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# Foliar mercury content from tropical trees and its correlation with physiological parameters *in situ*☆

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ABSTRACT

The terrestrial biogeochemical cycle of mercury has been widely studied because, among other causes, it presents a global distribution and harmful biotic interactions. Forested ecosystems shows great concentrations from Hg and Litterfall is known as the major contributor to the fluxes at the soil/air interface, through the superficial adsorption on the leaves and by the gas exchange of the stomatal pores. The understanding of which processes control the stage of Hg cycle in these ecosystems is still not totally clear. The influences of physiological and morphological parameters were tested against the Hg concentrations in the leaves of 14 endemic species of an evergreen tropical forest in south-eastern Brazil, and an exotic species from *Platanus* genus. Pathways were studied through leaf areas and growing tree parameters, where maximum rate of net photosynthesis (Pnmax), transpiration rate (E), stomatal conductance (Gs) were examined. The results obtained *in situ* indicated a positive correlation between Pnmax and the Hg concentration; *Cedrela fissilis* and *Croton floribundus* were the most sensitive species to the accumulation of Hg and the most photosynthetically active in this study. The primary productivity from Tropical forest should be a proxy of Hg deposition from atmosphere to soil, retained there while forests stand up, representing an environmental service of sequestration of this global pollutant. Therefore, forests and trees with great photosynthetic potential should be considered in predictions, budgets and non-geological soil content regarding the global Hg cycle.



## 1. Introduction

In the past few decades, the importance of forest biomes to the global mercury (Hg) cycle has been highlighted, since Hg transfer from atmosphere to soil certainly appears to be amplified through foliar uptake, which accumulates Hg continuously throughout the whole life of the leaf and further depositing through litterfall to the forest soil, enriching the surface soil layers with this element (Silva-Filho et al., 2006; Guédron et al., 2013). For example, fluxes of MeHg and total Hg under the canopy of subtropical Chinese forests were three times higher than their respective fluxes in wet deposition in the open area (Ma et al., 2015). Relatively high litterfall deposition fluxes suggest that even in remote forest areas Hg could be intensively transferred from atmosphere to soil, without a positive correlation to its local background air concentrations of Hg (Wang et al., 2016a,b). On the other hand, experiments with Hg isotope spikes mixed with an aqueous solution and sprayed over deciduous and conifer canopies by an aircraft, suggested that over 45% of the applied Hg is emitted back to the atmosphere, whereas only 14% were transferred to soils through litterfall (Graydon et al., 2012). A comparison of the fate of atmospheric Hg between 80-year-old stands of Douglas fir and a red alder, in close proximity under similar soil and atmospheric deposition, also showed significant differences between those plant groups in Hg concentrations and, therefore, in the Hg transfer process to soils (Obrist et al., 2012). Litterfall is composed by the non-living biological parts fallen over the superficial soil layer, which collectively consists of leaves, stems and reproductive elements, and there is a significant relation between leaf fall and season. Deciduous forests represent a physiological adaptation, mainly against water loss but also to enable species survival during periods of climatic restrictions (Reich and Borchert, 1984; De Vuono et al., 1986; Kozlowski.and Pallardy, 1997; Rizzini, 1997). Hence, it has been considered that water availability also controls different specific phenophases of species

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from tropical forests (Reich and Borchert, 1984). The annual rhythms of some tree species are significantly sensitive to changes in climatic conditions (Orlandi et al., 2016). In addition, water stress affects plant growth and cell expansion, and under more severe water conditions plants are unable to produce new bodies (De lucia and Heckathorn, 1989); the heterogeneity of a tropical rainforest, for example, can interfere in a direct correlation between precipitation and biomass production by litterfall. This occurs due to the ecological resilience of many species (Martinelli et al., 2017).

The Brazilian Atlantic Forest is considered one of the major productive biomes on Earth and the second in South America (Martinelli et al., 2017). In terms of biodiversity, it is considered an important centre of endemism and one of the 25 'hotspots' of the world. It is known by some as 'the hottest of the hotspots' (Cardoso da Silva et al., 2004; Laurance, 2009). Among the mega-biodiverse rainforests, the highly complex and structural variability of the Brazilian Atlantic Forest results in a highly productive mixed litterfall (Myers et al., 2000). Litterfall usually chemically corresponds to the composition of living tree parts, but some chemical compounds are translocated before the leaf abscission by the tree (Wood et al., 2005).

This litter machinery could be compared to dischargeable atmospheric filters with different surface areas, gaseous exchange pumps and morpho-anatomical particularities (Silva-Filho et al., 2006). Based on this, the litterfall brings atmospheric elements to the soil; the majorities are bioconstituents but some are pollutants, such as Hg, which are also discharged by plants (Grigal, 2002).

Known as a global pollutant (Schroeder and Munthe, 1998), Hg is mostly associated with the carbon cycle, since they share the same pathways after they are deposited in the ground of forested ecosystems. Once deposited on the forest soils, Hg could be mineralized by pedogenesis, taken up by the edaphic fauna (Buch et al., 2015) or be exported by run-off. Those processes turn the soil compartments into an Hg sink with a long retention time, mainly if the forest is not disturbed or suppressed (Roulet et al., 1998; Almeida et al., 2005).

Considering the Hg species transferred from the atmosphere to the soils by litterfall, 70–90% is associated with the leaves, compared with other litter components (Rea et al., 2000). To be in litterfall, Hg can take two pathways during the tree's life: non-stomatal adsorbed on the surface of the leaf epidermis or by absorption through epidermal cells (almost insignificant due to the parenchyma resistance and the fact that it is easily washed away by rain (Rea et al., 2000)); and the other by stomatal uptake (Hanson et al., 1995; Graydon et al., 2006; Millhollen et al., 2006a,b; Rutter et al., 2011). Additionally to the stomatal uptake process, there is a higher pore density and a higher rate of net photosynthesis in tropical tree leaves than in species of the temperate and boreal zones (Larcher, 2000), which corroborates the stomatal Hg entrance as the possible dominant pathway to litterfall (Laacouri et al., 2013). On the other hand, there is evidence that the non-stomatal uptake is also important, occurring even in the dark, regardless of the stomatal opening (Stamenkovic and Gustin, 2009). All the experiments describe above were made using controlled environment chambers and not *in situ*, and even with gymnosperms (Arnold et al., 2018).

There is apositive correlation of Hg concentration with the leaf's age (Wright et al., 2016), which indicates greater sequestration by evergreen forests, with longer retention time in the canopy (Millholen et al., 2006a,b). At sites where there is a wide inter-specific phenological diversity, as in the tropics, it is probable that there are also large differences between concentrations by species, since the leaves of each species have different lifespans, anatomy and physiology. The discrepancies in the Hg concentrations by tree species were found in all types of ecosystems, from the temperate and boreal zone (Rasmussen et al., 1991; Grigal, 2002; Bushey et al., 2008), to tropical forests (Mélières et al., 2003; De França et al., 2004; Teixeira et al., 2012). The ranges of Hg concentrations from those zones respectively.are between 10 - 50 and 21–215 ng.Hg.g$^{-1}$. Although there are relatively few data, the variability in global litterfall Hg deposition values is more dependent on the forest cover type than geographical region (Wright et al., 2016). This exposes a possible genetic/physiological control by species, correlated with the biomass production, which indirectly participates in this atmospheric Hg uptake. Wang et al. (2016a,b) did the first global map of Hg litterfall deposition and verified that tropical and subtropical biome are the greatest sequesters of Hg from the atmosphere, and Hg from the background atmosphere did not affect in the concentration of Hg in the litterfall. The southeast downlands of Atlantic Forest, the same in this study but different in altitude, are the top-ranked contributor, even thoug surrounded by average air loads of Hg. So, why do tropical trees have so much of this element? If one exists, what is the correlation between the morpho/physiological plant parameters and the concentration of Hg? To test the influence of photosynthesis over the Hg atmospheric sequestration by tree species from the Brazilian Atlantic Forest, the Hg concentrations were measured in senescent foliage of 14 endemic tree species and an exotic species from *Acer* genus, concomitantly with physiological parameters measured *in situ*, to confirm the hypothesis of the stomatal uptake mediated by photosynthesis, being the mainly biomagnificator and bioaccumulator motor of this cycle's stage through air to soil.

## 2. Materials and methods

### 2.1. Site description

The study was conducted from June 2009 to May 2011 at the Itatiaia National Park (INP), the first conservational unit created in Brazil, which is located in the states of Rio de Janeiro and Minas Gerais (22º18′56″S and 44º35′45″ W) and includes the highest part of the Mantiqueira Hills, with the culmination point at *Agulhas Negras* at 2787 m. In its lowest parts, the vegetation is typically identified as Atlantic Forest (AF), and gradually changes with increasing altitude, being replaced by typical non-arboreal vegetation (>1650 m). At higher altitudes, tree species of mountain and high mountain dense forest permeate the Atlantic Forest biome. In this regional ecotone, the boundary between these forested ecosystems is almost visually imperceptible. Botanical surveys accomplished by Pereira et al. (2006), just 8 km away from the study area, designated the ecotype as mixed high mountain forest. However, the main difference is in the presence of groups of *Arauacaria angustifolia*, not so evident in this study, due to sparse individuals. Also, it is important to mention that based on the altitude of the study area, forests could be classified as high mountain (1200–1600 m), but due to the hillside's orientation (north–south) the species distribution or appearance could be changed (Huggett, 1995). The microclimate parameters, such as rainfall accumulated and frequency, act more intensively over a hillside with that orientation. Regarding the Mantiqueira Hills, seasonal rains are more common over the oceanic hillside than in continental slopes like the watershed in question (Oliveira-Filho and Fontes, 2000). This scenery guarantees no hydric stress to the trees and the whole forest, which were confirmed by a soil psychrometer Wescor PST-55 stainless steel, that helps to calculate the soil water potential showing an almost saturated soil and never lower than the field capacity (- 0,33 bars). Although located between two of the largest urban centres in Brazil (~250 km), the study sites was considered remote from Hg anthropogenic sources (>40 km), at least until the end of the sampling.

The area at north-east (NE) of INP is formed mainly by a migmatite gneiss rock basement. The watershed studied is called Santa Clara Valley and is a sub-affluent of Paraíba do Sul River, the most important Brazilian river in south-east (SE). The area is a typical mountain relief with more than 35° of slope and ruled by a hydrologic morphostructural control. There are two types of main representative soils, latosol and cambisol, while at higher altitudes litholic neosols can be found. The region has predominantly medium-textured soils with low activity clays (with low cation-exchange capacity) interspersed with rocky outcrops. The climate can be considered as humid subtropical changing to subtropical highlands (Köppen climate climate classification – Cwa/Cwb - C = Subtropical; w = summer rains; a = hot summer and b = temperate summer, respectively (Alvares et al., 2013), depending on altitude and slopes, with two well-defined seasons: a short dry cold winter and a longer rainy warm summer.

### 2.2. Photosynthetic production

The maximum rate of net photosynthesis (Pnmax), transpiration rate (E) and stomatal conductance (Gs) were recorded after calibration and sample photosynthesis stabilization inside the cuvette of the portable infrared gases analyser Ciras-2 (PPSystems Inc.). Each of four fully expanded sunlight leaves of every three adult individuals of the same species were tested from 10 p.m. to 11 p.m. on fully sunny days. They were followed during 2 years of development, generating 12 samples of each the above mentioned parameters. In composite leaf species, leaflets were considered to be functionally similar to single leaves (Rijkers et al., 2000) and the median leaflet was used as the sample unit. The $CO_2$ cuvette reading set for this study was 380 ppm, the values of leaf temperature inside the cuvettewere set to 22.5 °C and relative humidity 62.5Once those values are indenpendently from each other, was taken an effort to record the Pn at the maximum values inside an acceptable range of Humidity and Temperature within the cuvette analysis apparatus. After photosynthesis is stabilized, which took no more than few minutes, the data generated by Ciras 2 was taken during this maximum rate of Pn and the outliers values from Humidity, Temperature and PAR radiation were discarded. Calculated from the relative humidity and the temperature, the Vapour Pressure Deficit (VPD) varied between 9 and 12.5 mb ($\mu = 10.5 \pm 0.8$ mb). The environmental photosynthetic active radiation (PAR) measured ranged from 800 to 1200 $\mu$mol m$^2$ s$^{-1}$ ($\mu = 1000 \pm 115$) during the measurements. Those values are very close to them registered in the weather station during found on sunny days between 10 and 11 p.m. after 3 days of the last rain event.

The leaf area index (LAI - is defined as the projected area of leaves over the same unit of ground surface area) and canopy cover (% of ground shaded) were measured by a digital canopy imager, CID-110. This device consists of a digital fisheye camera and canopy analyzer software (also developed by CID Inc.). The software calculates the coefficients of the transmission of diffuse radiation and the visible fraction of the sky above the canopy. It also works by providing the LAI and the average angle of the leaf canopy. In the case of the LAI of individual species, this was sampled every 6 months to monitor the plant growth concomitantly with the diameter at breast height (DBH). When the leaf is senescent it is cut, dried until constant weight and has its area measured to compose the specific leaf area (SLA, is the ratio of foliar area by corresponding leaf dry weight). All individuals were marked by GPS and data were collected in the canopy according to the tree climbing technique from Oliveira and Zau (1995).

The botanical material collection of each sampled individual was taken with pruning shears (secateurs-type) at a height of 5 m, which was also used in estimating the height of the trees, along with a sling and nylon thread. The identification of botanical material was made through academic literature, consultations by specialists and/or compared institutional herbaria (HPNI – Herbarium of Itatiaia National Park; RB- JBRJ - Botanical Garden of Rio de Janeiro). All litterfall data were taken from a previous work (Teixeira et al., 2016) in the same area of a major project focused on Hg and tropical biomes. The leaves were collected when senescent from the same branches as the photosynthesis analysis occurred. To quantify Hg, at the final and maximum sequestration period, four leaves from three individuals of the same species were chosen.

### 2.3. Soil sampling and Hg determinations

The cambisol were coarse-textured and very acidic due to the abundance of exchangeable ions generating acidity ($H^+$, $Al^{+3}$) and SOM-generating organic acids. Due to the proximity of the rock matrix the maximum of 1 m profiles could be reached, it was investigated regarding its total Hg concentration, at every 5 cm depth. Then the samples were homogenized and the mean Hg concentration by soil horizon was obtained, based on 10 profiles. The Hg concentration was determined by a cold vapor atomic absorption spectrophotometry (CVAAS). An acidic extraction in a concentrated 3:1 HCl:$HNO_3$ solution was used to digest 1.0 g of the dried sample (50 °C), pulverized (by a lab. Willey stainless steel grinder), homogenized (milled), and subsequently subjected to $Hg^{2+}$ reduction to volatile $Hg^0$ with $SnCl_2$ (Lechler et al., 1997). Certified material was tested along with the samples' chemical analysis, Buffalo River Sediment (SEM-2704, NIST, USA), with 97.5% of average recovery (n = 10, sd = 3.54) while leaves that, after being dried and ground, were analysed through the same methodology but followed by apple leaves as certified material (SRM-1515, NIST, USA), obtaining an average recovery of 93.5% (n = 12, sd = 2.32).

## 3. Results

### 3.1. The Hg accumulation by Atlantic Forest tree species

The species chosen (Table 1) are representative of the Atlantic Forest from the altitude of the INP and were selected based on their relative importance reported in other distribution studies in this region (Brade, 1956; Oliveira-Filho and Fontes, 2000; Carvalho et al., 2005; Pereira et al., 2006).

The highest Hg concentrations were observed in *C. fissilis, C.*

**Table 1**
List of tree species, their families and growth parameters used in this study to compare with measured Hg * DBH (diameter at breast height in cm), SS (successional strategy: pioneer = P and non-pioneer = NP), LLS (mean leaf life span in months), S (senescence: deciduous-D, semi-deciduous-SD or evergreen-EG).

| Tree species | DBH* | SS | LLS | S |
|---|---|---|---|---|
| *Cedrela fissilis* | 73.65 | P/NP | 9 | D |
| *Alchornea glandulosa subsp. Iricurana* | 39.78 | P | 12 | EG |
| *Croton floribundus* | 28.39 | P | 10 | SD |
| *Rapanea gardneriana* | 13.70 | P | 9 | D |
| *Ingá sessilis* | 2791 | P | >24 | D |
| *Nectandra oppositifolia* | 36.34 | P | >24 | EG |
| *Casearia sylvestris* | 29.87 | P | 21 | EG |
| *Araucaria angustifólia* | 70.56 | P | >24 | EG |
| *Eremanthus erythropappus* | 42.45 | P | 10 | SD/D |
| *Ocoteae odorifera* | 75.85 | NP | >24 | EG |
| *Bathysa australis* | 23.76 | NP | >24 | EG |
| *Vochysia tucanorum* | 35.34 | P/NP | >24 | EG |
| *Alsophila elegans* | 10.45 | NP | 14 | EG |
| *Cabralea canjerana* | 70.43 | NP | 10 | D |
| *Platanus acerifolia* | 36.87 | P | 9 | D |

floribundus, A. glandulosa, I. sessilis, N. oppositifolia and R. Gardneriana (Fig. 1), all of them pioneers and fast-growing species. The lowest concentrations were measured in *A. angustifolia, A. elegans* and *Platanus acerifolia*. *A. angustifolia* although presents a pioneer fitness, it belongs to the gymnosperm group with a medium to slow growth development and possible for this reason has low Hg in their needles. *A. elegans* is a pteridophyte, and this group is known as a low gaseous exchanger.

The net photosynthesis (Pn), evapotranspiration rate (E) and stomatal conductance (Gs) are presented in Fig. 2. We can highlight *C. fissilis* and *C. floribundus* as great gaseous exchangers. When testing the correlation of growth parameters of the trees against the mean Hg concentrations found in their leaves, all of them presented significant correlation: net photosynthesis - Pn ($r = 0.96$; $r^2 = 0.92$), stomatal conductance - Gs ($r = 0.77$; $r^2 = 0.59$) and foliar transpiration - E ($r = 0.78$; $r^2 = 0.61$) with significant level $p < 0.01$ in all cases.

The Hg concentrations in mature leaves of tree species here ($58.3 \pm 14$ ng $g^{-1}$) are statistically close to the Hg concentrations found in the litterfall for the same area (mean $57 \pm 16$ ng $g^{-1}$) (Teixeira et al., 2016), although by literature, a higher value is expected in the litterfall. But the average foliar Hg concentration found in the Atlantic Forest tree species, considering three Atlantic forest sites (De França et al., 2004; Teixeira et al., 2012; and the present study) is $79 \pm 10$ ng $g^{-1}$ ($n = 29$) (Fig. 4) against 130 ng $g^{-1}$ for the whole biome litterfall.

### 3.2. The Hg accumulation by Atlantic Forest soils

The soils of the region were classified in the field according to the Brazilian soil classification system (EMBRAPA, 2006). Among the three types present in the studied area, Hg concentrations were measured only in the most representative (cambisol). Average Hg concentration measured in Horizon O, whose first layer is composed basically of fragmented litter, decomposing microorganisms, carcasses and feces, was $57.5 \pm 7.5$ ng $g^{-1}$ (O*i*). This value is not significantly different from the average of $48.4 \pm 9$ ng Hg $g^{-1}$ found in litterfall in this area. However, there is a progressive reduction of Hg concentration through the B*i* -Horizon until it reaches the C-horizon. In the deeper C-horizon samples in contact with the decomposing rock matrix, the lowest Hg concentrations were demonstrated, (<3 ng $g^{-1}$), close to the detection limit of the analytical method used (CVAAS).

## 4. Discussion

The low gaseous exchange and the limited photosynthetic capacity from Samambaiaçu (*A. elegans,* from the Pteridophyte group) can be related to a reduced transport efficiency and greater xylem construction cost (Pittermann, 2010), probably contributing to the leaf having a lower Hg content. Brodersen et al. (2012) suggested that vascular organization might control the spread of air but possibly at the cost of hydraulic efficiency. Thus, the efficient water transport in plants allows an increased photosynthetic uptake of $CO_2$ for a given vascular investment and should improve fitness through enhanced growth and reproduction (Pittermann, 2010). Photosynthetic production by these species tends to be composed of a standard by the forest type (Larcher, 2000), within the genetic plasticity of each species being restricted by climate and, in turn latitude (insolation time), altitude and continentality.

The *C. canjerana,* despite its non-pioneer and a slow development type, can accumulate high loads of Hg, due to a high gaseous change rates and in addition, because of its high surface leaf area per weight ratio (SLA), which potentially stores more Hg (Laacouri et al., 2013). Thus concomitantly with this reason the *C. fissilis* surpassed the Hg mean concentration of the species sampled here, but mainly due to its Pn rate On the other hand, it is important to highlight the gymnosperm *Araucaria angustifolia* the SLA of which was as small as the Hg concentration in their needles, which is very similar to the values found in boreal forests for this plant group. But indeed, in this work, there was not a correlation between SLA and Hg by species, showing distinct behaviors, with no correlation even when analyzed in separate the group of pioneers and non-pioneers trees. But if we exclude *A. elegans, P. acerifolia* and *A. angustifolia* there is a significant correlation between Hg vs the mean leaf lifespan (Fig. 1), $r = -0.68$, $p = 0.01$, therefore, the deciduous trees showed more Hg content than evergreen trees. The non-pioneer group showed differences in the average when confronted against the pioneer group on Hg levels, showing lower values (means are between 35.8 – 45.6 and 71.3–87.7 ng Hg $g^{-1}$ respectively, inside a 99% interval of confidence) When we take into account the *principal components analysis* (PCA), using the physiological parameters and the Hg found per species correlated, we have groups linked to photosynthetic production and Hg values. Conversely DBH and especially LA and SLA are very different and even demonstrate an opposite behaviour in the distribution pattern of Hg values. *C. fissilis, C. floribundus* and *A. glandulosa* were the species in which these Hg sequestration factors through

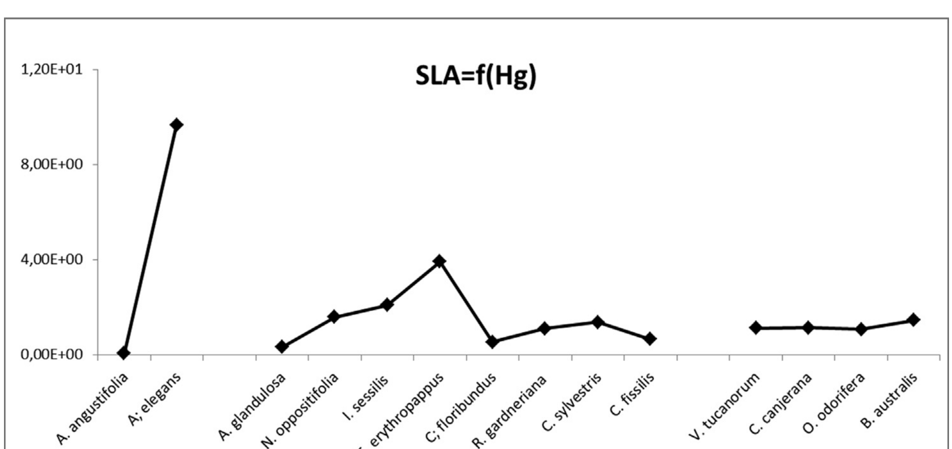


**Fig. 1.** SLA = f(Hg) - Hg concentration and SLA – specific leaf area means of full-blown living leaves from the INP. The exotic *P. acerifolia* is not shown here.

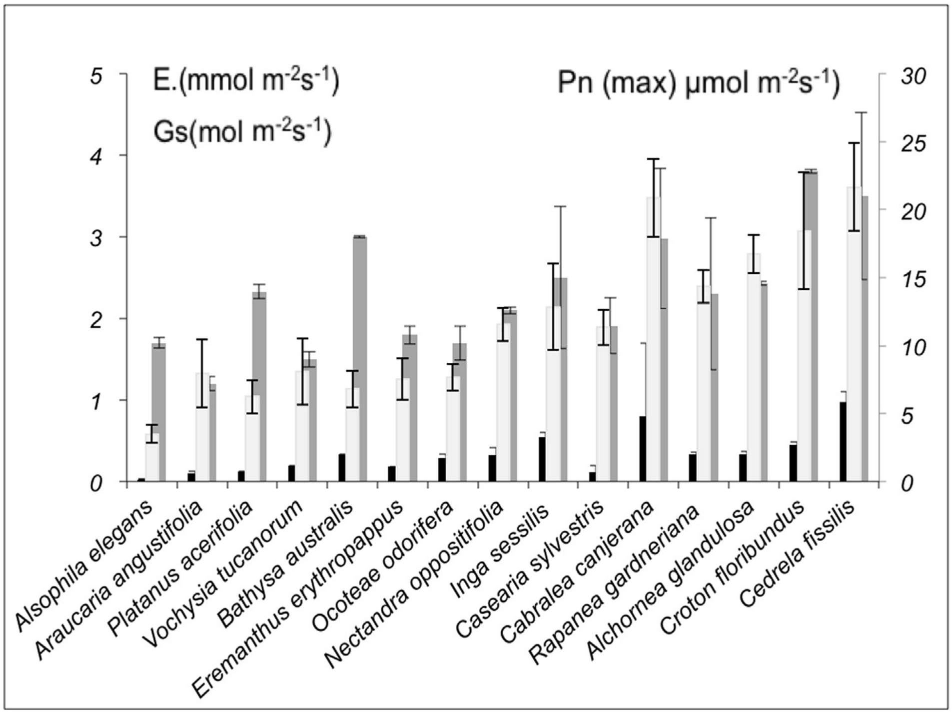


**Fig. 2.** Physiological parameter means of developed living leaves from the INP, *grey bar*– E (evapotranspiration) – mmol.m$^{-2}$.s$^{-1}$,– *black bar* Gs (stomatal conductance) – mol.m$^{-2}$.s$^{-1}$ (left axis) and *white bar* – Pn (max) (net photosynthesis) μmol.m$^{-2}$.s$^{-1}$ (right axis).

photosynthesis were determinant in this standard behaviour, whereas other species were grouped by LA or SLA, as in the case of *A. angustifolia B. australis* and *A. elegans* (Fig. 3 and Table S1-S4).

The Hg adsorbed is not considered as a significant variable as shown in a study conducted by Teixeira et al. (2012), the species of the Brazilian Atlantic Forest, *Alchornea iricurana* and *Piptadenia gonoachanta*, presented the highest concentrations of Hg in an inventory of five native species. Curiously, *P. gonoachanta*, despite having high values of Hg concentrations, presents low stomatal density by weight when compared to other high-Hg concentration species. The high-Hg concentration observed in this species was granted probably associated with the high density of trichomes found in their leaves. But, these physical parameters do not correlate significantly to the total Hg accumulated, and should indeed not be another very important way of Hg accumulation, maybe, to wash-off events in the tropics. On the other hand a high Pn rate must be the reason which agrees with the pioneer characteristics of *P. gonoachanta*, a fast-growing species. Another study concerning leaf morphology versus Hg content found a significant and positive correlation between the ratio of leaf surface to weight and Hg

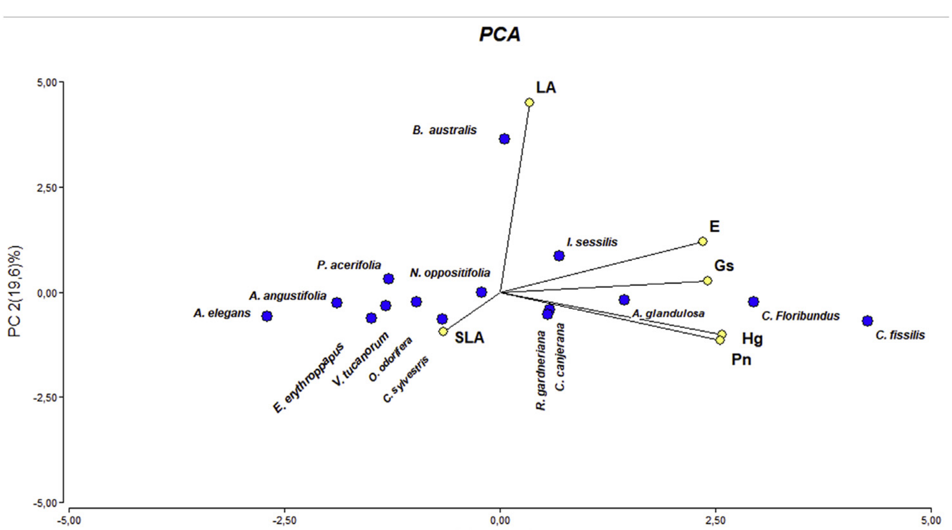


**Fig. 3.** Principal components analysis of the physiological parameters and Hg levels by trees: Alsophila elegans; Araucaria angustifolia; Platanus acerifolia; Vochysia tucanorum; Bathysa australis; Eremanthus erythropappus; Ocoteae odorifera; Nectandra oppositifolia; Inga sessilis; Casearia sylvestris; Cabralea canjerana; Rapanea gardneriana; Alchornea glandulosa; Croton floribundus; Cedrela fissilis.

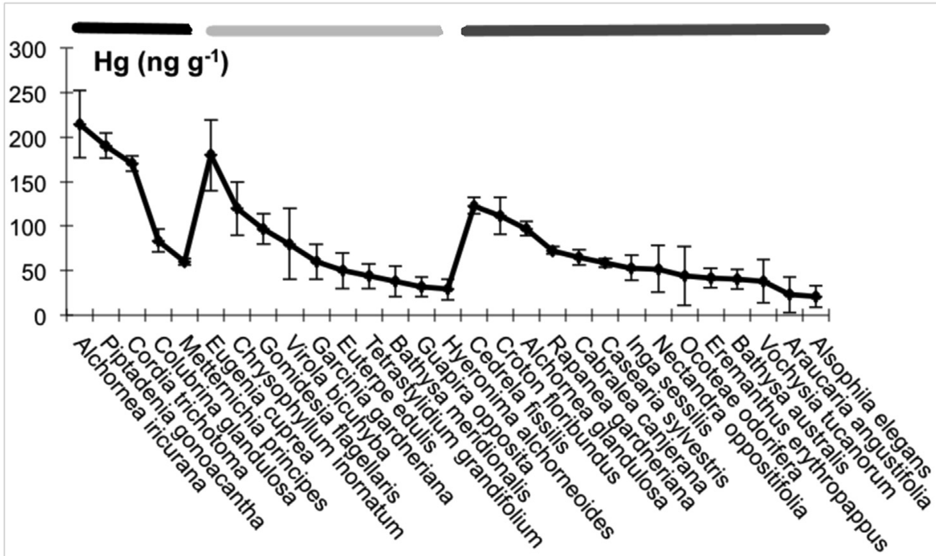


**Fig. 4.** Average foliar Hg concentration of species from the SE Brazilian Atlantic Forest of three different ecotypes. (**black bar**) Lowland Dense Forest – Rio de Janeiro, at 200 masl (39). (**light grey bar**) Mountain Dense Forest – São Miguel Arcanjo, SP – at 800 m (38). (**dark grey bar**) High Mountain Dense Forest – Bocaina de Minas, MG, at 1300 m.

concentration (Juillerat et al., 2012). Therefore, the fact that stomatal density per specific leaf area is not directly correlated with the concentration of Hg may be due to the photosynthetic capacity of each species being also related to their successional fitness. Finally, morphological characteristics alone should not be used to infer how much Hg the plant could capture, indeed there is (are) other(s) physiological factor(s) influencing the amount of Hg captured by the leaves.

Thus, a significant statistical relation was observed here between the gaseous exchange processes promoted by photosynthesis and the increase of Hg concentrations. The highest Hg concentrations of fast-growing pioneer trees and the same distribution of high Hg litterfall varying with the solar-induced fluorescence (Wang et al., 2016a,b) are evidence that the photosynthesis processes by stomatal uptake substantially rule the Hg sequestration in this ecosystem. This work boldly corroborates the idea that the combined effects of 1–2 years of leaf lifespan and stronger foliage photosysnthesis assimilation by fast growing evergreen species are the likely causes for the enhanced Hg accumulation in the litterfall of these forests. Our findings also are consonant with the recent research using satellite data (Jiskra et al., 2018), that showed that the photosynthetic activity of vegetation correlates with Hg(0) levels at individual sites and across continents. The terrestrial vegetation acts as a global Hg(0) pump, which the constant suppression of huge areas of forests, as such in the tropics, represents loss of sequestration, changing the whole global Hg balance.

With few inventories we tried to compare species among the foliar Hg accumulated, like in a remote Atlantic Forest area (800 m above sea level – a.s.l.) which values varied from 29 and 180 ng $g^{-1}$ (De França et al., 2004). The difference between these Hg levels found in leaves and with the present study must be related to the altitude, at 800 m s.l; the climate is warmer, which contributes to more photosynthesis and sequestration of gaseous compounds, the forest is even higher. A species within the same genus in our study area (*Bathysa meridionalis*) showed an average Hg concentration of $38 \pm 17$ ng $g^{-1}$, not significantly different from *Bathysa australis* in our study site of $40 \pm 9$ ng $g^{-1}$.

On the other hand, differences between distinct botanical families and the Hg accumulated in their leaves were found in our (Teixeira et al., 2012; Teixeira et al., 2016) and another regional study (De França et al., 2004). Therefore, a genetic approach is needed to clarify leaf physicochemical pathways and the morpho/physiological proximities within the same genus. It is interesting to observe that the *Alchornea* genus presented the higher Hg foliar concentrations in both studies. However, average Hg concentrations in *Alchornea* sampled from an urban Atlantic Forest's site were two times higher (Teixeira et al., 2012) than the concentrations observed in this study.

In order to compare the exotic species *Platanus acerifolia*, we chose the deciduous genus Acer, very well documented in the northern hemisphere. Rassmusen and colleagues (36) reported Hg concentrations in both *Acer saccharum* and *Acer rubrum* ($9.47 \pm 2.85$ and $7.40 \pm 2.70$ ng $g^{-1}$, respectively) in Ontario, Canada. In New York, USA, *Acer saccharum* showed an average Hg concentration of $44.1 \pm 1.3$ ng$g^{-1}$ (Bushey et al., 2008) and in Vermont, USA, of $41.4 \pm 7.6$ ng $g^{-1}$ (Juillerat et al., 2012). The highest Hg concentrations found at urban areas in the USA compared to Canada are closer to the lowest values found for *P. acerifolia* individuals at the INP. Probably, *P. acerifolia* presented an improved sequestration ability in the tropics, due to difference of quality and quantity of light received and others hydric/temperature supports offered by this biome, which raise the gaseous exchanges.

The increasing in Hg concentrations in litterfall compared with foliar averages was not found in this area, by the less with these tree species, but yes indeed there is an augment when compared the means for the whole biome. The enrichment of Hg in litterfall is normally found in the literature when compared with senescent leaves (Grigal, 2002), but in this case without a local phytosociological survey it is very difficult to check the real representative of these 14 species with those discussed above. The diversity is considered intermediary in the nearest survey 10 km from the study, in the same forest type and altitude, where the Shannon diversity index (*H*′) and the Pielou's evenness index (*J*′) were 4.15 nats ind.$^{-1}$ e 0.82, respectively (Carvalho et al., 2005).

Considering the first 20 cm of this soil (corresponding to humic horizon A) the observed average Hg concentration was higher ($93.74 \pm 44.3$ ng Hg $g^{-1}$) and is similar to the average of 110 ng Hg $g^{-1}$ found by Fostier et al. (2003) also in the south-east region of Brazil. Although it was a recent fallen and fragmented litter, it was noticed that in the stocked litter there was higher Hg concentration than in the litterfall (Juillerat et al., 2012). This enrichment could be associated with the humification process and the increased density of the soils (Lourençato et al., 2017).

Humification is a process of formation of humic substances (organic matter that has reached maturity) decomposed from biological material remain by the microbiota. The progressive reduction of Hg content downward to the soil is possibly related to the adsorption by organic soil components which in higher horizons are better adsorbents in acidic environments like this (Mark and Williamson, 2004; Miretzky et al., 2005). Thus, Hg has its mobility and distribution related to the same parameters controlling the mobility of dissolved organic matter (DOM) or the dissolved organic carbon (DOC) in tropical soils (Roulet et al., 1998).

In the Earth's crust, Hg abundance is not so high, varying from 0.02 to 0.06 mg $kg^{-1}$ with the highest concentrations found in argillaceous sediments and in coal (Kabata-Pendias and Mukherjee, 2007). Corroborating the hypothesis of a top-down deposition movement of Hg, the concentrations found in the gneiss saprolites from the studied area did not differ from the lowest Hg concentrations in other rock matrices found in Brazil, which show a typical range of concentrations varying between 1 and 10 ng $g^{-1}$ in basalts (Terashima, 1994), and around 10 ng $g^{-1}$ in granites (Telmer et al., 2006). In volcanic rocks from the Rio Iguaçu basin, South Brazil, Plawiak and colleagues (Plawiak et al., 2006) found mercury concentrations varying from 0.2 to 0.4 ng $g^{-1}$.

## 5. Conclusions

The species presented statistical variation of their means in foliar concentration of Hg, being the angiosperms, C. fissilis and C. floribundus the champions in sequestration, while the pteridophyte A. elegans and the gymnosperm A. angustifolia were the ones that presented the lowest concentrations of this one pollutant. In addition to the correspondence of the successional behavioral parameters with the Hg concentration, the photosynthesis was also positively correlated, evidencing the participation of this process in the bioconcentration of this element by the forest. The multifactorial analysis indicated that the leaf area parameters did not correlate with the Hg concentration, thus corroborating the fact that the physiological capture was more important than the leaf surface for the Hg Forestal sequestration. Thus, the soil profiles showed a positive relation between Hg concentrations with the organic layer's thickness. Through litterfall decomposition, Hg moves in the top-down direction into the forest soil. The most pronounced values at the upper profile's layers from tropical soils revealed a direct (openfall + rainfall) and an indirect (throughfall + litterfall) influence from atmospheric Hg deposition in tropical forests ecosystem, this last one managed by the primary production. The most productive forests of the world must be considered in the global cycle of this pollutant, not just after Anthropocene, but even to understand the prehistorical pools existent in present soils and to calculate future sceneries like with climate changes.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2018.07.120.

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