

## Changes in Lead and Mercury Atmospheric Deposition Due to Industrial Emissions in Southeastern Brazil

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Este estudo apresenta uma primeira estimativa de emissões de Pb e Hg para a Região Sudeste do Brasil, a região mais industrializada da América do Sul, durante o século XX, baseada na análise de perfis de sedimentos datados, coletados em lago ombrotófico da Serra do Itatiaia, na região do vale do Rio Paraíba do Sul, Estado do Rio de Janeiro. As concentrações médias de Pb ao longo dos perfis variaram de 40 a 180  $\mu\text{g g}^{-1}$ , enquanto que para Hg as concentrações variaram de 30 a 420  $\text{ng g}^{-1}$ . As concentrações de Hg se correlacionaram significativamente com as de Pb até os anos 80. A taxa de acumulação de Pb no período pré-industrial foi de cerca de  $8,0 \pm 2,0 \text{ mg m}^{-2} \text{ ano}^{-1}$ , com um máximo observado na superfície dos perfis variando de 40 a 80  $\text{mg m}^{-2} \text{ ano}^{-1}$ . Por outro lado, a taxa de acumulação de Hg foi de  $36 \pm 4 \mu\text{g m}^{-2} \text{ ano}^{-1}$ , entre 1910 e 1940, apresentando um máximo nos anos 60 de cerca de  $120 \mu\text{g m}^{-2} \text{ ano}^{-1}$ , e decrescendo novamente após os anos 70 para  $20 \mu\text{g m}^{-2} \text{ ano}^{-1}$ . O padrão de distribuição temporal da acumulação de Hg é similar aqueles relatados para diferentes regiões do hemisfério norte. Entretanto, as taxas de acumulação pré-industrial de Pb e Hg são de 3 a 6 vezes maiores que os valores relatados para o período pré-industrial no hemisfério norte. Emissões originadas na industrialização mais antiga no hemisfério norte podem ter influenciado a magnitude da acumulação pré-industrial na região em estudo, que se iniciou pelo menos 100 anos depois. No caso do Hg, a mineração de ouro e prata nos três séculos anteriores, pode também ter influenciado as taxas de acumulação pré-industrial estimadas neste estudo.

This study presents the first estimate of Pb and Hg loads to southeastern Brazil, the most industrialized region of South America, during the 20<sup>th</sup> century. This estimate was based on the analysis of dated ombrotrophic lake sediment cores, from the Itatiaia Mountains, at the Paraíba do Sul River valley region, in the Rio de Janeiro State. Average Pb concentrations along the cores ranged from 40 to 180  $\mu\text{g g}^{-1}$ , whereas for Hg, concentrations ranged from 30 to 420  $\text{ng g}^{-1}$ . Mercury concentrations correlated significantly with Pb concentrations up to the middle of the 1980's. Average regional pre-industrial (prior to 1940) Pb accumulation rate was  $8.0 \pm 2.0 \text{ mg m}^{-2} \text{ yr}^{-1}$ , with maximum at the surface of the cores ranging from 40 to 80  $\text{mg m}^{-2} \text{ yr}^{-1}$ . The average Hg deposition rate was  $36 \mu\text{g m}^{-2} \text{ yr}^{-1}$ , between 1910 and 1940. A maximum of  $120 \mu\text{g m}^{-2} \text{ yr}^{-1}$  was observed in the 1960's, with a further decrease after the late 1970's. The temporal Hg distribution pattern is similar to those reported in different regions of the northern hemisphere. However, regional pre-industrial Pb and Hg accumulation were from 3 to 6 times higher than those reported for the northern hemisphere. Emissions from the earlier industrialization of the northern hemisphere may have influenced the magnitude of regional pre-industrial Pb and Hg deposition in South America, where the industrialization started about 100 years latter. In the case of Hg, gold and silver mining during the previous three centuries, may have also affected regional pre-industrial values.

**Keywords:** mercury, lead, atmospheric deposition, ombrotrophic lakes, South America

### Introduction

Assessments of trace metals inputs to remote environments allow the characterization of their environmental impacts at the regional level. These

measurements have shown an increase in trace metals concentrations relatively to the background values in many parts of the world.<sup>1</sup> Surveys on trace metal concentrations in sediment cores have shown significant increases in the accumulation rates during the past 60 to 80 years. Debate still exists on the relative importance of the contribution of natural sources.<sup>2</sup> However, most authors agree with the

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anthropogenic origin as the main cause for the increase of trace metals deposition in remote areas, what is best demonstrated where independent information about inputs is available.

Mercury and lead are typical global scale contaminants, due to the dominance of the atmospheric transport, and the relatively long residence time of these elements in the atmosphere.<sup>1</sup> Estimates of the anthropogenic deposition of Pb and Hg in North America and Europe, showed increasing deposition rates during the 20<sup>th</sup> century. Maximum deposition occurred in the 1960's and 1970's, followed by a relative decrease, certainly due to emission control policies implemented in most industrialized nations in the last two decades. It was of particular importance the banning of Pb use in gasoline and the closing of chlor-alkali plants using Hg cells in the production process.<sup>3-5</sup>

In general, pre-industrial (prior to 1850) Pb and Hg atmospheric deposition in remote areas of the northern hemisphere range from 1 to 8 mg m<sup>-2</sup> yr<sup>-1</sup> and from 5 to 10 µg m<sup>-2</sup> yr<sup>-1</sup>, for Pb and Hg respectively. Maximum deposition occurred during the mid-seventies, reaching about 50 to 70 mg m<sup>-2</sup> yr<sup>-1</sup> and up to 100 µg m<sup>-2</sup> yr<sup>-1</sup>, for Pb and Hg respectively.<sup>3,6,7</sup> Present day rates estimated for those areas, however, are much lower *ca.* 4 mg m<sup>-2</sup> yr<sup>-1</sup> for Pb and ranging from 10 to 25 µg m<sup>-2</sup> yr<sup>-1</sup> for Hg.<sup>5,6,8,9</sup> Up to now, however, only few consistent data are available for South America, notwithstanding its significant anthropogenic contribution of trace metals release to the atmosphere, in particular from Brazil, the largest and most industrialized country of this sub-continent.<sup>10,11</sup> Few studies performed in the Brazilian Amazon, however, suggest that, at least for Hg, regional deposition rates are linked not only to regional, but also to global anthropogenic emissions.<sup>12</sup>

In Brazil, studies on local Pb emissions are available, but restricted to the southeastern coastal region<sup>13</sup> or to a single emission source, in particular related to energy generation.<sup>11,14</sup> These isolated data are not sufficient for interpreting changes in the regional deposition rates observed in remote sites. Studies on Pb accumulation rates are only available for areas receiving inputs from river, such as bays and lagoons and are not comparable to ombrotrophic water bodies.

Emissions of Hg in Brazil are better studied and consistent data exist at the regional scale. As for Pb, they are due to the accelerated industrialization of the country after World War II, particularly in the southeastern region. More recently, large amounts of Hg were emitted in the Amazon region due to gold mining, but most atmospheric deposition from this source is believed to occur in the Amazon region itself.<sup>15,16</sup> Monitoring data from local

environmental agencies and some few academic studies, have detected a decrease in Hg concentrations in fish and estuarine sediments in some highly polluted areas in the southeast. This decrease is generally believed to reflect the implementation of recent emission control policies,<sup>16,17</sup> although, bulk atmospheric deposition data from industrialized areas still show relatively large numbers (*ca.* 76 µg m<sup>-2</sup> yr<sup>-1</sup>).<sup>18</sup>

Available estimates industrial annual emissions of Hg in Central and South America was first published by Pirrone *et al.*<sup>10</sup> and reach 73 tons, but this is most probably an underestimation. Brazil imports all its Hg from other countries, and the origin and fate of imported Hg have to be declared to the Brazilian authorities. Therefore, very accurate information exists for Hg industrial uses in Brazil,<sup>19</sup> and this information contradicts the suggested<sup>10</sup> emissions. Industrial annual consumption of Hg in Brazil presented a maximum of 147 t in 1980, ranging from 110 to 147 t yr<sup>-1</sup> during the 1970's.<sup>19,20</sup> From 1980 onward, a decrease in industrial uses of Hg was observed in Brazil, which dropped to an annual average consume of about 70 t by 1989.<sup>19,20</sup> Nearly 80% of this amount is used in the southeast. This consume of Hg in Brazil resulted in annual industrial emissions to the atmosphere, estimated by emission factor statistics, of about 38 t, approximately 89% of them emitted in the southeastern region. Today, annual emissions from the Brazilian industrial park is even smaller<sup>11</sup> ranging from 16 to 25 t yr<sup>-1</sup>.

Gold mining is the major source of Hg to the atmosphere in Brazil. During its peak in the late 1980's, this activity contributed with about 110 t yr<sup>-1</sup>, nearly 65% of it to the atmosphere.<sup>15,20,21</sup> Today, gold mining is much reduced due to the exhaustion of easily mined deposits, but still contributes with about 31 t yr<sup>-1</sup>, about 20 t yr<sup>-1</sup> to the atmosphere.<sup>22</sup> However, the few data on Hg atmospheric deposition due to gold mining have been estimated for the Amazon only, where this activity is largely concentrated.<sup>15,23,24</sup>

The present study estimates the Pb and Hg atmospheric deposition rates in Southeastern Brazil based on the accumulation rates determined in dated sediment cores, collected in high altitude ombrotrophic lakes located at the Paraíba do Sul River valley, the most industrialized areas in Brazil.

## Material and Methods

### Study site

The Itatiaia National Park is located at the Serra da Mantiqueira, along the Paraíba do Sul River valley,

between the São Paulo and Rio de Janeiro cities (Figure 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 by highland prairies up to 2,800 m. In these prairies, ombrotrophic lakes are common. Rainfall in the area is over 2,300 mm per year, which keeps lakes permanently flooded. An alkaline rock complex dominates the geology of the region with alkaline granites covered by latossols, cambisols and litolic soils, at higher altitudes. This geology is particularly poor in heavy metals and no occurrence of Pb- or Hg-bearing rocks is known for the entire region. Thus Pb and Hg reaching the lakes are mostly from atmospheric origin.



**Figure 1.** Study site: The Itatiaia National Park (INP), Southeastern Brazil.

### Sampling and analysis

Samples were collected in one of the most remote and permanently flooded lakes of the highland prairies, located at approximately 2,460 m of altitude (22° 22' 24" S; 44° 42' 10" W), in accordance to accepted protocols.<sup>25</sup> In this lake, two cores were manually collected, inserting acrylic tubes into the sediment to a depth of 50 cm. The first 23 cm were sliced in 1.0 cm layers and in 5.0 cm layers from this depth onward. Samples were stored in acid-clean plastic bags and frozen for transport.

In laboratory, the sediment samples were oven-dried at 50 °C to constant weight (approximately 24 h). Approximately 1.0 g of the dried sample was digested in a closed system at 60-70 °C for 1.0 hour with 20 mL of 50% v/v. *aqua regia* solution (4 mL HCl + 6 mL HNO<sub>3</sub> + 10 mL H<sub>2</sub>O) in duplicate.<sup>26</sup> The resulting extracts were centrifuged during 15 min at approximately 2,000 rpm. Mercury was determined by Cold Vapor Atomic Absorption Spectrophotometry (CVAAS), in a Bacharat Model spectrophotometer. The detection limit, based on 3 times the standard deviation of the response of the reagent blank,

was 6 ng g<sup>-1</sup>. Simultaneously, the same analytical procedure was used to determine Hg in a certified reference material standard (NIST-USA, Buffalo River Sediment, with a certified value of 60 ng g<sup>-1</sup>). The found results of 58 ± 6 ng g<sup>-1</sup>, n=15, were in good concordance with the certified one.

Additionally, in one core, the organic matter content was determined in duplicate in the 1.0 g dried samples, after heating at 450 °C for 24 h. The ashes were dissolved with a strong acid mixture (2 mL HNO<sub>3</sub> + 3 mL HCl + 1 mL HF) at 60-70 °C for 2 h, in duplicate, for the determination of the total Fe and Pb contents by conventional flame atomic absorption spectrophotometry.<sup>27</sup> Simultaneously, the same analytical procedure was used to determine Fe and Pb in a certified reference material standard (NIST-USA, SRM 1646a - Estuarine Sediment). The found results showed recuperation of 105% for Fe and 95 for Pb, therefore in good concordance with the certified values.

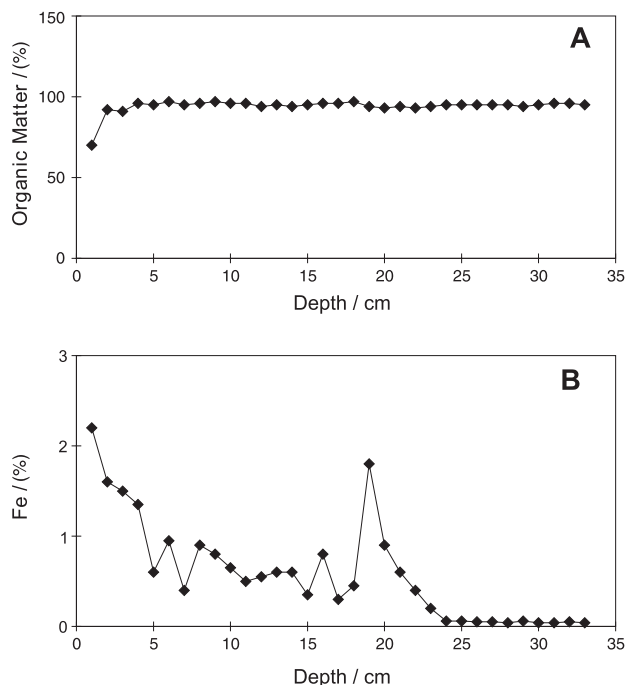
Sub-samples from the two cores used for Hg determinations were dated by the analysis of the excess of <sup>210</sup>Pb, at the Laboratory of Geochemistry from the University of Nice, France. Excess <sup>210</sup>Pb distribution in the cores were fairly consistent and gave an estimated sedimentation rate of 0.45 cm yr<sup>-1</sup>, constant for at least the past 60 to 80 years. Details on dating methodology and statistics, and on <sup>210</sup>Pb activity and temporal distribution in the cores, are published elsewhere.<sup>28</sup>

## Results and Discussion

### Concentrations distribution

The Pb concentrations were also used as tracers of major industrial inputs<sup>29</sup> to help interpret the Hg distribution, whereas the organic matter and Fe distribution was used to detect eventual post-deposition mobilization in the core, since water table fluctuations, which may result in redistribution of deposited Pb and Hg, would result in changes in the Fe redox state and organic matter oxidation.<sup>30</sup>

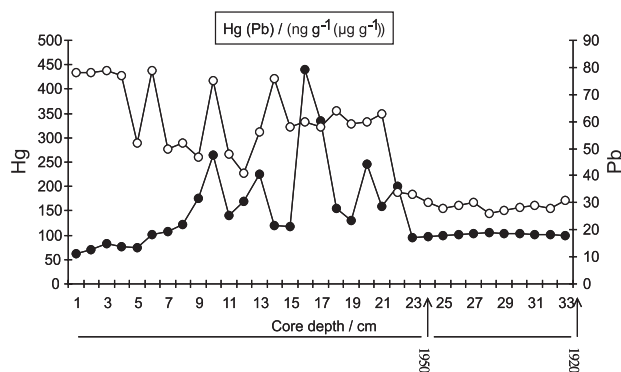
Organic matter and Fe distribution in core from Itatiaia, are presented in Figures 2A, B. Organic matter content is constant along the core and ranged less than 5%, from 92 to 97%, except in the first top slice where it drops to approximately 70%, probably due to more intense oxidation at the sediment-water interface. Concentrations of Fe were lowest (~ 0.06%) and nearly constant below 24 cm. From 24 cm, Fe concentrations increased to a maximum at 19 cm (1.8%), decreasing again to about 0.5% at 18 cm and increasing steadily from that depth to the top of the core, with peak concentrations in the first 1 cm reaching 2.2%. The largest peak between 18-20 cm of depth



**Figure 2.** Distribution of organic matter (A) and Fe concentrations (B) in core Itatiaia II. Concentrations are on a dry weight basis.

corresponds approximately to the beginning of the industrialization of the Paraíba do Sul Valley (see Figure 4 for corresponding dating). The extremely constant values of organic matter content suggest that water table fluctuations, which may result in the redistribution of deposited metals, is of minor, if any, importance to this lake. Likewise, the steady increase in Fe concentrations from 18 cm upward does not suggest any significant redox changes along the core. The Fe distribution along the core is difficult to interpret, but is probably due to anthropogenic emissions, since Fe is a major component of the effluents of various industries of the Paraíba do Sul river valley, which include one of the largest steel plant and iron smelter of the country. More detailed coring, however, is needed to fully interpret Fe deposition in the Itatiaia Mountains. Notwithstanding, for the specific objectives of the present work, the results on the organic matter and Fe distribution in the sedimentary column, suggest that any variation in Hg and Pb concentrations along the profiles, is mostly due to changes in loading rates, rather than post-depositional mobilization.

Lead concentrations (Figure 3) followed the same general trend as that of Fe, with lower concentrations of approximately  $40 \mu\text{g g}^{-1}$ , observed in the lower slices (up to 23 cm) and an increase from this depth to the top, reaching  $70 \mu\text{g g}^{-1}$  in sub-surface layers. A larger peak ( $180 \mu\text{g g}^{-1}$ ) was observed in the first cm, also found for the  $^{210}\text{Pb}$  data (not shown<sup>30</sup>). This may be due to the

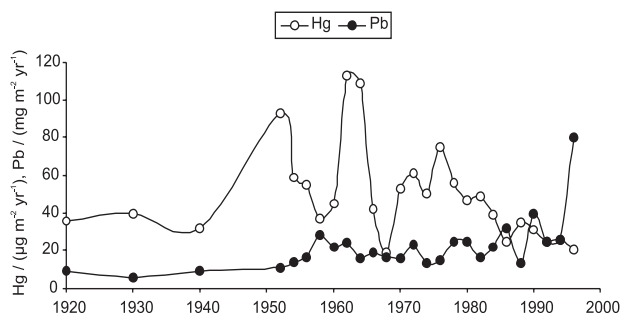


**Figure 3.** Distribution of Pb (open circles) and Hg (dark circles) average concentrations of Itatiaia I and II cores.

remobilization and oxidation at the sediment-water interface. This is also suggested by the drop in the organic matter content at the surface layer of the core. But since they only affect the first 1 cm layer, such processes have no importance in deeper layers.

Lead and Fe concentrations presented a significant positive correlation ( $r = 0.714$ ;  $P < 0.01$ ) but no significant correlation with the organic matter content. The lack of correlation with the organic matter content and the concentration increase of both metals from the 1940's (on Figure 4), suggest the industrialization of the Paraíba do Sul River valley as the major source of these two elements to the lake. In the case of Pb, another significant source is the use of gasoline as fuel, which was leaded up to 1986. The economic growth in the last 10 years of the 20<sup>th</sup> century, in particular the steel industry, which production increased from 20.6 Mt in 1992 to 26.7 Mt in 2000 (about 30%),<sup>31</sup> is probably responsible for the additional increase in the Pb and Fe concentrations in the first 5.0 cm of the core.

The variation of Hg concentrations is also presented in Figure 3. Average Hg concentrations ranged from 30 to  $420 \text{ ng g}^{-1}$ . Similar to Fe and Pb, Hg concentrations were lower and constant at deeper parts of the cores (up to 23 cm) with the maximum concentration occurring in the 16-18 cm layer ( $420 \text{ ng g}^{-1}$ ). However, contrary to the other



**Figure 4.** Average accumulation rates of Pb and Hg estimated from dated sediment cores from Itatiaia Mountains lake cores.

two metals, Hg concentrations showed a decrease towards the top of the core, starting around 8 cm, corresponding to the late 1980's. Surface concentrations ranged from 20 to 40 ng g<sup>-1</sup>. No anomalous Hg concentration peak was detected at the first 1.0 cm layer of the cores, suggesting that whatever processes causing the surface concentration peak observed for Fe and, in particular for Pb, do not affect the Hg distribution in the cores.

Decreasing Hg concentrations in surface layers of sediment cores has been frequently observed in lakes of the northern hemisphere, and at least in one study on the continental shelf sediments of the Rio de Janeiro coast.<sup>32</sup> However, this decrease has not been observed in similar studies in Amazon gold mining areas of Brazil, which consistently show increasing Hg concentrations toward the top of lake sediment profiles.<sup>12,22,33,34</sup> Surface Hg concentrations in the Itatiaia Mountains lake studied here are much lower than those measured in lake sediments in the Amazon. For example, in the Pantanal region, Central Brazil,<sup>22,34-36</sup> Hg concentrations in surface sediments of remote lakes range from 60 to 120 ng g<sup>-1</sup>. In the Carajás mountains,<sup>12,16</sup> southeastern Amazon, ombrotrophic lakes, similar to those of the Itatiaia Mountains, present Hg concentrations in surface sediments ranging from 80 to 310 ng g<sup>-1</sup>, while at the Alta Floresta mining area,<sup>16,34</sup> southern Amazon, concentrations ranged from 80 to 210 ng g<sup>-1</sup>. These results are in accordance to previous estimates<sup>15,16,19,21</sup> suggesting the larger importance of Amazon Hg emissions relatively to industrial emission<sup>5</sup> in Brazil, in the recent past.

#### *Accumulation rates*

Estimates of the Hg and Pb accumulation rates are presented in Figure 4. Since the studied lake is predominantly ombrotrophic, accumulation rates reflect principally the atmospheric deposition of the metals. As expected, Pb accumulation rates (Figure 4), increased from nearly constant values ( $8.0 \pm 2.0$  mg m<sup>-2</sup> yr<sup>-1</sup>) from 1910 to 1940, to approximately 20 mg m<sup>-2</sup> yr<sup>-1</sup>, between 1950 and 1980, and increased to a maximum of about 40 mg m<sup>-2</sup> yr<sup>-1</sup>, at sub-surface layers. At the top 1.0 cm, if the anomalous high concentration is considered, Pb accumulation rate would reach 80 mg m<sup>-2</sup> yr<sup>-1</sup>.

Notwithstanding the typical industrial emission-influenced profile of Pb, we still consider this lake as remote, since accumulation rates of Pb are at least one order of magnitude lower than those reported for other industrialized regions. For example, a survey of several Canadian lakes<sup>29</sup> showed Pb accumulation rates ranging from 400 to 950 mg m<sup>-2</sup> yr<sup>-1</sup>. Typical rates measured in

south Sweden also reach much higher values (2,000 to 4,500 mg m<sup>-2</sup> yr<sup>-1</sup>), whereas remote lakes in the same country showed similar values to those reported here.<sup>37</sup>

Mercury accumulation rates (Figure 4) ranged from a relatively constant value from 1910 to 1940 ( $36 \pm 4$  µg m<sup>-2</sup> yr<sup>-1</sup>) increasing from 1940 onward, following the industrialization of the Paraíba do Sul River valley, and reached a maximum in the 1960's, of approximately 120 µg m<sup>-2</sup> yr<sup>-1</sup>. Contrary to Pb however, Hg accumulation decreased from the late 1970's to the present, to values ranging from 15 to 30 µg m<sup>-2</sup> yr<sup>-1</sup>, at the top of the core. This decrease is probably resulting from emission control measures implemented by that time, in particular the banning of Hg-containing agro-chemicals and changing chlor-alkali plants technology, which have significantly reduced Hg industrial emissions in Brazil<sup>17,20,21</sup> and the Hg contamination of the aquatic environments of southeastern Brazil as well.<sup>19</sup> The 5 to 6 times decrease in Hg accumulation rates observed in the Itatiaia lake cores, compares well with the estimated decrease in Hg industrial emissions from about 150 t in 1979, to approximately 30 t in 1995.<sup>15,20</sup> This decrease also suggests that Hg emitted from gold mining areas in the Amazon has no influence on Southeastern Brazil and agrees with the regional differences between the Hg concentrations in surface sediments of aquatic environments in both areas.<sup>16</sup>

The temporal variation in Hg accumulation rates observed in the Itatiaia cores is similar to those reported for different regions of the northern hemisphere, which also reported peak values in the 1960's and 1970's.<sup>25,29</sup> Also, peak accumulation in the Itatiaia lake compares well with those reported for remote lakes in the Midwest USA<sup>5,38</sup> and with the average Hg accumulation rate estimated for the Great Lakes,<sup>10</sup> that is 135 µg m<sup>-2</sup> yr<sup>-1</sup>. However, pre-industrial Hg accumulation rates are from 3 to 6 times higher than those reported for remote areas in the northern hemisphere,<sup>5,37,39</sup> which range from 5 to 10 µg m<sup>-2</sup> yr<sup>-1</sup>. Emissions from gold and silver mining during the previous three centuries, which amounted nearly 200,000 t in Latin America,<sup>40</sup> with mean annual emissions of 316 t, may have influenced the magnitude of pre-industrial Hg accumulation 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.<sup>12</sup>

Alternatively, Hg atmospheric deposition in many regions of the northern hemisphere started raising by 1850 and were relatively high from 1900 to 1940,<sup>3,5,38</sup> frequently reaching values higher than 30 µg m<sup>-2</sup> yr<sup>-1</sup> and even surpassing 100 µg m<sup>-2</sup> yr<sup>-1</sup> during the Second World War.<sup>41</sup> Therefore, some Hg from the northern hemisphere

industrial revolution may have eventually reached the southern hemisphere, similarly to the Pb occurrence in the Antarctic ice.<sup>42</sup> Unfortunately, the scarce data on Pb (only one core) do not allow further discussion of its use as a tracer of industrial anthropogenic emissions prior to the 20<sup>th</sup> century. Better coring is needed for further discussion of the pre-industrial Hg atmospheric deposition in the region, but trans-hemisphere transport of Hg and/or the influence of colonial gold and silver mining, cannot be ruled out.

Present day average Hg accumulation rates measured in the Itatiaia mountains (15 - 30  $\mu\text{g m}^{-2} \text{y}^{-1}$ ), however, are similar to recent average deposition rates reported for North America<sup>3,5,8,25</sup> and for northern Europe,<sup>4,29,38</sup> which range from 9 to 30  $\mu\text{g m}^{-2} \text{y}^{-1}$ . Considering that the area is mostly affected by industrial emissions, these deposition rates are in agreement with emissions from industrial sources in southeastern Brazil.<sup>15</sup> Notwithstanding, they are much lower than those measured in areas receiving direct atmospheric effluents from industrial sources in this region of Brazil,<sup>18</sup> which may reach up to 76  $\mu\text{g m}^{-2} \text{y}^{-1}$ . Therefore, the accumulation rates estimated for the Itatiaia Mountains shall be viewed as a regional average for remote sites in southeast Brazil.

## Conclusions

Mercury atmospheric deposition measured in the Itatiaia Mountains provides a figure for South America similar to that of North America and Europe, with values showing a significant decrease in response to specific emission control measures implemented in the last 20 years. Unfortunately however, these measures seem to be only effective for Hg, since Pb accumulation, contrary to reports for the northern hemisphere, showed no similar decrease for the present day values. More data are needed to explain the relatively high pre-industrial Hg accumulation rates reported here. Both colonial silver and gold mining and the earlier industrial revolution in the north hemisphere may have influenced these values.

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