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Review

Mercury sequestration by rainforests: The influence of microclimate and different successional stages

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HIGHLIGHTS

- Global climate change could increase mobilization of mercury to the atmosphere.
- Litterfall transfers mercury from the atmosphere to forest soils.
- Mercury in tropical forest soils and litter is 10 times higher than in temperate zones.
- Scenarios affecting the global mercury cycle must consider the role of tropical rainforests.

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ABSTRACT

Mercury (Hg) concentrations in tropical forest soils and litter are up to 10 times higher than those from temperate and boreal forests. The majority of Hg that has been stored in tropical soils, as the forest is left intact, could be trapped in deeper layers of soil and only small quantities are exported to water bodies. The quantitative approach to the Hg cycle in tropical forests is uncommon; the South America Atlantic Forest indeed is a hotspot for species conservation and also seems to be for the Hg's cycle. This study reports on a biannual dynamics of Hg through different species assemblage of different successional stages in this biome, based on 24 litter traps used to collect litterfall from 3 different successional stages under a rainforest located at Brazilian Southeast. The mean Hg litterfall flux obtained was 6.1 ± 0.15 μg ha^{-1} yr^{-1}, while the mean Hg concentration in litter was 57 ± 16 ng g^{-1} and the accumulation of Hg via litterfall flux was 34.6 ± 1.2 μg m^{-2} yr^{-1}. These inventories are close to those found for tropical areas in the Amazon, but they were lower than those assessed for Atlantic Forest biome studies. These low concentrations are related to the remoteness of the area from pollution sources and probably to the climatic limitation, due to the altitude effects over the forest's eco-physiology. The mercury fluxes found in each different successional stage, correlated with time variations of global radiation, suggesting a mandatory role of the forest primary production over Hg deposition to the soil.

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Contents

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1. Introduction

Brazil holds two of the most important forested biomes on Earth, the Amazon and the Mata Atlântica forests. The later biome is considered a hotspot because of the combination of high biodiversity and continuous loss of territory (Myers et al., 2000). The fate of tropical forests in Brazil and elsewhere is highly important because they are efficient carriers of chemical compounds among different biosphere reservoirs (Malhi and Phillips, 2004). Additionally, when their high potential for nutrient losses is considered (Jordan et al., 1980), biogeochemical cycles play a crucial role for the maintenance of forest's homeostasis. The larger leaf surface area of tropical forests is a key step to their nutrient cycles, since it facilitates the adsorption of several substances, linking atmosphere and soil compartments through various processes, such as the uptake and sinking of CO_2 (Waring and Running, 2007) and other gases, unfortunately among them, atmospheric pollutants.

The faster dynamic found in the tropics, due to high temperature, rainfall and solar radiation, is an evidence of the important role played by these ecosystems in recycling elements at local, regional and global scales (Larcher, 2000). The incorporation of trace elements by plants such as Rb, Sc, Sr, As, Br, Cd, Cr, Hg, Sb and lanthanides supports this connection even if the element is not an essential plant nutrient (Aidid, 1988). In recent decades a growing body of literature has shown the damage to the biota caused by the association of Hg to organic matter and forests' structure and functioning may play a key role in this association (Roulet et al., 1998). With a well-known trophic biomagnification and worldwide distribution, Hg is considered a global pollutant (Schroeder and Munthe, 1998) with severe legal restrictions to its use in many countries as indicated by UNEP in the Minamata convention (Schroeder and Munthe, 1998).

In the Brazilian Amazon Basin, for example, local people and top predators show high Hg concentrations in muscle, blood, hair, and feathers (Malm et al., 1990). The contamination of humans and other living organisms by Hg may not be related just to past or present anthropogenic sources such as colonial and present day gold mining and others economic activities (Nriagu et al., 1992; Bastos et al., 2006), but it may be associated with the remobilization of deposited Hg from natural and anthropogenic by the natural cycling processes of elements within the forest (Lacerda et al., 2012). High Hg concentrations have been found in tropical soils, even in the most remote areas. Reported values can reach up to 400 ng g^{-1} in French Guyana and in parts of the Brazilian Amazon and have been associated with the typical paedogenesis of these tropical soils (Lechler et al., 2000; Roulet et al., 1998; Oliveira et al., 2001). However, the difference between the concentrations of Hg in the upper (<20 cm) and in deeper (>30 cm) layers of soil provides evidences of an additional atmospheric contribution (Oliveira et al., 2001). Measurements made since the beginning of the Industrial Revolution indicate that this additional Hg load from atmospheric deposition has increased continuously and is positively correlated with human activities, even when tropical regions are considered (Hylander and Meili, 2003; Lacerda and Ribeiro, 2004; Fiorentino et al., 2011; Pérez-Rodríguez et al., 2015; Chakraborty et al., 2016). Following atmospheric deposition, the Hg stocked in tropical soils has three possible fates: 1. immobilization in soils (mainly in deeper layers); 2. re-emission to the atmosphere, especially during forest burn or volatilization (mainly after the exposition of the soil surface due to the suppression of the forest (Almeida et al., 2009), and 3. leaching from the soil profile.

In forested areas, Hg air-soil deposition occurs through dry and wet precipitation, and/or by throughfall and litterfall. Wet deposition by rain and throughfall resultant from leaves rain-wash is responsible for removing approximately one quarter of all Hg captured by the canopy (Rea, 1999). The larger proportion interacts with leaves and epiphylls and can be incorporated by stomata. In Eco chambers experiments used to measure exchange of Hg concentrations under light and dark conditions, Stamenkovic and Gustin (2009) suggested that the nonstomatal pathway (epidermal entrance) might also be an important route of foliar accumulation of atmospheric Hg. Although it is not yet well defined whether the Hg in litterfall direct correlates with the *in situ* atmospheric Hg concentration (Hanson et al., 1995), there is a consensus that litterfall is the most important mechanism of Hg transfer from the canopy to forest soils (Frescholtz et al., 2009; Grigal, 2002). Studies in the Brazilian Atlantic Rain Forest has shown considerably higher Hg concentrations in litterfall when compared to Amazon forests (Oliveira et al., 2005; Silva-Filho et al., 2006; Teixeira et al., 2012) and even higher than temperate and boreal forests (Grigal, 2002). Specific surveys in leaves from ten different tropical trees show that Hg concentration can vary up to six times, depending on the species. Methodological differences have been dismissed as the cause of such variations (França et al., 2004). Different authors (Ericksen et al., 2003; Frescholtz et al., 2009; Silva-Filho et al., 2006) suggest these differences are caused by different variables such as leaf area, lifetime; foliar trichomes; leaf epicuticular waxes; stomatal density, and roughness, which may lead to different photosynthetic activity and absorption/adsorption processes.

This work contributes to a better understanding of the Hg biogeochemical cycle in tropical forests by providing new data on Hg concentrations in litterfall and the respective fluxes in the Brazilian Atlantic Forest from three different successional stages using canopy closure as the classification parameter. In the same site, physicochemical and biological data were collected to test the relationship of the forest's heterogeneity and the ecophysiological attributes of the canopy with Hg cycling. Simultaneously, micrometeorological data were recorded during two years to infer more precisely about the local environment.

2. Materials and methods

2.1. Site description

The area of study is located at the Serra da Mantiqueira, a mountain range located in Southeastern Brazil, among the three most industrialized Brazilian states: Minas Gerais, Rio de Janeiro and São Paulo. The study sites are located inside the Itatiaia National Park at an altitude of 2000 m (Fig. 1). The dominant ecotype found in the area is the evergreen *mountain rainforest*. Three successional stages were selected for data gathering conducted over

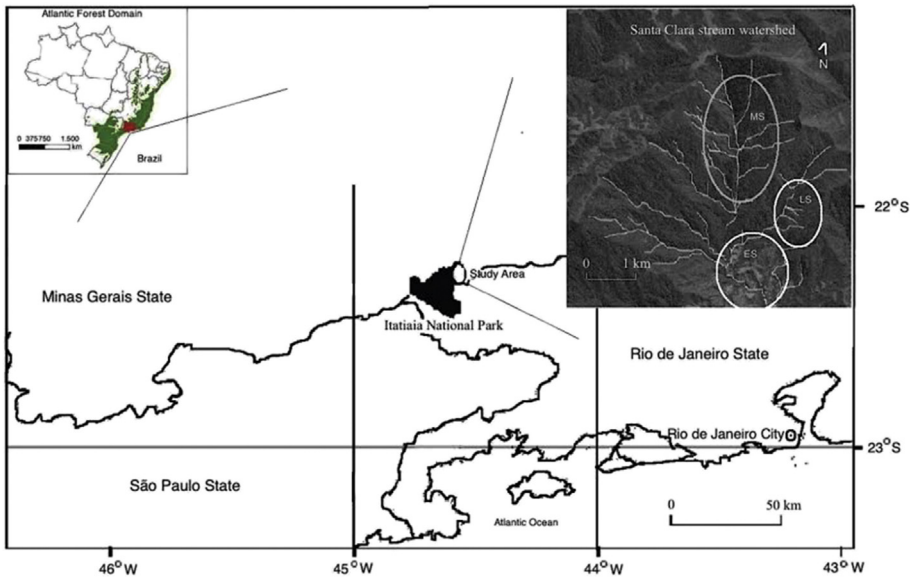

Fig. 1. Study area with location map showing studied successional stages, National Park of Itatiaia, SE - Brazil.

two whole years divided as follow according to their canopy closure characteristics: early-secondary (ES), late-secondary (LS) and mature stage (MS). The ES stand has been undisturbed for approximately twenty-five years, with almost no trees in the middle-level canopy. In the high-level canopy there are many heliophytes species from the Cecropiaceae, Melastomaceae and Euphorbiaceae families, with an average of 20 cm of diameter at breast height (DBH), ~15 m of height and poor tree species diversity. The LS stand has been undisturbed for thirty years and holds greater plant heterogeneity with species from the Bromeliaceae and Orchidaceae, and larger trees with an average of 80 cm of DBH and 25 m of height. The MS stand is at least two hundred years old and contains many ancient trees with DBH reaching until 130 cm and 35 m of height. Their canopies are densely colonized by numerous and diverse epiphytic families of Araceae, Moraceae (hemiepiphytes), Cactaceae besides the Bromeliaceae and Orchidaceae.

The local geology is characterized by the presence of migmatite orthogneiss, and the two main soil types are latosol and cambisol, but on higher slopes, litholic neosols can be found. Regional climate is tropical with mesothermal characteristics (Cwa—Köppen classification), with two defined seasons: a short dry and cold period in winter and a rainy and hot one in summer. Maximum monthly average temperature is 24° C (February) and minimum of 17° C (July). The historical annual rainfall is 1327 mm (measured at 1200 m, near 20 km).

The Santa Clara River, a third order stream, is the main watercourse in the studied area, with a watershed about 11.34 km^2. The headwater is located about 2000 m a.s.l. and has a rectilinear pattern with a southward flow. Santa Clara is one of the indirect tributaries of the Paraíba do Sul River, the most important river in Southeastern Brazil.

2.2. Sampling and chemical analysis

The sampling locations were situated between 1200 and 1600 m a.s.l. Litterfall samples were collected in the three successional stages from June 2009 to May 2011. Circular plastic litter traps (8 traps by forest type) were placed 70 cm above the forest floor, each one with an area of 0.25 m^2 used for litterfall sampling. Litter samples were taken off from the trap every fifteen days to avoid excessive rain-wash and the gathered material were composed to form a monthly sample. Samples were packed inside paper bags and transported to the laboratory. The collected litter was manually separated in leaves, small branches (below 2 cm in diameter), reproductive material and debris (miscellaneous plant material) and weighted separately. After, composite samples of all litter fractions from each monthly collection were dried under 50° C (Lechler et al., 2000) until constant weight, and then pulverized by a stainless steel Willey grinder disintegrator.

Total Hg concentration was measured in 1.0 g of homogenized samples (composed of all litter fractions) digested by an acid mixture of 3:1 HCl:HNO_3 (Lechler et al., 1997). A Cold Vapour Atomic Absorption Spectrophotometry (CVAAS) quantified total Hg after reduction of Hg with $SnCl_2$. Samples were analysed in duplicate and, when necessary, triplicate, showing a repeatability rate within 23%. Hg recovery from a standard reference material (NIST SRM 1515 — Apple Leaves) had an average value of 93%. Reagent blanks were analysed simultaneously, and blank signals were lower than 0.2% of the sample signals.

2.3. Climatic and physical parameters

A Digital Plant Canopy Imager (CI-110 from CID Inc.) was used to measure the canopy closure (CC); and further information on this procedure can be found in Campbell and Norman (1989). Twenty samples were used to measure the CC for each of the three successional stages. The measurements were taken during 10 and 11 h on sunny cloudless days.

A complete weather station made by Campbell Sci. S.A. provided records every 15 min for the following parameters: wind direction and speed, relative humidity, rainfall, solar radiation and temperature. The weather station was located in the upper middle section of the Santa Clara river watershed (Latitude 22°18′40, 49″S Longitude: 44°35′49, 52″W). All data were statistically analysed using the Statistica 10.0 software from Statsoft, INC.

3. Results and discussion

The micro environmental data collected over two whole years

agreed with the weather data from the Köppen Classification for the regional climate by showing a short dry winter and a long rainy summer. These two defined seasons divide the hydrologic year into four dry months (May to August − 240 mm accumulated rainfall) and eight rainy months (September to April − 2141 mm). The orographic rainfall and the valley shape and N-S orientation create a unique wet micro weather (Santos et al., 2011). During summer months, precipitation events commonly exceeded 5 mm in 15 min, sufficient to wash out particulate Hg from leaf surfaces (Rea et al., 2000). This process is even more pronounced if rain persists for several days or weeks.

The mean annual temperature was 17.0 ± 2.7° C, with an absolute maximum of 31.6° C (November 2011) and an absolute minimum of −0.5° C (August 2010). Winter had a few days of frost but with no apparent damage to the forest. Relative humidity is very high with annual mean of 88 ± 2%, with March showing the highest humidity (92%) and August the lowest (82.5%). March and August were respectively the last months of the wet and dry seasons.

The annual mean of the daily-accumulated solar radiation was of 14.6 ± 1.5 MJ. The first year of the study had 185 sunny days against 214 in the second year. When analysed in a monthly basis, global daily radiation is negatively correlated with daily rainfall accumulation and relative humidity but positively correlated with temperature (all Pearson's correlation test, $p \leq 0.01$).

There is a significant difference between the canopy closure levels for each successional stage as measured by a One-Way ANOVA test. Canopy closure of ES, LS and MS are, respectively, 42 ± 13%, 67 ± 16% e 92 ± 11% (Table 1). Canopy closure shows percentages inversely proportional according to the severity of disturbances to the forest covered area. Past studies about the healthiness of the Itatiaia National Park preservation areas showed, through satellites imagery data, that areas with more than 90% of the tree cover could be considered as pristine. The MS presented more than 70% of the measurements between 75% and 100% of canopy closure. These canopies have the most efficient spatial exploitation inside the forest; showing an uninterrupted growth of photosynthetic available areas over the soil surface.

3.1. Litterfall production

The annual mean litterfall production, considering the three successional stages together, was estimated to be 5.97 ± 0.14 Mg ha^{-1} $year^{-1}$. This value is consistent with that reported by Fostier et al. (2015) for an Amazon old-growth tropical rainforest 7.37 ± 1.80 Mg ha^{-1} y^{-1}. The litter from each trap was collected individually and distributed into the following three categories: 79.6% leaves, 12.3% twigs, 8.1% reproductive elements and other debris. These results point to a slightly higher leaf litter production and slightly lower reproductive contribution when compared to other South American Atlantic Forest of 71% and 9%, respectively; but in the same range of values found for highland forests (Chave et al., 2010).

Seasonally, the lowest litterfall production was observed in June of 2009, April and June of 2010 and March, April and May of 2011; with approximately 0.3 Mg ha^{-1} $month^{-1}$. Maximum production occurred in September, October and November of 2009, August, September and October of 2010 with values higher than 0.6 Mg ha^{-1} $month^{-1}$ (Fig. 2). Dry and windy months appeared to be when litterfall shows highest production. The months with intense litterfall production were preceded by two months of short photoperiod, with cold days and clear sky.

The mean litterfall flux from (ES) stand was estimated to be 4.8 ± 0.18 Mg ha^{-1} $year^{-1}$, without significant annual difference (Fig. 2). The calculated standard deviations were high even with a large number of litterfall traps. This result could have been caused during autumn by deciduous trees interferences (representing ~ <15% of tree species), and also by trees of one-year leaf cycle which are very common in the early successional stages.

The LS is denser than the ES stage because the canopy cover was left undisturbed during the last 30 years. The mean litterfall flux measured at the LS stand was 7.3 ± 0.13 Mg ha^{-1} $year^{-1}$ (Fig. 2).

The mean litterfall flux measured at MS stage was of 5.5 ± 0.12 Mg ha^{-1} $year^{-1}$ (Fig. 2). The small standard deviation reflects the smaller fluctuations of the micro-weather parameters. The monthly distribution of these groups were analysed by Kruskal-Wallis Test which showed a significant difference between the average litterfall fluxes of LS and MS stages ($p < 0.01$) and between ES and LS ($p < 0.01$).

Several growing decades of a very closed and stratified canopy makes up the mature forest stage, and it led to the greatest aboveground biomass out of the three successional stages. However, the MS stage has not shown a higher production compared to the others. This variation may be due to the remaining presence of high productive pioneer in the LS stage while in MS their presence is rare. Pioneer trees are primary growth specialists with a short life span (Larcher, 2000). At the same time, the age of MS guarantees a more constant humidity and temperature within the canopy, without any hydric stress.

3.2. Hg litterfall concentration

The observed Hg concentrations in the litterfall of the different successional stages (ES, LS and MS) were 74.1 ± 12 ng g^{-1}; 52.8 ± 11 ng g^{-1}; 48.4 ± 9 ng g^{-1}, respectively.

Early-secondary (ES) stage showed significant difference when compared to the monthly means of each other stage (Kruskal-Wallis Test - $p < 0.001$). The LS and MS results not significantly different, likely due to the higher quantity of pioneer trees present in the ES stage that are more susceptible to Hg capture. We assume that the highest measured concentrations reflect a higher Hg concentration captured by pioneer species, which have more net photosynthesis and larger green surface area. Silvestrini et al. (2007) showed that in Brazilian Semideciduous Tropical Forests, pioneer species present higher photosynthetic capacity and saturation light levels than mature stage species. According to Rea (1999), stomata uptake could represent around 70%–80% of the total Hg entering the ecosystem from the atmosphere. Moreover, the fact that plants have more pores (stomata) by leaf surface area in the tropical biomes (Larcher, 2000) is crucial to reach this conclusion. It should also be taken into account that dry deposition is more significant at higher temperatures (Lindberg et al., 1991)

Table 1
Canopy closure values from the three successional stages.

		Canopy closure (CC) %				
Successional stage	Samples by stage (n = 20)	0 ≤ 5%	5 < 25%	25 ≤ 50%	50 < 75%	75 ≤ 100%
ES		0	2	14	3	1
LS		0	0	7	11	2
MS		0	0	0	6	14

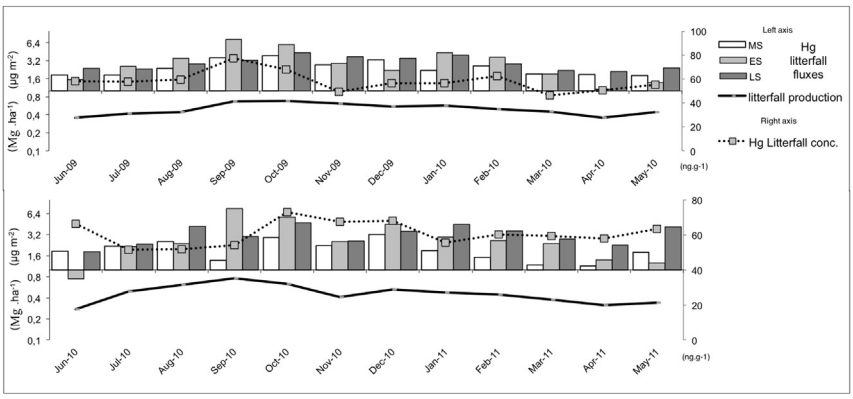

Fig. 2. Litterfall production, Hg concentrations and fluxes along the studied period at the Itatiaia National Park, SE – Brazil.

and can slightly interfere in both pathways (adsorption and uptake). To better understand the real importance of stomatal uptake it is fundamental to study adult trees "in locus".

Considering all three forest stages, the annual mean Hg concentration measured in the litterfall of the Itatiaia National Park was 58.2 ± 7 ng g^{-1} ranging from 48 ng g^{-1} (May and July of 2010) to 70 ng g^{-1} (September and October of 2010). The months with the most elevated Hg concentrations presented two pulses during the hydrologic year. The first pulse started during the end of the winter and increased until October, and the second was during the summer period (January and February). Torrential rains begun in November of 2010 and marked the division between two principal trends of Hg transport through the leaves. A climatic control over the transfer of Hg found in the forest canopy is expected, especially if they are captured from the atmosphere by stomatal uptake or by surface adsorption (Rea et al., 2000, 2001). After long and strong rain events, the litterfall collected presented the lower Hg concentrations, probably due to the low dry-deposited Hg concentrations which were washed away by the rain and became part of the throughfall fluxes. In January 2011, a catastrophic rain event (300 mm/24 hs) devastated many cities in the mountains of Rio de Janeiro state, including the study area.

At the end of summer, when the rainy season combines with the growing season (more elevated solar radiation) higher Hg concentrations were measured, reflecting greater stomatal uptake during photosynthesis. Corroborating with this assumption, this highest Hg values were obtained in the ES stage during the growing season, a fact that can be explained by the presence of species which leaves display short life span, showing higher photosynthetic efficiency and are physiologically more suitable to support hydric stress.

Oliveira et al. (2005) measured Hg in litterfall at the Camorim Forest, in Rio de Janeiro city, registering 1187 mm of annual rainfall, whereas Teixeira et al. (2012) repeated their measurement at the same place, under an annual rainfall of 1620 mm.

The augmenting of about 30% in annual rainfall, resulted in an increase in the mean Hg concentrations in litterfall of about 70 ng g^{-1} (from 170 ng g^{-1}, 2005 to 237 ng g^{-1} in 2012) suggesting stronger stomatal uptake in higher rainfall years. Obrist et al. (2011) showed a positive correlation between Hg concentrations in litterfall with annual precipitation in 14 USA forests. These findings suggest that once absorbed, Hg is difficult to be removed from inside the plant structure. Silva-Filho et al. (2006), in an area with similar altitude (sea level) but with significant higher rainfall (2400 mm) in the south of Rio de Janeiro city (>40 km far from Rio de Janeiro urban and industrial area), showed literfall average Hg concentrations of 131 ng g^{-1}, lower than in the studies of Oliveira et al. (2005) and Teixeira et al. (2012), which are much closer than urban and industrial Hg sources. Annual mean temperature can reflect another environmental dominant variable which influences directly the litterfall Hg concentration, and, consequently, it varies with altitude. The dry deposition from gaseous elementary Hg (the Hg species most commonly found in the atmosphere) increases with the temperature (Schroeder and Munthe, 1998), and temperature also increases the gaseous diffusion between the mesophyll cells (Lindberg et al., 1991). Forest altitude is a parameter that may influence Hg deposition and it must be investigated especially in tropical zones, once the available literature focusing temperate and boreal biomes is ambiguous with studies indicating both a negative (Gong et al., 2014) and a positive correlation (Reiners et al., 1975; Bushey et al., 2008; Stankwitz et al., 2012; Zhang et al., 2013) between Hg concentrations in litter and altitude.

The results also showed a significant ($P < 0.05$) correlation between the Hg concentrations in litterfall and solar radiation along the studied period in the Itatiaia forests.

The biological association between photosynthetic active radiation (PAR) and the primary development of plants, their leaves and green stems (Larcher, 2000), results in larger stomata absorption during the lifespan of a tree. Although the relatively low *r* value ($r = 0.380$) suggests that adsorption and diffusion also play a concomitant role in Hg incorporation into leaves and eventually control Hg concentrations in litterfall.

Among the three studied forests stages the only one that showed significant correlation with radiation when analysed separately was the ES ($r = 0.41$; $p < 0.05$). If the photosynthesis pathway is responsible for the most part of the Hg uptake (Laacouri et al., 2013), this finding indicate that in the mature forest the solar radiation has less effect over Hg capture than in the others stages, since in the MS stage there is a predominance of the diffuse radiation, with a canopy closer than in ES and LS, which are more open. With more species dependent of direct sunlight, the physiology of these stages was more sensitive to solar radiation showing a significant correlation between the Hg concentrations in litterfall and radiation.

Litterfall represents a large portion of Hg dry deposition to forested soils in terrestrial ecosystems (Johnson and Lindberg, 1995; St. Louis et al., 2001; Grigal, 2002), directly and/or indirectly controlled by solar and photosynthetically-active radiation and its interception by canopies (Baynton, 1968; Aylett, 1985; Cavelier and Mejia, 1990; Bruijnzeel et al., 1993). In this sense, since the light quality and quantity are so important to the plants ecophysiology and strongly influence on the net canopy photosynthesis (Larcher, 2000), it will also strongly affects Hg incorporation into leaves. Solar radiation has a significant association with

temperature ($p < 0.05$) which has higher value in December (summer) and lower in June (winter).

Passive adsorption of Hg reaches a saturation point when the atmospheric Hg levels are maintained high, but there are no more binding sites inside the leaf parenchyma (Graydon et al., 2006). The study area can be considered as being remote from Hg sources. Loureiro et al. (2010) monitored total gaseous Hg in the atmosphere of the region during one year and found values ranging from 0.4 to 1.3 ng m^{-3}; typical of background concentrations over the southern hemisphere. Lacerda and Ribeiro (2004) found total Hg atmospheric deposition over the Itatiaia Mountains of 20 μg m^{-2} yr^{-1}. Therefore, the saturation point has most probably not been reached. This and the high frequency and intensity of wash out events, strongly suggests that photosynthesis can be assigned as the main direct process controlling Hg accumulation in leaves in the Itatitaia tropical forests.

The mean Hg concentrations founded in litterfall in this study were in the higher range of values reported for temperate and boreal biomes in the North Hemisphere (Schwesig and Matzner, 2001; St. Louis et al., 2001; Grigal, 2003; Risch et al., 2012) (Table 2). For example, Hg mean concentrations found in the Itatiaia forests are twice higher than the mean from 80% of the 11 cases reviewed by Grigal (2002) from Europe and North America.

Mercury concentrations in the litterfall of the Itatiaia forests are the lowest ever reported for rainforests in the Brazilian Southeast (Fostier et al., 2003; Oliveira et al., 2005; Silva-Filho et al., 2006). The reported Hg concentrations for the Itatiaia Mountains are more close to those reported from different Amazon forest sites (Roulet et al., 1998; Mélières et al., 2003; Magarelli and Fostier, 2005). On the other hand, they are much lower than those values reported for urban forests at the Rio de Janeiro metropolitan area (Silva-Filho et al., 2006; Oliveira et al., 2005; Teixeira et al., 2012), or lower than intermediate values found for example, in the Subtropical Forest on Northeastern China (1600 m.a.s.l.), where mean Hg concentration reached up to 137 ng g^{-1} (Wang et al., 2009). Thus, high local pollution could be interfering with Hg present in litterfall, even in high altitude forests. For example, in the Subtropical Forest in Northeastern China (1600 m.a.s.l.), Hg mean concentration reached up to 137 ng g^{-1} (Wang et al., 2009). On the other hand, at higher latitudes even at sea level and/or in polluted zones (Grigal, 2002), there are no equivalent concentrations of Hg in litterfall that can be compared to tropical biomes.

3.3. Hg flux via litterfall

Monthly means of Hg concentration and the litterfall production were used in order to determine Hg litterfall fluxes (Fig. 2). While the accumulation of Hg via litterfall flux was 34.6 ± 1.2 μg m^{-2} yr^{-1}, the annual mean of monthly Hg fluxes was 2.8 μg m^{-2}, with the lowest value obtained in June 2010 (1.47 μg m^{-2}) and the highest in August and September 2009 (4.7 μg m^{-2}) (Fig. 2). The maximum values in September and October and the minimum in May and June repeat for the three years and are in agreement with other seasonal variation reported for the other Atlantic Forest sites (Teixeira et al., 2012; Silva-Filho et al., 2006), suggesting a strong association between climate, phenology, productivity and Hg capturing.

Mercury fluxes showed a positive and significant correlation with the production of litter during this study ($r = 0.88$, $p < 0.01$) (Fig. 2). A significant correlation was also found between monthly Hg concentration in litter and litterfall Hg fluxes, ($r = 0.62$, $p < 0.01$). When litterfall fractions are analysed separately, only the leaves fraction production presented a significant correlation with Hg litterfall fluxes ($r = 0.92$, $p < 0.01$ and $n = 24$). However, these correlations support the importance of leaf metabolism as a major mechanism of Hg interception by the canopy.

In a study on a mature stage forest in Ilha Grande, also in SE Brazil, Silva-Filho et al. (2006) reported a strong correlation between Hg fluxes and litterfall ($r = 0.88$, $p < 0.001$). Also, at higher latitudes, several authors found that the correlation of litterfall production and the Hg litterfall flux was more significant than with Hg litterfall concentration (Sheehan et al., 2006; St. Louis et al., 2001; Teixeira et al., 2012). In the rainforests, the most advantageous strategy for trees is to enhance the retention of old leaves until the development and maturing of the new ones to avoid a loss of photosynthetic activity and increase nutrient uptake directly from the atmosphere (Jackson, 1978; Jordan et al., 1980).

Due to the species lifespan the dynamic of Hg litterfall fluxes of the secondary forests is influenced more by Hg litterfall concentrations than the litterfall production variation. It secondary forests, the species have faster growth and short lifespan, investing energy in the primary biomass (Budowski, 1965; Vásquez-Yanes, 1980). In the rainforests, the most advantageous strategy for trees is to enhance the retention of old leaves until the development and maturing of the new ones to avoid a loss of photosynthetic activity and increase nutrient uptake directly from the atmosphere (Jackson, 1978; Jordan et al., 1980). At secondary forests, the species have faster growth and short lifespan, investing energy in the primary biomass (Budowski, 1965; Vásquez-Yanes, 1980). This fact was in agreement with the positive correlation found between foliar lifespan, photosynthesis and biomass production (Reich et al., 1992). Consequently, we can assume that different successional

Table 2
Annual litterfall Hg mean concentration and flux from different types of Biomes.

Biome	References	ng g^{-1}	μg m^{-2} yr^{-1}
Temperate Forest (North-Hemisphere)	Grigal, 2002	38 ± 1.4	12
Temperate Mixed Forest (eastern USA)	Risch et al., 2012	41.1 (21.4–62.7)	12.3 (3.5–23.4)
Boreal Mixed Forest (Canada)	St. Louis et al., 2001	42 ± 2	12
Boreal Coniferous Forest (Germany)	Schwesig and Matzner 2001	70 ± 2	15
Amazon Forest (South-America)	Roulet et al., 1998.	92 ± 1	52
Amazon Forest	Mélières et al., 2003.	64 ± 1	45
Amazon Forest	Magarelli and Fostier 2005	48 ± 1	43
Amazon Forest	Fostier et al., 2015	60,5	49
Atlantic Forest (SE-Brazil)	**present study**	58 ± 7	34
Atlantic Forest	Fostier et al., 2003	97	72
Atlantic Forest	Fostier et al., 2003	70	60
Atlantic Forest	Silva-Filho et al., 2006.	131 ± 7	122
Atlantic Forest	Oliveira et al., 2005.	170 ± 7	128
Atlantic Forest	Teixeira et al., 2012	237 ± 7	184
Subtropical Mixed Forest–NE–China	Wang et al., 2009	135.1 ± 31.7	78,3

stages of tropical forests lead to different dynamic on Hg transfer from atmosphere to soil. In the same way the ecotypes from each Biome could influence the dynamic of different ways of Hg deposition, Blackwell et al. (2014) showed that the fate of Hg depends on the trees species that define a given forest ecosystem. They found that much more Hg was deposited in a conifer forest via throughfall while at a hardwood forest, the litterfall plays a more important role, as well as retaining the Hg in soil for a much longer time.

The annual means of Hg fluxes in the successional stages were: ES: 37.2 ± 1.7; LS: 37.7 ± 1.2; MS: 26.9 ± 1.1 μg m^{-2}. Significant difference was observed between mean Hg fluxes from LS and MS stages (Kruskal-Wallis Test $p < 0.05$). The ES and LS stages presented a significant correlation, ($r = 0.54$, $p < 0.01$ and $r = 0.63$, $p < 0.01$), respectively, with solar radiation. Given the fact that solar radiation is closely related to photosynthesis, this correlation between Hg flux and radiation intensity in the ES and LS stages suggest how this process can be regulating the Hg uptake by leaves. Indirectly, radiation intensity influences the leaf microenvironmental parameters, such as: temperature, relative humidity, rainfall dynamics and the wind intensity, which may also influence Hg uptake by canopy leaves.

When compared to world litterfall Hg fluxes, the result of our study (34 μg m^{-2} yr^{-1}) is about 3 times higher than the mean found for 21 temperate forests surveys (10 μg m^{-2} yr^{-1}) (Grigal, 2002), and similar to a 75 years-old mature conifer forest in Canada and an Amazonian forest (St. Louis et al., 2001, Mélières et al., 2003; Magarelli and Fostier, 2005; Fostier et al., 2015). However, our value is lower than most Hg litterfall fluxes reported for other tropical forests (Table 2).

4. Conclusion

Notwithstanding the lower Hg concentrations and fluxes in litterfall at this high altitude tropical forest, compared to other Atlantic Forests of lower altitude, the observed concentrations and fluxes are higher than those reported for most temperate and boreal forests. If all other tropical forests are considered, these higher values are even clearer. This suggests that uptake of gaseous Hg from each tropical tree species, and therefore, by the forest as a whole is more efficient in tropical latitudes, in agreement with the ecology of such biomes in coping with nutrient-poor soils and deriving a significant portion of their nutritional requirements from the atmosphere. The biological activity plays an important role in the recycling of Hg in such ecosystems, and its magnitude is variable according to the successional stage. These forests are presently witnessing significant transformations, due to land use alterations and global climate change. Hence any effort of creating future scenarios related to the global Hg cycle, must consider the occurrence, distribution and successional stage of evergreen tropical rainforests.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2016.10.081.

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