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Article

Atmospheric Deposition of Mercury over Sepetiba Bay, SE Brazil

***R.V. Marins*[a,b], *E.V. Silva Filho*[b] *and L.D Lacerda*[b]**

[a] *Centro de Tecnologia Mineral, CNPq, Ilha do Fundão, Rua 4, Quadra D, 21941-100 Rio de Janeiro - RJ, Brazil*

[b] *Dept. Geoquímica, Universidade Federal Fluminense, 24020-007 Niterói - RJ, Brazil*

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Através da amostragem anual da deposição atmosférica total sobre a Baía de Sepetiba, estimou-se a deposição atmosférica de mercúrio.

As concentrações de mercúrio nas amostras mensais variaram na faixa de 30 a 164 ng.L^{-1}, resultando em uma deposição total de 76 $\mu g.m^{-2}.ano^{-1}$. Esse valor encontra-se na mesma faixa dos resultados publicados para outras regiões industrializadas na Europa e América do Norte. Comparando-se esses valores à deposição total de mercúrio na Baía, estimada através da análise de testemunhos de sedimentos da área, o componente atmosférico é responsável por 54 a 84% da deposição total anual de mercúrio na baía. A solubilidade das diferentes espécies mercuriais na precipitação pluviométrica sugere que o mercúrio particulado é a principal forma de mercúrio na deposição total atmosférica.

Atmospheric deposition of mercury over Sepetiba Bay was estimated through collection of bulk precipitation during one year.

Mercury concentrations in monthly samples ranged from 30 ng.L-1 to 164 ng.L^{-1}, resulting in a total annual deposition of 76 $\mu g.m^{-2}.yr^{-1}$.This is in agreement with published results from other industrialized areas in Europe and North America. In comparison with the total mercury deposition in the bay, estimated through sediment core analysis, the atmospheric component is responsible for 54 to 84% of the total annual deposition of mercury in the bay. The solubility of different mercury species in rain water suggests that particulate Hg is the major form of this element in the bulk atmospheric deposition.

Keywords: *atmospheric deposition, mercury, SE Brazil*

Introduction

The state of Rio de Janeiro is the second most important industrial and urban area in Brazil, with about 15 million inhabitants living in the region of the city of Rio de Janeiro. In the last three decades industrial and urban expansion have been explosive, leading to a series of impacts on the regional environment. Sepetiba Bay, about 60 km south of the city and relatively pristine, shows the fastest growing industrialization and urbanization in the state of Rio de Janeiro, and significant environmental pressure is expected.

The lowlands of the eastern shore of Sepetiba Bay, with good transportation facilities, cheap and ample land, a good fresh water supply and a low population density, became an interesting area for industrial development, further facilitated by the building of large harbor facilities in the late 70's. The population of the bay has increased from 600,000 people in 1978 to 1.2 million, mostly concentrated along the northeastern shore as a result of industrial growth.

As a result of this fast and unplanned development, environmental contamination of the bay is now reaching alarming levels, and an accelerated increase is expected in the next few years, in direct conflict with the need for environmental conservation and large scale tourism with its economic benefits[1].

Presently, there are 400 industries, mostly pyrometallurgic, including two large steel plants, aluminum plants, a Cd-Zn smelter, and the "Casa da Moeda" where for about eight years gold was refined on a large scale. This industrial park is responsible for the input of trace metals into Sepetiba Bay. Although most metals reach the bay through

rivers, a significant input comes from atmospheric deposition[2].

Mercury in both inorganic as well as organic chemical forms is known to be widely distributed in the environment[3]. It can reach the coastal environment through many routes, such as river inputs, runoff and tides. However dry and wet atmospheric deposition is frequently the major route of Hg to coastal environments[4]. Atmospheric processes may also significantly affect the global distribution of Hg, and provide a means for Hg transfer between the continents and oceans[5].

There does not seem to be a single point-source of Hg in the Sepetiba Bay. Mercury sources are probably diffuse, coming from effluents from the metallurgic plants in the area, from the leaching of landfills, and from urban and rural runoff[6].

There are few studies dealing with the destiny of Hg in Sepetiba Bay. Three recent investigations[7,8,9] showed increasing Hg concentrations in sediment cores taken from the eastern shore of the bay, indicating a progressive Hg accumulation in the bottom sediments of the bay. Since sediment profiles may be strongly related to Hg loading rates[10], it is reasonable to advance increasing Hg inputs into Sepetiba Bay. Therefore, the objective of the present study is to quantify the bulk atmospheric deposition of Hg in Sepetiba Bay as a first step in quantifying the inputs of this heavy metal into the area, and evaluate its behavior and fate in the bay environment.

Materials and methods

Sepetiba Bay is a semi-enclosed body of water with an area of 447 km^2 and an average depth of 6 m, located at latitude 23° S and longitude 44° W. The region has a hot, humid tropical climate, with a mean annual precipitation ranging from 1,400 mm to 2,500 mm, depending on the location along the shore. Nine rivers draining the quaternary plain on the northeastern shore of the bay are responsible for almost the totality of freshwater inputs[11], reaching an annual flow of 7.6 million m^3. Therefore, annual atmospheric precipitation over Sepetiba Bay (0.5 to 10 x 10^7 $m^3.yr^{-1}$) equals and may even surpass the fluvial inputs[2,11], increasing the importance of atmosphere-derived pollutants, such as mercury.

All devices used for bulk precipitation sampling were cleaned using normal procedures for the analysis of trace metals. They were soaked in dilute HNO_3 and rinsed with metal-free water. The collection apparatus consisted of an acrylic funnels with an area of 0.25 m^2, connected to a polyethylene bottle by a high density plastic tube. The samplers were fixed on a roof *c.a.* 3 m above the soil surface, and at least 1.5 m above the roof surface, and were left open during the sampling intervals, thus collecting bulk (wet + dry) precipitation. This sampling procedure has been exaustively and successfully tested in Sepetiba Bay[2] and other coastal areas[12,13] for the collection of heavy metals from atmospheric deposition.

Sampling intervals range from 7 to 22 days depending on the intensity of the rains during one year, from August 1993 to August 1994. The samples from May, June and November were lost. Sampling points are located in Fig. 1.

After the measurements of the total volume collected, the samples were preserved by adding concentrated HNO_3, and were kept in Teflon bottles. The addition of concentrated HNO_3 prevents the loss of monomethyl mercury[14]. Also, this treatment transforms non-reactive forms of mercury into reactive forms, *i.e.*, Hg^{+2} [15].

To destroy any organo-mercury compounds we used bromine monochloride[16,17], adding ascorbic acid for the pre-reduction[18]. The technique with oxidation by bromine monochloride was tested[19] and showed better results than the traditional methodology with permanganate-persulfate oxidation. It is easier to use and requires smaller amounts of reagents, which can be readily purified, resulting in very low blanks.

The bromine monochloride method occasionally gave no or a very low signal response related to the generation of chlorine or bromine gas during treatment of the sample, which interferes with the collection of Hg on the gold collector of the detector apparatus. However, the analytical procedure[20] employed involved the pre-cleaning of the fluxes containing Hg on the gold collector, first with NaOH and then with water, preventing possible interferences caused by chlorine and bromine release.

Mercury compounds were reduced to Hg^0 by $SnCl_2$ in acid solution. Hg^0 was liberated from the solution by bubbling with Hg-free air. The mercury released was collected on Au amalgamation (one stage) and the measurements were carried out through cold vapor atomic absorption spectrometry.

Results and Discussions

The smallest concentrations of Hg in the atmosphere over the open ocean have been observed in the Southern

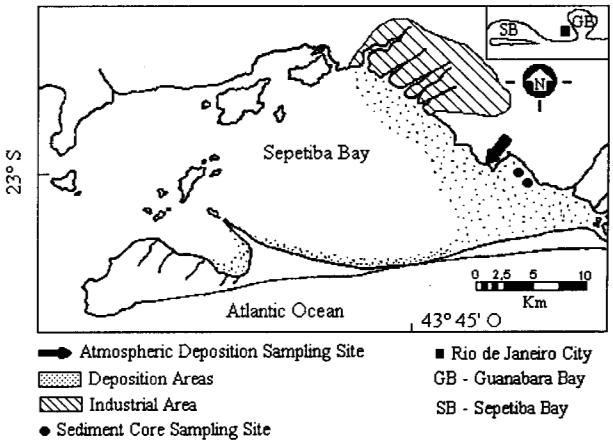

Figure 1. Location of sampling sites.

Hemisphere (~1.0 $ng.m^{-3}$), and the concentrations of Hg in rains in the open ocean are also quite low (~2.0 $ng.L^{-1}$)[5]. Over pristine continental areas[21] these concentrations range between 10 and 30 $ng.L^{-1}$.

Most of the near-surface atmospheric Hg species over both the open ocean and coastal regions are in the vapor phase[5] in most of the regions studied. However, Keeler *et al.*[22] denote that measurements of Hg associated with particles (Hg(p)) in the air have been limited over the past two decades. With the recent advances in instrumental sensitivity and the application of clean techniques, knowledge of Hg(p) concentrations and behavior has improved. Recent measurements of particulate Hg in several urban/industrial areas documented Hg on large particles and in concentrations similar to those of the vapor phase Hg ($ng.m^{-3}$)[22]. Therefore, bulk deposition sampling techniques are the best way of evaluating the total atmospheric contribution of Hg to a given system.

Mercury concentrations in bulk precipitation ranged from 30 to 164 $ng.L^{-1}$, with an average of 80 $ng.L^{-1}$. This mean concentration is 2 to 3 times higher than in pristine areas, and suggests a moderate contamination of the Sepetiba Bay atmosphere. The highest concentrations (up to 164 $ng.L^{-1}$) occurred in the summer (January and February), whereas, the lowest concentrations (30 $ng.L^{-1}$) occurred in the winter (July - September) (Fig. 2).

Higher deposition also occurred in the summer when the highest Hg concentrations and stronger and more frequent rains occur in the area, leading to a more efficient washout of the atmosphere[21]. Similar behavior has been reported for other metals in bulk precipitation over Sepetiba Bay[2].

We estimated the total anual mercury atmospheric deposition over Sepetiba Bay to be 76 $\mu g.m^{-2}.yr^{-1}$. This value is in agreement with those reported for moderately industrialized coastal areas (50 - 90 $\mu g.m^{-2}.yr^{-1}$)[4,23], and up to five times higher than those from remote continental sites[21] (15 $\mu g.m^{-2}.yr^{-1}$).

Previous results on mercury distribution in sediment cores from Sepetiba Bay[7,8], sampled in front of a mangrove-dominated shore (Fig. 1), permitted the estimation of the rates of mercury deposition in bottom sediments of this area. Sedimentation rates[24] were estimated based on excess ^{210}Pb distribution being 0.4 $cm.yr^{-1}$.

Undisturbed sediment profiles gave approximate mercury anthropogenic deposition rates[9] ranging from 90 to 140 $\mu g.m^{-2}.yr^{-1}$. This estimate is in the same range found for other industrialized coastal areas. Natural deposition rates estimated from pre-industrial sediment layers range[9] from 40 to 60 $\mu g.m^{-2}.yr^{-1}$.

Since sediment deposition patterns and metal concentrations vary spatially across the bay, we must consider this rate of mercury deposition only for the sampled area. However, it is a good indicator of the diffuse contamination by mercury in Sepetiba Bay, so we can compare them with bulk atmospheric deposition. Also, these two methods for the determination of Hg deposition are both integrators of the rates of deposition, and we can assume that they reduce the sampling "noise", mainly for the atmospheric deposition.

Comparing both atmospheric and sedimentation rates, atmospheric deposition can significantly contribute to the total Hg accumulation in the sediments in the bay. This

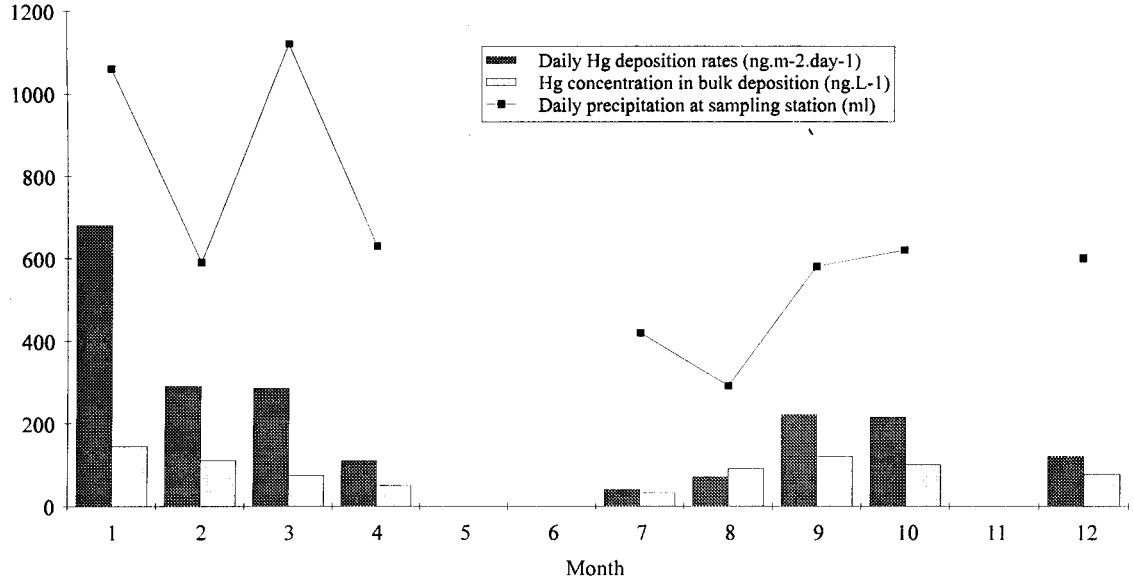

Figure 2. Seasonal variation in Hg concentrations in bulk deposition, daily Hg deposition rates and daily bulk precipitation, in Sepetiba Bay, Rio de Janeiro.

contribution can range from 54 to 84%, being mostly anthropogenic in origin. In a similar study in the Gulf of St. Lawrence, atmospheric deposition was also compared with the total accumulation in the sediments. The authors also found atmospheric deposition to be responsible for over 60% of the total Hg accumulation in the gulf sediments[4].

Other information concerning the nature and behavior of Hg in the environment in Sepetiba Bay could be obtained if the vapor and particulate species could be identified and quantified as well as the chemical species making up the vapor phase. Elemental mercury is very insoluble in both fresh and salt water. For example, the Hg^0 concentration in rainwater in equilibrium with an atmosphere containing 1.5 $ng.m^{-3}$ at 20 °C would be 5 x 10^{-12} $g.L^{-1}$, suggesting that mercury present in rain would primarily reflect the particulate Hg that is washed out of the atmosphere[5]. If this is true for Sepetiba Bay, and considering that the techniques used are not the best for sampling volatile Hg, based on the values of mercury in bulk deposition obtained over Sepetiba Bay, we can predict that the greater portion of the mercury inputs to Sepetiba Bay is from anthropogenic sources, and that particulate mercury is being washed and deposited in the bay. Our results indicate that even considering the absence of significant point sources of mercury in Sepetiba Bay, it is necessary to establish a system of control for mercury emission into the bay, since diffuse sources may significantly increase mercury inputs in the region.

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References

1. Lacerda, L.D.; Koudstaal, R.; Blower, B.T.; Pfeiffer, W.C. *The Sepetiba Bay Management Study*; IFIAS Research Program in Coastal Management. International Federation of Institutes of Advanced Studies, Rio de Janeiro, 1988.
2. Pedlowiski, M.A.; Lacerda, L.D.; Ovalle, A.R.C.; Watts, P.P.R.; Silva Filho, E.V. *Ciênc. Cult.* **1991**, *43*, 380.
3. Schroeder,W.H. *Canadian Research.* **1981**, *May*, 33.
4. Gobeil, C.; Cossa, D. *Can. J. Fish. Aquat. Sci.* **1993**, *50*, 1794.
5. Fitzgerald, W.F.; Gill, G.A.; Hewitt, A.D. *Trace Metals In Seawater*; NATO Symposium Proceeding Series: NewYork, 1983; p 297
6. Marins, R.V.; Lacerda, L.D. Sources of Mercury to Sepetiba Bay, in preparation.
7. Quevauviller, P.; Donard, O.F.; Wasserman, J.C.; Martin, F.M.; Schneider, J. *Appl. Organometallic Chem.* **1992**, *6*, 221.
8. Wasserman, J.C. (pers. comm)
9. Lacerda, L.D.; Marins, R.V.; Gonçalves, G.O.; Paiva, E.C. *Proc. Intern. Conf. Biogeochemistry on Trace Metals*, Paris, **1995**; abstract.
10. Rasmussen, P.E. *Environ. Sci. Technol.* **1994**, *28*, 2233.
11. Watts, P.P.R. *Entradas Fluviais de Metais Pesados para a Baía de Sepetiba e seu Comportamento na Região Estuarina*; MSc. Thesis, Dept. Geoquímica, Univ. Fed. Fluminense: Niterói, 1990.
12. Vale, J.A.; Harrison, S.J.; Watts, C.D. *Changes in Fluxes in Estuaries*; Olsen & Olsen: Fredensborg, 1993; p 219.
13. Lacerda, L.D.; Barcellos, C. *Proc. Int. Symp. Perspect. Environ. Geochem. Trop. Countries*: Niterói, 1993; p 137.
14. Cossa, D.; Courau, P. *Appl. Organometallic Chemistry.* **1990**, *4*, 49.
15. Lindqvist, O.; Jernelöv, A.; Johanson, K.; Rodhe, H. *Mercury in the Swedish Environment - Global and Local Sources; Solna: Sweden*, 1984.
16. Nelson, L.A. *Environ. Sci. Technol.* **1979**, *28*, 2233.
17. Szakacs, O.; Lasztity, A.; Horvath, Z.S. *Anal. Chim. Acta* **1980**, *121*, 219.
18. Krogmann, D. *Optimierung der Ultraspurenanalytik für Quecksilber inn Meerwasser*; MSc. Thesis, Fachhochschule, Hamburg, 1993.
19. Bloom, N.S.; Crecilius, E.A. *Mar. Chem.* **1983**, *14*, 49.
20. Marins, R.V.; Gonçalves, G.O.; Silva Filho, E.V.; Paiva, E.C. *Proc. VIII Enc. Nac. Química Analítica*, Belo Horizonte, 1995; abstract.
21. Glass, G.E.; Sorensen, J.A.; Schmidt, K.W.; Rapp Jr., G.R.; Yap, D.; Fraser, D. *Water, Air & Soil Pollut.* **1991**, *56*, 235.
22. Keeler, G.J. *Proceedings of Int. Conf. on Mercury as a Global Pollutant,* Whilster, Canada, **1994**; abstract.
23. Mason, R.P.; Morel, F.M.M. *Proc. Int. Symp. Perspect. Environ. Geochem. Trop. Countries*, Niterói, **1993**; 409.
24. Patchineelan, S.R., pers. comm.

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