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## Litterfall mercury deposition in Atlantic forest ecosystem from SE - Brazil

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#### 1. Introduction

Mercury is known to be a global pollutant, with harmful effects on human health that is largely accumulated through respiratory organs from the atmosphere (WHO, 2000). In order to understand the global mercury cycle, it is mandatory to take into account the transference processes between its pools. The forest ecosystem has been recognized as a temporary dynamic mercury reservoir, linking the lithosphere and the atmosphere. Considering that the major Hg path is through atmosphere, increasing dry and wet depositions processes, the litterfall may significantly contribute to an incremental soil mercury input (Ericksen et al., 2003; Fleck et al., 1999; Grigal, 2002; Lindberg et al., 1991; Rea et al., 2002; St-Louis et al., 2001). Mercury can be incorporated to leaves via three processes: oxidation and adsorption of gaseous Hg (Hg°) (Munthe et al., 1995); Hg° uptake by stomata (Lindberg et al., 1992) or particulate Hg by adsorption (Rea et al., 2000).

The measurement of total Hg in litterfall is important to evaluate how much this input has enriched the soils in the tropical soil. When compared to temperate and boreal forests Hg in litterfall from tropical forests reaches values up to one order of magnitude higher. In a review containing pertaining to temperate and boreal ecosystems made by Grigal (2002), it was determined an average Hg deposition value of 21  $\mu$ g m<sup>-2</sup> y<sup>-1</sup>. This value is much lower than obtained from seven sites at tropical zone (74  $\mu$ g m<sup>-2</sup> y<sup>-1</sup>; Roulet

### ABSTRACT

Litterfall is believed to be the major flux of Hg to soils in forested landscapes, yet much less is known about this input on tropical environment. The Hg litterfall flux was measured during one year in Atlantic Forest fragment, located within Rio de Janeiro urban perimeter, in the Southeastern region of Brazil. The results indicated a mean annual Hg concentration of  $238 \pm 52 \text{ ng g}^{-1}$  and a total annual Hg deposition of  $184 \pm 8.2 \text{ µg m}^{-2} \text{ y}^{-1}$ . The negative correlation observed between rain precipitation and Hg concentrations is probably related to the higher photosynthetic activity observed during summer. The total Hg concentration in leaves from the most abundant species varied from 60 to 215 ng g<sup>-1</sup>. Hg concentration showed a positive correlation with stomatal and trichomes densities. These characteristics support the hypothesis that Tropical Forest is an efficient mercury sink and litter plays a key role in Hg dynamics. © 2011 Elsevier Ltd. All rights reserved.

et al., 1998; Mélières et al., 2003; Magarelli, 2006 ; Fostier et al., 2003; Silva-Filho et al., 2006).

Specifics surveys in ten tropical trees show that Hg concentration varies up to six fold, depending on the species (França et al., 2004). This difference may be due to the leaves lifetime, foliar trichomes, surface foliar waxes, stomatal density and roughness, which could contributes to different photosynthetic activity and absorption/adsorption processes.

Oliveira et al. (2006) and Silva-Filho et al. (2006) suggest a higher photosynthetic activity from tropical forest, due to temperature and luminosity, as a reason for the higher soil mercury input via litterfall, considering the stomatal Hg gaseous uptake as the main path to foliage accumulation.

The high mercury content in Amazonian soils (Nriagu et al., 1992) cannot be exclusively explained by the long term gold mining activities, but also by the natural Hg inputs, as suggested by the literature (e.g., Lacerda et al., 1995; Cordeiro et al., 2002; Wasserman et al., 2003; Almeida et al., 2005). Therefore this work aims to quantify one of these Hg inputs that enter through the literfall in a law protected area named Parque Estadual da Pedra Branca (PEPB), in order to discuss the contribution of this process to the soil Hg incorporation.

#### 2. Location and methods

The studied forest is located within the Rio de Janeiro urban perimeter (Fig. 1) and belongs to the Atlantic Forest Biome. Rio de Janeiro city is known as the second most urbanized and industrial area of Brazil (FEEMA, 2006). Within the urban limits, two great forested areas remains barely touched and were stablished as protection areas: Tijuca and Pedra Branca Forests.



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Fig. 1. Sampling area in Camorim Forest, Pedra Branca State Park (PBSP), Rio de Janeiro, Brazil.

This fragment of the Atlantic Forest is located some four kilometers inland and was established as a protection area for the last 50 years and is classified as oligotrophic (Oliveira et al., 2006). The regional geology is basically characterized by the presence of melanocromatic gnaisse and granites and the mean soil depth reaches 50 cm. Regional climate is hot and humid, without a well defined dry season. The annual average temperature is 23.7 °C. During this study the total annual precipitation reached up 1620 mm, with a very dry month of August (60 mm).

The sampling location (situated 200–300 m above m.s.l., with a slope of about 40°) is a secondary forest stand, on which litterfall samples were collected from November 2005 to October 2006. It was previously identified 92 tree species belonging to 34 families, with an average height of 9 m, a D.B.H. (Diameter at Breast Height) average of 15 cm and basal area of 26 m<sup>2</sup> ha<sup>-1</sup> (Solórzano et al., 2005). From those, ten species are dominant: *Piptadenia gonoacantha, Cordia trichotoma, Meternichia princeps, Colubrina glandulosa, Alchornea iricurana, Miconia tristis, Chrysophyllum flexuosum, Guapira opposita, Senefeldera multiflora and Allophylus sericeus, represent 47.7% of the tree density in the area (Solórzano et al., 2005).* 

Twelve plastic litter traps  $(0.25 \text{ m}^2)$ , situated 70 cm above the forest floor and representing an area of 2500 m<sup>2</sup>, were used to sample litter monthly (the litter was taken off from the trap each fifteen days to avoid excessive rain wash and every two collections constituted one sample). Those samples were packed into paper bags and transported to the laboratory. Canopy living leaves from the five most representative species were collected, after an intense rainfall period, in order to analyze its anatomical parameters. These samples were collected according to the tree climbing method described by Oliveira and Zaú, (1995).

In the lab, litter material was manually separated in leaves, twigs (below 2 cm in diameter), reproductive material and debris (miscellaneous plant material) in order to characterize the deposited material. All litter fractions were dried at 60 °C until constant weight. After that, composite samples were prepared by mechanically grinding all fractions with a stainless steel grinder, and then by careful homogenization of the powder.

For the determination of total Hg concentration, approximately 1.0 g of homogenized samples of the total deposited litter (composed of all litter fractions) was submitted to an acidic extraction in a 3:1 HCI:HNO<sub>3</sub> solution. Glass and plastic ware were decontaminated by immersion during 2 days in 10% (v/v) Extran<sup>®</sup> solution (MERCK), followed by immersion during 3 days in diluted HNO<sub>3</sub> (10% v/v) and final rinsing with Milli-Q water. All chemical reagents used were of at least analytical grade.

Cold Vapor Atomic Absorption Spectrophotometry (CVAAS) was used for Hg determination, after  $Hg^{2+}$  reduction to volatile  $Hg^{\circ}$  with SnCl2. All samples were analyzed in duplicates, showing reproducibility within 27%. The analysis of a standard reference material (NIST SRM 1515 – Apple Leaves) provided an average

recovery of 92%. Reagent blanks were simultaneously analysed with all sample analysis. In all cases blank signals were lower than 0.3% of sample signals. The concentration values obtained were not corrected for the recoveries found in the certified material.

Anatomic parameters like stomatal density, stomata pore length, trichomes length and trichomes density were measured on an Imaq Vision Builder<sup>®</sup> from National Instruments, the images were captured by a Leitz, Diaplan model and Olympus AX 70 microscopes. For this analysis, samples from three tree specimens were used from each one of the five most representative species. Twenty leaves from each tree were cut in the one third, resulting in a 1 mm<sup>2</sup> from each leave, totalizing sixty laminas by specie (Wallis, 1985). The anatomical material was prepared with ethylic alcohol (70%) and clarified with NaOH (5%) solution and sodium hypochlorite for three minutes. Previously, the samples were washed off and dried in a progressive ethylic series, colored with safranine (1% aqueous solution) and astrablau (Bukatsch, 1972).

#### 3. Results and discussion

Total litterfall deposition in the study site ranged from  $0.39 \text{ t ha}^{-1} \text{ month}^{-1}$  (May) to 1.17 t ha<sup>-1</sup> month<sup>-1</sup> (September), resulting in a total litter input to the forest floor of 7.6 t ha<sup>-1</sup> y<sup>-1</sup>. These results were similar to the ones obtained by Vitousek and Sanford (1986) in a study of thirty-two different tropical forests (3.6–12.4 t ha<sup>-1</sup> y<sup>-1</sup>). The major litter fraction (83.7%) was composed by leaves, followed by twigs (10.1%), while other fractions (reproductive material and debris) presented a lower contribution (6.2%).

Fig. 2 shows the temporal variability of the total litterfall deposition as well as rainfall distribution during the sampling period. The higher litterfall fluxes occurred during the winter and the lowest during the autumn. These results are probably related to the presence of deciduous species, which looses their leaves during lower rainfall periods (Santiago and Mulkey, 2003). Wang et al., (2009) showed that the amount and periodicity of leaves fall-out may be influenced by air pollution pressure and defoliant insects. Fig. 2 presented an increased litterfall during the summer that

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