

Mercury Concentrations in Bulk Atmospheric Deposition over the Coast of Rio de Janeiro, Southeast, Brazil

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As concentrações totais de Hg foram medidas em amostras de deposição atmosférica total coletadas em três regiões costeiras do Estado do Rio de Janeiro, sudeste do Brasil entre Outubro de 1998 e Dezembro de 1999. Amostras foram coletadas em Campos dos Goytacazes, área agrícola no norte do estado, em Niterói, região urbanizada e industrializada, e em Itacuruçá, um pólo turístico no litoral sul. As concentrações de Hg em Campos apresentaram uma média de 0,51 ng L⁻¹, variando de 0,07 a 1,01 ng L⁻¹, e mostraram uma tendência sazonal aparentemente afetada pela queima da cana de açúcar no inverno. Em Niterói, foram medidas as maiores concentrações, com média de 0,73 ng L⁻¹ e variando de 0,06 a 2,95 ng L⁻¹, sem padrão de distribuição sazonal definido. Em Itacuruçá, 35% das amostras apresentaram concentrações menores que o limite de detecção do método (<0,02 ng L⁻¹), com média de 0,24 ng L⁻¹ e variando entre <0,02 a 1,04 ng L⁻¹.

Total Hg concentrations were measured in bulk atmospheric deposition from three sampling stations along the Rio de Janeiro State coast, Southeast, Brazil, from October 1998 to December 1999. Samples were collected at Campos dos Goytacazes, an agriculture center at the North coast; Niterói, an industrialized metropolitan area and at Itacuruçá, a tourist town at the South. Concentrations at Campos average 0.51 ng L⁻¹, ranging from 0.07 to 1.01 ng L⁻¹, and showed a seasonal trend, probably affected by burning of sugar cane plantations in winter. At Niterói, concentrations were highest, averaging 0.73 ng L⁻¹ and ranging from 0.06 to 2.95 ng L⁻¹. No pattern of temporal variation was observed and concentration peaks are probably related to industrial emissions. At Itacuruçá, Hg concentrations were below the detection limit of the method (0.02 ng L⁻¹) in 35% of the samples, with an average of 0.24 ng L⁻¹ and ranging from <0.02 to 1.04 ng L⁻¹.

Keywords: mercury, rain water, atmospheric deposition, Rio de Janeiro coastal region

Introduction

Atmospheric deposition is a significant source of Hg to surface environments. The large residence time of Hg in the atmosphere results in large-scale transport and in the input of significant amounts of Hg to remote sites through atmospheric deposition.¹ Since the consume of contaminated aquatic biota is the major pathway of Hg exposure to humans and Hg levels in these organisms are directly linked to bulk atmospheric deposition rates,^{2,3} knowing Hg concentrations in bulk atmospheric deposition is a key step

to model the environmental dynamics and forecast Hg contamination.

Data on Hg concentrations in bulk atmospheric deposition abound in the northern hemisphere, but very few studies were published in the southern hemisphere. The few examples are from areas close to industrial sites⁴ or from gold mining areas in the Amazon,^{5,6} which frequently show extreme values. A recent extensive survey by Silva Filho *et al.*,⁷ reported only on the particulate fraction of the atmospheric deposition, which has no direct correlation with contamination of aquatic food webs. Therefore we have designed this study to characterize the range of Hg concentrations in bulk atmospheric deposition over a gradient of landscapes, from a nearly pristine site,

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which can provide local background concentrations, an intensive agriculture region, to an industrialized metropolitan area. It was not the objective of the present work to study rates of deposition, since daily precipitation volume data do not exist for the sites. However, whenever volume data were available they were used to help interpret the variations in Hg concentrations and preliminary estimate deposition rates for these areas.

Sampling sites

Samples were collected in 3 coastal areas of Rio de Janeiro State (Figure 1). The Campos dos Goytacazes site is located at the northern coast in a region poorly industrialized but with extensive sugar cane agriculture, with annual yields from 4.6 to 8.8 million tons.⁸ Pre-harvest burning of sugar cane plantations occurs by the end of autumn to the end of the winter (May to October) during the dry season⁸ and may significantly contribute to atmospheric deposition. Precipitation events are due to cold fronts and average 1,000 mm per year. The Niterói site is located at the Universidade Federal Fluminense, downtown Niterói city, by the Guanabara Bay. The site is surrounded by Rio de Janeiro metropolitan area, which harbors about 14 million inhabitants and over 6,000 industries, including two large petrochemical plants, emitting heavy loads to the atmosphere. Precipitation events are also due to cold fronts and annual rainfall average 1,200 mm. The Itacuruçá site is located by Sepetiba Bay, but about 30 km upwind from the local industrial park, between the Serra do Mar Mountains and the Island of Itacuruçá, which allows the formation of intense orographic rains apart from the cold fronts. Annual rainfall can reach up to 2,300 mm.

Material and Methods

Two bulk deposition samplers were installed less than 10 km from the sea in all sites, at least 1.5 m from the soil or roof surface to avoid splash water to enter the samplers.

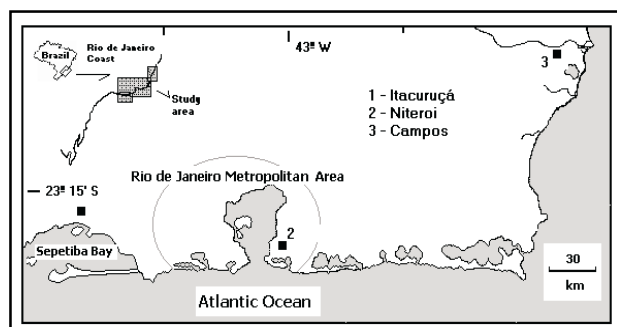


Figure 1. Map of the Rio de Janeiro coast showing sampling sites

Samplers were made of permanently open Teflon funnels and tubes and samples were collected in pre-cleaned Teflon bottles and frozen for transport. These bulk deposition samplers contain 100% of the wet deposition and whatever dry deposition collected in the funnels and is rinsed into the receiving bottle.⁹ We used un-acidified Teflon bottles deployed from 6 h to 28 days, depending on precipitation volume. An intensive study exercise on methods comparison for measuring Hg in rainfall¹⁰ showed no difference in Hg content of bulk atmospheric deposition collected in pre-acidified or un-acidified bulk deposition samples, during deployments of up to 35 days. Since our deployment periods were always less than the limit established by this study,¹⁰ contamination or loss of Hg due to this variable were unlikely.

Open collectors deployed for longer periods of time tend to collect relatively more dry-deposition than short-period deployments, and may result in systematically higher Hg concentrations.¹¹ By using relatively short deployment times our results show no relationship between deployment period and Hg concentrations (Figure 2), although it does underestimate the total Hg concentrations in the atmospheric deposition, by minimizing the effect of dry particle deposition. Also, evidence exists showing no difference between bulk and wet Hg concentrations and fluxes for short deployment periods, suggesting the small importance of the dry deposition component of the bulk data for short deployment periods.⁹

Sample volume ranged from a minimum of about 200 mL to over 2 L. In 60% of the samples more than one bottle was filled during deployment. We analyzed all bottles from any event separately and an average concentration for those sampling periods was recorded. Differences among bottles range widely, since the beginning of rain is frequently enriched relative to the end of the rain period.¹¹ Variation in Hg concentrations among bottles of a single event averaged 30%. All samples were immediately analyzed, in duplicate, after collection (within 48 h maximum).

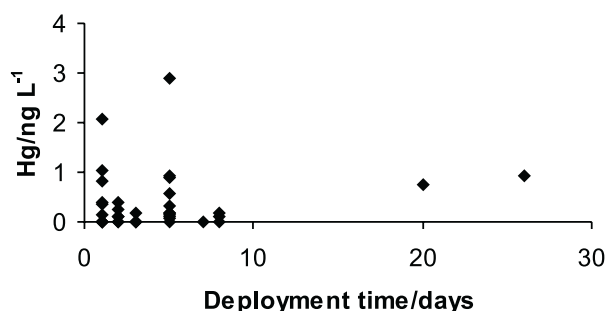


Figure 2. Relationship between mercury concentrations and deployment periods of samplers for all sampling sites along the coast of Rio de Janeiro State, Southeast, Brazil

Total Hg was determined after oxidation with 0.2 mL of a bromine monochloride solution (0.1 mL KBrO_3 1% m/v + 0.1 mL HCl 20% v/v). After oxidation, 0.1 mL of 1% m/v ascorbic acid solution was used to reduce the excess BrCl, this was followed by a reduction with 1.0 mL of acidic (2.6 mol L^{-1} HCl) 1.0% m/v SnCl_2 solution.⁴ The Hg^0 resultant from the reduction reaction 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 gold wool trap connected to the outlet of the reaction vessel. Two Au traps in the gas line stripped any Hg from the carrier gas. All connecting tubing was made of Teflon with glass-Teflon connections made of clean silicone tubing. Mercury determination was performed at a wavelength of 253.7 nm, in a Tekran Model 2500 Cold Vapor Atomic Fluorescence Spectrophotometer.¹² Under the operational conditions described, the analytical detection limit of the method, based on three standard deviations of the average Hg concentrations of the reagents blank, was 0.02 ng L^{-1} . All samples were analyzed in duplicate. Differences between duplicates remained below 15% for all samples. The extraction method used oxidizes all dissolved Hg in the sample but do not release Hg eventually present in deposited atmospheric particles, *i.e.* no digestions of samples were performed.

Results and Discussion

Table 1 summarizes the Hg concentrations measured in bulk atmospheric deposition collected in the three sites while Figure 3 shows its temporal variability. At the Itacuruçá site Hg concentrations were lowest with average concentrations of 0.24 ng L^{-1} ($n = 19$), ranging from a maximum concentration per event of 1.04 ng L^{-1} to a minimum of <0.02 ng L^{-1} . Maximum concentration in a single bottle reached 2.08 ng L^{-1} . At this site 35% of the samples showed Hg concentrations below the detection limit of the method. This is probably a result of the very short deployment times of this sampling resulting in very small effect of particle deposition. Since at this site sampling period was only of 3 months, no temporal distribution trend could be detected (Figure 3). Eventual changes in dominant wind direction from SW to NE may bring Hg from the Sepetiba Bay industrial park, and this

may be responsible for the two peaks observed in early November. Marins *et al.*⁴ showed very high Hg concentrations in bulk atmospheric deposition close to and downwind from the Sepetiba Bay industrial park and using long deployment times. They measured concentrations ranging from 30 to 164 ng L^{-1} closer to industrial point sources, and associated these high values with the washout of Hg-rich particles. This has also been shown to occur in urban centers close to gold dealer shops where gold smelting at high temperatures emits Hg-rich particles.^{5,6} Particulate emissions however, seldom spread too much long distance, as have been shown for many types of point sources.⁵ Therefore, at Itacuruçá, the position of the sampling site relative to winds and the dominance of orographic rains in the atmospheric deposition result in very low Hg concentrations.

At the Campos dos Goytacazes site, average concentrations were twice those measured at Itacuruçá (0.51 ng L^{-1} , $n = 15$). Maximum concentration per event reached 1.01 ng L^{-1} and minimum of 0.07 ng L^{-1} . Peak concentration in a single bottle reached 1.85 ng L^{-1} . The distribution of Hg concentrations suggests a seasonal trend, with higher concentrations occurring during the dry season, particularly from March to May and in August and September (Figure 3). During these samplings, bottles frequently presented soot and coal particles, suggesting an influence of the pre-harvest burning of the sugar cane plantations. No sample showed Hg concentrations below the detection limit of the method.

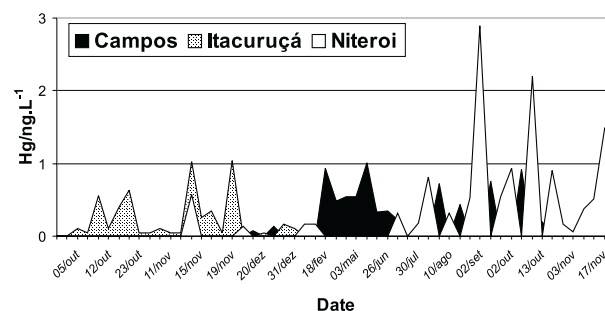


Figure 3. Mercury concentrations in bulk atmospheric deposition in three different sites along the coast of Rio de Janeiro State, Southeast, Brazil. Samples from Itacuruçá with concentrations below the detection limit are plotted as equal to the detection limit (0.02 ng L^{-1}), to avoid confusion with dates without sampling

Table 1. Summary of Hg concentrations (ng L^{-1}) in bulk precipitation from three sampling sites along the Rio de Janeiro coast, Southeast, Brazil

Site	Range of concentrations in individual bottles	Range of concentrations in deployment periods	Average concentration per deployment period
Itacuruçá	$<0.02 - 2.08$	$<0.02 - 1.04$	0.24
Campos	$<0.02 - 1.85$	$0.07 - 1.01$	0.51
Niterói	$0.06 - 4.3$	$0.06 - 2.95$	0.73

Sugar cane agriculture may contribute with atmospheric Hg emissions due to the burning of bagasse at sugar mills and pre-harvest burning in the field, typical of this type of agriculture. Also, during pre-harvest burning, significant emissions of Hg may happen from soils through vaporization,¹³ in particular in areas where organo-mercurials were used as fungicides in seedling protection, a common practice in Campos dos Goytacazes sugar cane agriculture until 1980, when it was banned by federal law.¹⁴

A comparable study in Florida everglades sugar cane area, where no Hg containing chemicals were ever used notwithstanding, showed that pre-harvest burning is the most significant source of Hg and that volatilization from soils is negligible.¹³

At Niterói, Hg concentrations were highest, with an event average of 0.73 ng L⁻¹. Maximum event concentrations reached 2.95 ng L⁻¹ and minimum of 0.06 ng L⁻¹. Peak concentration in individual bottles reached 4.3 ng L⁻¹ and no sample presented Hg concentrations below the detection limit of the method. No seasonal trend was observed, although high frequency of maximum concentration peaks occurred mostly between September and October (Figure 3). These peaks are probably associated with events of high atmospheric emissions from the industrial park of Rio de Janeiro metropolitan area. No significant point source of Hg exists in the region. However, many industries have Hg as a component of their atmospheric effluent, in particular oil refineries and iron and steel plants. Therefore Hg emissions are quite variable in time and space, being dependent on type of raw material used (*e.g.* iron ore *vs.* scrap metal in steel plants, or the origin of the oil burnt in a refinery). Thus seasonal patterns are frequently absent from this type of emission. Clearly, however, the concentrations obtained in Niterói show the influence of the industrial metropolitan area of Rio de Janeiro, with average values nearly 4 and 2 times higher than those found at Itacuruçá and Campos, respectively.

Table 2 compares the results found along the Rio de Janeiro coast with recent values reported in the literature for the northern hemisphere. Notwithstanding the relative high concentrations measured at Niterói, bulk atmospheric deposition along the coast of Rio de Janeiro shows much lower Hg concentrations than other coastal sites in the northern hemisphere (Table 2). Even considering peak bottle concentrations, our values are in the lower range of those reported for the northern hemisphere and are much lower than those reported for areas close to point sources of Hg. The lack of significant point sources of Hg and the strong influence of marine air masses over the sampling sites are probably the major reasons for this result.

As stated before, reliable daily precipitation volume data

for the sites are not available. Historical precipitation data for the regions where the sites were located, however, do exist and allow at least a preliminary estimate of the order of magnitude of the atmospheric Hg deposition, at least on a yearly basis. This is obviously an underestimation since for properly assessing Hg atmospheric deposition, a longer; at least one year-period of deployment would be necessary. Notwithstanding, taking into consideration this limiting aspects and considering average concentrations per deployment period (Table 1), bulk atmospheric deposition would range from about 0.4 $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ at the more pristine site of Itacuruçá to about 3.3 $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, at Niterói. As expected these values compare well with the lower range of wet deposition values for continental sites in the northern hemisphere during the 1900's decade,^{13,15-17} which ranged from about 5 to 11 $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, and present-day deposition estimated for remote sites in northern South America,¹⁸ but are at least one order of magnitude lower than values found close to point sources,^{4-6,19} where a significant contribution of dry deposition and washed out particles characteristically results in elevated bulk atmospheric deposition rates.

Regarding the possible contamination of receptor environments, the estimates of atmospheric deposition based on this limited set of data, shows that although fairly low compared to the northern hemisphere, deposition rates estimated here can be 2 to 3 times higher than background deposition over remote areas in the open South Atlantic Ocean, which typically range from 0.13 $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ around Antarctica to 4.1 $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ at mid latitudes^{20, 21} and twice pre-industrial values measured in the Amazon region,¹⁸ suggesting that at least for the agricultural region of Campos and the urban-industrial site at Niterói, notwithstanding being far from Hg point sources, surface ecosystems are already submitted to anomalous high deposition rates of Hg, exposing their biota to anomalous high Hg levels.

Table 2. Mercury concentrations in bulk atmospheric deposition over Rio de Janeiro State coast compared with other industrial and remote sites

Location	Hg (ng L ⁻¹)
Southern Sweden coast ¹⁶	10.6 - 13.8
Southern Florida, USA ¹³	15 - 23
Northwestern Ontario, Canada ¹⁷	0.95 - 9.31 (4.04)
Midwest USA ¹⁵	4.3 - 28.9 (14.3)
Oak Ridge, Tennessee, USA ¹¹	7.6 - 17.4 (11.5)
Wisconsin, USA ¹⁵	3.2 - 15.2 (10.5)
Cheasapeak bay, USA ¹⁹	<2.0 - 80 (17)
Northern South America ¹⁸	2.6 - 11.4
Over the Central Pacific Ocean ²⁰	<2.0
Itacuruçá, Northern Sepetiba Bay, Southern Rio de Janeiro coast	<0.02 - 2.08 (0.24)
Campos dos Goytacazes, Northern Rio de Janeiro coast	< 0.02 - 1.85 (0.51)
Niterói, metropolitan Rio de Janeiro	0.06 - 4.3 (0.73)

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