Atmospheric mercury deposition over Brazil during the past 30,000 years

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Atmospheric Hg deposition over Brazil is presented for the past 30,000 years as a tracer of the different natural and anthropogenic processes affecting the atmospheric environment of Brazil. During most of the prehistoric period, atmospheric deposition rates were rather constant with an average of about 2 μg m^{-2} yr^{-1}. Peak deposition, ranging from 4 to 6 μg m^{-2} yr^{-1}, occurred at least during two periods between 3,300 and 3,600 BP and between 8,500 to 12,000 BP, and during the last glacial maximum (LGM), at about 18,000 years BP. These periods were characterized by drier, colder climates with high frequency of forest fires, as shown by correlation with coal and pollen distribution data. During the colonial period Hg atmospheric deposition rates were much higher, about four times the prehistoric background and reached 6 to 8 μg m^{-2} yr^{-1}. These increasing Hg deposition rates can only be explained by the large Hg emissions in South and Central America from Spanish silver mines, which emitted to the continent's environment about 200,000 tons of Hg from 1580 to 1820. During the present century, Hg deposition rates varied according to the region of the country. In the Amazon region, where gold mining is the major source of Hg emission to the atmosphere, deposition rates increased continuously during the last 40 years, reaching 8 to 10 μg m^{-2} yr^{-1}. In the industrialized Southeast, Hg deposition was higher during the mid 1960s and 1970s, ranging from 80 to 130 μg m^{-2} yr^{-1}, but decreased to 20 to 30 μg m^{-2} yr^{-1} in the 1990s, due to the enforcement of emission control policies. However, where Hg emissions are mostly from urban, nonpoint sources, such as along the high urbanized coastal area, Hg deposition, although smaller, increased steadily from the 1940s reaching a maximum at surface sediment layers of about 40.0 μg m^{-2} yr^{-1}. The results presented suggest Hg as a reliable tracer of natural (paleoclimatic changes) and anthropogenic (industrial and mining emissions) processes able to affect the atmosphere in Brazil.

Foram estimadas as taxas de deposição atmosférica de Hg sobre o Brasil, durante os últimos 30.000 anos. As estimativas foram utilizadas como traçadores de processos naturais e antropogênicos que afetaram e afetam o ambiente atmosférico no país. Durante a maior parte do período pré-histórico, a deposição atmosférica de Hg foi bastante constante, variando em torno de 2 μg m^{-2} yr^{-1}. Dois picos de deposição ocorreram em períodos secos, caracterizados por maior freqüência de incêndios florestais, entre 3.300 e 3.600 BP e entre 8.500 e 12.000 BP, e durante o último máximo glacial, por volta de 18.000 anos BP. Nesses períodos as deposições variaram de 4 to 6 μg m^{-2} yr^{-1}. Durante o período colonial, a deposição atmosférica de Hg aumentou em até 4 vezes em relação à deposição pré-histórica, atingindo cerca de 6 a 8

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µg m^{-2} yr^{-1}. Este aumento só pode ser explicado pela imensa emissão de Hg (cerca de 200.000 toneladas) oriunda da mineração de prata nas América do Sul e Central pelos espanhóis, entre 1580 e 1820. Durante o presente século, a deposição de Hg variou de acordo com a região amostrada. Na Amazônia, onde a principal fonte de Hg é o garimpo de ouro, a deposição aumentou progressivamente durante os últimos 40 anos atingindo 8 to 10 µg Hg m^{-2} yr^{-1}. Na industrializada região sudeste, as deposições atingiram um máximo nos anos 1960 e 1970, variando de 80 to 150 µg m^{-2} yr^{-1}, mas decresceram para valores em torno de 20 a 30 µg m^{-2} yr^{-1} nos anos 1990, em razão de um controle mais efetivo das emissões industriais. Em áreas onde as emissões de Hg são devidas à fontes urbanas, não-pontuais, entretanto, a deposição de Hg, embora menor que na área sob influência industrial, aumentou progressivamente a partir dos anos 1940, atingindo um máximo na superfície dos sedimentos em torno de 40 µg m^{-2} yr^{-1}. Os resultados aqui apresentados sugerem o Hg como um traçador confiável de processos naturais (mudanças paleoclimáticas) e antropogênicos (industrialização e mineração), capazes de afetar a atmosfera no Brasil.

Mercury is a typical global scale contaminant, due to the dominance of the atmospheric transport, and the long residence time of this element in the atmosphere. Atmospheric deposition of Hg has demonstrated its potential to assess the impacts of natural and anthropogenic processes activities on the global Hg cycling (1,2,3). Atmospheric deposition of Hg is a key step in the biogeochemical cycle of this element, due to the dominant role of gaseous Hg species. Atmospheric deposition rates are linked to soil Hg concentrations (4), concentrations in remote lake waters and sediments (5), and the Hg content in freshwater (6) and marine fish (7). Thus estimating atmospheric Hg deposition rates and their variability, is fundamental to model Hg transport and accumulation in the environment.

Surveys on Hg concentrations in lake and peat bog sediment and ice cores have shown significant changes in prehistoric deposition rates during glacial periods, due to changes in aridity and temperatures, and consequent changes in soil cover (1,2,8). In historic times, deposition rates have shown an increase in concentrations relative to background values in many parts of the world, in particular because of mining operations (9). Most significant changes, however, occurred during the past 60 to 80 years, due to industrialization (3,10,11).

Estimates of the anthropogenic deposition of Hg in North America and Europe during the present century showed increasing deposition rates, with a peak of maximum deposition occurring in the 1960s and 1970s. More recently a relative decrease in deposition rates is observed, due to emission control policies implemented in the industrialized nations in the last two decades (11,12,13). In general, preindustrial atmospheric Hg deposition in remote areas of the northern hemisphere ranges from 5 to 10 µg m^{-2} yr^{-1}, whereas present-day rates range from 10 to 25 µg m^{-2} yr^{-1}, although during the peak deposition in the 1960s and 1970s it reached over 100 µg m^{-2} yr^{-1} (5,11,14). Up to now, however, no consistent data are available for South America, notwithstanding its significant anthropogenic Hg contribution to the atmosphere, in particular from Brazil, the largest and most industrialized country of this subcontinent.

Natural emissions of Hg in Brazil are most probably very small, since no volcanoes or significant Hg ore deposits exist in the country. Therefore, natural emissions are solely from revolatilization of deposited Hg from soils and waters, from long-range atmospheric transport. This reemission of deposited Hg is highly influenced by climatic changes and changes in land use (1,2,15,16).

Anthropogenic emissions of Hg in Brazil are due to the accelerated industrialization of the country after the Second World War, particularly in the southeast. More recently, large amounts of Hg are being emitted into the Amazon region due to gold mining, but most of the resultant atmospheric deposition is believed to occur in the Amazon region itself (17,18). Monitoring data from local environmental agencies and a few academic studies, have detected a decrease in Hg concentrations in fish and estuarine sediments in localized, highly polluted areas in the southeast, generally believed to reflect the implementation of recent emission control polices. However, bulk atmospheric deposition data in these areas still show relatively large numbers (> 70 µg m^{-2} yr^{-1}) (19).

Changes in atmospheric Hg deposition rates are both due to natural and anthropogenic causes. Among the natural causes, climatic changes, volcanic emissions, and changing the vegetation cover are the major factors affecting deposition rates (2,20). Among the anthropogenic causes, mining and industrialization, and further emission control policies, changes in soil uses and technological changes, are among the most important controllers of deposition rates (3,9,15,16, 18,21,22). Therefore the study of atmospheric Hg deposition rates through time, may also be used as a tracer of natural and human introduced changes affecting the atmospheric environment of a given region. In this context, we present here the first estimates of atmospheric Hg deposition over Brazil during the past 30,000 years, in order to characterize the different sources of Hg emission variability during this period, and comparing with similar historical data from the northern hemisphere.

Recording past atmospheric Hg deposition

Past atmospheric Hg deposition rates may be recorded in tree rings, peat bog deposits and lake sediments. These compartments may be used according to the objectives of a given research. Tree rings are accurate in temperate climates, but difficult to use in the tropics. Also, since trees have a relatively short lifespan, records are restricted to times of decades to a few centuries. Ombrotrophic bogs, those receiving water and materials only from the atmosphere, can record deposition over thousands of years (2,23,24). However, water table variation may cause postdepositional move-

ment of Hg (24). Also, the fast growing rate of peat, makes the sampling of long cores, frequently many meters long necessary, in order to record prehistorical deposition, which may prove to be of difficult logistics. Lake sediment cores are in general the easiest way of recording past atmospheric Hg deposition. However, some characteristics must be achieved in order to fully interpret results from this type of samples. Proper environments for recording past atmospheric deposition rates, are those where the basin area to lake surface ratio is very small, as in headwater lakes, thus decreasing the importance of input from basins, which may be of only local scale. Lakes are to be located in remote sites, in order to avoid direct inputs of trace metals from point sources. Such groups of lakes are not frequent. In general the remoteness of the site creates additional logistic problems (23,24). Also, with the described above characteristics, these groups of lakes characteristically show very low sedimentation rates, of the order of 0.1 to 0.01 cm yr^{-1}, decreasing the temporal resolution obtained from cores. Notwithstanding this, remote headwater lakes sediment cores are the best material to analyze past deposition rates of Hg.

Taking the above considerations into account, we studied five lakes, three in the Amazon region and two in the southeast (Fig.1) (25), which presented most of the above characteristics allowing the interpretation of deposition rates based on careful Hg analysis (26) and dating of sediment cores (27).

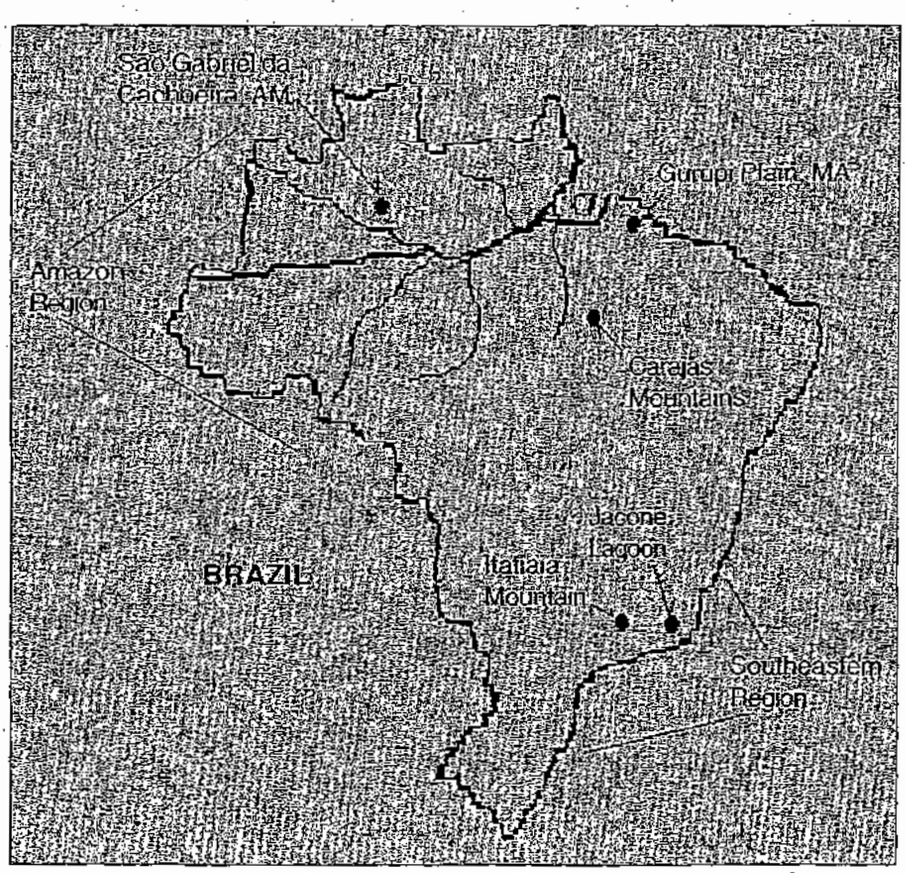

Figure 1. Map showing location of the studied lakes in Brazil.

Atmospheric Hg deposition over southeastern Brazil during the present century

Mercury deposition rates from Itatiaia and Jaconé cores are presented in Figure 2. At Itatiaia, Hg deposition rates ranged from a relatively constant value, of 36 ± 4 μg m^{-2} yr^{-1}, from 1910 to 1940, increased thereafter following the industrialization of the Paraíba do Sul river valley, and reached a maximum deposition peak of approximately 120 μg m^{-2} yr^{-1} in the 1960s. Hg deposition decreased from the late 1970s to the present, to values ranging from 15 to 30 μg m^{-2} yr^{-1}, at the top of the core. This decrease probably results from emission control measurements implemented by that time, in particular the banning of Hg-containing agrochemicals and changing chlor-alkali production plant technology, which has significantly reduced industrial Hg emissions in Brazil (21,28,29). The 5 to 6-fold decrease in Hg deposition rates observed in the superficial sediments of Itatiaia lake, compares well with the estimated decrease in industrial Hg emissions from about 150 tons in 1979, to approximately 30 tons in 1995 (17,21,28). This decrease is also in agreement with decreasing Hg concentrations observed in freshwater fish from São Paulo state rivers (18).

The temporal variation in Hg deposition rates observed in the Itatiaia cores is similar to those reported in different industrial regions of the northern hemisphere, which also reported peak deposition occurring in the 1960s or 1970s (30,31). Also, peak depositions in the Itatiaia lake compare well with those reported for remote lakes in Midwest USA (5) and with the average of 135 μg m^{-2} yr^{-1} Hg deposition estimated for the Great Lakes (11). However, preindustrial Hg depositions are from 3 to 6 times higher than those reported from remote areas in the northern hemisphere, which range from 5 to 10 μg m^{-2} yr^{-1} (5,11). Emissions from gold and silver mining during the previous three centuries, which amounted to nearly 200,000 tons in Latin America, with an average annual emissions of 316 tons (9), may have influenced the magnitude of preindustrial Hg deposition observed in the Itatiaia mountains. Preliminary evidence of the influence of the colonial mining on Hg deposition rates in South America, has already been reported, at least for the Amazon region (18).

Alternatively, atmospheric Hg deposition in many regions of the northern hemisphere started to increase by 1880 and was relatively high from 1900 to 1940, frequently reaching deposition rates higher than

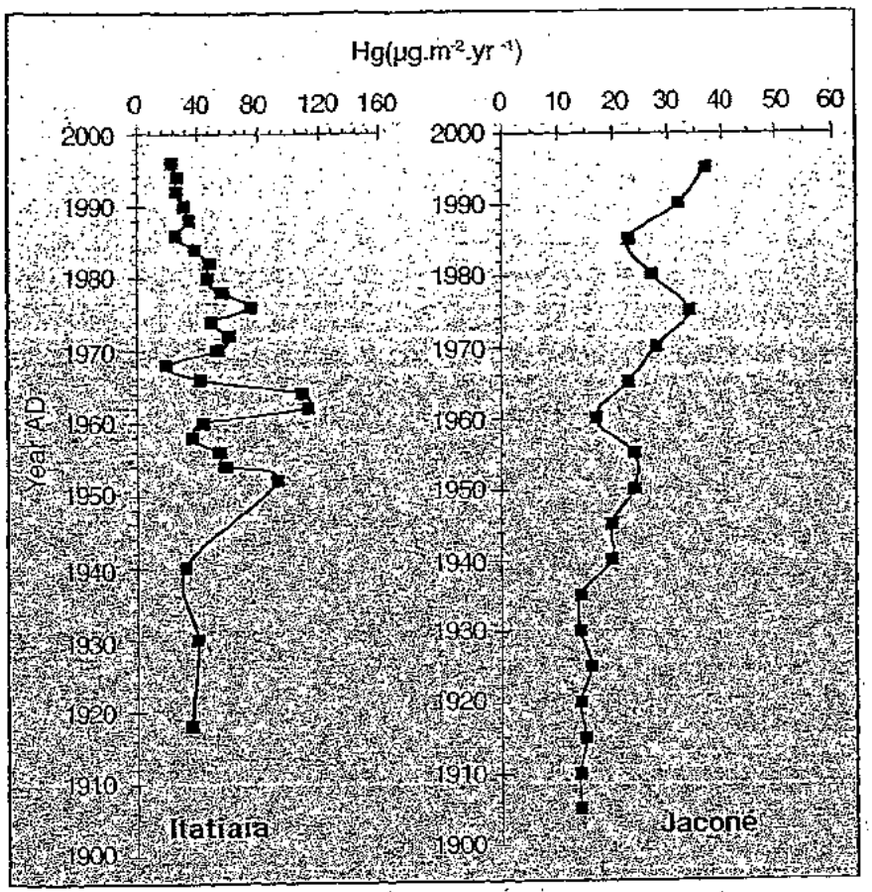

Figure 2. Mercury deposition rate distribution along sediment cores from southeastern Brazil, at Itatiaia mountains, SW Rio de Janeiro and Jaconé lagoon, SE coast of Rio de Janeiro. Data are average values of two replicates from two cores.

Table 1. Reported pre-cal. (1990s) Hg deposition rates from diverse remote, industrial, urban, affected areas of the world, compared to Brazilian data (μg m⁻² yr⁻¹).

Site	Region	Hg deposition	Reference
North Sea	remote	10-30	14
Scandinavia	remote	10-30	11
Northern Minnesota, USA	remote	10.4-15.4	30
Lake Michigan, USA	remote	12.0	31
Rural, Mid-West USA	remote	12	31
Upper Mid-W, USA	remote	5.8-8.3	32
Mid-continental, USA	remote	7	32
Norway	remote	3-30	33
Finland	remote	2-50	33
Caracas mountains	remote	17	This study
Itatiaia mountains	remote	15-20	This study
Southern USA	industrialized	6-50	34
Sepetiba Bay, Brazil	industrialized	5	15
Finland	industrialized	170	34
Denmark	industrialized	30-700	35
Poconé, Central Brazil	Au mining operation	90-120	36
Poconé, Central Brazil	Au mining operation	62-721	37
Peñudo Vello, Spain	Hg mining operation	26.1-75.7	2
Jaconé, SE Brazil	metropolitan	23-37	This study
Peñudo Vello, Spain	Holocene	1.6-8	2
Amazon	Holocene	1.7-5.6	This study

30 μg m^{-2} y^{-1} (5) and even surpassing 100 μg m^{-2} y^{-1} (10,11). Therefore, some Hg from the northern hemisphere industrial revolution may have eventually reached the southern hemisphere, in a manner similar to Pb occurrence in the Antarctic and Arctic ice cores (32,33). Unfortunately, the scarcity of data does not allow further discussion and better coring is needed to further discuss preindustrial atmospheric Hg deposition in the region, but transhemisphere transport of Hg and/or influence of colonial gold and silver mining cannot be ruled out.

Present-day average atmospheric Hg deposition measured in the Itatiaia mountains (15-30 μg m^{-2} y^{-1}), however, are similar to recent average deposition rates reported for North America (12,14,31,34) and from northern Europe (11,35,36,37), which ranges from 9 to 30 μg m^{-2} yr^{-1} (Table 1). Considering the area affected by the industrial emissions, these deposition rates are in agreement with emissions from industrial sources in southeastern Brazil (17), although being much lower than those measured in areas receiving direct atmospheric effluents from industrial sources in this region of Brazil, which reach up to 76 μg m^{-2} yr^{-1} (19).

Jaconé lagoon presented a different Hg deposition rate pattern than Itatiaia. Like in Itatiaia, Hg deposition rates were constant and lower from the early 1900s to the 1930s, ranging from 14 to 23 μg m^{-2} yr^{-1}. After this period however, deposition rates started to present a significant increase from the 1940s, and showed a peak of maximum deposition of about 34 μg m^{-2} yr^{-1} during the 1970s. However, contrary to the industry influenced Itatiaia site, deposition rates continue to increase in more recent sediments, reaching a maximum at the surface layer of the core, corresponding to about 40 μg m^{-2} yr^{-1}, in the late 1990s. Major sources of Hg in this lagoon is from nonpoint sources, mostly of urban origin. There are no industrial sources of Hg in the vicinities of Jaconé lagoon. It has been shown (38) that Hg concentrations in the coastal lagoons of Rio de Janeiro, including Jaconé, are directly related to inputs from metropolitan areas, which have witnessed an enormous

growth during the last two decades. Control policies to reduce heavy metal pollution, including Hg, in Brazil have been applied only for industrial point sources. Urban, nonpoint sources of trace metals have been totally neglected by environmental authorities, resulting in a continuous increase in their emissions (17,21,28). This may explain the contrasting behavior of the two areas. In Sepetiba bay, also affected by metropolitan development, the same pattern has been reported with increasing Hg deposition in recent years due to nonpoint sources (19).

Atmospheric Hg deposition over northern Brazil during prehistoric times

The results from the lake cores from Maranhão state and São Gabriel da Cachoeira (Fig. 3) present some difficulties of interpretation. The very small sedimentation rates observed in the lakes result in poor temporal resolution in most cores, which hampers the interpretation of Hg deposition rates during the past 1,000 years for the majority of the cores sampled. However, a good evaluation of Hg deposition during the period between 1,000 to 30,000 years BP can be drawn. Figure 3 shows Hg deposition in the three areas during the Holocene, between 30,000 and 1,000 years BP. Deposition rates are rather constant regardless of the area studied. The three regions (Carajás, São Gabriel da Cachoeira and Maranhão) presented average Hg deposition ranging between 1.7 and 2.6 $\mu g\ m^{-2}\ yr^{-1}$, and this is, most probably, the background deposition for the entire Amazon region. Interesting to note is that these values are from two to four times lower than the reported deposition in the northern hemisphere during the same period (2). Large land masses relative to sea and larger Hg deposits in the northern hemisphere relative to the southern hemisphere probably explain these results.

During the prehistoric period covered by the cores, peaks of Hg deposition rates, ranging from 4.0 to 6.0 μg Hg $m^{-2}\ yr^{-1}$, occurred at least during two periods between 3,300 and 3,600 BP, at the Maranhão site, and between 8,500 to 12,000 BP, and during the last glacial maximum (LGM), at about 18,000 years BP, at the São Gabriel da Cachoeira sites. These periods were characterized by drier, colder climates with higher frequency of forest fires, as shown by coal and pollen distribution data (39-43). Forest fires are an important source of Hg in the atmosphere in the Amazon region, due to enhanced reemission of deposited Hg, because of increasing albedo and microclimate at soil level, as well as by volatilizing Hg present in the biomass itself (15,16,22,44). Also, black carbon ashes may nucleate and reduce Hg residence time in the atmosphere, increasing its deposition (8,45) A good correlation between black carbon distribution and Hg deposition rates was obtained, at least for the Maranhão cores. Although still based on very few studies, increase in Hg deposition during dry periods in the Holocene has been reported, at least for Europe (2) and Antarctica (1). More consistent data from cores are needed to test for similarities among the different regions in the Brazilian Amazon.

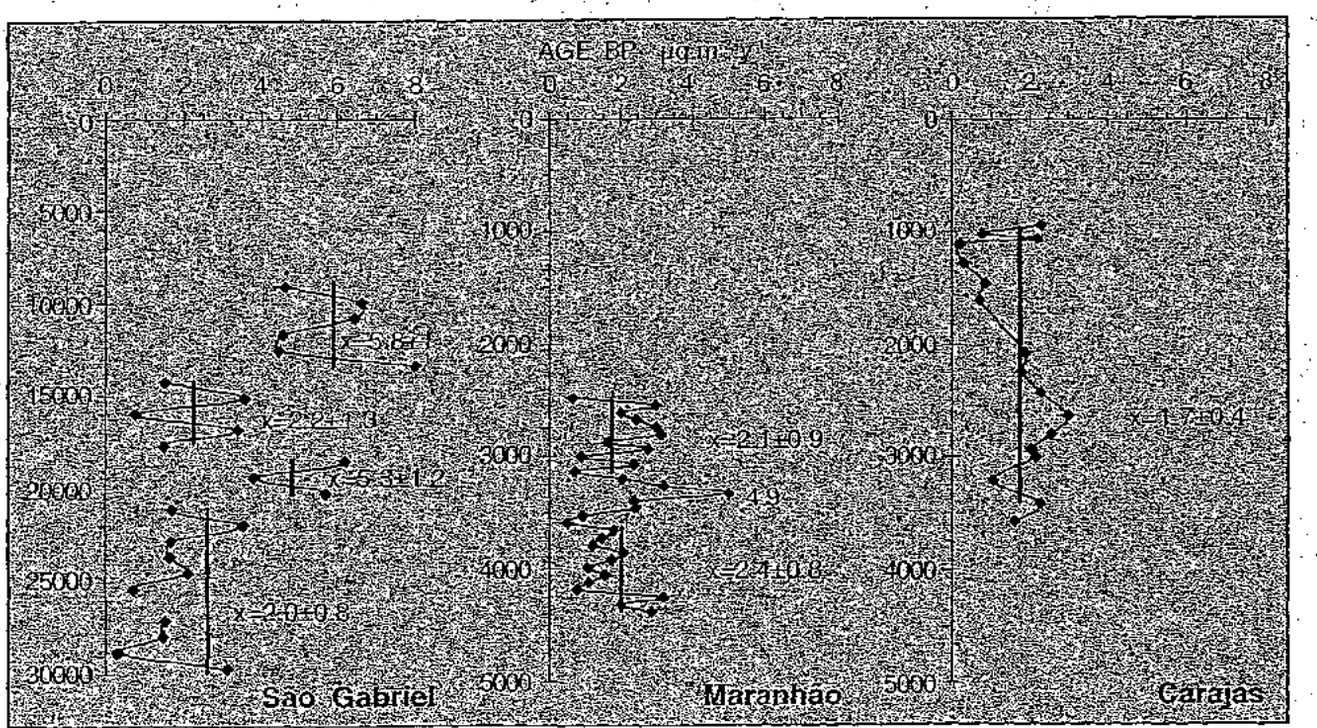

Figure 3. Mercury deposition rate distribution along sediment cores from there different regions of the Amazon region from 1,000 to 30,000 BP. Average of two samples from each area.

Atmospheric Hg deposition over northern Brazil during the past 1,000 years

Figure 4 shows Hg deposition rate distribution in a sediment core from Lake CSN93.3, in the Carajás mountains (39), the only core retrieved intact at 20 cm of depth, with sedimentation rates high enough for providing good temporal resolution. Recent estimates of Hg emissions from Spanish silver mines in colonial America (9) are also shown.

Comparing Hg distribution in Lake CSN93.3 with the estimated Hg emissions from the Spanish silver mines, the two curves match well. Mercury deposition in the profile increases from assumed background values, ranging from 0.7 to 2.6 μg m^{-2} yr^{-1} before 1600 AD, similar to the prehistorical background values discussed above, to about 7.0 to 9.0 μg m^{-2} yr^{-1} from 1700 to 1840, when the largest annual emissions of Hg from Spanish colonial silver mines occurred. Silver mining in South and Central America between AD 1580 to 1900 resulted in an average annual loss of Hg of 612 tons (with a range from 292 to 1,085 tons yr^{-1}) and totaled about 196,000 tons, whereas the total amount of Hg emitted to the environment in North America during last century's gold rush is reported to be 61,380 tons (9). Present-day gold mining in South America emits nearly 300 tons yr^{-1}, and totaled nearly 4,000 tons during the past 30 years (21).

Figure 5 shows estimated Hg deposition rates and sediment characteristics which may affect Hg distribution in Lake CSN93.3. Sediment is mostly composed of organic matter (Org-C = 46%) deposited under a constant and low regime at a rate of 0.03 cm yr^{-1}. Since the lakes have very small basins and no fluvial inputs, Hg deposition is mostly from the atmosphere. No relationship between distribution of fluxes of organic matter, chlorophyll derivatives and charcoal particles in the core, and Hg deposition rates was shown, strongly suggesting that variations in Hg deposition is due to variation in Hg inputs into the lake, rather than to recycling. Also, natural events, such as periods of more intense biomass burning, represented by the flux of charcoal particles, which seemed to have affected Hg deposition during the Holocene, or change in lake productivity, as indicated by organic matter and chlorophyll derivative fluxes, have no effect on Hg distribution. Therefore, we may assume that any Hg variability in the core is due to anthropogenic input (46).

Natural and man-made emissions into the atmosphere likely enter the global cycle if they are in the form of Hg(0), but deposit locally or regionally if they are oxidized (Hg(II)) (30), since from 65 to 85% of Hg emissions from gold and silver mining enter the atmosphere as Hg(0) – vapor (47). Emissions from the Spanish silver mines and lately the present Amazon gold rush are likely to reach at least a regional scale and may easily reach the entire Amazon basin (18). The small sedimentation rates of this Carajás lake, represent all present century Hg emissions, i.e. industrial and from gold mining, at the top 3 cm of the core. At this depth, Hg deposition ranges from 9 to 11 μg m^{-2} yr^{-1}, and this may be considered to be the present deposition for remote Amazon areas. Although this value is close to those observed in remote areas of the northern hemisphere, it is from 3 to 6 times higher than the local

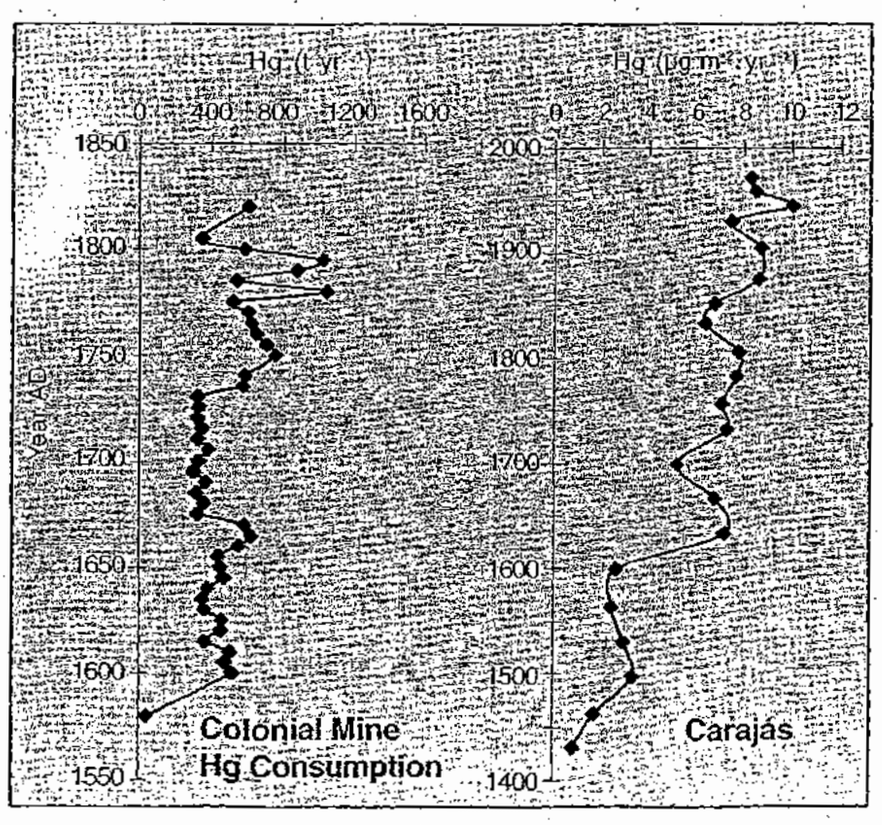

Figure 4. Mercury deposition rate distribution in sediment cores from Lake CSN93.3, at Carajás mountain, PA, compared to mercury consumption rates in Spanish colonial silver mines in Central and South America during the past three centuries. Modified from (9).

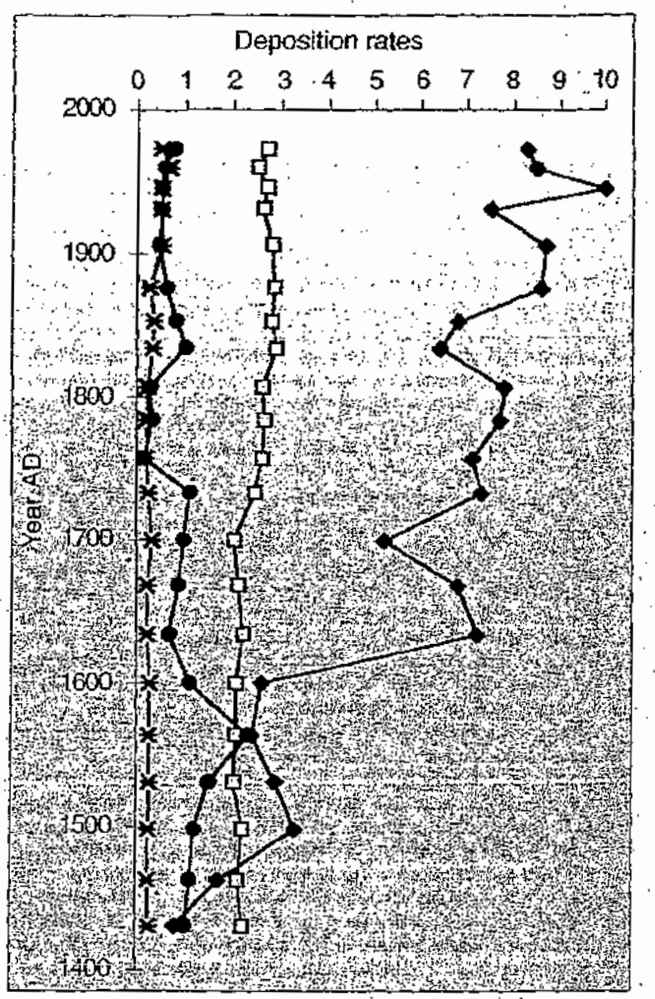

Figure 5. Mercury deposition rates distribution in μg m⁻² yr⁻¹ (◆) in sediment cores from Lake CSN93.3, at Carajás mountain, PA, compared to deposition rates of organic matter in kg m⁻² yr⁻¹ (×), of chlorophill derivatives in SPDU dm⁻² yr⁻¹ (□), and charcoal particles in 10^8 cm⁻² yr⁻¹ (●).

background, as shown for the prehistoric rates presented in Figure 3. However, since only one intact core was obtained, our results should be taken as preliminary, but since no other Hg source in South America is known from this period, we conclude that the variations found between 1600 AD to the beginning of the present century are, most probably, due to the colonial silver mines.

Comparing Hg deposition in Brazil

Prehistoric deposition of Hg over the Amazon, is somewhat lower than the values reported for the northern hemisphere (see Table 1), and also shown to be influenced by regional paleoclimatic changes. The mechanism involved, however, may include changes in vegetation cover and forest fires, rather than simply changes in overall temperature. Mercury deposition during the past millenium, notwithstanding the few results evaluated, seems to be strongly influenced by colonial mining activities. Presently, although with deposition rates similar to those reported for other remote areas in the northern hemisphere, the estimated Hg deposition rates are several times higher than the region's prehistoric background, suggesting the importance of anthropogenic sources even in such remote environments.

Atmospheric mercury deposition measured in industrialized Brazil, based on the cores collected at Itatiaia Mountains, provides a similar figure for South America as those in North America and Europe, with values showing a significant decrease after the 1970s peak, in response to specific emission control measurements implemented in the last 15 years, as shown in Table 1. When compared to areas affected by urbanization rather than by industrial development, although the two distribution trends showed similar peaks of maximum deposition and similar deposition during the beginning of the present century, they were completely different regarding the present deposition pattern. No significant decrease in Hg deposition was verified in the urban influenced area. Different source categories of Hg for the two areas (point industrial sources versus nonpoint urban sources) caused different deposition patterns, particularly during the last 2 decades. This highlights the importance of nonpoint sources of Hg as compared with industrial sources during the past 20 years, and reflects the effectiveness of control policies for industries, emphasizing the necessity of control policies for nonpoint sources of Hg. On the other hand, more data are needed to explain the relatively high preindustrial (before 1940) Hg deposition reported for southern Brazil. Both, the colonial silver and gold mining and the earlier industrial revolution in the northern hemisphere may prove to have influenced this deposition.

A final interesting analogy can be traced regarding the economic development of Brazil. Economists of the 1980s used the expression *Bel-India*, to characterize the unequal economic growth distribution between the industrialized south and southeast and the underdeveloped north and northeast regions of the country. The results presented on Hg deposition rates, clearly categorized the country into two different regions based on pollution sources and characteristics. In the industrialized southeast, Hg emissions are mostly of industrial origin, and following the same trend observed in industrialized nations, these sources have been submitted to an effective control, resulting in a strong reduction in emissions, as verified by the Itatiaia mountain results. On the other hand, increasing urbanization of the coast, resulted in increasing emission from nonpoint urban sources, as shown by the data from the Jaconé lagoon. In contrast, the north region, presents increasing Hg deposition as a result of increasing emission from an activity characterized by low technological investment, such as artisanal gold mining, and directly linked to the socioeconomic problems of the region's population. ■

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25. Studied lakes: Southeastern Brazil - Two areas were investigated for Hg atmospheric deposition in this region. The first located at the Itatiaia mountain chain, which receives emissions from industrial point sources located at the Paraíba do Sul river valley. The second, the Jaconé lagoon, is a brackish water coastal dune lagoon, northeast of Rio de Janeiro city, which receives, via atmosphere, emission from nonpoint urban sources, of the metropolitan area of Rio de Janeiro. The Parque Nacional de Itatiaia is a national park located in the Serra da Mantiqueira along the Paraíba do Sul river valley, between São Paulo and Rio de Janeiro cities (see Fig. 1). Most of the area is occupied by the Atlantic tropical rain forest formation, a high density forest dominating altitudes up to 1,500 m. Intermediate altitudes from 1,500 to 2,100 m, are dominated by clouded evergreen forest, substituted for highland prairies up to 2,800 m. In these prairies, peat bog lakes are common. Rainfall in the area is over 2,300 mm per year, which keeps lakes permanently flooded. The geology of the region is dominated by an alkaline rock complex, dominated by alkaline granites covered by latossols, cambisols and litolic soils, at higher altitudes. This geology is particularly poor in heavy metals and no occurrence of Hg-bearing rocks is known for the entire region. Thus any Hg reaching the lakes is mostly of atmospheric origin. Samples were collected in one of the most remote and permanently flooded peat bog lake of the highland prairies, located at approximately 2,700 m of altitude. Jaconé lagoon, is a small (1.5 km^2), shallow (1.2 m), euthrophic brackish water lagoon, located inside a dune field, approximately 30 km from Rio de Janeiro city. Sediments consist of autochthonous materials, mostly organic matter, over a base of quaternary sands. There is no significant fluvial input to this lagoon, and most Hg input is from the atmosphere. Samples were collected along the seaward margin of the lagoon, less influenced by eventual runoff from its basin (38). Northern Brazil - Three areas were investigated in this region: The lakes on the Carajás mountains, in Pará state, southeastern Amazon. The Six Lakes Hill at São Gabriel da Cachoeira, about 600 km north of Manaus, and the Gurupi plain on the coast of Maranhão state. The Carajás lakes studied are located at latitude 6°07'S and longitude 50°12'W and at latitude 6°22'S and longitude 50°25'W. Small depressions on a 750 m elevation plateau covered with hard and thick lateritic crust form the lakes. Lake basins are from 100 to 100 ha, covered with Amazonian rain forest and poorly developed steppe vegetation. Clastic inputs are rather small, and sediments are mostly of organic origin (about 50% organic carbon) (39). Sampling sites at São Gabriel da Cachoeira were located at the Hill of Six Lakes, at latitude 0°16'N and longitude 66°41'W, in the Amazon lowland of northwestern Brazil. The lake studied is surrounded by dense tropical rain forest, in a hot humid climate. All lakes of the Hill occupy small closed, steep-sided basins with flat or shelving bottoms under 7 to 15 m of water. Two twin cores of about 1.0 m length were collected, dating back to about 30,000 years. Details of lake stratigraphy and pollen register are published elsewhere (40). At the Maranhão site, samples were collected from lake Caço, latitude 2°58' and longitude 43°25'W, at approximately 100 km from the coast. The lake is located at an old dune field covered by *cerrado* vegetation, under tropical semihumid climate, influenced by the seasonal changes of the intertropical convergence zone
26. Sampling and analysis: Samples we collected in accordance with accepted protocols (31). From each lake, two cores were collected by hand, inserting acrylic tubes into the sediment to a depth of 50 cm. Each core was sliced into 1.0 cm layers to a depth of 23 cm and into 5.0 cm layers to the bottom of the core. Samples were stored in acid-clean plastic bags and frozen for transport. In the laboratory, the sediment samples were oven-dried at 50°C to constant weight. Approximately 1.0 g of the dried sample was digested in a closed system at 60-70°C for 1 h with a 50% aqua regia solution (4 mL HCl + 6 mL HNO_3 + 10 mL H_2O) in duplicate. The resulting extracts were centrifuged during 15 minutes at approximately 2,000 rpm. Mercury was analyzed through CVAAS, in a Bacharat Model spectrophotometer, with a detection limit, based on 3 times the value of 6 ng g^{-1} of the reagent blank. Simultaneously, we used the same analytical procedure to determine Hg in reference standards (NIST-USA, Buffalo river sediments, 60 ng g^{-1}). Our results gave 58 ± 6 ng g^{-1} (n = 15). Mercury concentrations and their variability as well as sediment density and sedimentation rates were used to estimate deposition rates. However, concentrations will not be discussed in the present paper. Most results are published and are discussed in detail elsewhere (38).

27. Dating: Subsamples from the two cores from the Itatiaia mountains and from the Jaconé lagoon were dated through the analysis of excess ^{210}Pb, at the Laboratory of Geochemistry of the University of Nice, France. Excess ^{210}Pb distributions in the cores were fairly consistent and gave an estimated sedimentation rate of 0.45 cm yr^{-1}, constant for at least the past 60 to 80 years, for the Itatiaia mountains and of 0.20 cm yr^{-1}, for the Jaconé lagoon. Details on dating methodology and statistics, and on ^{210}Pb activity and temporal distribution in the cores, are published elsewhere (48,49). Samples from Carajás mountains, Maranhão coast and São Gabriel da Cachoeira were dated using ^{14}C, since low sedimentation rates compared to the two other lakes in the Southeast, cover up to 30,000 years in the first 40 cm of the cores. Carbon isotope analysis were performed at the IRD laboratory at Bondy. Details of dating analysis may be found elsewhere (39). The main advantage of the Amazonian lakes is their low clastic input from restricted basins which results in slow organic sedimentation and Hg concentrations reach measurable values. On the other hand low sedimentation make an absolute chronology difficult. Short half-life radionuclides cannot be used and ^{14}C is the only way to correlate sediment depth with time using calibration curves (41,42). It has been recently shown that these calibration curves formerly established for the northern hemisphere can be used in the southern hemisphere (42). These curves are not completely linear and in particular show marked irregularities for the past 310 years. However, all Amazonian lakes studied until now presented a very constant sedimentation rate (41,42,43). Microscopic observations also revealed good preservation of thin horizontal layers indicating that vertical mixing is of little importance (42). Constant sediment characteristics and sedimentation rate counterbalance the uncertainties of ^{14}C calibration curves for the last 310 years, considering the whole set of dating for each core for the last 1,500 years. To avoid compaction influences, chronologies where elaborated by linear extrapolation based on constant accumulation rate (g cm^{-1} yr^{-1}) rather than sedimentation rate (cm yr^{-1}). Regarding the upper 30 cm, correlation coefficients for these curves were > 0.997 for all lakes cores. A twin core collected from Lake CSN93.3 (Lake CSN93.4) gave exactly the same radiocarbon results as that from the core where Hg was analyzed (39). Dating of sediment cores using ^{14}C concentration is, unfortunately, not the best for the recent past. In particular for those lakes in Maranhão and São Gabriel da Cachoeira, where sedimentation rates are very low. As a result, actual dates presented may vary at least 100 years for these lakes. Therefore, the past 1,000 years were only interpreted for the Carajás lakes
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