Decadal and spatial variation of Hg concentrations in sediments of a multi-stressor impacted estuary

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ABSTRACT

The present study has evaluated temporal and spatial mercury trends based on surficial sediment samples and ^{210}Pb-dated sediment profiles. The obtained results show that there are areas close to the main bay's tributary rivers where the Hg content has doubled during the last 15 years and regions where it has decreased by a factor of 2, mainly the area close to the navigation channel, which is submitted to periodic dredging. In the inner part of the bay, the most contaminated region, mercury shows a strong association with sulfide. In the same region, based on the ^{210}Pb results, it was possible to calculate the yearly increment on the Hg concentration in the surface sediment, $0.62\,\mu g\,kg^{-1}\,y^{-1}$ to $0.29\,\mu g\,kg^{-1}\,y^{-1}$, according to the distance to the bay's main tributary rivers.

1. Introduction

Sepetiba Bay, in the metropolitan area of Rio de Janeiro, exists in a conflicting situation. While an important recreational and touristic region, where fishery is still a significant economic activity, the bay's watershed harbors several large industries, including two steelwork plants, two commercial ship terminals for containers, and iron ore and coal transport, which require frequent large-scale dredging, and a population of approximately 2 million, served by poor or no sewage and solid waste treatment. These pollution sources contribute significant loads of sediment and toxic metals, in particular Zn, Pb, Cd and Hg. Sediment accumulation rates vary from 160 to 650 mg·m^{-2}·yr^{-1}, from a total basin input to the bay of approximately 1 million tons of sediment annually (Molisani et al., 2006). Although no recent inventory is available, estimates of metals discharges in the past decade reach figures on the order of hundreds of tons annually (200, 7.7, 2 and 0.75 tons for Zn, Pb, Cd and Hg, respectively) (Molisani et al., 2004).

Between 2000 and 2005, the Rio de Janeiro state environmental authority (actual INEA former FEEMA) prepared a large environmental survey at Sepetiba Bay, including evaluation of heavy metals in surface sediments (FEEMA, 2006). Possibly due to the high sedimentation rate, as well as the decommissioning of the largest Cd-Zn smelter in the

region, the Inga Metallurgical, one of the major metal (Zn, Cd and Pb) contributors to the bay, a reduction of contamination levels of these metals relative to the late 1980s was observed. This trend was confirmed by biological monitoring of oysters (Lacerda and Molisani, 2006). Mercury was an exception to this trend, with an expansion of areas with sediments containing high Hg content. Veeck et al. (2007) observed that higher Hg concentrations were mostly localized close to river outfalls and related to fluvial sources and inputs, particularly in the northeast portion of the bay, in agreement with what was reported by Paraquetti et al. (2004) and Molisani et al (2007) who associated the Hg input to Sepetiba Bay with the transport of particulate material from rivers reaching the bay.

This paper reevaluates the present-day contamination by Hg of Sepetiba Bay sediments. Additionally, in order to test the Hg association with the organic matter content in sediments, as previously only reported based on statistical correlation, the stable isotope composition of carbon and nitrogen ($\delta(^{13}C)$ and $\delta(^{15}N)$) and C/N ratio was determined, to detail this metal-organic association.

2. Material and methods

Bottom sediments were taken using a Petersen grab, stored in acid-

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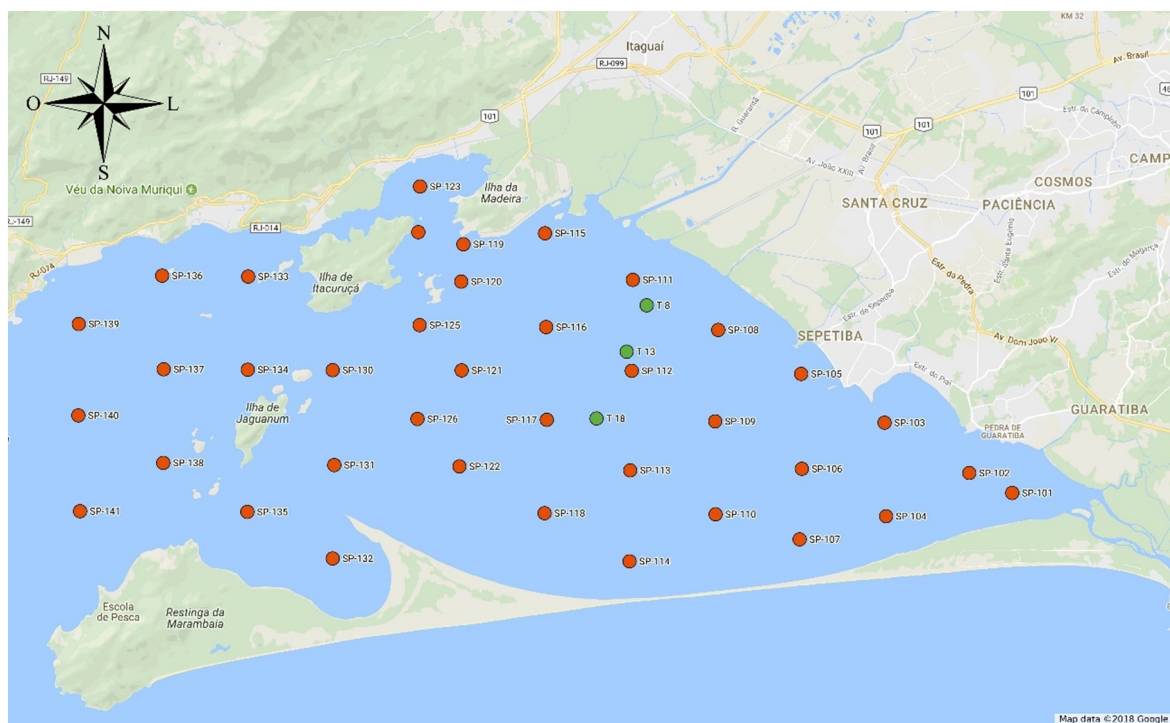**Fig. 1.** Sepetiba Bay and the surface sediment sampling points (red dots) and sediment cores (green dots). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

cleaned glass jars, kept cool using a cooler and ice for transport to laboratory, where samples were preserved in a refrigerator (3 °C). Sampling stations are shown in Fig. 1 and follow the same grid established by the Rio de Janeiro State Environmental Agency (FEEMA, 2006) involving 38 stations. Details on Sepetiba Bay hydrodynamics and geographical settings can be found in Cunha et al. (2006).

Half gram wet sediment samples were analyzed for total Hg concentrations by cold vapor atomic absorption, following the procedure described by Limaverde Filho and Campos (1999), in a RA-915 M Lumex Instruments Hg analyzer. The achieved detection limit was $0.002 \, \mu g \, g^{-1}$. Acid volatile sulfide (AVS) was determined following EPA-Method-376.2 and the APHA 4500-S^{2-} colorimetric determination method. Particle size determination was performed using a Cilas 1190 Particle Size Analyzer. All results were corrected for the wet/dry weight ratio. Distribution plots were drawn using Ocean Data View version 4 and the GEBCO1 Southern Ocean-Atl map.

All sediments were initially dried by lyophilization and homogenized, and approximately 8 mg was placed in tin vials to determine total carbon and nitrogen (TC and TN, respectively) and nitrogen isotopic composition. Then, approximately 8 mg was placed in silver vials, and 25 μL of HCl 2.0 mol L^{-1} was added slowly, 3 times, until the reaction finished, to determine organic carbon (OC) content and organic carbon isotopic composition. After that, the vials were dried in an oven at 110 °C (boiling temperature) for 24 h. Samples were then combusted on a continuous flow elemental analyzer (Flash 2000 Organic Elemental Analyzer), which measured elemental concentrations of C and N, coupled to a stable isotope ratio mass spectrometer (IRMS Delta V Advantage, Thermo Scientific, Germany), which measured isotopic composition of C and N. Pee Dee Belemnite (PDB) and atmospheric N were used as standard values for C and N analyses, respectively. The analytical precision was ± 0.1‰ for δ13C and ± 0.2‰ for δ15N, and the accuracy for elemental and isotopic compositions were determined by certified standard (Protein OAS/Isotope Cert 114,859; Elemental Microanalysis).

Sediment dating was carried out on three sediment profiles (T-08, T-13 and T-17; Fig. 1). The sediment cores were sampled by applying a

6.0 cm diameter UWITEC gravity sediment corer, and two-centimeter-high slicing was applied. Lead-210 was determined as described by Godoy et al. (1998), and the sedimentation rate was calculated applying the Constant Rate-Constant Flux (CR-CF) and the Constant Rate of Supply models.

3. Results and discussion

Concentrations of Hg found in surficial sediments from all sampled stations in Sepetiba Bay are listed in Table S1 in the Supplementary Material. There is no Brazilian guideline for sediment quality relative to Hg, and as such, it is typical to apply the limits established by the National Environmental Council (CONAMA) resolution 454/2012, which are based on the "Canadian Sediment Quality Guidelines for the Protection of Aquatic Life". In this interim sediment quality guideline (ISQG), the Hg concentration limit is $130 \, \mu g \, kg^{-1}$. Considering this limit, only one station, SP-111, had a Hg concentration higher than the ISQG (Table S1).

Descriptive statistics on sediment Hg concentrations are shown in Table 1, with a comparison to previous values reported in the literature. Concentrations are quite variable, since all these previous studies, as well as this one, covered the entire area of the bay. There is no evidence of any temporal trend from the 1990s to the present, at least when considering the entire area of the bay. However, for sediment samples collected from stations close to river mouths, present-day maximum concentrations are nearly double those reported in 1998.

Table 1
Mercury concentrations in surficial sediments from Sepetiba Bay – Descriptive statistics and comparison to the literature (values in $\mu g \, kg^{-1}$).

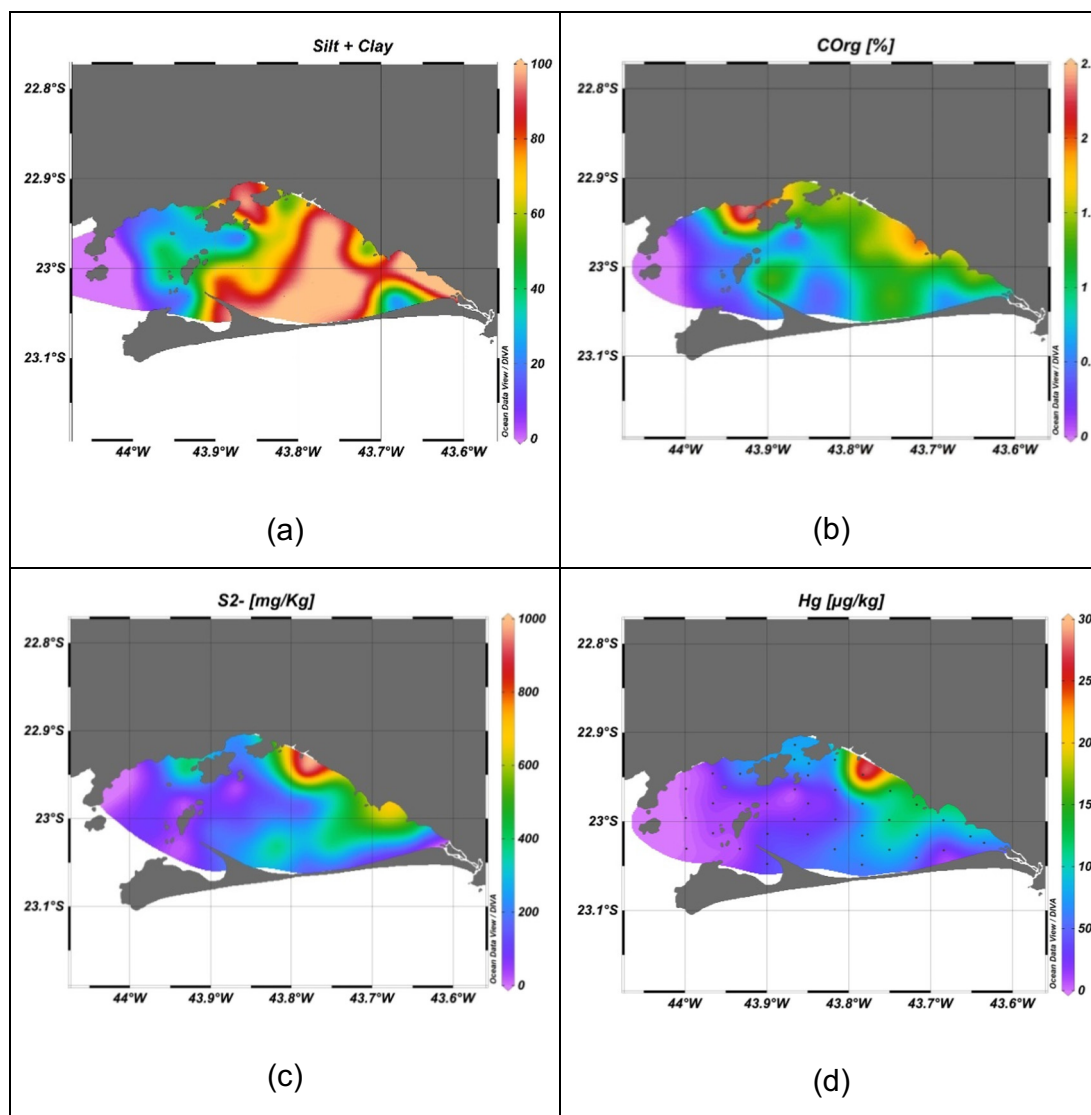| Reference	Mean value	SD	Range	Median
Present work	57	54	0.04–290	62
Veeck et al. (2007)	57	26	18–108	58
FEEMA (2006)	91	36	40–200	100
Marins et al. (1998)	–	–	17–163	

Fig. 2. Sepetiba Bay isosurface plots for silt + clay (a), organic carbon (b), sulfide (c) and mercury (d).
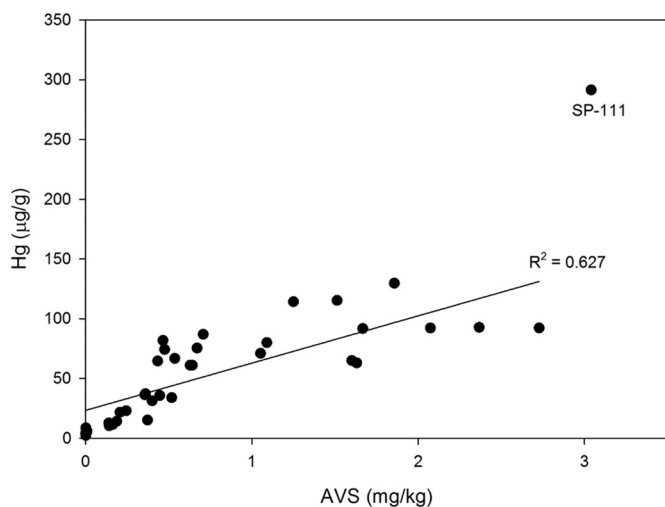

Fig. 3. Mercury and acid volatile sulfide (AVS) correlation on Sepetiba Bay surface sediments.

Isosurface plots for clay, organic carbon, sulfide and mercury were generated using Ocean Data View version 4.7.10 software and are shown in Fig. 2a–d.

The lower content of fine fractions are localized at the outer part of the bay (Fig. 2a) and include the main navigation canal. To some extent this area also contains lower organic carbon and AVS (Fig. 2b and c). High silt and clay percentages are observed on the inner bay region, with the exception of an area close to the sand barrier that isolates the bay from the open sea. Wind erosion in this region was previously cited in the FEEMA (2006) report and at the main channel area (Central region, between the Itacuruça and Juguanum Islands.

There is an organic carbon hot spot behind Itacuruça Island, which could be influenced by the high density of summer houses in this region. A second high organic carbon area is Sepetiba beach, which is known as an unsuitable beach due to non-treated sewage discharge; this region also represents a sulfide hot spot. Rezende et al. (2010) have studied the organic matter in Sepetiba Bay and its tributary river, and for the common sampling points, mainly 111 and 115, the obtained results were similar to the present values. According to the same authors, the organic matter end members were continental forest (wood and leaves), including mangroves, and plankton, approximately 50% each. As there is a larger difference in the C/N ratio than on the $\delta(^{13}C)$ value, for the continental forest and plankton end members, the leaf
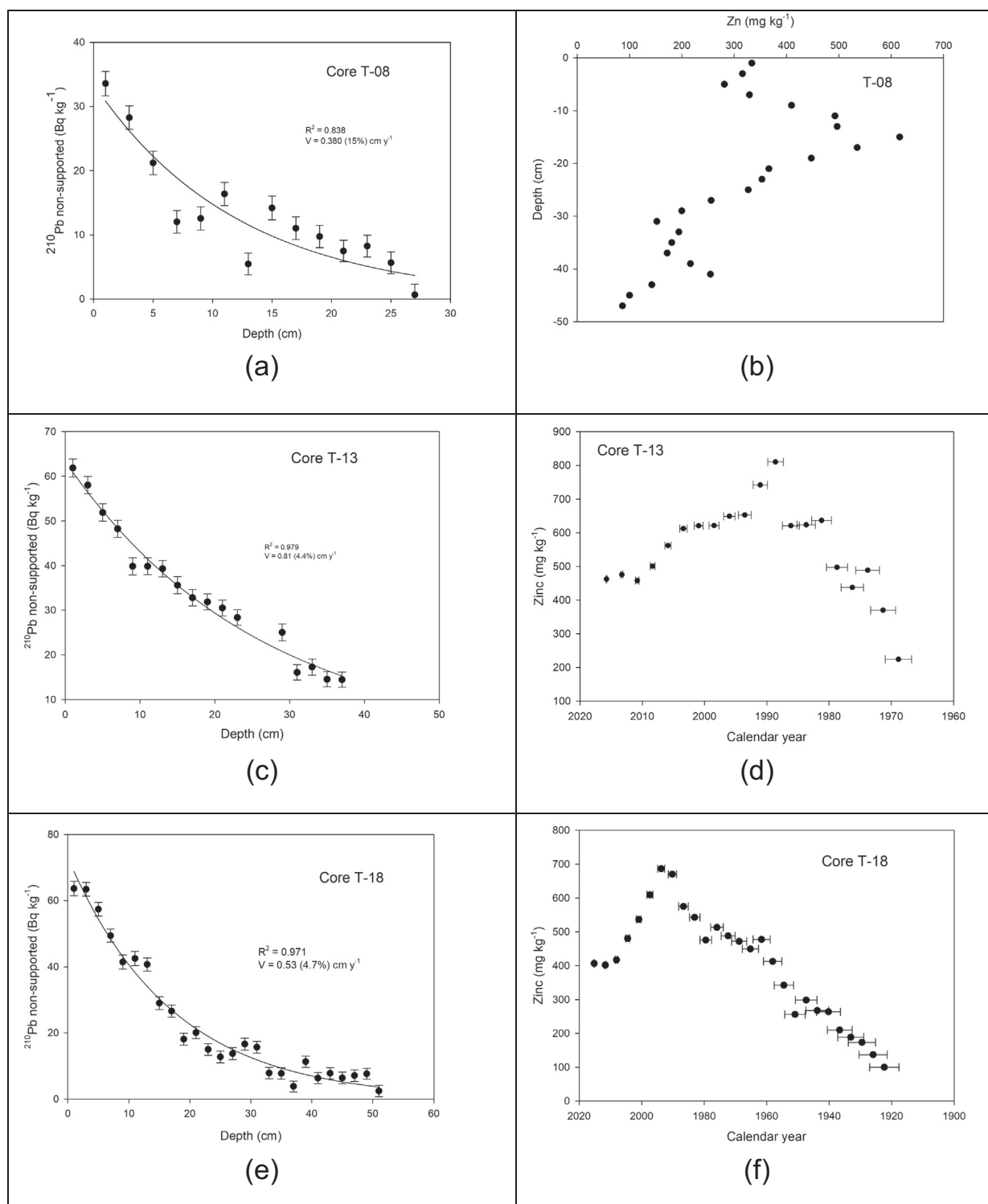
Fig. 4. Pb-210 dating of sediment cores T-08, T-13 and T-18 showing the non-supported ^{210}Pb profile (a, c and e) and the Zn temporal variation applied for the age validation (b, d and f).

and plankton contribution for organic carbon in Sepetiba Bay was calculated using the C/N ratio which showed that the calculated planktonic contribution ranged between 75% to 100%, with the lowest contribution along the shoreline from sampling point 123 to 103, where mangroves and tributary rivers are present.

The largest sulfide concentration was observed close to the main river discharge, which corresponds to the main BOD load to the bay (Cunha et al., 2006) and, consequently, anoxic sediments. The mercury

contamination pattern is quite similar to sulfide distribution (Fig. 2d) and agrees with those described by Paraquetti et al. (2004) and Molisani et al. (2004) with a hot spot close to the São Francisco Channel and Guandu River discharge, where the highest concentrations were observed. Using Itacuruça Island (Fig. 1) as a geographical reference, dividing the bay into two sectors: an oceanic sector at the left-hand side and an inner sector at the right, it is possible to observe a statistically significant difference between the two sectors (z = 4.8). Comparing
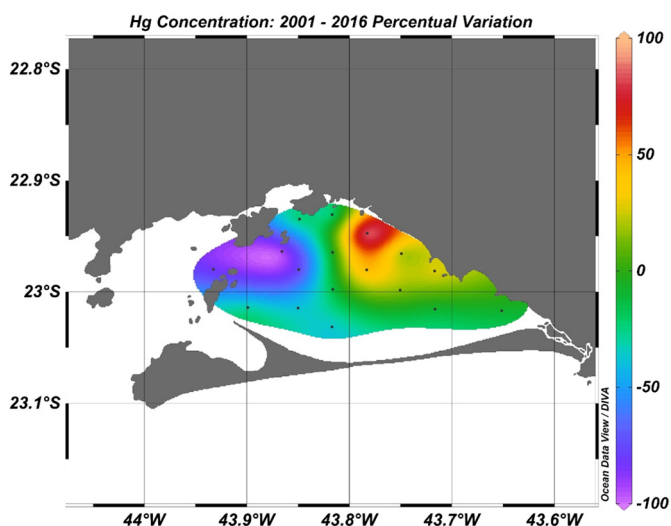
Fig. 5. Temporal variation of Hg concentration in surficial sediments from Sepetiba Bay in percent relative to concentrations reported in 2001.

sulfide and Hg distribution (Fig. 2c and d), it is possible to verify that both are relatively equal; to test this, Hg concentrations were plotted against the sulfide content (Fig. 3). Based on this comparison, it appears that this correlation exists, with an outlier corresponding to sampling point 111, due to the influence of the São Francisco Channel and Guandu River. In fact, Hg affinity for S is well documented, and even the correlation between Hg and organic matter is attributed to S containing functional groups (Schartup et al., 2014). The methyl-mercury content was very low < 0.1%, in agreement with reports by other authors (Belzile et al., 2008; Bratikic et al., 2013; Schartup et al., 2014), that the mercury methylation on sulfide rich anoxic sediments is very low.

In the São Francisco Channel and in the Guandu River, total Hg in the water column is routinely determined on a monthly basis at two depths (surface and bottom), and on sediment samples, by the Companhia Siderúrgica do Atlântico (CSA), as a component of its environmental monitoring program. It was possible to obtain these data for the period of 2014–2016 and to apply them to validate present findings. No water samples contained Hg above the limit of quantification (0.05 µg L^{-1}). As shown previously, the larger contribution to Hg input from these rivers to the bay is associated with suspended particles, which account for a net flux varying from 1575 to 13,111 µg·s^{-1},

compared to a dissolved flux varying from 47 to 485 µg·s^{-1}, in the dry and rainy season respectively (Paraquetti et al., 2004). On the other hand, according to this report, the Guandu River sediment contains a Hg concentration (210–580 µg kg^{-1}) higher than that obtained for the sampling point 111. Consequently, the transport of Hg to the bay should occur during the river flooding events, which happen during the summer monsoons, fluxing contaminated sediments to the bay instead of a continuous input.

Distribution of Zn in sediment cores from Sepetiba Bay is a good proxy of internal sources of metals to the bay, since a major Zn-Cd smelter had contributed the near totality of Zn, Cd and Pb loads to the bay until 2010, when the smelter was decommissioned. Therefore, based on the observed zinc and ^{210}Pb profiles and on the proximity to the Guandu River and the São Francisco channel, Hg sources and loads (Fig. 2d), can be better ascertained. Fig. 4(a) shows the T-08 ^{210}Pb$_{total}$ profile, the sedimentation rate estimate of 0.38 cm y^{-1} is 50% of the value based on the Zn profile, 0.75 cm y^{-1}. Therefore, ^{210}Pb dating was not considered for this sediment core. Figs. 4c–f present the non-supported ^{210}Pb, the calculated ages and the Zn profiles, applied to the age validation, for the two sediment cores, T-13 and T-18. Despite all man-made interferences in the bay, an exponential variation of the ^{210}Pb concentration with the depth was observed for these two cores, indicating a nearly constant sedimentation rate. As T-13 is closer to the shoreline than T-18, the calculated sedimentation rate, 0.81 cm year^{-1}, is higher than that verified at T-18, 0.53 cm year^{-1}. For core T-13 the Zn maximum was observed in 1992 (± 4) which fits with the Inga Metallurgical smelter waste dam rupture which occurred in 1996. For the core T-18 the Zn maximum was observed in 1993 (± 4), which also fits with the Inga Metallurgical waste dam rupture (Lacerda and Molisani, 2006).

The Hg temporal variation was evaluated following two different approaches: 1) Comparing the obtained results with those from 2001 and constructing isosurfaces based on the differences observed during these 15 years (Fig. 5). 2) Based on the dated sediment profiles, verifying the Hg archive during the past 80 years (Fig. 6a–b).

There is a 100% increase in present-day Hg concentrations relative to those found in 2001 (Fig. 5) closest to the main Hg source to the bay: the Guandu River and the São Francisco Channel. These two rivers are responsible for over 95% of the total Hg input into Sepetiba Bay (Lacerda et al., 2004), and their influence on Hg distribution in bottom sediments of the bay has been previously reported (Marins et al., 1998). On the other hand, in other areas of the bay roughly corresponding to the main navigation canal to reach Sepetiba harbor, concentrations decreased over 100%, likely the result of periodic dredging.
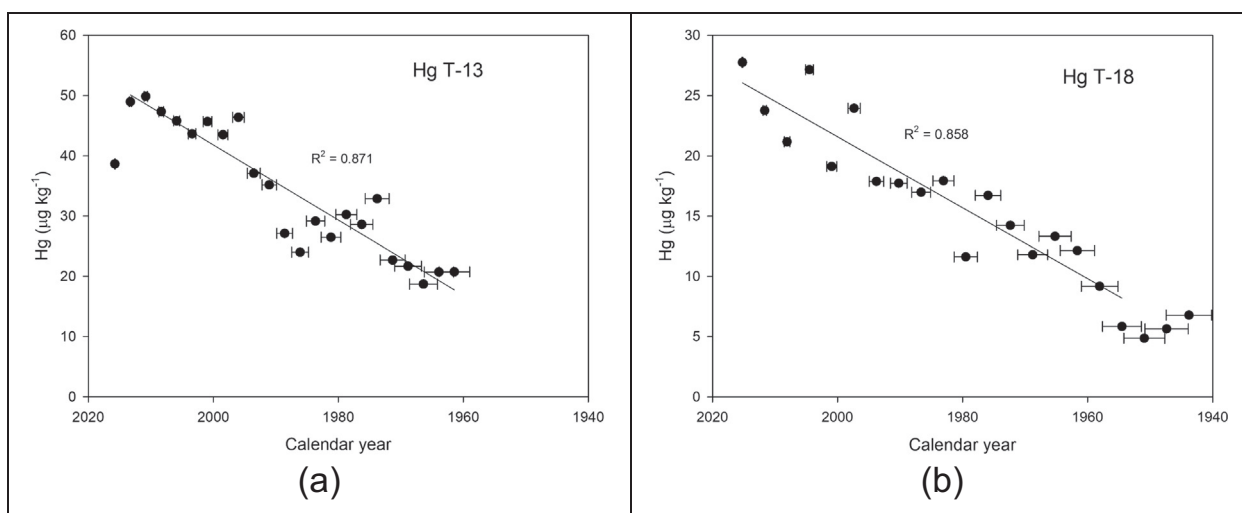

Fig. 6. Mercury temporal variation (a) sediment core T-13 and (b) sediment core T-18.

Based on the temporal variation of Hg concentration along sediment cores T-13 and T-18, it is possible to observe an almost linear increase with time for cores T-13 and T-18. As the sedimentation rate for these two cores is constant, it is possible to conclude that the Hg flux to the bay has linearly increased throughout the years, and the yearly increment of the Hg concentration in the surface sediments is $0.62\,\mu g\,kg^{-1}\,y^{-1}$ at T-13 and $0.29\,\mu g\,kg^{-1}\,y^{-1}$ at T-18 (Fig. 6). As there is not an industry in this region utilizing mercury in its processes, the Hg sources are diffuse, e.g., sanitary waste deposits, non-treated domestic sewage and city rainwater drainage systems, and have increased with population growth in the region. The sediment core data allow an estimate of the Hg concentration baseline value, $5\,\mu g\,kg^{-1}$ at sampling point T-18, which represents ¼ of the value proposed by Marins et al. (2004) for clay rich sediments from Sepetiba Bay.

4. Conclusions

The actual Hg distribution in Sepetiba Bay surface sediments did not present a uniform pattern, as proposed by the state environmental authority circa ten years ago; rather, it shows a concentration gradient, with the highest values in the region close to its main fresh water contributors, São Francisco Channel and Guandu River, a pattern that has not changed during the last twenty years.

Itacuruça Island can be applied as a geographic reference to divide the bay into two regions: to its left, the oceanic region where sandy sediments are found and to the its right, the inner region of the bay where silt-clay sediments are observed. In general, the same criteria apply to organic carbon, sulfide and other heavy metals, being higher in the inner part of the bay than in its oceanic region.

Based on ^{210}Pb-dated sediment cores, it is possible to conclude that, in the region under direct influence from the land-based sources, Hg concentrations in surface sediments have increased steadily during the last 80 years and confirm the concentration differences of maximum values observed when comparing the literature. This increment is probably due to the augmenting of emissions from diffuse sources associated with population growth in the region.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2018.08.053.

References

Belzile, N., Lang, C.Y., Chen, Y.W., Wang, M., 2008. The competitive role of organic carbon and dissolved sulfide in controlling the distribution of mercury in freshwater lake sediments. Sci. Total Environ. 405, 226–238.

Bratikic, A., Ogrinc, N., Kotnik, J., Faganeli, J., Zagar, D., Yano, S., Tada, A., Horvat, M., 2013. Mercury speciation driven by seasonal changes in a contaminates estuarine environment. Environ. Res. 125, 171–178.

Conselho Nacional do Meio Ambiente Resolução 454/2012. avaliable at. http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=693 (accessed in May 2018).

Cunha, C.L.N., Rosman, P.C.C., Ferreira, A.P., Monteiro, T.C.N., 2006. Hydrodynamics and water quality models applied to Sepetiba Bay. Cont. Shelf Res. 26, 1940–1953.

Fundação Estadual de Engenharia do Meio Ambiente (FEEMA), 2006. Baía de Sepetiba, Rios da Baixada da Baía de Sepetiba, Diagnóstico de Qualidade de Águas e Sedimentos. Fundação Ricardo Franco, Rio de Janeiro, RJ, Brazil.

Godoy, J.M., Moreira, I., Wanderley, W., Simões Filho, F.F.L., Mozeto, A.A., 1998. An alternative method for the determination of excess ^{210}Pb in sediments. Radiat. Prot. Dosim. 75, 111–115.

Lacerda, L.D., Molisani, M.M., 2006. Three decades of Cd and Zn contamination in Sepetiba bay, SE Brazil evidence from the mangrove oyster *Crassostrea rhizophorae*. Mar. Pollut. Bull. 52, 974–977.

Lacerda, L.D., Marins, R.V., Barcellos, C., Molisani, M., 2004. Sepetiba Bay: a case study on the environmental geochemistry of heavy metals in a subtropical coastal lagoon. In: Lacerda, L.D., Santelli, R.E., Duursma, E.K., Abrão, J.J. (Eds.), Environmental Geochemistry in Tropical and Subtropical Environments. Springer Verlag, Heidelberg, pp. 293–318.

Limaverde Filho, A.M., Campos, R.C., 1999. Redução Seletiva Aplicada à Especiação de Mercúrio em Peixes: Uma Adaptação do Método de Magos. Química Nova 22, 477–482.

Marins, R.V., Lacerda, L.D., Paraquetti, H.H.M., Paiva, E.C., Villas Boas, R.C., 1998. Geochemistry of mercury in sediments of a sub-tropical coastal lagoon, Sepetiba Bay, southeastern Brazil. Bull. Environ. Contam. Toxicol. 61, 57–64.

Marins, R.V., Paula Filho, F.J., Maia, S.R.R., Lacerda, L.D., Marques, W.S., 2004. Distribuição de mercúrio total como indicador de poluição urbana e industrial na costa brasileira, Quim. Nova 27, 763–770.

Molisani, M.M., Marins, R.V., Lacerda, L.D., 2004. Environmental changes in Sepetiba Bay, Brazil. Reg. Environ. Chang. 4, 17–27.

Molisani, M.M., Kjerfve, B., Lacerda, L.D., 2006. Water discharge and sediment load to Sepetiba Bay from an anthropogenically-altered drainage basin, SE Brazil. J. Hydrol. 331, 425–433.

Paraquetti, H.H.M., Ayres, G.A., Molisani, M.M., Lacerda, L.D., 2004. Mercury distribution, speciation and flux in the Sepetiba Bay tributaries, SE Brazil. Water Res. 38, 1439–1448.

Rezende, C.E., Pfeiffer, W.C., Martinelli, L.A., Tsamakis, E., Hedges, J.I., Keil, R.G., 2010. Lignin phenols used to infer organic matter sources to Sepetiba Bay – RJ, Brazil. Estuar. Coast. Shelf Sci. 87, 479–486.

Schartup, A.T., Balcon, P.H., Mason, R.P., 2014. Sediment-porewater partitioning, total sulfur, and methylmercury production in estuaries. Environ. Sci. Technol. 48, 954–960.

Veeck, L., Silva-Filho, E.V., Wasseman, J.C., Sella, S.M., Santos, I.R., Lacerda, L.D., 2007. Mercury distribution in sediments of a sub-tropical coastal lagoon, Sepetiba Bay, SE, Brazil. Geochim. Bras. 21, 50–57.