive Hg that is reduced and therefore released from solution after adding acidic 10% $SnCl_2$ solution. (Bloom and Crecilius, 1983). The total dissolved Hg fraction was determined in sub-samples after oxidation with bromine monochloride solution at room temperature. After oxidation, 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 (Marins et al., 2002).

Sub-samples were collected from each sampling time and site to obtain total suspended solids (TSS) retained on a 0.45-μm pore size filter, cleaned with 50% HNO_3, after pressure filtration using Teflon apparatus (Leermakers et al., 1995; Krabbenhoft et al., 1998). Filtration was conducted in laboratory within 4 h maximum after sample collection. The particulate Hg was obtained after partial digestion of the retained material on the filters with 50% v/v aqua-regia solution at 80 °C followed by reduction with the same $SnCl_2$ solution used to reduce the reactive Hg fraction (Lacerda and Gonçalves, 2001). For each batch, blank membranes samples were simultaneously analyzed and values subtracted from the sample concentrations.

Hg^0, resultant from the reduction reaction, was analyzed by Cold Vapor Atomic Fluorescence Spectrophotometer. Under the operational conditions described, the analytical detection limit of the method was 1.0 pg for dissolved Hg and 15 ng g^{-1} for particulate Hg, based on the ratio between three standard deviations of blank reagents (Miller and Miller, 1993). All samples were analyzed in duplicate. Differences between duplicates remained below 10% for DGM, reactive and total Hg, while for particulate Hg differences were approximately 30%. In the present study, duplicates represent any two samples collected sequentially, each analyzed once, and not replicates from a single homogenized sample. Thus, relatively high differences of particulate Hg concentrations between duplicates include not only the precision of analytical procedure but also the particulate Hg concentration variability of the river system. During sampling, dissolved oxygen, conductivity, pH, Eh and temperature were measured in situ, using portable electrodes.

One sediment core was sampled at Vigário reservoir in August 2001. The sediment core was sectioned in 2 cm thick discs and each layer was dried at room temperature. The sediment samples were digested in duplicate with 50% aqua regia for 1.0 h at 70 °C in a close system (Marins et al., 1998b). Mercury was analyzed electrochemically by CVAAS, in a

Bacharach Hg analyzer system. Differences between duplicates were always smaller than 6%. Simultaneous determination of Hg in reference standards (NIST-USA no. 2704, Buffalo River, with 60 ng g^{-1} of Hg) were performed using the same analytical procedure and the results gave 57 ± 5 ng g^{-1}. Detection limit of the method based on three times the value of reagent blanks was 5.0 ng g^{-1}.

2.3.   Calculation of mass-balance budgets

Our Hg mass balance is a first order estimation based on average concentrations of Hg, mean water discharge, and average sediment loads. Differences between reservoir inputs and outputs, and river transports enabled us to calculate Hg losses, gains, and fluxes to the coast. Calculations of water and sediment fluxes to Sepetiba Bay from Paraiba do Sul River and the local Sepetiba Bay drainage basin have recently been detailed by Molisani et al. (2006a). Here we only summarize the methods.

2.3.1.   Water and sediment mass-balance budgets
Because hydrological measurements are not done routinely, we have modeled both water discharge (m³ s^{-1}) and sediment load (t yr^{-1}) to develop mass balance. We also compiled and used available data on pumped discharges, outflow from dams, and measurements of suspended sediment concentrations (LIGHT, unpublished data, 2002).

The water discharge model is based on a steady state climatic water balance (Schreiber, 1904); assuming that on an annual basis rainfall equals evapotranspiration and runoff. Input data consist of monthly precipitation and temperature obtained during 30 years at six locations within the Sepetiba basin, provided by LIGHT (unpublished data, 2002) and Ministério da Agricultura (unpublished data, 2000). To obtain water budgets, we calculated annually area-average estimates of precipitation and temperature separately to the Piraí, Guandú, Vigário Reservoir basins, from which evapotranspiration, runoff ratio, and discharge were calculated, as detailed by Molisani et al. (2006a). The calculated water discharges from the sub-watersheds were coupled with long-term discharges based on data from hydroelectric power generation and water supply demands (LIGHT, unpublished data, 2002) to obtain the mass balance for the entire watershed.

Long-term annual sediment load from the anthropogenically altered watershed was estimated by using a numerical model and coupled to sediment load transported by regulated discharges from operating rules of water diversion scheme. The numerical model takes into account the climatic and morphologic characteristics of the watershed based on global dataset (Mulder and Syvitski, 1995, 1996) from which general relationships represented by one equation was determined for predicting sediment load (Q_s) (Morehead et al., 2003). Input data consists of basin relief, basin area and long-term mean annual temperature. The same procedure adopted for the water discharge model was used for the sediment load calculation, as described in Molisani et al. (2006a). The simulated results were related to the sediment load pumped from the Paraíba do Sul River and transferred between reservoirs were provided by LIGHT, unpublished data (2002)

and by Governo do Estado do Rio de Janeiro (2000) for estimating the overall sediment mass balance.

2.3.2. Calculation of Hg flux and mass-balance budgets

The Hg mass balance was obtained by using Hg measurements the simulated water discharge and sediment load at the seven locations. The Hg concentrations were measured in sampling sites are presented in Fig. 1. These sampling sites were chosen to coincide with water discharge and sediment load transported though the most critical points across the overall watershed such as water diverted from Paraíba do Sul River, outlet discharge from dams, middle Guandú river basin and resulting discharge into Sepetiba Bay (Fig. 1). To obtain Hg mass-balance budget for the entirely watershed, we cross-multiplied Hg concentrations with long-term simulated water discharge and sediment load for each sampling site, calculating instantaneous fluxes, which were then averaged. The results represent an annual mean, as our data do not warrant seasonal differentiation.

3. Results and discussion

The physical chemical parameters characterize the water characteristics of the entire watershed as neutral to basic (pH: 6.6–7.0) and oxidant (Eh: 146–178 mV). The conductivity (85–$100 \, \mu s \, cm^{-1}$) and dissolved oxygen (4.1–$6.2 \, mg \, L^{-1}$) ranges indicate that this artificial watercourse is lesser impacted than others rivers draining the Sepetiba Bay basin (Paraquetti et al., 2004). The concentrations of Hg species measured along the engineered-modified watershed until the discharge into the Sepetiba Bay is shown in Table 1. Seasonal variability was not observed for Hg species, thus all samples were integrated in a single analysis.

Dissolved gaseous Hg (DGM) presented concentrations varying from 0.01 to $0.10 \, ng \, L^{-1}$ while reactive Hg concentrations ranged from 0.02 to $0.69 \, ng \, L^{-1}$ during the sampling period. Total dissolved Hg concentrations ranged from 0.12 to $2.13 \, ng \, L^{-1}$ and these concentrations are similar to concentrations from non-polluted watersheds or moderately polluted areas (Hurley et al., 1995, 1998; Schroeder, 1989; Balogh et al., 2005), as well as for the most rivers draining into Sepetiba Bay (Paraquetti et al., 2004) and other Brazilian Rivers (Roulet et al., 2001; Maurice-Bourgoin et al., 2003; Lechler et al., 2000). The DGM, reactive Hg, and total dissolved Hg concentrations did not show any significant spatial difference ($P > 0.05$).

Particulate Hg concentrations presented large variation (0.23–$1.8 \, \mu g \, g^{-1}$). For rivers draining to coastal areas, particulate Hg concentrations are rather variable ranging from 0.05 to $1.4 \, \mu g \, g^{-1}$ in non-contaminated areas and from 1.2 to $30 \, \mu g \, g^{-1}$ in contaminated sites (Horvat, 1996). Thus, compared with literature data, some of our measurements of particulate Hg show an enrichment of this metal in suspended sediments. The seasonal and spatial variability was also not statistically observed for this Hg species ($P > 0.05$).

The Hg mass balance is shown in Fig. 3, as a steady-state description of relative magnitudes of fluxes, reservoir contents and resulting Hg discharge into Sepetiba Bay. The water diverted from Paraíba do Sul River transfers 4 and $460 \, kg \, yr^{-1}$ of total dissolved and particulate Hg, respectively, into Santana reservoir, which is the dammed lower Piraí River basin. At the outlet of Santana reservoir, where a second water diversion occurs by pumping water uphill, we estimated that 4 and $100 \, kg \, yr^{-1}$ of total dissolved and particulate Hg, respectively, are diverted downstream into Vigário reservoir. The Hg balance between input and outflow of Santana reservoir indicated that $360 \, kg \, yr^{-1}$ of particulate Hg is trapped in this reservoir. It is important to note that the Hg transfers from Paraíba do Sul River and Hg retention in Santana reservoir are probably overestimated, as the suspended sediment concentration time-series used to calculate the Hg load from Paraíba do Sul river was obtained in river channel upstream from St Cecília reservoir. This sediment concentration is the best value available, but could differ substantially from concentrations within the St. Cecília reservoir, where water is collected for diversion.

In Vigário, the mass balance indicates that more Hg leaves the reservoir than enters (Fig. 3). This is a result of higher average dissolved and particulate Hg concentrations (Table 1), but needs to be confirmed with additional long-term field data. Further, the suspended particle load retained by the Vigário reservoir ($46 \times 10^3 \, t \, yr^{-1}$) (Fig. 4) obviously buried particulate Hg, following the same pattern as in other reservoirs (Aula et al., 1995; Diamond et al., 2000). From the Hg mass balance, we cannot accurately estimate the amount of Hg retained in the Vigário reservoir. However, considering the predominance of Hg flux in the particulate phase, we assume that the burial of particulate Hg occurs at the same rate as the sediment trapping efficiency for the Vigário reservoir (14%). Based on this assumption, the suspended particulate load retained and buried in the reservoir corresponds to $30 \, t \, Hg$ annually (Fig. 3).

From Vigário reservoir, Hg is discharged into Guandú River basin at rates of 5 and $260 \, kg \, yr^{-1}$ for total dissolved and particulate Hg, respectively. These loads represent the con-

Table 1 – Mercury speciation (mean and range) in water samples collected along the water diversion scheme (number of samples = 7)

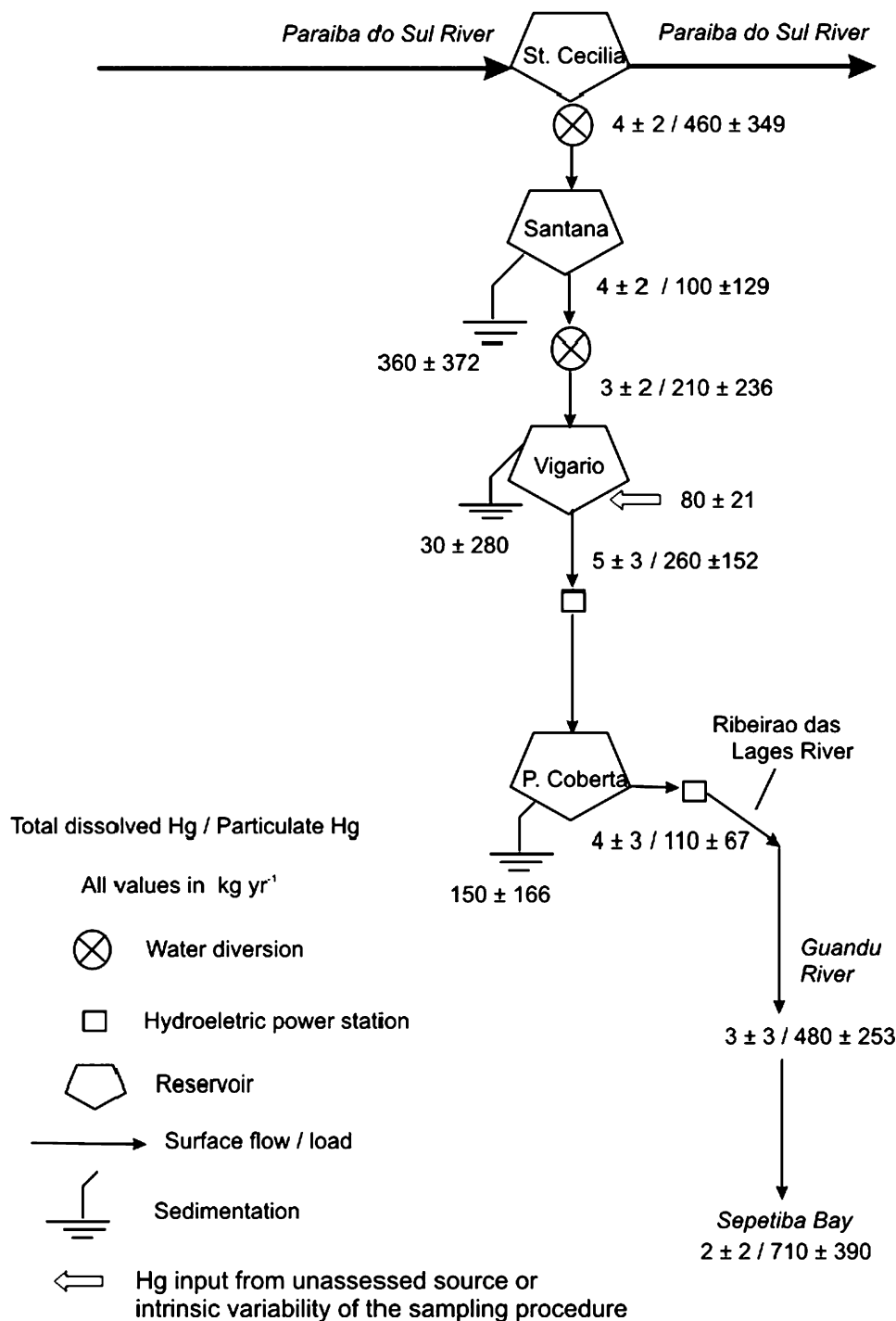| Sampling site	Dissolved gaseous Hg ($ng \, L^{-1}$)	Reactive Hg ($ng \, L^{-1}$)	Total dissolved Hg ($ng \, L^{-1}$)	Particulate Hg ($ng \, g^{-1}$)
1	0.04 ± 0.03	0.36 ± 0.24	0.74 ± 0.40	782 ± 567
	0.01–0.10	0.07–0.69	0.25–1.55	338–1.801
2	0.05 ± 0.05	0.28 ± 0.12	0.82 ± 0.42	747 ± 452
	0.01–0.15	0.09–0.42	0.37–1.76	240–1.501
3	0.04 ± 0.02	0.43 ± 0.15	0.60 ± 0.32	650 ± 175
	0.01–0.07	0.02–0.56	0.15–1.24	347–915
4	0.05 ± 0.03	0.30 ± 0.12	0.91 ± 0.58	964 ± 450
	0.01–0.11	0.17–0.49	0.27–1.99	330–1.358
5	0.05 ± 0.03	0.27 ± 0.14	0.71 ± 0.60	540 ± 217
	0.01–0.10	0.12–0.49	0.15–2.02	233–840
6	0.05 ± 0.03	0.35 ± 0.25	0.58 ± 0.63	731 ± 350
	0.01–0.09	0.12–0.49	0.12–1.83	244–1.178
7	0.06 ± 0.04	0.26 ± 0.15	0.63 ± 0.68	837 ± 278
	0.01–0.10	0.12–0.50	0.14–2.13	336–1.134

Fig. 3 – Mass-balance budget of Hg (mean ± standard deviation, kg yr^{-1}) along the engineered-modified watershed.

tribution of water diversion scheme to Sepetiba Bay drainage basin confirming our hypothesis which stated the water diversion scheme as an additional source of Hg to Sepetiba Bay basin. These additional loads explain the differences between Hg emissions and discharges for the Sepetiba Bay basin, reported in previous mass balance (Marins et al., 1999).

The water flow is also dammed by the last reservoir of the water diversion scheme (Ponte Coberta) and the mass balance shows that 540 kg yr^{-1} of particulate Hg is retained along successive reservoirs reducing the downstream transport of

sediment load from Paraíba do Sul River. Chronological Hg concentration within reservoirs could be exemplified from the sediment profile collected in Vigário reservoir. The down core Hg concentration increases from 32 ng g^{-1} in the bottom of the sediment core to 97 ng g^{-1} in the surface layer (Fig. 5). The actual enriched Hg condition relative to the last time period must be related to changes in loading rates due to anthropogenic emissions (Lacerda and Ribeiro, 2004) and/or post-depositional mobilization (e.g. diffusion, bioturbation, sediment resuspension). Whatever processes causing the
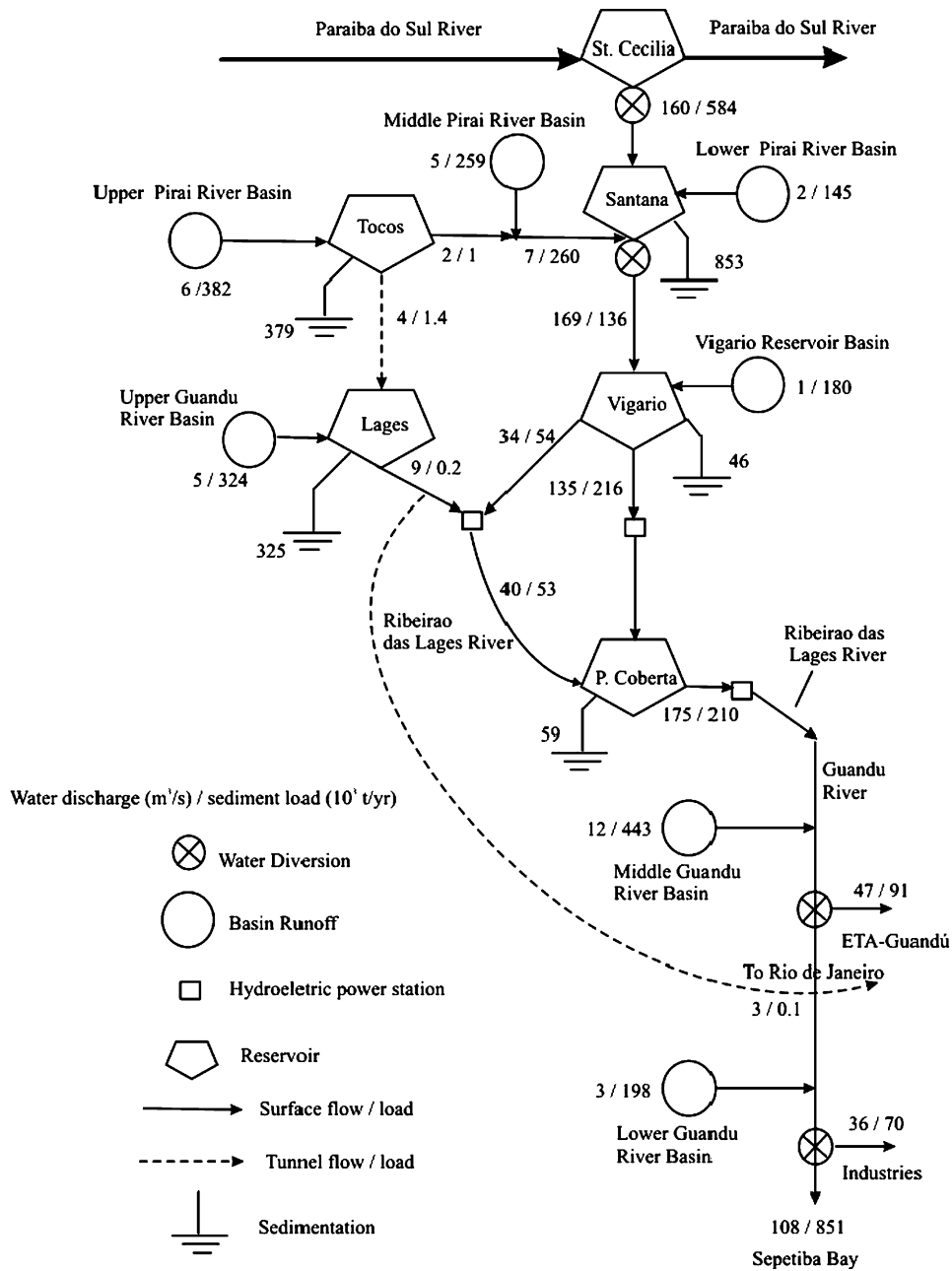
Fig. 4 – Long-term water discharge $(m^3\,s^{-1})$ and sediment load $(103\,t\,yr^{-1})$ transported from Paraíba do Sul River to Sepetiba Bay (from Molisani et al., 2006a).

actual higher Hg levels compared to early conditions, trace metal enrichment in reservoirs could increase the exposure and availability for biota (Jackson, 1998).

Relatively high Hg concentration was found in aquatic macrophytes from reservoirs in the study area (Molisani et al., 2006b). These concentrations were higher than those reported from uncontaminated lakes in Brazil and other tropical areas and similar to those from moderately contaminated sites. As trace metal pollution in freshwater environments can be recorder in the aquatic plants, Hg concentration found in such macrophytes colonizing both reservoirs may be also related to an actual significant enriched Hg condition relative to the early periods.

Downstream fluxes from Ponte Coberta reservoir was estimated as 4 and $110\,kg\,yr^{-1}$ for total dissolved and particulate Hg, respectively. Total dissolved Hg flux decreases downstream along the Guandú River and the estimated discharge of total Hg into the Sepetiba Bay is $2\,kg\,yr^{-1}$. Although the downstream water flow decreases along the Guandú River, the particulate Hg load presents an opposite trend with increasing loads until the most seaward site that represents the Hg discharge into Sepetiba Bay calculated at a rate of $710\,kg\,yr^{-1}$. Higher fluxes associated with particulate phases can simply be a result of increased suspended sediments loading from different particle pool inputs along the Guandú River basin since spatial Hg concentrations was
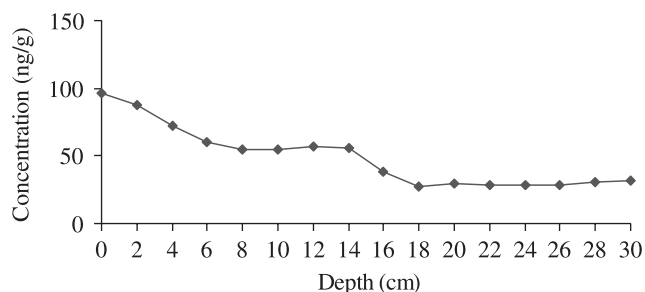
Fig. 5 – Distribution of Hg in a sediment core profile taken from Vigário reservoir.

not significantly different between sampling sites. The speciation showed that the fate of riverine Hg inputs to Sepetiba Bay may be closely linked to the primarily association with particles since more than 90% of total Hg flux to the coast is associated to particulate phase. Thus, Hg dynamics are similar to that of other highly particle-reactive metals, which fate is determined by particles transport.

Rivers represent an important pathway for Hg mobilization to coastal ecosystems and therefore understanding the mechanisms controlling Hg transport by rivers is essential to assess its downstream fate. In the present study, the engineered-modified watershed is subject to water and sediment inputs from the Paraíba do Sul River and involved basins that compose the water diversion scheme from which Hg dispersal along the watercourse is determined. The qualitative importance of such sources may indirectly provide footprints of the controlling mechanisms of Hg transfers along the watercourse until Sepetiba Bay. The importance of the main water and sediment sources along the watershed was obtained by the long-term water and sediment mass-balance budgets (Fig. 4).

Discharge into Sepetiba Bay has increased threefold since the water redistribution began and water from the Paraíba do Sul River is the main source of water to the Bay (Molisani et al., 2006a). On the other hand, sediment budget calculations indicate retention of a large fraction of the sediment load from the Paraíba do Sul by reservoirs along the watercourse. As a consequence the water diversion scheme has lead to a 28% increase in sediment delivery to Sepetiba Bay or $270 \times 10^6\,t\,yr^{-1}$. Of the total 28% increased sediment yield to Sepetiba Bay, 14% is attributed to the watershed and 14% to the Paraíba do Sul River thought the water diversion. Therefore, the Paraíba do Sul River contributes most of the freshwater input into Sepetiba Bay, whereas the sediment load to the bay is mainly originated from the local drainage basins (Molisani et al., 2006a).

According to the proposed mass-balance budget and considering that a great extent of Hg transported along the watercourse is particulate Hg, the resultant Hg input into Sepetiba Bay may be mostly governed by the involved drainage basins and to a lesser extent by the Paraíba do Sul River proper. For some drainage basins, Hg levels are consistent with those reported for soils and therefore Hg concentration in river particulate matter probably reflects the erosion of soil-derived particles (Roulet et al., 2001; Maurice-Bourgoin et al., 2003). Although no consideration was made in

the present study on the relationships between Hg concentration in soils and riverine loads, mass-balance calculations proposed by Marins et al. (1999) shows that more than 90% of total Hg emission from activities located within Sepetiba Bay basin is to the atmosphere and soils. As 90% of total atmospheric emission is deposited within Sepetiba Bay basin (Marins et al., 1996), soils are important stocks of Hg along the catchment, highlighting the importance of erosion of soil-derived particles from the involved basins along the water-course as a major source of Hg to Sepetiba Bay.

4. Conclusions

Water diversion provides an additional source of Hg to Sepetiba Bay. The design of the water diversion scheme and the operational rules are key factors controlling the Hg transport along the engineered-modified watershed. Successive reservoirs and water volume transfers determine the amount of Hg retained or transferred downstream. According to mass-balance budgets, most of Hg load diverted from the Paraíba do Sul River is retained behind successive dams. Sediment balance shows the importance of contribution of the involved basins on the composition of suspended sediments transported along the watercourse suggesting a progressive dilution effect of sediment influx from Paraíba do Sul River. Thus, as the Hg load is predominantly composed by the particulate phase and the data from literature point out the soils of Sepetiba Bay basin as an important stock of Hg emitted from activities placed along the basin, the Hg flux along the water diversion scheme and resulting load to the Sepetiba Bay is most probably governed by erosion of soil-derived particles of the involved basins along the water diversion scheme and a to lesser extent of the Paraíba do Sul River.

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