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Litter mercury deposition in the Amazonian rainforest

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ABSTRACT

The objective of this work was to assess the flux of atmospheric mercury transferred to the soil of the Amazonian rainforest by litterfall. Calculations were based on a large survey of published and unpublished data on litterfall and Hg concentrations in litterfall samples from the Amazonian region. Litterfall based on 65 sites located in the Amazon rainforest averaged 8.15 ± 2.25 Mg ha^{-1} y^{-1}. Average Hg concentrations were calculated from nine datasets for fresh tree leaves and ten datasets for litter, and a median concentration of 60.5 ng Hg g^{-1} was considered for Hg deposition in litterfall, which averaged 49 ± 14 μg m^{-2} yr^{-1}. This value was used to estimate that in the Amazonian rainforest, litterfall would be responsible for the annual removing of 268 ± 77 Mg of Hg, approximately 8% of the total atmospheric Hg deposition to land. The impact of the Amazon deforestation on the Hg biogeochemical cycle is also discussed.

1. Introduction

Mercury (Hg) is considered by the Word Health Organization as one of the top ten chemicals of major public health concern (WHO, 2013). In aquatic environment, inorganic mercury can be converted to methylmercury, one of the most toxic species of Hg, which bioaccumulates in aquatic food chains and adversely affects human health on a global scale through fish consumption (Karagas et al., 2012; Li et al., 2014).

When compared with natural levels, mercury concentrations in many areas have significantly increased over the two last centuries (*e.g.,* 300–500% in the atmosphere, 200% in surface oceans) due to anthropogenic activities (Mason et al., 2012). The main sources of anthropogenic emissions of mercury are primarily coal burning, artisanal and small-scale gold mining and production of cement and metals (Horowitz et al., 2014; UNEP, 2013). Nevertheless, along the last decades, some countries from the northern hemisphere began to limit their anthropogenic mercury emissions and a decrease of mercury concentrations in the air of the northern hemisphere is observed since the nineties (Weigelt et al., 2015).

Estimates of total global Hg emissions range from 6500 to 8200 Mg yr^{-1} (Driscoll et al., 2013) with approximately 10% originating from natural geological sources, 30% from anthropogenic emissions and the rest (60%) from "re-emissions" of previously released mercury that has built up over decades and centuries in surface soils and oceans (Pacyna et al., 2006; UNEP, 2013). When considering natural emissions and re-emissions, oceans and biomass burning are the two primary sources, which account for 54 and 13% of the emissions, respectively (Pirrone et al., 2010).

The atmosphere is a major pathway for the biogeochemical cycle of mercury. Atmospheric mercury may occur as gaseous elemental mercury (Hg^0 or GEM), gaseous oxidized mercury (Hg(II) or GOM) and as particulate-bound mercury (PBM) (Lindberg et al., 2007). Once in the atmosphere, Hg can remain airborne or be deposited in aquatic and terrestrial surfaces by wet and dry deposition, where ~55% is deposited in oceans and 45% is deposited on land (Driscoll et al., 2013; Mason et al., 2012).

Forest canopies are highly effective in trapping atmospheric mercury due to the large surface area, which allows the Hg retention through the stomata, particularly for GEM, and/or through foliar adsorption of GOM and PBM (Ericksen and Gustin, 2004; Laacouri et al., 2013; Zhang et al., 2009). The efficiency of a canopy in trapping Hg increases with its surface area and canopies become more enriched along their lifetime (Guentzel et al., 1998; Rea et al., 2002)

Because the translocation of Hg between tree roots and vegetation is virtually nonexistent, Hg mass accumulated in forest canopies is believed to be largely atmospheric in origin (Ericksen and Gustin, 2004; Fay and Gustin, 2007; Grigal, 2003; Rea et al., 2000; Risch et al., 2012). Mercury compounds that accumulate on foliage are then transferred to the soil through litterfall and its decomposition, and via throughfall (rainfall that passes through the

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canopy and becomes enriched in Hg because of the wash-off of dry deposited Hg compounds from the leaf surfaces) (Fostier et al., 2000; Melieres et al., 2003; Rea et al., 1996; Silva et al., 2006, 2009). Although several mercury compounds that accumulate on foliage are washed away by precipitation, which increase their concentration in soil, many studies have suggested that in many locations litterfall and its subsequent decomposition can be considered the primary sources of Hg in soil, ranging from 52 to 60% of the total inputs (Bushey et al., 2008; Grigal, 2003; Melieres et al., 2003; Silva et al., 2009).

Therefore, forest ecosystems act as Hg sinks by limiting the mobility of this element in the environment. In many regions, deforestation is destabilizing the entire ecosystem, and among others impacts, it has been suggested that the Hg biogeochemical cycle is strongly affected (UNEP, 2013). For example, Hg stocked in soil and vegetation can be volatilized during forest burning and therefore can be reemitted to the atmosphere (Friedli et al., 2009; Melendez-Perez et al., 2014; Michelazzo et al., 2010), enhancement of soil Hg emissions has also been observed after deforestation (Almeida et al., 2005; Carpi et al., 2014; Magarelli and Fostier, 2005). It has also been shown that after deforestation Hg leached from soils is partially transferred toward water courses (*e.g.,* Fostier et al. (2000); Mailman and Bodaly (2005); Patry et al. (2013); Silveira et al. (2009)).

The Amazon basin (10° N–10° S, 80° W–50° E) covers more than 8.10^6 km^2 distributed over nine countries, and represents over half of the planet's remaining rainforests. The vegetation in the region is mainly semi-deciduous or evergreen tropical forest, but the species composition varies widely due to the differences in soil type and altitude across the basin (Sombroek, 2000). The general vegetation types are: old-growth terra firme forests, partially flooded forests, secondary forests (i.e., recently disturbed), short-statured forest and montane forest (Chave et al., 2010), and the biomass is generally >300 Mg ha^{-1} (Saatchi et al., 2007). It is also the location of large deforestation, mainly in the Brazilian Amazon where the rate of deforestation in the past last ten years was around 10.10^3 km^2 yr^{-1} (INPE, 2015). Nevertheless, only a few datasets have been published on Hg concentration in litterfall and the role of this forest as a sink for atmospheric mercury has been poorly studied.

Therefore, the objective of this work is to assess the flux of atmospheric mercury transferred to the soil of the Amazonian rainforest by litterfall. We compiled a number of published and unpublished data regarding litterfall and Hg concentrations in litterfall samples reported in the Amazonian region, which allow the average Hg litterfall deposition to be calculated. No study has been published regarding the monitoring of Hg deposition by litterfall in the Amazonian region and the present study is the first one that presents global data on litterfall Hg deposition in the Amazon. We also discuss the impact of Amazon deforestation on the Hg biogeochemical cycle.

2. Methods

2.1. Litterfall

For the Amazonian forests it has been shown that the net primary production (amount of carbon that is fixed from the atmosphere into new organic matter) is strongly correlated with total litterfall (Aragao et al., 2009; Clark et al., 2001). A number of studies have therefore been performed on litterfall in the Amazonian forest in the last several decades to quantify the carbon cycle in tropical forest ecosystems. Chave et al. (2010) performed a review that included 81 sites in South American forests (not all located in the Amazon basin). Most of the published data on quantified litterfall were obtained by using litter-traps (with sizes between 0.25 and 1 m^2), which were generally placed 1–2 m aboveground level to avoid animal interferences; the amount of vegetation deposited in these traps was measured monthly. The authors also reported that across their dataset, 70.8 ± 8.5% of the litterfall was attributed to leaves. In the present work, litter flux calculations were achieved by considering only the data related to the studies performed in the Amazon rainforest (65 sites) reported by Chave et al. (2010). We also included four sites from works published after 2010 that reported quantified litter fluxes in the Amazon rainforest (Silva et al., 2011; Wagner et al., 2013; Zeilhofer et al., 2012). The majority of the sites were old-growth tropical rainforest (OG) (61%). However, the dataset also included a number of secondary rainforest (SEC) (12%), periodically or permanently flooded rainforest (FLO) (17%), and short-statured tropical forest (LOW) (10%).

2.2. Mercury concentration in fresh leaves and litterfall

The mean Hg concentration was calculated from an exhaustive compilation of published data on Hg concentration in leaves sampled on trees (fresh leaves) and litter samples collected in the Amazonian rainforest. The dataset was completed using several unpublished data on Hg concentration in litter and tree leaves samples we collected at different periods and localities in the Brazilian Amazon. In addition to Roulet et al. (1999) and Melieres et al. (2003), who reported Hg concentration of samples collected in the French Guiana, all the others data refer to samples from the Brazilian Amazonian rainforest. All the litterfall samples were collected in OG and FLO forests.

In 1999 (Fostier, unpublished data), nineteen leaf samples were collected along the middle Negro river floodable forest (geographical coordinates: 62° 58′ 48″ W and 1° 24′ 18″ S); each sample was a composite with 20 leaves of the same tree, which were collected at different height (different tree species were sampled, but were not identified). All of the samples were oven-dried at 60 °C for a 24 h period. The concentration of total Hg was determined after wet digestion of ground samples at 75 °C with a mixture of concentrated HNO_3 and 30% v/v H_2O_2, by cold vapor atomic absorption spectrometry (CVAAS, Buck Scientific-Mercury Analyser Vapor 400-A). Recovery of Hg in the SRMs peach leaves (NIST 1547) and apple leaves (NIST 1515) was 97% and 98%, respectively, showing the good accuracy of the method; precision was lower than 17% (N = 5).

The Hg concentration was also determined in litter samples collected in a forest near Alta Floresta (MT) in 2013 and Candeias do Jamari (RO) in 2013 and 2014. Both locations are part of the so called "Arc of Deforestation" of the Brazilian Amazon. In 2013, the Alta Floresta samples were collected at 6 different places in a ~0.5 ha forest plot while the Candeias do Jamari samples were collected in 4 different places in a ~0.5 ha forest plot. In 2014, a new campaign was performed in Candeias do Jamari, where a composite sample was collected by sampling litterfall in 6 different places in a ~0.5 ha forest plot located approximately 30 km far from the 2013 experimental plot. All samples were dried at room temperature in a laminar flux for 48 h and ground manually with liquid nitrogen. Total Hg was determined by thermal desorption (DMA-80, Milestone) according to Melendez-Perez and Fostier (2013). Recovery of Hg in the SRMs peach leaves (NIST 1547) and apple leaves (NIST 1515) was 103% and 104%, respectively, showing the good accuracy of the method; precision was lower than 5% (N = 5).

3. Results and discussion

3.1. Litterfall

The spatial distribution of litterfall dataset is presented in Fig. 1a. The litterfall was 9.27 ± 1.72 Mg ha^{-1} y^{-1} for FLO,