Atmos. Chem. Phys. Discuss., 15, 35857–35880, 2015
www.atmos-chem-phys-discuss.net/15/35857/2015/
doi:10.5194/acpd-15-35857-2015


Atmospheric Chemistry and Physics Discussions
Open Access



# Mercury dynamics and mass balance in a subtropical forest, southwestern China

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Received: 14 November 2015 – Accepted: 27 November 2015
– Published: 21 December 2015

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Published by Copernicus Publications on behalf of the European Geosciences Union.

## Abstract

The mid-subtropical forest area in southwest China was affected by anthropogenic mercury (Hg) emissions over the past three decades. We quantified mercury dynamics on the forest field and measured fluxes and pools of Hg in litterfall, throughfall, stream water and forest soil in an evergreen broad-leaf forest field in southwestern China. Total Hg (THg) input by the throughfall and litterfall were assessed at 32.2 and 42.9 $\mu g\, m^{-2}\, yr^{-1}$, respectively, which were obviously higher than those formerly observed from other forest fields in the background of North America and Europe. Hg fluxes across the soil/air interface (18.6 $\mu g\, m^{-2}\, yr^{-1}$) and runoff/stream flow (7.2 $\mu g\, m^{-2}\, yr^{-1}$) were regarded as the dominant ways for THg export from the forest field. The forest field hosts an enormous amount of atmospheric Hg, and its reserves were estimated to 25 341 $\mu g\, m^2$. The ratio of output to input Hg fluxes (0.34) is higher comparing with other study sites. The higher output/input ratio may represent an important ecological risk for the downstream aquatic ecosystems, even if the forest field could be an effective sink of Hg.

## 1 Introduction

Mercury (Hg) can cause damage to the environment and human health due to its extreme toxicity. It is well established that Hg as a gas phase can travel a long distance in the atmosphere so that aquatic systems in remote regions can be impacted by Hg pollution through deposition from the atmosphere (Lindberg et al., 2002a, b; Feng et al., 2009a, b). As a consequence, atmospheric deposition is the principal form of total Hg (THg) input to aquatic systems in remote pristine regions. Although Hg emissions must be reduced to mitigate current Hg contamination in surface water and fishes, the magnitude of that reduction is a critical policy debate.

Forest ecosystem is generally regarded as an active pool of Hg. Hg transformation processes in the forest is considered as a vital part of global Hg cycling and possible climate changes (Ericksen et al., 2003; Sigler et al., 2009). Most of the Hg accumulated in canopy foliage comes from atmospheric sources, rather than root uptake (Ericksen et al., 2003; Stamenkovic and Gustin, 2009). The forest canopy is a major receptor of Hg in forested landscapes (St. Louis et al., 2001). The deposited Hg to the forest may produce a certain ecological risk on the biogeochemical cycle of Hg in the forest watersheds. Hg accumulated in the forest soil may be considered as a source of both total and methyl Hg (MeHg) to aquatic ecosystems through runoff/stream flow. Moreover, Hg in the forest soil and decomposed litterfall can transfer into MeHg, resulting in increased MeHg levels in downstream wet areas. Thus the release of Hg compounds from the forest field can be considered as an initial step of Hg mobilization in forested catchments, and seems to be of high importance for its mobility.

Biogeochemical mass balance studies quantifying Hg pools and fluxes in the whole forest ecosystem are essential for assessing current rates of Hg inputs to, retention within, and release from terrestrial ecosystems. Major research initiatives have improved our understanding of current Hg pools and fluxes (Grigal et al., 2000; Schwesig and Matzner, 2001), however, knowledge of the internal cycling dynamics controlling retention within and release from these ecosystems which are located in the elevated Hg emitting regions is still limited (Demers et al., 2007). China's rapid economic development is predicted to increase the emission of atmospheric Hg (Fu et al., 2008, 2010b). The coal burning leads to Hg pollution in industrial and urban areas, as well as remote areas due to the long-range atmospheric transport of Hg (Feng and Qiu., 2008; Fu et al., 2009). In this study, we conducted a full-scale investigation on the distribution of Hg in the throughfall, litterfall and precipitation for a whole year. At the same time, we calculated the output and input of Hg during the study period. Thus, the objectives of this study were to: (1) evaluate the deposition and output fluxes of Hg in the forest field and the accumulation of THg in a subtropical forest soil pool of southwest China, (2) discuss Hg import and export characteristics via deposition and runoff/stream flow in the study field, and (3) explore the main factors affecting Hg deposition, retention within and output fluxes in the subtropical forest ecosystem.





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## 2 Materials and methods

### 2.1 Site description

We conducted this research at Mt. Simian National Natural Reserve (106°22′–106°25′ E, 28°35′–28°39′ N), which is situated about 200 km away from Chongqing city (Fig. 1). Chongqing is the largest industrial city in southwest China, where combustion of coal accounted for more than 75 % of the regional energy supplies in recent years. The study area has a subtropical monsoon climate, which means that this area has abundant rainfall every year. The mean annual temperature is 13.7 °C, with the highest and lowest records in August (average: 31.5 °C) and January (averages: −5.5 °C) respectively. The mean annual precipitation in the study area is 1522.3 mm with a daily maximum up to 160.5 mm. The study area is typical of the region with hills of 1394 m and watersheds of about 100.1 $km^{-2}$. The evergreen broad-leaf forest selected in our research is believed to be one of the most representative vegetation types preserved in the study reserve. And it is also the only largest and intact forest in the same latitude of the earth. Therefore, the evergreen broad-leaf forest was selected as the representative forest of subtropical vegetation in this research.

### 2.2 Sampling methods and analysis

#### 2.2.1 Sampling method of throughfall and precipitation

The throughfall samples were obtained from the evergreen broad-leaf forest where Hg dynamics have been investigated for one whole year, from March 2012 to February 2013. The precipitation samples were collected by self-made automatic precipitation samplers (APS-3A, Changsha Xianglan Scientific Instruments Co., Hunan, China), which were placed on the forest field of the sampling site. The throughfall was collected and measured using the same rain gauges (APS-3A, Ma et al., 2015). Four rain gauges were randomly placed in each of the three 20 m × 20 m permanent observation plots in





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each plantation, resulting in 12 throughfall sampling points for each plantation. The containers were pre-washed with dilute (5 %) HCl and thoroughly rinsed with deionized water after each sampling. Moreover, the through and precipitation samples were collected after each precipitation event from each site during the whole sampling period.

### 2.2.2 Sampling method of the stream

The stream/runoff was carried out at the edge of the forest catchment. The measured data of the stream/runoff for calculating flow rate were collected by the local hydrological departments in the outlets. Stream water samples for analysis were collected in 7 sampling sites every two weeks from March 2012 to February 2013. The 250 mL Teflon bottles were used to collect the stream water samples. The bottles were rinsed by the water samples for three times before collection. Trace-metal grade HCl was immediately treated to the samples to acidify them. It should be noted that the water samples were not filtered and thus represented the stream load of THg. The annual precipitation of the sampling site is slightly lower than the annual discharge. Therefore, it can be assumed that the calculation has a certain representativeness. Volume weighted concentrations were computed by the stream/runoff collected during the whole study period. The fluxes were achieved by multiplying the average Hg concentration by the total amount of runoff during the whole year. The robustness of the approach for THg and MeHg was 5 and 9 % respectively.

### 2.2.3 Sampling method of litterfall and soil pool

The litter samples were collected by self-made litter collectors (0.25 $m^2$), which were made from treated lumber with a screen bottom. During the study period, the collectors were placed at four different sites within the study field. The litter collected was saved in brown paper bags and transported to the laboratory under 4 °C, and then air-dried in clean environment in the laboratory until analysis. Soil samples were collected at five different sites in each field using polyvinyl chloride pipes (2.54 cm). THg in the $O_i$, $O_e$,





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and $O_a$ horizons of the forest floor were based on two replicate soil cores from each of the five litter decomposition plots in each forest stand. After freeze-dried, the samples were preserved in acid-cleaned polypropylene containers at room temperature until further analysis. Litter and soil collections were done monthly from March 2012 to February 2013.

The ultimate fate of Hg in the forest field may be fixed by the delivery of Hg into the forest floor. Hg delivered to the forest floor through litterfall is likely retained in the soil profile, whereas Hg delivered to the forest floor through throughfall is either incorporated into decomposing leaf litter or re-volatilized. At the same time, Hg accumulation in soil is a long process so the pool in soil is not comparable with Hg deposition fluxes, and delivered Hg might not be considered to be a new output on the basis of origin in forest soil. It would still be considered to be a more biologically available form of Hg. Thus, new and recycled Hg are difficult to differentiate in the soil pool. There may be very few errors of estimates of Hg output from the soil pool.

### 2.2.4 Hg volatilization from the forest field

A dynamic flux chamber (DFC) in series with Tekran 1110 synchronized dual-port sampling unit and Tekran automated Hg analyzer (2537X) were used to measure the emission rates of $Hg^0$ (Fu et al., 2010a). The DFC used here can measure 20 cm × 20 cm × 60 cm. The volume of the DFC is 0.024 $m^3$. It is made by quartz glass due to its transparency to light and potential to achieve low chamber blanks. The special DFC method was described in detail at Ma et al. (2013). Tekran 1110 can be used to alternately sample the ambient air (inlet) and vapor from soil substrate (outlet) within the chamber consecutively at five minute intervals. Hg emission fluxes were calculated by the equation below (Ma et al., 2013):

$$F = C_{\text{out}} - C_{\text{in}} \times Q/A \quad (1)$$





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Where $F$ is the flux (ng m$^2$ h$^{-1}$); $C_{out}$ and $C_{in}$ are $Hg^0$ levels at the outlet and inlet of the Hg analyzer (ng m$^3$); $Q$ is the flushing flow rate through the chamber (m$^3$ h$^{-1}$); and $A$ is the surface area of the soil exposed in the chamber (m$^2$).

Hg emission fluxes across the air/soil interface were monitored seasonally from spring 2012 to winter 2013. Hg emission flux were monitored at three sampling sites in the evergreen broadleaved forest of Mt. Simian. And the Hg emission fluxes were measured continuously for 7 days for each sampling. Quality assurance was conducted by manually injected Hg to the ambient air and soil vapor of the Tekran analyzer before and after data collection. At the beginning and end of each measurement date, the Hg fluxes over a clean TeflonTM sheet in the field was measured and regarded as the chamber blanks. The chamber blanks in our research ranged from 0.48 to 0.64 ng m$^{-2}$ h$^{-1}$, with an average of 0.54 ± 0.07 ng m$^{-2}$ h$^{-1}$ ($n = 12$). No blank value was needed to be subtracted from the flux results due to no significant difference found.

### 2.3 Sample analysis and quality control

For THg and MeHg in water samples, the special method was described at Ma et al. (2015). Detailed introduction of the measurement of THg and MeHg in soil and litter samples can also be found at Ma et al. (2015).The detection limits of THg and MeHg in this research were 0.02 and 0.01 ng L$^{-1}$ respectively. The method blank was lower than detection limits in all cases. And the equipment blanks for THg and MeHg were 0.04 and 0.02 ng L$^{-1}$, respectively. The average relative standard deviation for the duplicate analyses of THg and MeHg were 5.2 and 5.4 %, respectively. Matrix spikes recoveries for THg and MeHg were both within acceptable range, 89 to 115 % for THg, and 91 to 117 % for MeHg.





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## 3 Results and discussion

### 3.1 Hg concentrations and deposition fluxes in throughfall and litterfall

THg concentrations in the throughfall ranged from 3.2 to 62.5 ng $L^{-1}$ for the individual samples, and the average level of throughfall was 24.1 ± 7.9 ng $L^{-1}$. Canopy density did have an effect on THg and MeHg concentrations (the forest cover is more than 90 % and the canopy density is 0.9). THg concentrations measured in the throughfall of the subtropical evergreen broad-leaved forest (24.1 ± 7.9 ng $L^{-1}$) were significantly higher than those measured in the open field (10.9 ± 3.1 ng $L^{-1}$). Similar to THg concentrations, MeHg concentrations in the throughfall were nearly 2.5 times higher than that in precipitation ($p = 0.004$, $n = 49$).

THg concentrations in the throughfall were consistently at their highest in the cold season (Fig. 1), which was probably due to the lower rainfall but elevated atmospheric Hg in this season. In the subtropical region of China, the monsoon-driven climate of northwest China does not bring much precipitation in cold season. At the same time, atmospheric stability is high during the cold period, and pollutants like atmospheric Hg do not spread easily, which contributes to the higher scavenging ability of Hg of the atmosphere. While the warm season (from April to September) is influenced by the southeast monsoon, and the rainfall increases greatly, which leads to lower concentration of Hg (Fig. 1). The study station has obscure seasons and clear rainy and dry seasons. The deposition fluxes of THg through throughfall also showed the seasonal variation characteristics, with higher data appearing in wet-season (June to August). The deposition fluxes of THg through throughfall in summer at Mt. Simian accounting more than 40 % of total annual Hg deposition. It is, however, still in September and October that a higher throughfall flux is observed. This may because that the rainfall in the two months is mainly effected by Indian Monsoon, contributing to a higher rainfall (Fu et al., 2010b) comparing with other months. The minimum values for THg deposition occurred in the cold season.





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During the surveillance, THg in the throughfall was evaluated to be 32.2 $\mu g\,m^{-2}\,yr^{-1}$. The deposition fluxes of THg through throughfall in Mt. Simian were lower than those investigated in the southwestern cities of China, such as Guizhou and Chongqing (Precipitation: 8.4–62.1 $\mu g\,m^{-2}\,yr^{-1}$, throughfall: 15.6–292.1 $\mu g\,m^{-2}\,yr^{-1}$, Guo et al., 2008; Feng et al., 2009a, b; Wang et al., 2007). However, the deposition fluxes of THg through throughfall in Mt. Simian were approximately 2–10 times higher than those reported in remote areas of North America and Europe (Precipitation: 3.1–10.0 $\mu g\,m^{-2}\,yr^{-1}$, throughfall: 6.7–23.0 $\mu g\,m^{-2}\,yr^{-1}$, St. Louis et al., 2001; Keeler et al., 2005). It was obviously that the THg fluxes at Mt. Simian were higher than other sites at home and abroad. The reason perhaps was that Mt. Simian had considerably more dense forest canopies. As one of the National Natural Reserves of China, it has preserved the best subtropical evergreen broad-leaved forest of China. The forest cover in the reserves reaches over 90 %. The increased THg concentrations in throughfall mainly resulted from the dry deposition of Hg on the vegetation, followed by the washout of throughfall. Another possible reason, which may be the most important one, for the elevated deposition fluxes were probably bound up with the increased atmospheric Hg concentrations in the past 30 years due to China's fast economic development. This area, especially Chongqing city, has a large demand for energy consumption, about 70 % of which is from coal combustion. The annual mean gaseous elemental Hg (GEM) concentration in the middle of Chongqing city (more than 200 km away from the study site) tripled comparing with global background level (Yang et al., 2009), which corresponded to the high annual deposition flux of Hg in the study area. It is also reported that the GEM concentration in the study area is as high as $3.8 \pm 1.5\,ng\,m^{-3}$ (Ma et al., 2015), even if it is situated in a natural subtropical forest reserve. The MeHg flux was 0.45 $\mu g\,m^{-2}\,yr^{-1}$, which was higher than those measured in other areas. While MeHg/THg in the throughfall samples was 1.3 %, which was a relatively high value compared with other studies (Lee et al., 2000; Demers et al., 2007; Choi et al., 2008; Fu et al., 2010b; Guo et al., 2008; Larssen et al., 2008). Here, the higher ratio of MeHg to THg in throughfall samples may suggest that the contribution of MeHg from throughfall cannot be ignored





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and should be taken care of in future studies. After all, accumulation of MeHg in the soil might have caused serious risks in the functioning of natural downstream ecosystems.

The deposition fluxes of THg through litterfall were shown in Table 1. The average concentrations of THg and MeHg in leaf litter were $106.7 \pm 18.3\,\mathrm{ng\,g^{-1}}$ (SE = 2.6, $N = 60$) and $0.8 \pm 0.4\,\mathrm{ng\,g^{-1}}$ (SE = 0.2, $N = 60$), respectively. The deposition flux of THg through litterfall was estimated to be $42.9\,\mathrm{\mu g\,m^{-2}\,yr^{-1}}$ in the measurement field, which was obviously higher than the input flux through throughfall. And it is also considerably higher than litterfall fluxes reported from other regions (St. Louis et al., 2001; Demers et al., 2007). GEM can be absorbed by stomata and detained in the leaf tissue (Ericksen et al., 2003; Fu et al., 2008, 2010b). Therefore, we believed that the elevated litterfall input fluxes were directly related to the increased GEM concentrations, even in remote areas.

### 3.2 Mercury emission from soils under the canopy

The emission characteristics and air–surface exchange of GEM from the subtropical forest field have been investigated during eight intensive field campaigns from 2012 to 2013. At the forest field, GEM released from soils had the characteristic of obvious diurnal and seasonal variations. Day and night GEM fluxes were statistically different ($t$ test, $p < 0.001$), with nighttime emissions considerably lower than daytime fluxes in all seasons (Fig. 2). Average fluxes of Hg in spring, summer, autumn and winter were $12.2 \pm 5.1$, $14.2 \pm 4.7$, $9.9 \pm 2.5$, and $3.1 \pm 1.1\,\mathrm{ng\,m^{-2}\,h^{-1}}$, respectively. It can be seen that the highest value occurred in summer, followed by spring and fall, while the lowest value was observed in winter. Unlike some other studies, in which average fluxes of Hg in spring ($12.2 \pm 5.1\,\mathrm{ng\,m^{-2}\,h^{-1}}$) were slightly lower than that in summer ($14.2 \pm 4.7\,\mathrm{ng\,m^{-2}\,h^{-1}}$), it appeared that warm temperature with low canopy density in spring at the mid subtropical forest were more likely to release GEM. One of the possible reasons perhaps was that the forest canopies were lushly and well spaced in spring, and thus the forest can receive more sunlight. Therefore, the reduction rate of $Hg^{2+}$ by photochemical, thermal and biogenic processes probably increased.

This research indicated that Hg fluxes of forest field were far lower than those observed from contaminated areas such as heavily air-polluted areas in eastern Guizhou (33–3638 $ng\,m^{-2}\,h^{-1}$) (Wang et al., 2007), some cities in southwest China (15.0–44.4 $ng\,m^{-2}\,h^{-1}$) (Qiu et al., 2006), dry landfills (46.5–22.8 $ng\,m^{-2}\,h^{-1}$) (Zhu et al., 2010) and wetlands (20–500 $ng\,m^{-2}\,h^{-1}$) (Lindberg et al., 2002b). But the emission of GEM elevated in comparison with those reported from other places (Lindberg et al., 2002a, b; Travnikov, 2005). At Mt. Simian, the estimated net GEM fluxes were released from soils during the warm season (spring, summer and fall) and slightly volatilized during the cold season (winter), and thus only several data were observed with Hg deposition in the night. Hg released from the snow/air interface was extremely low comparing with the soil/air interface. Normally it was supposed that the $Hg^0$ flux was zero from snow-covered surface (Huang et al., 2012). At most subtropical areas, especially mid-subtropical forests, however, there were short winter seasons with unstable snow cover, and the snow cover season only tended to occur in January. So we assumed that there still existed $Hg^0$ emission in December and February in winter. Therefore, the annual total net Hg emission flux was 18.6 $\mu g\,m^{-2}\,yr^{-1}$.

### 3.3 Hg concentrations and out-flux in stream water

Annual volume-weighted concentrations of THg and MeHg were measured at the outlet stream of the forest field of Mt. Simian. The mean concentrations of THg and MeHg in the outflow stream were $3.9 \pm 2.0$ and $0.2 \pm 0.08$ $ng\,L^{-1}$, respectively. THg and MeHg concentrations in stream water draining the upland in our research were slightly higher than those reported in literature (Fu et al., 2008, 2010b; Larssen et al., 2008). THg concentrations in runoff/stream water in rainy seasons ($4.6 \pm 2.0$ $ng\,L^{-1}$) were significantly higher than those in dry seasons ($3.3 \pm 1.8$ $ng\,L^{-1}$), which can probably be attributed to the soil erosion and runoff. It is known that if a remote forest field does not have other obvious Hg pollution sources, Hg concentrations in the runoff/stream water can represent risks from a solitary watershed. Numerous studies showed that the remote forest already considered the forested catchments as filters between atmosphere and hydrosphere. The fate of Hg stored in the forest soils can be divided into three parts. One part of them transfers through food webs, threatening the balance of forest ecosystems; the second part of them is released into the atmosphere again; the third part of them probably transfers with the runoff/stream, becoming one of the Hg sources of downstream aquatic ecosystem. Therefore, to a certain extent, the role of forested catchments as Hg filters can be characterized by Hg output (runoff/stream) from the forest field. This study shows that, even though Hg deposition fluxes in throughfall is high, THg concentration in stream/runoff is lower than that in contaminated sites under the same geological background. This indicated that subtropical forest field had the filtering effect of Hg in precipitation and throughfall. On the other hand, the lower concentration in stream/runoff indicated that the study area did not suffer from severe anthropogenic Hg pollution. Steam output of THg was calculated by multiplying the average THg concentration in stream water ($3.9 \pm 2.03\,\mathrm{ng\,L^{-1}}$) by the water discharge rate in the forest field of the study site (annual water discharge: $1.86 \times 10^8\,\mathrm{m^3}$, from hydrological departments of Jiangjin district). The export mass flux of THg via runoff/stream was $0.73\,\mathrm{kg\,yr^{-1}}$. The subtropical forest field in the study area is $100.1\,\mathrm{km^{-2}}$. So the export mass of THg through stream water was $7.23\,\mathrm{\mu g\,m^{-2}\,yr^{-1}}$, which tripled the values reported in the catchments of Sweden ($1.6$–$1.8\,\mathrm{\mu g\,m^{-2}\,yr^{-1}}$, Lee et al., 2000; $2.4\,\mathrm{\mu g\,m^{-2}\,yr^{-1}}$, Larssen et al., 2008). Our results indicated that the output fluxes of MeHg via stream water were $0.08\,\mathrm{\mu g\,m^{-2}\,yr^{-1}}$, which was similar to or slightly larger than other results ($0.03$–$0.07\,\mathrm{\mu g\,m^{-2}\,yr^{-1}}$, Lee et al., 2000; $0.05\,\mathrm{\mu g\,m^{-2}\,yr^{-1}}$, Schwesig and Matzner, 2001). Here the elevated Hg fluxes in stream water were probably attributed to the great atmospheric Hg depositions. At the same time, our preliminary research results also illustrated that forest runoff and soil erosion could increase Hg output from subtropical forest catchments (Ma et al., 2013). But the total output fluxes of THg and MeHg were far lower than the input fluxes via wet deposition ($32.2\,\mathrm{\mu g\,m^{-2}\,yr^{-1}}$





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for THg and 0.5 µg m$^{-2}$ yr$^{-1}$ for MeHg). This study showed that the subtropical forest was able to exert purification effect of filtration, even with elevated deposition of Hg.

### 3.4 Dynamics and transport of Hg based on forest field

THg content in the forest field (forest floor and soil profiles) of Mt. Simian was shown in Table 2. The THg stocked in the forest soil was approximately 20 192 µg m$^{-2}$ (mean average soil depth is 98 cm), while that in the organic floor was 5148 µg m$^{-2}$ (mean average litter depth is 19 cm). THg content in soil profile were three times more than the organic horizon in the subtropical forest field. The active pool (the upper 22 cm, $O_i$) of THg represented 41 % of the total storage of the study area. In the soil profile, THg content in the organic horizon ($O_i$) is obviously higher than those in the other horizons. At the same time, the organic matter is well decomposed under warm and rainy subtropical climate, which has high affinity to Hg in soil. Due to the good adsorption and reduction of organic matter, the organically bound contents of Hg could be released into the environment again during decomposition of organic matter.

The ultimate fate of Hg in the terrestrial ecosystem may depend upon the means of delivery and incorporation of Hg into the forest floor. And the average Hg fluxes were also estimated. Input of THg to the forest field of Mt. Simian included net throughfall and litterfall depositions (St. Louis et al., 2001; Fu et al., 2010a). Annual throughfall and litterfall deposition fluxes of THg in Mt. Simian were 32.2 and 42.9 µg m$^{-2}$ yr$^{-1}$, respectively (Fig. 3). Litterfall deposition inputs were estimated as 134 % of throughfall deposition at the forest field. In the studied forest field, the predominant pathway of Hg fluxes to the forest floor was via ltterfall (57.1 %). An amount of the atmospherically deposited THg was released through $Hg^0$ emission at a rate of 18.6 µg m$^{-2}$ yr$^{-1}$. Steam outflow of THg from the wetland was 7.2 µg m$^{-2}$ yr$^{-1}$. The ratio between output and input of THg was 0.34 at the subtropical forest field of Mt. Simian, which was significantly higher than others (Lee et al., 2000; Larssen et al., 2008; Fu et al., 2010a). The appar-





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ently higher ratio between the output/input fluxes of THg may represent an important ecological risk.

The THg stored in the forest field was 982.2 times larger than the annual THg output by stream/runoff outflow and soil volatilization, and 337.6 times larger than the input estimated from wet and dry depositions (Fig. 3). The estimates of the deposition flux of THg in this study were much higher than values reported from the northeastern American (3.8–12.6 $\mu g\,m^{-2}\,yr^{-1}$; Driscoll et al., 2007) and Norway (7 $\mu g\,m^{2}\,yr^{-1}$; Larssen et al., 2008), probably indicating a significant impact of heavy regional Hg emissions from industry and urban on local Hg deposition. The reason perhaps was that highly soluble $Hg^{2+}$ was easily stripped from the atmosphere and deposited locally. And higher wet deposition can illustrate the obvious influence of local Hg emissions on Hg accumulation in the regional forest field. The THg flux through litterfall was 1.5 times larger than that through throughfall due to greater input of litter mass and higher Hg concentrations in the litter. Annual exports of THg in stream water of the study area (3.2–9.5 $\mu g\,m^{-2}\,yr^{-1}$) were not accorded with those reported from northern forest catchments (1.0–3.4 $\mu g\,m^{-2}\,yr^{-1}$; St. Louis et al., 2001; Grigal et al., 2000). An amount of the atmospherically deposited THg was lost via emissions at a rate of 18.6 $\mu g\,m^{-2}\,yr^{-1}$. Compared with stream outflow, the evasion of Hg from forest soil played a more essential role in THg outputs. Compared the ratios of output flux with other places (Larrsen et al., 2008; Fu et al., 2010a), the higher output flux may be greatly affected by the elevated deposition. Therefore, regional emission of Hg may have stronger influence on forest ecosystems, in which the deposition of THg through litterfall and throughfall, being affected more by local and regional changes of Hg emissions and cycling, were the main paths for Hg entering into soil surface (Demers et al., 2007). However, in this study, the outflow of Hg via runoff output and the soil–air interface accounted for a small fraction of Hg budget in the study area. And the accumulation pattern of Hg in forest floor and soil profiles was seasonal. Therefore, the accumulation of Hg in soil would be enhanced with time. At the same time, the ultimate fate of deposited Hg depends upon the biogeochemical processes that have not been well quantified within the ecosys-





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tem. Hg dynamics during litter decomposition, for instance, need to be considered as a whole so that we can better understand controls on long-term accumulation of Hg in the forest ecosystem and its delayed release to surface water.

## 4 Conclusions

In this study, the mass balance and transport of Hg in southwestern China were first measured at a subtropical forest, Chongqing, China. Results revealed that litterfall deposition inputs were the predominant pathway (42.9 $\mu g\,m^{-2}\,yr^{-1}$, account for 57.1 %) of Hg flux to the forest floor. Annual deposition fluxes of Hg through throughfall were 32.2 $m^{-2}\,yr^{-1}$, accounting for 40 % of the Hg inputs. Researchers should pay more attention to the higher ratio of MeHg to THg in the throughfall deposition when they model the biogeochemical cycling in a typical local forest watershed. For the output process, the exchange of Hg (18.6 $\mu g\,m^{-2}\,yr^{-1}$) across the forest field–air interface is an essential part of the biogeochemical cycle of Hg. Runoff/Steam outflow of THg from the wetland was 7.2 $\mu g\,m^{-2}\,yr^{-1}$. The forest field (forest floor and soil profiles) plays an important role in the cycling of THg and MeHg. In reality, it is just another problem created by the accumulation of Hg, which would be a potential risk affecting the output of Hg in the long term. Terrestrial ecosystems that have accumulated more Hg may ultimately emit them to wetlands and surface water, finally affecting the entire aquatic ecosystems. Therefore, it is a signal that we should not ignore. In this case, however, any changes in the forest floor like deforestation or forestland degradation may strongly affect Hg budget of the region.

## Data availability

Data in this research is available from the email of Professor D. Y. Wang, dywang@swu.edu.cn.





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*Author contributions.* Ma, M., Sun, T., Du, H., and Zhao, Z. collected the litterfall, throughfall, stream water and forest soil samples. Wang, Y. measured the concentrations of THg and MeHg from all samples. Sun, T. made the analysis of Hg volatilization from forest field. Ma, M. wrote the main manuscript text and drew all the figures, with contributions from all co-authors. Wang, D., Wei, S., and Ma, M. designed the research. All authors reviewed the manuscript.

*Acknowledgements.* We are also grateful to Vincent Grondin (University of Québec at Montreal) for his language modification on the early draft of the manuscript. This study was supported by the Natural Science Foundation of China (41573105), the National Basic Research Program of China (973 Program, 2013CB430003), and the Fundamental Research Funds for the Central Universities (XDJK2013B044).

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**Table 1.** Mean values of THg and MeHg concentrations and deposition fluxes in throughfall and litterfall.

| | THg Concentration ($ng\,L^{-1}$) | | | MeHg Concentration ($ng\,L^{-1}$) | | |
|---|---|---|---|---|---|---|
| | THg | DHg | PHg | MeHg | DMeHg | PMeHg |
| Precipitation | 10.94 ± 3.1 | 4.43 ± 2.2 | 6.52 ± 2.9 | 0.24 ± 0.34 | 0.11 ± 0.04 | 0.13 ± 0.10 |
| Throughfall | 24.04 ± 7.9 | 6.68 ± 4.2 | 16.35 ± 5.7 | 0.33 ± 0.24 | 0.25 ± 0.12 | 0.31 ± 0.14 |
| Litterfall | THg Concentration ($ng\,g^{-1}$) | | | MeHg Concentration ($ng\,g^{-1}$) | | |
| | 106.7 ± 18.3 | | | 0.79 ± 0.36 | | |
| Annual deposition flux | THg ($\mu g\,m^{-2}\,yr^{-1}$) | | | MeHg ($\mu g\,m^{-2}\,yr^{-1}$) | | |
| Precipitation (1508 mm) | 15.45 | | | 0.36 | | |
| Throughfall (1336 mm) | 32.17 | | | 0.45 | | |
| Litterfall (402 $g\,m^{-2}\,yr^{-1}$) | 42.89 | | | 0.32 | | |



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**Table 2.** The concentrations and contents of THg in forest floor and different soil layers.

| | | THg ($ng\,g^{-1}$) | Density ($g\,cm^{-3}$) | Thickness (m) | THg content ($\mu g\,m^{-2}$) | |
|---|---|---|---|---|---|---|
| Forest floor | Initial leaf litter | 46.30 ± 14.2 | 0.28 ± 6.2 | 0.06 ± 0.02 | 774.8 | 5148.7 |
| | Half decomposition | 51.22 ± 9.4 | 0.49 ± 18.1 | 0.08 ± 0.03 | 2000.8 | |
| | decomposition | 57.88 ± 10.3 | 0.82 ± 9.9 | 0.05 ± 0.02 | 2373.1 | |
| Soil profile | $O_i$ | 297.8 ± 15.2 | 1.27 ± 2.1 | 0.22 ± 0.10 | 8320.5 | 20 192.6 |
| | $O_e$ | 117.4 ± 32.3 | 1.65 ± 16.2 | 0.34 ± 0.08 | 6586.1 | |
| | $O_a$ | 68.4 ± 13.6 | 1.84 ± 20.7 | 0.42 ± 0.06 | 5286.0 | |





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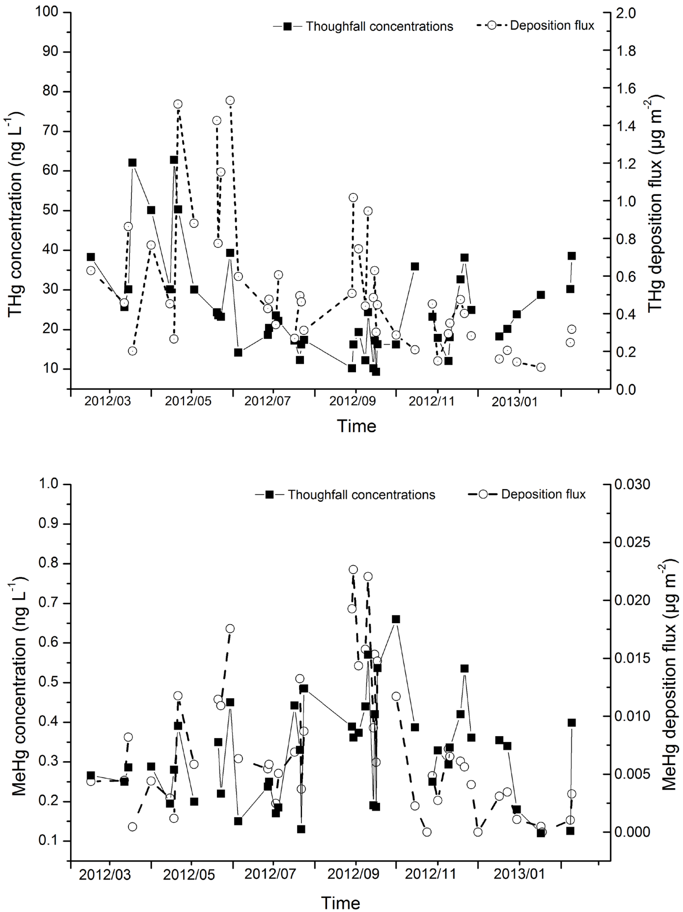


**Figure 1.** Volume-weighted mean concentrations of THg and MeHg and deposition fluxes of throughfall in evergreen broad-leaf forest from March 2012 to February 2013.





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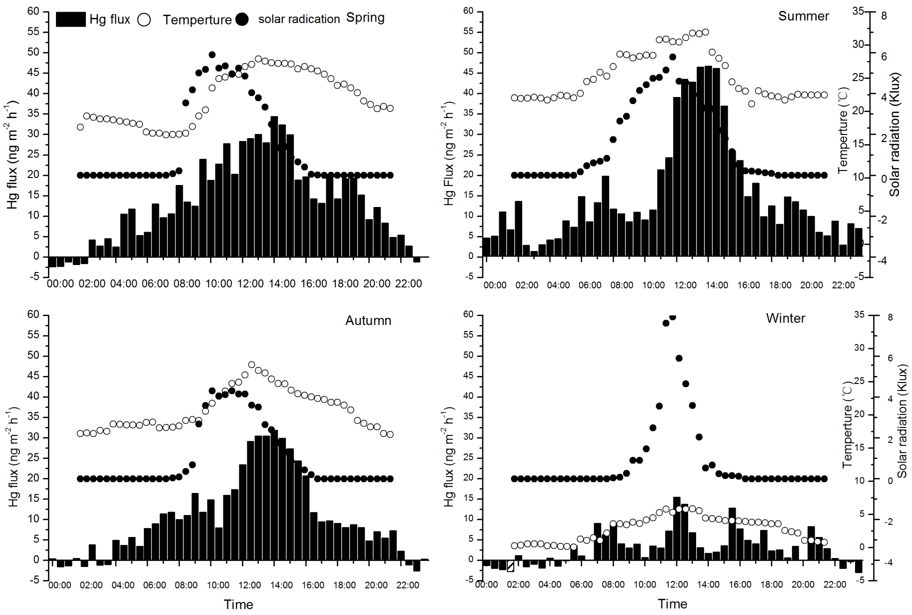


**Figure 2.** Soil emission fluxes of Hg and air temperature in the evergreen broad-leaf forest field.



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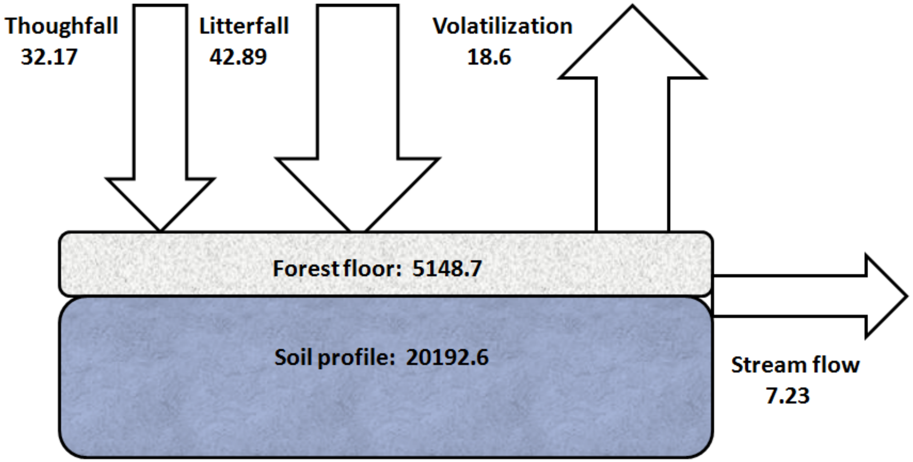


**Figure 3.** Annual ecosystem Hg fluxes and pools in the evergreen broad-leaf forest field. Fluxes ($\mu g\,m^{-2}\,yr^{-1}$) were represented by arrows, while pools ($\mu g\,m^{2}$) by boxes.





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