

RESEARCH ARTICLE

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Key Points:

- Hg input through litterfall at evergreen broadleaf forest sites is 1 order of magnitude greater than that of temperate broadleaf forest
- Steady Hg accumulation in decomposing litter biomass and Hg uptake from the environment were observed during experimental period
- Hg accumulation in soils is closely linked to sulfur and nitrogen during carbohydrate mineralization of litter

Supporting Information:

- Supporting Information S1
- Table S5
- Table S6

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Enhanced accumulation and storage of mercury on subtropical evergreen forest floor: Implications on mercury budget in global forest ecosystems

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Abstract Forest ecosystems play an important role in the global cycling of mercury (Hg). In this study, we characterized the Hg cycling at a remote evergreen broadleaf (EB) forest site in southwest China (Mount Ailao). The annual Hg input via litterfall is estimated to be $75.0 \pm 24.2 \mu\text{g m}^{-2} \text{yr}^{-1}$ at Mount Ailao. Such a quantity is up to 1 order of magnitude greater than those observed at remote temperate/boreal (T/B) forest sites. Production of litter biomass is found to be the most influential factor causing the high Hg input to the EB forest. Given their large areal coverage, Hg deposition through litterfall in EB forests is appropriately $9 \pm 5 \text{ Mg yr}^{-1}$ in China and $1086 \pm 775 \text{ Mg yr}^{-1}$ globally. The observed wet Hg deposition at Mount Ailao is $4.9 \pm 4.5 \mu\text{g m}^{-2} \text{yr}^{-1}$, falling in the lower range of those observed at 49 T/B forest sites in North America and Europe. Given the data, the Hg deposition flux through litterfall is approximately 15 times higher than the wet Hg deposition at Mount Ailao. Steady Hg accumulation in decomposing litter biomass and Hg uptake from the environment were observed during 25 months of litter decomposition. The size of the Hg pool in the organic horizon of EB forest floors is estimated to be up to 2–10 times the typical pool size in T/B forests. This study highlights the importance of EB forest ecosystems in global Hg cycling, which requires further assessment when more data become available in tropical forests.

1. Introduction

Terrestrial forest has been regarded as a largely underestimated sink for atmospheric Hg on a global scale [Gustin *et al.*, 2005; Lindberg *et al.*, 2007; Obrist, 2007]. Hg cycling in different types of forest exhibits unique characteristics in Hg input, transformation, and sequestration [Demers *et al.*, 2007; Obrist *et al.*, 2012]. Recent data showed elevated concentration of Hg in soil of evergreen broadleaf (EB) forest in China relative to the level measured in temperate/boreal (T/B) forest [Luo *et al.*, 2014; Obrist *et al.*, 2011; Shi *et al.*, 2013], which was attributed to higher Hg deposition [Luo *et al.*, 2014]. In a forest ecosystem, Hg deposition flux through litterfall often exceeds that from rainfall by a factor of 2 or more [Grigal, 2002]. Elevated Hg input contributed by litterfall in EB forest has been reported and could be up to $220 \mu\text{g m}^{-2}$ in rural southwest China [Fu *et al.*, 2010; Ma *et al.*, 2015a; Wang *et al.*, 2009; Zhou *et al.*, 2013]. The most common explanation for the elevated Hg input is the high atmospheric Hg concentration ($2\text{--}5 \text{ ng m}^{-3}$) in these regions, which enhances Hg uptake by foliage. However, the earlier studies did not pay attention to the contribution caused by the higher production of litter biomass (2–10 times the quantity of T/B forest) in EB forest [Ni and Song, 1998; Wang *et al.*, 2009; Zhou *et al.*, 2007, 2013]. This calls for a reassessment on the factors leading to elevated Hg input through litterfall in EB forest (~50% global forest areas), which has important implications on global Hg cycling.

A large fraction (>60%) of Hg input to forest floor is retained in soil [Demers *et al.*, 2007; Fu *et al.*, 2010; Grigal, 2003; Ma *et al.*, 2016; Selvendiran *et al.*, 2008; St Louis *et al.*, 2001b; Wang *et al.*, 2009]. However, the fate of deposited Hg and its biogeochemical processes in this important environmental compartment have not been well understood. For example, Pokharel and Obrist [2011] reported 5–23% of Hg mass loss to Hg evasion during litter decomposition under artificial laboratory conditions. On the contrary, field data showed that total Hg mass in litter can increase by 37%–147% in 1–2 years of litter decomposition via the uptake of

Table 1. Summary of the Observed Hg Concentrations in Litterfall (LC, ng g^{-1}), Open Rainfall (OC, ng L^{-1}), and Throughfall (TC, ng L^{-1}) and of Hg Fluxes ($\mu\text{g m}^{-2} \text{yr}^{-1}$) Through Litterfall (LF), Open Rainfall (OF), and Throughfall (TF)^a

Site	Latitude	Longitude	LC	LF	OC	OF	TC	TF	O
ASSFERS	23.96°	101.52°	58 ± 8	75.0 ± 24.0	4.9 ± 3.0	4.9 ± 4.5	22.9 ± 11.4	22.9 ± 16.5	26.9
SLJ	31.45°	109.91°	92 ± 78						
JFL	19.18°	109.73°	78 ± 42						
WYM	28.04°	117.57°	45 ± 14						
XSBN	21.68°	101.42°	74 ± 32						

^aAll data are presented as mean ± SD. The estimated Hg pool size (mg m^{-2}) in the organic horizon (O) is calculated by the Hg concentration, soil depth of O-horizon, and soil bulk density in O-horizon. ASSFERS is a remote EB forest site, and the others are the rural forest sites.

“external” Hg (absorption from the environment during decomposition) [Demers *et al.*, 2007; Hall and Louis, 2004; Pokharel and Obrist, 2011]. During the decomposition process in T/B forest, Hg to carbon ratio (Hg/C) increases with decreasing carbon to nitrogen ratio (C/N), suggesting relatively faster mineralization of C compared to N and continuous sorption of external Hg to the organic matters in soil [Demers *et al.*, 2007; Grigal, 2003; Obrist *et al.*, 2011]. The strong affinity between Hg(II) and reduced organic S in the soil of T/B forest is well documented [Grigal, 2003; Skyllberg *et al.*, 2006; Xia *et al.*, 1999]. Compared to T/B forest, the timescale of the carbon and nutrient cycle in subtropical forest is typically shorter [Vitousek, 1984] because temperature is an important factor influencing the rates of litter decomposition and C, N, and S sequestration [Aerts, 1997; Fierer *et al.*, 2005; Wang *et al.*, 2012]. However, no studies have reported the interplays among the mass change of Hg, C, N, S, and temperature during litter decomposition in EB forest where the processes of Hg accumulation and sequestration may be distinct from T/B forest.

In this study, we present the data of Hg input through litterfall and Hg transformation during litter decomposition over 2 to 7 years at a remote EB forest site in Southwest China. In addition, the importance of litter production in contributing to the Hg input in EB forests and the difference in the fate of deposited Hg between EB and T/B forests are assessed. Conclusions are drawn in terms of the importance of EB forest in global Hg cycling.

2. Materials and Methods

2.1. Site Description

Mount Ailao is located between the Yunan-Guizhou Plateau, Hengduan Mountains, and Tibet Plateau in Yunnan, Southwest China. The weather is controlled by the southwest monsoon and has distinct dry (November to May) and rainy seasons. The annual precipitation, temperature, and relative humidity are 1400 ± 700 mm (mean ± standard deviation, SD), $13.0 \pm 5.0^\circ\text{C}$, and $84 \pm 5\%$, respectively. The study site, Ailaoshan Station for Subtropical Forest Ecosystem Research Studies (ASSFERS, $24^\circ32'\text{N}$, and $101^\circ01'\text{E}$), has an altitude of 2450 m above sea level. The ASSFERS is a pristine remote forest site with $\sim 2 \text{ ng m}^{-3}$ mean atmospheric Hg concentration [Fu *et al.*, 2015a]. The forest is a montane EB forest with a canopy height of 20–30 m and a canopy coverage of $\geq 85\%$. The dominant plant species are *Castanopsis wattii*, *Lithocarpus xylocarpus*, *Schima noronhae*, and *Manglietia insignis*. The forest soil is mainly *Luvisol* (World Reference Base) with a soil pH of 3.5–4.8 [Yang and Yang, 2011]. Litter samples were also collected at four other EB forest sites in the region (Table 1), including Xishuangbanna (XSBN: 21.68°N and 101.42°E), Jianfengling (JFL: 19.18°N and 109.73°E), Shenlongjia (SLJ: 31.45°N and 109.91°E), and Mount Wuyi (WYM: 28.04°N and 117.57°E). The most dominant plant species at these sites include *Gironniera subaequalis* Planch, *Pometia pinnata*, *Barringtonia racemosa*, and *Alseodaphne hainanensis* Merr.

2.2. Litterfall Sample Collection and Measurement

The collection of litterfall samples and the Hg measurement have been described in our previous work [J Zhou *et al.*, 2013]. Monthly litterfall samples were collected by $1 \text{ m} \times 1 \text{ m}$ nylon nets hanging 1 m above ground at eight random locations (Figure S1 in the supporting information) at the ASSFERS during 2011–2014. The eight sampling sites were based on the tree species at the ASSFERS (which include the five most dominant species *Manglietia insignis* (Sample #1), *Lithocarpus chintungensis* (Sample #2), *Blueberry* (Sample #3), *Castanopsis wattii* (Sample #4), and *Lithocarpus xylocarpus* (Sample #5)) and three other random species (Samples #6–#8) under the five dominant species [J Zhou *et al.*, 2013]. The sampling period at the

other four sites (three to four random locations) is shown in Table S1. Litterfall samples were placed in paper bags, air-dried in a clean room, ground in an agate mortar, and sieved by a 200 mesh sieve (74 μm) [Zhou *et al.*, 2013]. The total Hg concentrations were measured by a Lumex RA-915+ multifunctional Hg analyzer equipped with a pyrolysis attachment. Total carbon (C), total sulfur (S), and total nitrogen (N) were measured by an Elementar vario macro cube [Zhou *et al.*, 2013]. Duplicated measurements for Hg, C, N, and S were performed, and the accepted variation of three replicated measurements was below 5%. Standard samples were measured in every 10 samples with recoveries in the range of 95%–105% using GBW07405 (GSS-5) as the soil Hg standard, GBW10020 (GSB-11) as the litter Hg standard, IVA99994 as the soil C/N standard, AR-4018 as the soil S standard, and AR-2026 as the litter C/N/S standard.

2.3. Precipitation Sample Collection and Measurement

The collection of precipitation samples, the aqueous Hg measurement, and the quality control procedure have been described in detail in our previous work [Zhou *et al.*, 2013]. Briefly, the precipitation water was collected from June 2011 to April 2014 in an open area at the ASSFERS (i.e., no canopy coverage) with an automated wet-only precipitation collector and borosilicate glass bottles at 1.5 m above ground. Water samples were not collected during the winter of 2012 and spring of 2014 because of the extreme dry weather leading to low precipitation (<10 mm) in both seasons. After each rainfall event, the precipitation sample was immediately transferred to a precleaned 250 mL Teflon bottle. Then, 1.25 mL of trace metal grade HCl was added to preserve the sample. The total Hg concentration in precipitation samples was determined following U.S. Environmental Protection Agency (EPA) Method 1631 using Tekran 2500 as the Hg detector [U.S. Environmental Protection Agency, 1999]. The average concentrations of Hg from blank solutions (55 mL) were below $0.02 \pm 0.01 \text{ ng L}^{-1}$. A 200 μL calibration standard sample (1 ng mL^{-1}) diluted with 55 mL double distilled water (DDW) was measured in every six samples with an analytical recovery of 98%–102%. Throughfall samples ($n = 135$) from three dominant tree species (*Castanopsis wattii*, *Lithocarpus xylocarpus*, and *Schima noronhae*) were collected during August to October 2015. The average monthly amount of throughfall was obtained from field data collected at the site 1 km away from the study site during 2011–2015 (Table S2).

2.4. Litterfall Decomposition Experiments

Litter samples were collected under one of the dominant tree species (*Castanopsis wattii*) in March 2012 at the study site. To ensure homogeneity of litterfall samples, the samples were washed by DDW to remove deposited dust and soil, which have much higher Hg concentrations (typically 2–3 times higher), and air dried to remove surface water. Then, the samples were divided into two batches. One batch (~500 g) was dried to a constant weight (mass variation <0.03% over 8 h) in an oven at 40°C to obtain the dry mass. After drying, the initial concentrations of Hg, C, N, and S were measured to be $77 \pm 4 \text{ ng g}^{-1}$, $45.7 \pm 0.2\%$, $1.6 \pm 0.1\%$, and $0.14 \pm 0.02\%$, respectively. The other batch was divided into smaller samples (15 g) used in litter decomposition experiments. Although the water content in litter could influence the rate of microbial and fungal growth, the disturbance caused by the initial air drying of litter samples does not play a significant role during the experiments [Berg, 2014]. In each experiment, 15 g of a well-mixed litter sample was placed in a 15 cm \times 15 cm nylon bag that had 1 mm \times 1 mm mesh size [Ribeiro *et al.*, 2002]. Fifteen replicates divided into five groups were placed in five 2.0 m \times 2.0 m ground cells at 2450 m above sea level on 1 April 2012. Two sets of experiments were performed. One set allowed the litter to decompose naturally at ambient temperature while the other set decomposed the litter at a 2°C elevated temperature using infrared radiators (800 W, 45 cm \times 15 cm) that were hung 1.5–2 m above the cells depending on the season. From April 2012 to May 2014, 30 bags of samples (15 replicates \times 2 groups) were collected every other month starting from May 2012. Each sample bag was lightly rinsed by DDW to remove surface soil and dust. The loss of Hg caused by the water rinse, assessed by exposing litter to water upon harvest, was negligible (<0.20 ng Hg g^{-1} dry mass), comparable to results showed in an earlier study [Pokharel and Obrist, 2011]. After carefully removing the impurities (roots and rubble) by visual inspection, the decomposed samples were dried to constant weights in an oven at 40°C. Finally, each sample was analyzed for Hg, C, N, and S as previously described.

2.5. Soil Sample Collection and Measurement

Soil samples were collected from the forest floor through the Chinese Ecosystem Research Network (CERN) during 2007–2013 at the ASSFERS. The sample plot is 30 m \times 40 m and divided into 12 10 m \times 10 m subplots.

Two groups of six subplots were sampled in alternation at the end of dry and rainy seasons. For each subplot, 12 replicated organic horizon soil samples (15 cm depth) were selected in the sampling plot to form an "S" shape and then mixed into a composite sample (1–2 kg). The soil profile samples were utilized to estimate soil Hg pool size as described in our previous work (soil profiles information in Table S3) [Zhou *et al.*, 2013]. After air drying at room temperature by placing the samples on kraft paper in a clean room and removing the impurities, each composite soil sample was ground in an agate mortar and sieved by a 200 mesh sieve (74 μm). Total Hg, C, N, and S were analyzed using the same procedure as the litter samples.

2.6. Data Collection and Analysis

To ensure data comparability, relevant data reported in peer-reviewed literature published during 1995–2015 were collected, analyzed, and then compared to the results in this study. The study locations include 99 T/B background forest sites in North America and Europe, 107 EB forest sites in China, and 22 EB forest sites in the tropical region. The data sets (Table S4–S6) include Hg concentration in foliage, Hg depositions, Hg emissions, Hg runoff, Hg soil pool sizes, litterfall biomass production, annual precipitation, and annual mean temperature. The statistical analysis was performed using SPSS 18.0.

3. Results and Discussion

3.1. Hg Input Through Litterfall in EB Forest

Based on the data collected in 2011–2014, the annual Hg input through litterfall at the ASSFERS is estimated to be $75.0 \pm 24.2 \mu\text{g m}^{-2} \text{yr}^{-1}$. This input is ~ 2 times higher than the values (26.0 – $42.9 \mu\text{g m}^{-2} \text{yr}^{-1}$) observed at three rural EB sites (SMM, i.e., Simianshan and GGM, i.e., Gonggashan in Southwest China and DMS, i.e., Dameishan in East China, 2 – 4 ng m^{-3} mean atmospheric Hg concentrations, Table S4) [Fu *et al.*, 2015a; Ma *et al.*, 2015a]. Given the comparable Hg concentrations in the litter samples at these sites (43 – 66 ng g^{-1} at the ASSFERS versus 47 – 107 ng g^{-1} at the three rural EB sites), the much higher production of litter biomass at the ASSFERS (1112 – $1560 \text{ Mg km}^{-2} \text{yr}^{-1}$ versus 402 – $657 \text{ Mg km}^{-2} \text{yr}^{-1}$ at three rural EB sites) is the primary cause of the elevated Hg input through litterfall. However, the litterfall Hg input (104.0 – $135.0 \mu\text{g m}^{-2} \text{yr}^{-1}$) at two other EB forest sites near anthropogenic emission sources (TSP, i.e., Tieshanping and LGS2, i.e., Leigongshan2 in southwest of China, 4 – 10 ng m^{-3} mean atmospheric Hg concentration, Table S4) [Fu *et al.*, 2015a] is 1 – 2 times higher than the values observed at the ASSFERS. Figure 1 shows the litterfall Hg input observed at 76 T/B forest background sites in Europe and North America (data shown in Tables S5–S6). Compared to the data range of 2.7 – $59.5 \mu\text{g m}^{-2} \text{yr}^{-1}$ in Figure 1, the Hg input at the ASSFERS is much elevated and can be up to 1 order of magnitude greater than the fluxes observed at these T/B forest sites.

The observed Hg input through litterfall at the EB forest sites in China ranges from 26.0 to $135.0 \mu\text{g m}^{-2}$ (Tables 1 and S4). Both the mean (Figure 1) and median values (mean = $65.4 \pm 40.9 \mu\text{g m}^{-2} \text{yr}^{-1}$, median = $42.9 \mu\text{g m}^{-2} \text{yr}^{-1}$, seven sites) are much higher than those observed at T/B forest sites (mean = $15.2 \pm 8.4 \mu\text{g m}^{-2} \text{yr}^{-1}$, median = $14.1 \mu\text{g m}^{-2} \text{yr}^{-1}$, 76 sites). The Hg concentration in the litter samples collected from different forest types are comparable (e.g., $47 \pm 23 \text{ ng g}^{-1}$ Hg concentration for DMS and $58 \pm 8 \text{ ng g}^{-1}$ for ASSFERS, both at EB forest sites are comparable to $45 \pm 11 \text{ ng g}^{-1}$ at T/B forest sites), and therefore, the elevated Hg input through litterfall in the EB forest cannot be solely explained by the Hg concentration in litterfall.

Furthermore, based on the data of Hg concentration in litter samples at 29 subtropical EB forest sites in China and at 69 T/B forest sites in Europe and North America, the interquartile ranges (i.e., 25th to 75th percentile) for the T/B and EB forests are 38 – 51 ng g^{-1} (Figure 2a) and 37 – 73 ng g^{-1} (Figure 2b), respectively. Both mean ($60 \pm 30 \text{ ng g}^{-1}$) and median (57 ng g^{-1}) Hg concentrations for the EB forests are significantly higher than the values for the T/B forests (mean = $45 \pm 11 \text{ ng g}^{-1}$, median = 44 ng g^{-1} , $P < 0.05$). After removing four data ($\geq 93 \text{ ng g}^{-1}$, 85th to 100th percentile) collected at polluted EB forest sites, the difference on Hg concentration between EB and T/B forest sites is not significant ($P = 0.251$). Although the measured atmospheric Hg concentrations (2 – 5 ng m^{-3}) at these EB forests sites are generally higher than the values (1 – 2 ng m^{-3}) at the background T/B forest sites [Fu *et al.*, 2012, 2015a; Lindberg *et al.*, 2007], the Hg concentration in litterfall does not appear to be elevated by the higher ambient Hg concentration.

Based on the consecutive 3 year data observed at the ASSFERS (Figure 3a), the Hg concentration in litter exhibits a consistent seasonal pattern, higher in autumn/spring and lower in summer/winter. Neither the litter production by different vegetation species (Figure S1) nor the seasonal trend of atmospheric Hg

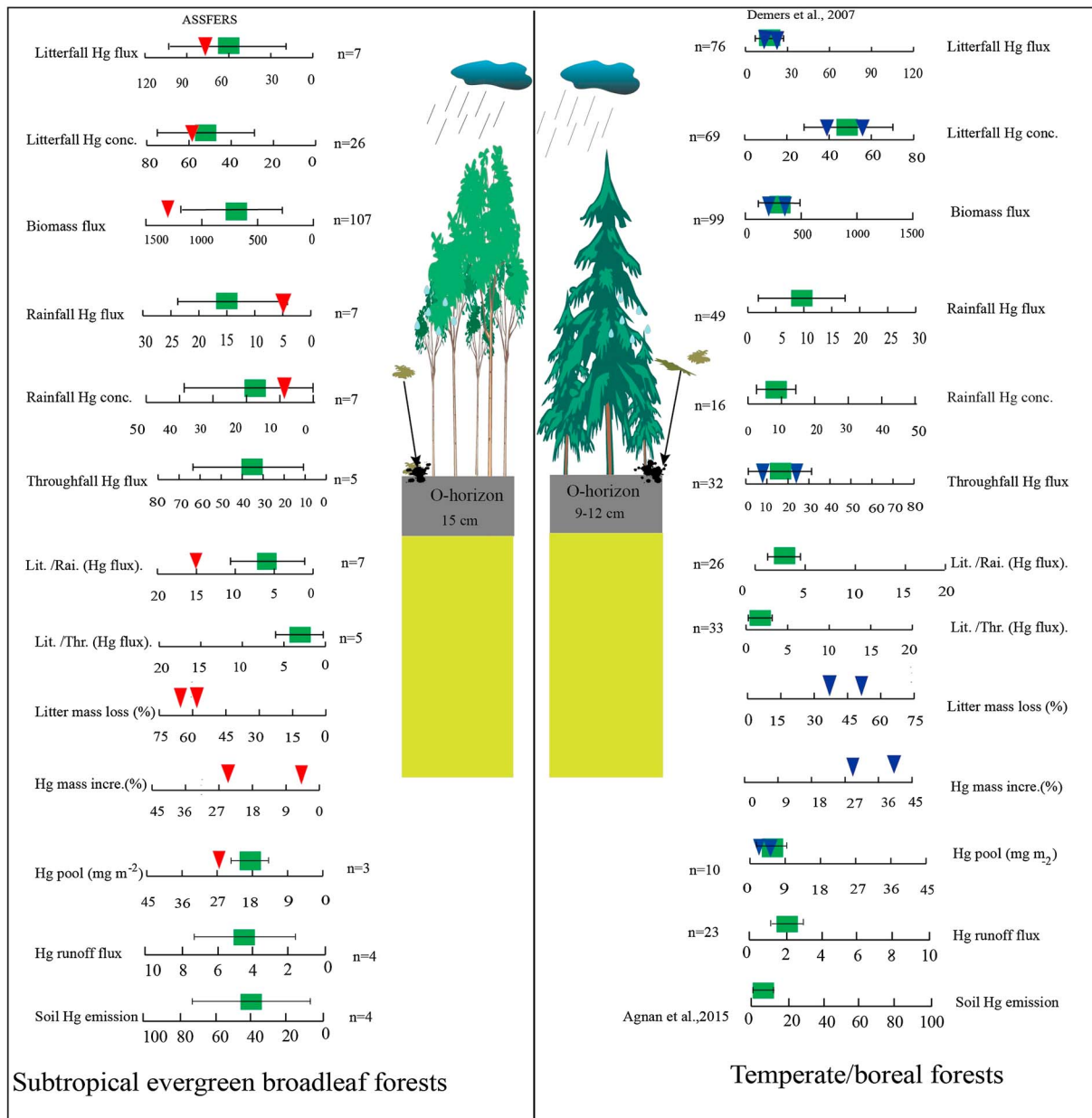


Figure 1. Differences in Hg input and accumulation (mean \pm SD) between EB and T/B forest ecosystems (Hg fluxes in $\mu\text{g m}^{-2}\text{yr}^{-1}$; rainfall Hg concentration in ng L^{-1} ; litterfall Hg concentration in ng g^{-1} ; biomass fluxes in $\text{Mg km}^{-2}\text{yr}^{-1}$; Lit./Rai. is the ratio of Hg flux contributed by litterfall over rainfall; Lit./Thr. is the ratio of Hg fluxes contributed by litterfall over throughfall; Hg mass incre. indicates the increment of Hg mass after 25 months of litter decomposition). The red triangle represents the data from ASSFERS. The blue triangle represents the data from Demers et al. [2007], soil Hg emission for T/B forests is from Agnan et al. [2015] and soil Hg pool size in O-horizon for T/B forests are from Obrist et al. [2011] and Navratil et al. [2014]. Hg concentration and flux data are available in Tables S5–S6 and obtained from previous references [Blackwell et al., 2014; Bringmark et al., 2013; Demers et al., 2007; Fisher and Wolfe, 2012; Fostier et al., 2000, 2015; Fu et al., 2010, 2015b; Graydon et al., 2008; Grigal et al., 2000; Hultberg et al., 1995; Johnson et al., 2007; Juillerat et al., 2012; Larssen et al., 2008; Lee et al., 1998, 2000; Ma et al., 2015b; Munthe and Hultberg, 2004; Munthe et al., 1995; Niu et al., 2011; Rea et al., 1996, 2001, 2002; Risch et al., 2012; Schwesig and Matzner, 2000, 2001; Selvendiran et al., 2008; Sheehan et al., 2006; Silva et al., 2006; St Louis et al., 2001a; Teixeira et al., 2012; Wang et al., 2009; Zhou et al., 2013].

(Figure S2) explains the pattern. Instead, litter in autumn and spring in an EB forest is produced from the leaves with a longer lifetime and accumulate more Hg in foliage [Luo et al., 2005; Zhang et al., 2010; Zhang, 2012]. Overall, the range of seasonal variation for Hg concentration data is 5–20% (Figure 3a). The seasonal variation of Hg concentration does not significantly change the result of previous comparison between EB and T/B forest sites (e.g., a 20% increase in mean Hg concentration at the EB forest sites does not make it significantly higher than the mean concentration observed at the T/B forest sites, $P=0.193$).

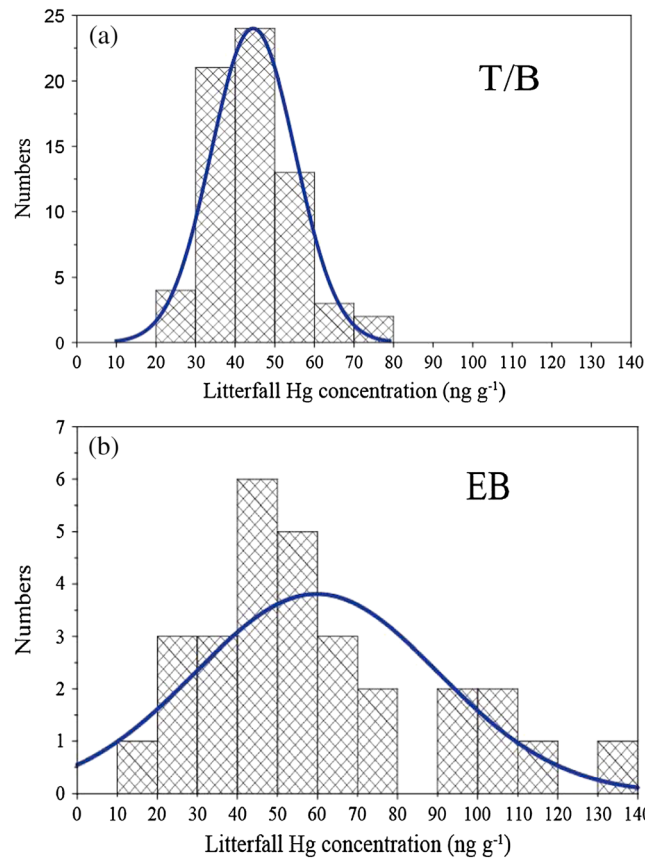


Figure 2. (a) Histogram of Hg concentration ($n = 69$) in T/B forests of Europe and North America (data in Tables S5–S6) and (b) Histogram for Hg concentration ($n = 29$) in subtropical EB forests of China.

ests, Figure 1). The annual flux is highly correlated to the litterfall production ($R^2 = 0.92$) rather than to the litterfall Hg concentration ($R^2 = 0.43$) based on 3 years of measurements at the ASSFERS; and exhibits a similar seasonal trend to the litterfall production (Figure 3b). Based on the data of litterfall biomass production at 99 T/B forest sites and at 107 EB forest sites (Figures 4a and 4b), the mean ($558 \pm 244 \text{ Mg km}^{-2} \text{ yr}^{-1}$) and median ($490 \text{ Mg km}^{-2} \text{ yr}^{-1}$) of the litter production in EB forests are ~ 2 times higher than the values (mean = $269 \pm 112 \text{ Mg km}^{-2} \text{ yr}^{-1}$, median = $258 \text{ Mg km}^{-2} \text{ yr}^{-1}$) in T/B forests ($P < 0.001$). The high litter biomass production is attributed to the rainy and warmer weather that leads to dense canopy in the subtropical regions (Figures 4c and 4d).

The present understanding of Hg mass budget in East Asia highlights strong anthropogenic Hg emissions but overlooks the potentially important Hg sink caused by the forest ecosystems [Chen et al., 2014; Lin et al., 2010]. Based on the data sets of Hg concentration ($n = 29$) and litterfall biomass production ($n = 107$) in the EB forests of China, the Hg input through litterfall is estimated to be $37.0 \pm 19.0 \mu\text{g m}^{-2} \text{ yr}^{-1}$. Considering the $249,500 \text{ km}^2$ subtropical EB forest cover in South China [Ran et al., 2012], Hg deposition through litterfall is $9 \pm 5 \text{ Mg yr}^{-1}$. Such a Hg sink alone offsets $\sim 5\%$ of total anthropogenic Hg emissions in South China [AMAP/UNEP, 2013]. In addition, Hg uptake from the atmosphere by vegetation can translocate to branches, stems, and roots [Siwik et al., 2010; Yin et al., 2013]. Even with the low Hg concentrations in these live biomasses (typically ≤ 24 ppb), Hg stored in the biomass other than the litter is considerable because of its two- to three-fold higher biomass production compared to litterfall production [Obrist, 2007]. Hence, the total Hg uptake by EB forest ecosystems could be 1–3 times higher than the estimated Hg input to the forest floor via litterfall.

Globally, production of litter biomass in EB forests is $450\text{--}1450 \text{ Mg km}^{-2} \text{ yr}^{-1}$, 2–4 times higher than T/B forests at global scale ($n = 604$ sites) [Zhang et al., 2014]. In addition, the litterfall Hg concentrations in EB forests are $\sim 50\%$ higher than those in T/B forests (Figure 5). Earlier studies in pristine tropical EB forests have suggested that the high production of litter biomass ($815 \pm 225 \text{ Mg km}^{-2} \text{ yr}^{-1}$) led to large Hg deposition via

Hg uptake by stomata has been suggested as the predominant pathway for Hg uptake by foliage [Laacouri et al., 2013], and leaf lifespan of leaves is also an important factor to shape Hg accumulation in foliage [Blackwell and Driscoll, 2015; Blackwell et al., 2014; Ericksen et al., 2003]. Generally, the leaf stomatal conductance in EB forest is lower than that in deciduous forest [Eamus, 1999; Ishida et al., 2006; Sobrado, 1991; Wang et al., 2015]. A higher stomatal conductance induces a larger air-foilage Hg^0 exchange [Graydon et al., 2006]. Leaf lifespan for evergreen needle forest is 2–5 years, in contrast to 1–2 years for EB forest [Luo et al., 2002]. A longer lifespan leads to a longer time of exposure to atmospheric Hg. The combined effect caused by the leaf lifespan and stomatal conductance of EB vegetation is likely to be the predominant driver, rather than elevated atmospheric Hg concentration, for Hg accumulation in foliage in EB forest.

Litterfall biomass production is the primary reason for the elevated Hg input from litterfall in EB forest (e.g., $1304 \pm 161 \text{ Mg km}^{-2} \text{ yr}^{-1}$ at the ASSFERS versus $318 \pm 163 \text{ Mg km}^{-2} \text{ yr}^{-1}$ in T/B for-

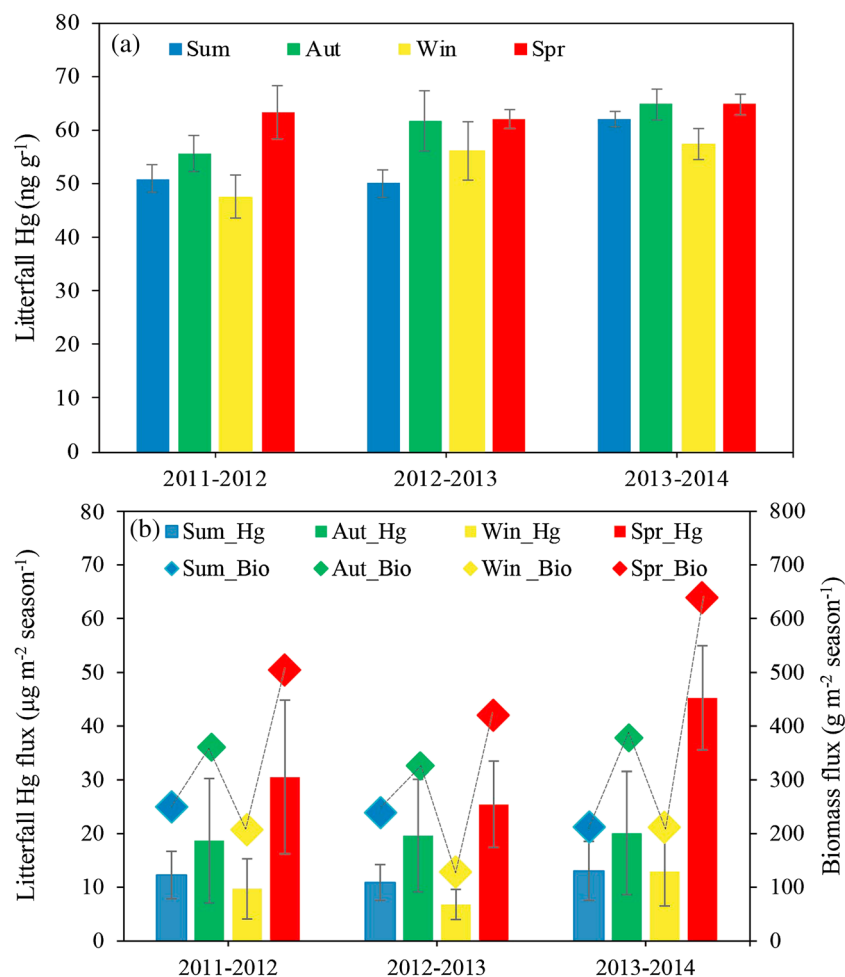


Figure 3. (a) Seasonal variation of total Hg concentrations in litterfall and (b) Seasonal variation of litterfall Hg flux and litter biomass flux during 2011–2014 for EB forests. Sum: summer, Aut: autumn, Win: winter, Spr: spring, and Bio: biomass flux. The 2011–2012 litterfall Hg concentrations/fluxes data were obtained from Zhou *et al.* [2013].

litterfall ($49.0 \pm 14.0 \mu\text{g m}^{-2} \text{yr}^{-1}$) [Fostier *et al.*, 2015]. Based on the data shown in Figure 5, the higher Hg deposition via litterfall in tropical EB forests is also caused by the elevated litterfall biomass production. Using the data collected at 107 subtropical EB and 121 tropical EB forest sites [Zhang *et al.*, 2014], the global litterfall biomass production is $773 \pm 319 \text{ Mg km}^{-2} \text{yr}^{-1}$. Given the mean Hg concentration of $72 \pm 42 \text{ ng g}^{-1}$ in litter ($n = 51$) and $19,490,000 \text{ km}^2$ land cover [Pan *et al.*, 2011], Hg deposition through litterfall in global EB forest is approximately $1086 \pm 775 \text{ Mg yr}^{-1}$, sufficiently large enough to remove 20% of Hg mass from the atmosphere ($\sim 5000 \text{ Mg Hg}$ in atmosphere) annually [Lindberg *et al.*, 2007] and offset $\sim 50\%$ of global anthropogenic Hg emission [AMAP/UNEP, 2013].

3.2. Hg Input From Precipitation in EB Forest

Figure 6a shows the 3 year seasonal Hg concentration in open-field precipitation water and the resulted wet deposition at the ASSFERS. Hg concentration in rainwater ranges from 1 to 13 ng L^{-1} with a mean value of $4.9 \pm 3.1 \text{ ng L}^{-1}$. This concentration is comparable to those observed at DMS and LGS1 (LGS1 in Southwest China, Table S4) yet is much lower than those observed at the other four rural/polluted EB forest sites ($10.9\text{--}55.3 \text{ ng L}^{-1}$, Table S4) in China. The Hg concentration in precipitation water at the ASSFERS is in the lower range of the values observed at the T/B forest sites in Europe and North America (range = $5.9\text{--}19.0 \text{ ng L}^{-1}$, median = 8.4 ng L^{-1} , $n = 16$). However, the Hg concentration in throughfall water at the ASSFERS ($22.9 \pm 11.4 \text{ ng L}^{-1}$, August–October 2015) is comparable to the values observed at the T/B forest sites (range = $9.5\text{--}40.0 \text{ ng L}^{-1}$, median = 17.8 ng L^{-1} , $n = 16$). Such differences are likely caused by the

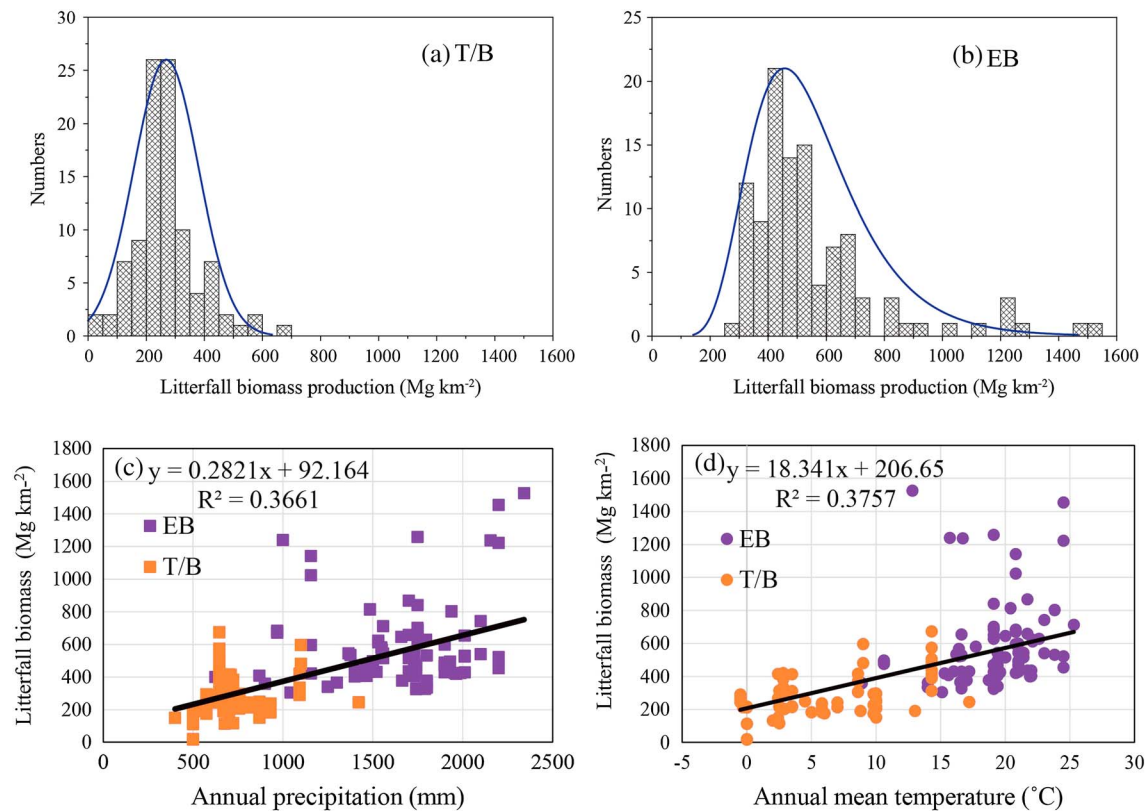


Figure 4. (a) Histogram of litterfall biomass production in T/B forests ($n = 99$), (b) histogram of litterfall biomass production in EB forests of China ($n = 107$), (c) correlation between litterfall biomass production and annual precipitation, and (d) correlation between litterfall biomass production and annual mean temperature.

high dry deposition of particle-bound Hg (PBM) in Asia [Fu *et al.*, 2015a] and can be evidenced by the elevated PBM concentration compared to reactive gaseous Hg, i.e., RGM (unpublished data, PBM concentration of mean = $31 \pm 33 \text{ pg m}^{-3}$, median = 19 pg m^{-3} , compared to RGM concentration of mean = $6 \pm 6 \text{ pg m}^{-3}$, median = 5 pg m^{-3}) during 2014–2015 at the ASSFERS.

The low Hg concentration in open-field precipitation water leads to the relatively small wet Hg deposition at the ASSFERS (mean = $4.9 \pm 4.5 \text{ } \mu\text{g m}^{-2} \text{ yr}^{-1}$). The wet deposition flux is highly correlated to the precipitation

depth ($R^2 = 0.61$). The interannual variability of wet deposition flux is mainly caused by the aqueous Hg concentration in the rainwater. Judging from the fact that the gaseous elemental Hg concentration did not vary significantly over the measurement period, the higher aqueous Hg concentration after Spring 2013 could be caused by the higher PBM/RGM during the period. Given that 40% of the precipitation occurred during August through October in 2015 (Table S2) and a total of $12.1 \text{ } \mu\text{g m}^{-2}$ Hg inputs occurred by throughfall during the period, the Hg input from throughfall at the ASSFERS is estimated to be $20\text{--}30.0 \text{ } \mu\text{g m}^{-2} \text{ yr}^{-1}$, in the higher range of those observed at the typical T/B forest sites in Europe and

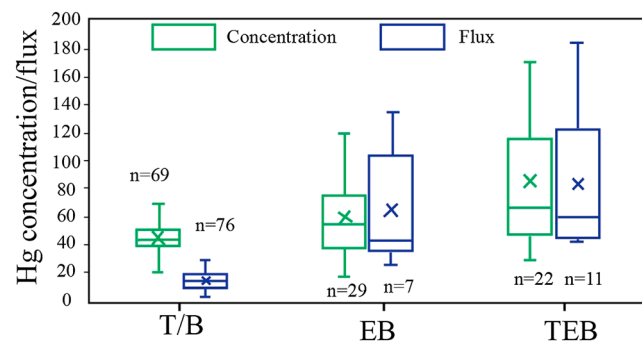


Figure 5. Hg concentration in litterfall (ng g^{-1}) and Hg deposition flux through litterfall ($\text{ } \mu\text{g m}^{-2} \text{ yr}^{-1}$). TEB: the tropical evergreen broadleaf forests. The box and whisker chart shows the maximum, 75th percentile, mean, median, 25th percentile, and the minimum. The Hg concentrations/fluxes in subtropical EB and TEB forests are significantly higher than values in T/B forests, and the Hg concentration in TEB forest is significantly higher than the value in subtropical EB forest ($P < 0.05$, by the post hoc tests, i.e., Tukey's HSD), honest significant difference test.

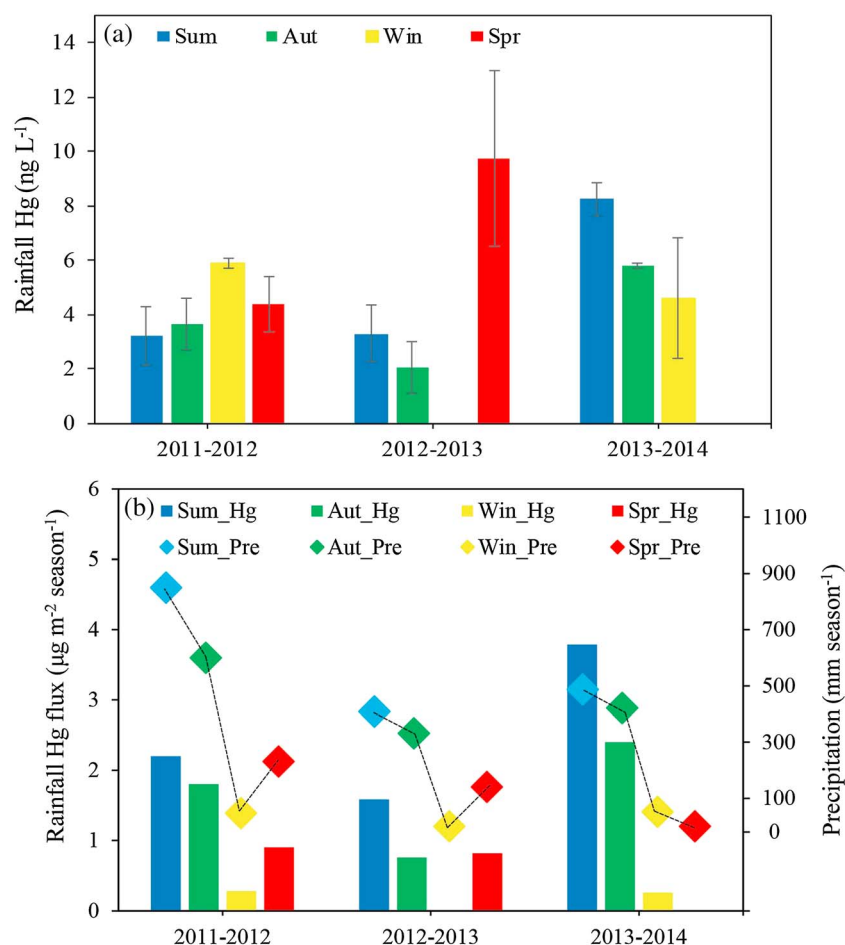


Figure 6. (a) Seasonal variation of total Hg concentrations in precipitation water during 2011–2014 and (b) seasonal variation of wet Hg flux and precipitation intensity. Sum: summer, Aut: autumn, Win: winter, Spr: spring, and Pre: precipitation. The 2011–2012 rainfall Hg concentrations/fluxes data were obtained from Zhou *et al.* [2013].

North America ($2.1\text{--}40.1\ \mu\text{g m}^{-2}\text{ yr}^{-1}$, mean = $13.8 \pm 9.5\ \mu\text{g m}^{-2}\text{ yr}^{-1}$, median = $13.4\ \mu\text{g m}^{-2}\text{ yr}^{-1}$, $n = 32$). Using the data shown in Table S4 and Figure 1, the total Hg flux through litterfall and throughfall to subtropical EB forests is 2–10 times greater than the flux to the T/B forests.

The relative importance of Hg deposition caused by litterfall and precipitation in EB forests is largely different from T/B forests. The ratio of litterfall Hg deposition over open-field wet Hg deposition up to 15 at the ASSFERS has never been observed elsewhere. Compared to other rural/polluted subtropical EB forest sites listed in Table S4, the ratio observed at the ASSFERS is also significantly higher due to the much lower wet Hg deposition at this remote EB forest site [Fu *et al.*, 2015a]. Similarly, the ratio of Hg deposition from litterfall over throughfall is in the range of 0.5–2 at the T/B forest sites, which is significantly lower than the ratio of up to 2–4 at the ASSFERS. These indicate that Hg input through litterfall in EB forests is a more predominant pathway of Hg removal than in T/B forests. More observations in EB forests are needed to quantify the contribution of EB forests to global Hg mass budget.

3.3. Accumulation of Hg in Litter During Biomass Decomposition in EB Forest

The field experiments of litter decompositions at the ASSFERS show that Hg concentration in litter biomass increases by 2.2 times over 25 months (Figure 7). The loss of biomass caused by the mineralization of litter is responsible for 90% and 75% of the Hg concentration increase in the ambient and heat-incubated samples, respectively. Total Hg mass in the decomposing litter shows a decreasing trend in both groups during the first 5 months and then continues to increase. After the 25 month experimental period, total Hg mass in litter increases by 25% in the heated samples. The 2°C higher temperature decreases the rate of Hg mass loss in the

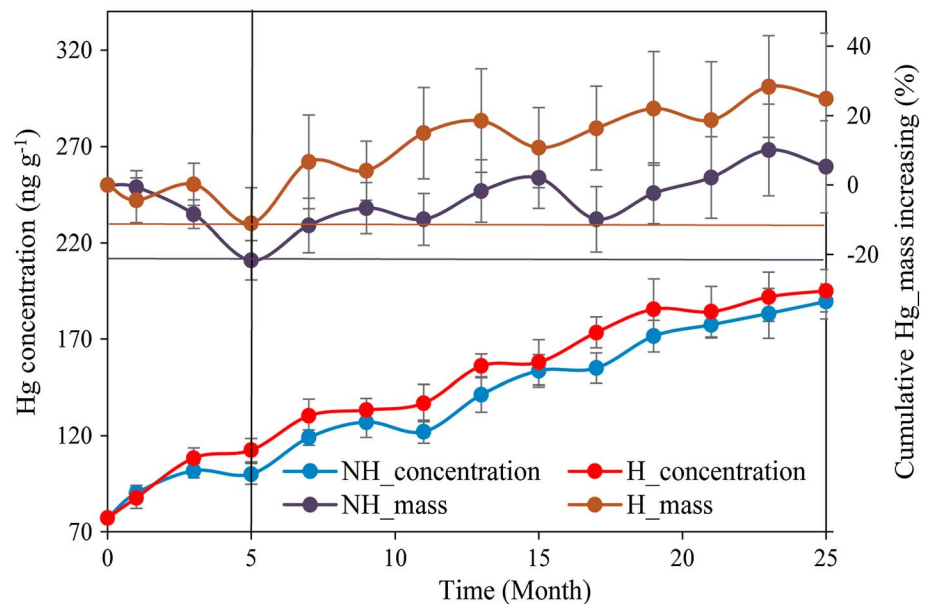


Figure 7. Changes of Hg concentration and cumulative Hg mass ratio compared to initial Hg mass in litter during 25 months of litter decomposition. NH: naturally decaying decomposition under ambient condition and H: heated decomposition at 2°C elevated temperature.

first 5 months (e.g., 22% and 11% Hg mass loss in the ambient and heated samples, $P = 0.036$ by paired t test), possibly due to the difference in microbial activities at the two temperature levels. The various degrees of cellulose and hemicellulose decomposition [Berg, 2014; Berg and McLaugherty, 2008; Cheng et al., 2010; Ferreira and Chauvet, 2011; Graca, 2001] facilitate the formation of Hg binding sites (e.g., O/N and reduced organic S functional groups) in the biomass.

The initial loss of the total Hg mass in decomposing litter has also been observed at the T/B forest sites in North America [Demers et al., 2007]. Two possible explanations have been proposed: (1) Hg^0 evasion due to the rapid carbon mineralization, and (2) Hg leaching with the newly formed dissolved organic carbons during decomposition by precipitation. The former has been verified under laboratory conditions, and the latter is partially supported by the observed Hg mass loss during litter decay in wetland and flooded reservoirs [Hall and Louis, 2004; Heyes et al., 1998]. During the early decomposition stage, the easily degradable cellulose and hemicellulose are rapidly converted to smaller organic molecules that form complexes with Hg in the biomass [Berg et al., 2008]. The water soluble fraction of the Hg-organic complexes can be washed out during precipitation events.

After the fifth month, the continuous increase of both Hg concentration and total Hg mass suggest Hg uptake from external sources. The rate of Hg mass increase is $6.1\text{--}8.9 \mu\text{g m}^{-2} \text{yr}^{-1}$ for the unheated and heated groups, slower than the rate of Hg accumulation typically observed at T/B sites over the same period of time (5–25% versus 25–48%, Figure 1). Given the greater loss of litter mass at the ASSFERS in 2 years (59–65% versus <43%, Figure 1), it is possible that the higher mineralization rates of N and S in subtropical forest [Vitousek, 1984] cause the slower Hg accumulation during litter decomposition at the study site.

Hg uptake from throughfall has been suggested as an important source of Hg accumulation in decomposing litter through adsorption and complexation of aqueous Hg(II) or through trapping of particulate Hg [Demers et al., 2007; Hall and Louis, 2004; Pokharel and Obrist, 2011]. Hg input from throughfall is estimated to be $20.0\text{--}30.0 \mu\text{g m}^{-2} \text{yr}^{-1}$ at the ASSFERS, more than sufficient to supply the accumulated Hg mass in the decaying biomass. Another possible source is through biotic Hg uptake and translocation from the O-horizon layer to the decaying litter [Demers et al., 2007]. Both mechanisms indicate a consistent sink of atmospheric Hg on the EB forest floor.

The mechanism of Hg accumulation during litter decomposition has not been well understood. One hypothesis is that existing binding sites are sufficiently abundant for continued uptake even before litter

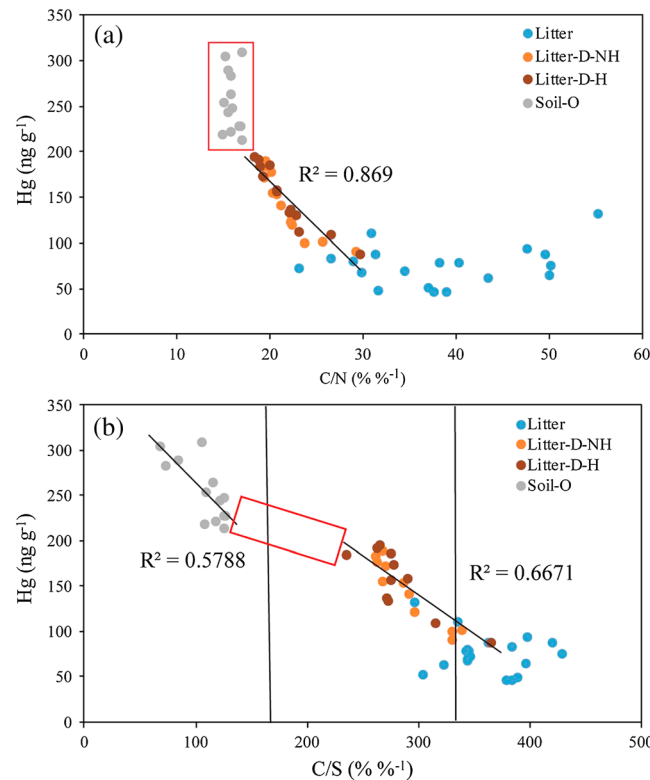


Figure 8. (a) Changes of Hg concentration in decomposing litter biomass with respect to C/N ratio and (b) changes of Hg concentration in decomposing litter biomass with respect to C/S ratio during soil development. All regression curves are significant ($P < 0.01$). Litter-D-NH is for litter decaying naturally under ambient condition, and Litter-D-H is for litter decaying at 2°C higher than ambient temperature. Soil O is for O-horizon. The red block in each figure represents the projected trend after 25 months of litter decomposition.

known that the immobilization of S occurs during litter decomposition, which produces reduced organic S (up to 65% of total S in decomposing litter biomass) [Likens et al., 2002; Ribeiro et al., 2002; Schowalter et al., 1998; Schroth et al., 2007]. In this process, the C/S ratios gradually transition from 400 to 200, suggesting dynamic transformation of S from microbial sulfur immobilization (≥ 400) to mineralization (≤ 200), then reach the low ratios typically found in O-horizon soil (Figure 8b) [Demers et al., 2013]. Figures 8a and 8b show that the C/N ratios of the decayed product at the end of 25 month decomposition experiment are close to the ratios found in the O-horizon, whereas the C/S ratios are 2 times higher and the Hg concentration is 27% lower than the values in the O-horizon. Using the Hg/C/S/N data in the O-horizon, Hg content is negatively correlated to C/S but not to C/N (Figures 8a and 8b). This suggests that the association of Hg with S continues to evolve beyond the 25 month experimental period. It is well documented that reduced organic S has a strong affinity to soft Group B metals such as Hg compared to O/N groups based on EXAFS/XANES analysis [Hesterberg et al., 2001; Schroth et al., 2007; Skyllberg et al., 2006; Xia et al., 1999]. Judging from the continuous trend of Hg and C/S, it is plausible to attribute the accumulation of Hg in the O-horizon to the organic S resulting from litter decomposition.

3.4. Soil Hg Pool Sizes in EB Forests

The Hg concentration and Hg pool size in the O-horizon soil samples collected from 2007 to 2013 at the ASSFERS are $257 \pm 14 \text{ ng g}^{-1}$ and $26.9 \pm 4.1 \text{ mg m}^{-2}$, respectively. Both are without significant year-to-year variation ($P > 0.05$). The Hg pool size in the O-horizon at the ASSFERS is up to 2–10 times greater than the pool size in T/B forests ($2.1\text{--}14.0 \text{ mg m}^{-2}$, mean = $5.8 \pm 2.9 \text{ mg m}^{-2}$, median = 6.3 mg m^{-2} , Figure 1). Although the observed Hg runoff and soil Hg evasion at rural and polluted EB forest sites are also significantly

decomposition, similar to Hg sorption on a cuticle surface [Stamenkovic and Gustin, 2009]. This process is unlikely the sole reason because Hg absorbed at the litter surface tends to be released through photochemical reduction or wash off by precipitation [Graydon et al., 2006; Laacouri et al., 2013; Stamenkovic and Gustin, 2009; Zhang et al., 2009]. Another hypothesis is built on the stoichiometric ratios of Hg, C, and N, stating that the original Hg in litter remains during litter decomposition and uptake of external Hg (adsorption of Hg wet deposition or fungal translocation) by organic matter occurs when C is gradually mineralized [Demers et al., 2013; Grigal, 2003; Navratil et al., 2014; Obrist et al., 2011].

During the litter decomposition experiments, Hg concentration increases with decreasing C/N ratio (Figure 8a) when fast initial carbohydrate mineralization takes place during the litter decomposition. The concentration increase can be attributed to the production of O/N functional groups and subsequent complex formation of Hg(II) [Hesterberg et al., 2001; Schroth et al., 2007; Skyllberg et al., 2006; Xia et al., 1999]. Interestingly, the Hg concentration also increases with decreasing C/S ratio (Figure 8b). It is well

higher than those found at the T/B forest sites ($P < 0.01$, Table S4 and Figure 1), 60–85% of the deposited Hg remains stored in the forest floor at EB forest sites [Fu *et al.*, 2010; Wang *et al.*, 2009]. The elevated soil Hg pool at the ASSFERS can be attributed to the much greater input by litterfall in the EB forest. The large Hg pool size at the ASSFERS suggests that the EB forest is at least a “past Hg sink.” Measurements for runoff and soil Hg evasion at the ASSFERS is needed to further understand the current state of Hg characteristics of source and sink in the forest floor. In addition, we recommend a longer-term study of litter decomposition to test whether or not the litter decomposition beyond the 25-month experimental period can effectively sequester Hg captured from the atmosphere.

4. Conclusions

In this study, we characterize the mass budget of Hg cycling in EB forests of China. The 3 year continuous observations at the ASSFERS, a remote EB forest site, show that Hg input via litterfall, mainly governed by the litterfall biomass production, is ~15 times greater than the input from wet deposition. The Hg accumulation in biomass and Hg uptake from external sources were observed during litter decomposition over a period of 25 months at the ASSFERS. The observed Hg accumulation in soil is closely linked to sulfur and nitrogen during the carbohydrate mineralization of litter biomass. The O-horizon soil represents a Hg pool of $26.9 \pm 4.1 \text{ mg m}^{-2}$, 2–10 times greater than the typical pool size in T/B forests. The Hg deposition through litterfall is approximately $9 \pm 5 \text{ Mg yr}^{-1}$ in the EB forests of China and $1086 \pm 775 \text{ Mg yr}^{-1}$ in global EB forests based on the observed Hg concentration and litterfall biomass production. Measurements for runoff and soil Hg evasion in remote EB forests are needed to further understand the role of EB forest ecosystems in the global biogeochemical cycling of Hg.

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