Response to the Referees

Thanks for the reviewers and editors' comments concerning our manuscript entitled "Mercury dynamics and mass balance in a subtropical forest, southwestern China" (acp-2015-664).
Here are our point-by-point response to all comments.

Anonymous Referee #1

P35858, L11: Too many significance digits (25 341).

We appreciate very much for this advice of the referee about the digits in L11. These are exact results of real-time investigation by our research. More significant digits, more accurate.

No change in the manuscript.

P35860, L12: Why is most representative?

We add the reasons in 2.1, before the last sentence "Therefore, the evergreen broad-leaf forest was selected as the representative forest of subtropical vegetation in this research.

"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 due to the following reasons. First, it is one of the most complete forest located in the place between Chongqing and Guizhou. Second, it is almost all subtropical forest and until recent decades is one of Asia's least populated and most inaccessible areas. Third, it is the only largest and intact forest in the same latitude of the earth."

P35860, L21: Delete self-made.

"self-made" has been deleted.

P35860, L23: Precipitation collector should be set up on open land?

We are sure the precipitation samples were collected at an open-air site near a meteorological station, which belongs to the Simian Mountain Alpine Ecosystem station of the Southwest University. Precipitation was taken from the nearest meteorological station (1318 m from the sample site) at an catchment of Mt. Simian with an elevation of 1427 m, which can be fully representative of the study area. Precipitation samples were collected by automatic APS-3A rain collectors (Changsha Xianglan Scientific Instruments Co., Hunan, China) installed in an unshadowed field at the sampling sites. We calculated the annual ratio (0.91) between precipitation amount and water discharge from the lake catchment.

No change in the manuscript.

P35861, L6: Since the catchment is so big, measure stream Hg in some sub-catchment may be better. As mentioned later, the runoff is even higher than the precipitation got in the site!

Steam outflow of THg was estimated by multiplying the mean THg concentration in stream water (3.89 ±2.03 ng L^{-1}) and water discharge rate in the forest field of Mt. Simian (annual water discharge: 1.86×108 m^3, from hydrological departments of Jiangjin district). The export mass flux of THg via runoff/stream was 0.73 kg yr^{-1}, and subtropical forest field in the study area is 100.1 km^{-2}. So the export mass of THg via stream water was 7.23 μg m^{-2} yr^{-1}, which was 3 times higher than those reported in the catchments of Sweden. Soil erosion and runoff were additional sources to stream water. THg concentrations in streamwater were slightly higher compared with precipitation, which was probably derived from soil erosion and runoff during stream transport.

No change in the manuscript.

P35861, L11: The bottle should be washed by acid.

Yes, the collected rain samples were transported in rigorously acidcleaned Teflon bottles (250 ml) and preserved by adding trace metal grade HCl. All Teflon bottles were cleaned with detergent, thoroughly rinsed with tap water, boiled in a 30% HNO3 solution (v/v) for 1.5 h and rinsed and filled with Milli-Q water.

According to the referee's suggestion, we made the following changes:

"All Teflon bottles were cleaned with detergent, thoroughly rinsed with tap water, boiled in a 30% HNO_3 solution (v/v) for 1.5 h and rinsed and filled with Milli-Q water."

P35861, L13: Not good for Hg balance! Better choosing smaller catchment or using soil water Hg leaching instead?

As far as the catchment are concerned, this is by far the most ideal place. Choosing smaller catchment or using soil water Hg leaching instead may be better, we will pay attention to this in future research.

No change in the manuscript.

P35861, L19: How to define robustness and how to obtain the values?

We appreciate very much for this question of the referee. Precision was determined by relative standard deviations. For duplicate samples, which were 5% for THg analysis in water samples, 9% for MeHg analysis inwater samples, 8% for THg analysis in soil samples, and 4.1% for THg analysis in leaf tissues.

We made the following changes in section 2.3:

"Precision was determined by relative standard deviations. For duplicate samples, the precision were 5% for THg in water samples, 9% for MeHg in water samples, 8% for THg in soil samples, and 4.1% for THg in leaf tissues."

P35861, L19: Diameter?

*We think the referee means the diameter of our self-made litter collectors in P35861, L21. It is a rectangle,0.5 m*0.5 m.*

We added this data (0.5 m×0.5 m) in P35861, L21, section 2.2.3.

P35862, L7-9: References?

We appreciate very much for this advice of the referee. We added the references at L7-9 in page 35862(Rea et al., 2001; St. Louis et al., 2001), this will be modified in the coming manuscript. This paragraph was deleted later (see reply to referee 2)

We added the references at L7-9 in page 35862(Rea et al., 2001; St. Louis et al., 2001).

P35862, L25: (C_{out}–C_{in})!

We appreciate very much for this advice of the referee. We added the bracket to the formula.

We add the bracket in the equation below:

$$F= (C_{out}–C_{in}) \times Q/A$$

P35863, L12: Was the blank too high to the detection limit? Need the results be adjusted?

Blanks of the flux sampling system were routinely measured by placing the chamber on a Quartz glass surface. Here we thought the blanks were small based on the background values of TGM of China. And we did not need to make blank correction for measured flux.

No change in the manuscript.

P35863, L18: The detection limits of Tekran 2537X is 0.1 ng/L for GEM.

We appreciate very much for this advice of the referee. We added the detection limits of Tekran 2537 X is 0.1ng L^{-1} for GEM.

According to the advice of the referee, we add the following sentence in P35863, L18, section 2.3: "The detection limits of Tekran 2537X was 0.1 ng L^{-1} for GEM."

P35865, L9: "at home" changed to "in China".

Combined with the editorial comments/suggestions, "4. Example of contradicting statements", we deleted "at home and".

So, we made the following changes based on the referee and editorial's comments:

"Obviously, the THg fluxes at Mt. Simian were higher than other sites abroad."

P35866, L5: Seasonal variation need to be introduced.

Thanks for the reviewer's suggestion. Mercury that is delivered to the forest floor with litterfall is likely retained in the soil profile, whereas mercury delivered to the forest floor in throughfall is either incorporated into decomposing leaf litter or re-volatilized. At the same time, Hg accumulation in soil is a long process that the pool in soil is not comparable with Hg deposition fluxes, and delivered Hg might not be considered a new output on the basis of origin in forest soil, it would still be considered a more biologically available form of Hg. Thus, new and recycled mercury are difficult to differentiate in the soil pool. The next step should consider this problem. There may be very little errors of estimate of Hg output from the soil pool.

We appreciate very much for this advice of the referee. We plan to add the following text to the coming manuscript: "Unlike some other studies, in which average litter fluxes of Hg in spring was slightly higher than that in autumn, it appeared that warm temperature with low canopy density in spring at mid subtropical forest were more likely to release Hg through litterfall. Although the branches and leaves were not so luxuriant, they received more deposition Hg in winter, which increased the Hg deposition in litterfall."

No change in the manuscript.

P35867, L18: Du et al. (2014) in Tieshanping, Chongqing showed different seasonal variation of soil Hg emission and indicated the importance of atmospheric Hg concentration. Some discussion added?

We have different objectives comparing with Du et al. (2014). To get accurate Hg emission data during our study period is more important in our research. So we think we do not need to add discussion of our results with Du (2014) in Tieshanping Chongqing.

No change in the manuscript.

P35868, L21: Why the MeHg not so high?

Yes, Research in recent years showed that if there is no other obvious mercury pollution sources, mercury levels in its runoff/stream water can reflect the characteristics of mercury inputs and risks of a remote forest. Studies in remote areas of forest already emphasized the role of forested catchments as filters between atmosphere and hydrosphere. THg concentration in stream/runoff was lower than that in contaminated sites under the same geological background, indicating that the study area did not suffer from severe anthropogenic Hg pollution. As for MeHg, we found that the methylation rate was not so high, the mechanisms of this may need to do further work in the future.

So, no change in the manuscript.

P35868, L24: When you concluded that the elevated Hg fluxes in stream water were probably attributed to the great atmospheric Hg depositions, you need explain there is not a geological Hg hotspot.

The referee is totally right. In the coming manuscript, we'd like to change the sentence "Here the elevated Hg fluxes in stream water were probably attributed to the great atmospheric Hg depositions" to:

"As we mentioned above that Mt. Simian was one of the most complete forest and until recent decades was one of Asia's least populated and most inaccessible areas. Average Hg concentration in soil detected in previous research was 0.28 mg kg^{-1}(Ma et al., 2013), which indicated that it was not an obvious geological Hg hotspot. Therefore, the elevated Hg fluxes in stream water were probably attributed to the great atmospheric Hg depositions."

We changed the sentence "Here the elevated Hg fluxes in stream water were probably attributed to the great atmospheric Hg depositions" (section 3.3) to:

"As we mentioned above that Mt. Simian was one of the most complete forest and until recent decades was one of Asia's least populated and most inaccessible areas. Average Hg concentration in soil detected in previous research was 0.28 mg kg^{-1} (Ma et al., 2013), which indicated that it was not an obvious geological Hg hotspot. Therefore, the elevated Hg fluxes in stream water were probably attributed to the great atmospheric Hg depositions."

P35869, L5: How deep the soil layer considered?

Soil samples were collected from soil profiles; 3 layers (nearly 98 cm) were collected from each profile according to diagnostic horizons (O_i, O_e, and O_a horizons). Horizon thickness was measured and soil cores were taken to measure soil bulk density. The average thickness of the organic soil horizon (O horizon) was 98 cm.

According to the advice of the referee, we made the following changes in 2.2.3:

"Soil samples were obtained from 5 soil profiles. Three layers (O_i, O_e, and O_a horizons) were collected from each profile according to diagnostic horizons. The average thickness of the organic soil horizon (O horizon) was ~98 cm. The O_i and O_e combined were ~38 cm in thickness, and the O_a horizon was ~60 cm."

P35869, L20: The stream flux of Hg was overestimated!

The steam outflow of THg was estimated by multiplying the mean THg concentration in stream water and the water discharge rate in the forest field of Mt. Simian. The export mass flux of THg via runoff/stream was 0.73 kg yr^{-1}, and subtropical forest field in the study area is 100.1 km^{-2}. So the export mass of THg via stream water was 7.23 $\mu g\ m^{-2}\ yr^{-1}$. The referee is right that choosing smaller catchment or using soil water Hg leaching instead may be better, so we will pay attention to it in future research. But now, this area is still the ideal area considering on all aspects.

No change in the manuscript. Please see the explanation in "reply to referee 1".

P35870, L20: Very high Hg pool in soil here (equal to many years' Hg deposition), mainly from other source than atmospheric deposition! It might not be concluded that high emission relates to high deposition. Better to show the Hg content in mineral soil and bed rock.

The referee is totally right. In the coming manuscript, we'd like to add the following sentences before "Therefore" in line 21:

"As we mentioned above that Mt. Simian was one of the most typical subtropical forest systems and the least

accessed area, average Hg concentrations in all soil surfaces of this area were below 0.30 mg kg^{-1}(Fu et al., 2010a; Ma et al., 2013).”

According to the advice of the referee, we added the following sentences before “Therefore” in line 21, P35870, section 3.4:

“As we mentioned above that Mt. Simian was one of the most typical subtropical forest systems and the least accessed area, average Hg concentrations in all soil surfaces of this area were below 0.30 mg kg^{-1}(Fu et al., 2010; Ma et al., 2013).”

Figure 2: I suggest to add Hg concentration in the atmosphere.

We’ve already showed some GEM data and discussions as references in 3.1:

“The area, especially the Chongqing city, has a large demand of energy, about 70% of which is derived from coal combustion. The annual mean GEM concentration of Hg in the main districts of Chongqing (more than 200 km away from the study site) is three-fold higher than the global background level (Lindberg et al., 2002a,b), corresponding 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 ±1.5 ng m^{-3}(Ma et al., 2015), even it located in a natural subtropical forest reserve.”

So, no change in the manuscript.

Anonymous Referee #2

Major concerns：

1. The title reads “Mercury dynamics and mass balance in a subtropical forest, southwestern China”. However, the reviewer could not find any analysis of the dynamics. If data were indeed collected in different seasons, a seasonal analysis would provide the changes of Hg in different compartments of the forest system throughout the year.

We did collect continuous data of Hg fluxes through throughfall, litterfall and runoff (stream) in different seasons (Fig.1). We collected the air-surface exchange of gaseous elemental Hg from the subtropical forest field during eight intensive field campaigns in 2012 and 2013 (Fig.2). We introduced the changes in throughfall deposition flux in the whole year in the cold and warm seasons; we also analyzed the Hg exchange fluxes between forest soil and air in the four seasons during the whole year, respectively.

“The study station has obscure seasons and clear rainy and dry seasons, throughfall deposition fluxes were also seasonal, with higher monthly THg deposition appearing during rainy months (June to August) (Fig. 1). THg throughfall deposition in summer at the study sites represents over 40% of total annual Hg deposition. It is, however, still a higher throughfall flux observed in September and October. This may because that the rainfall in this month was influenced by Indian Monsoon resulting in a high rainfall (Fu et al., 2008a). The lowest monthly values of THg deposition appeared in the cold season.” in 3.1.

“Unlike some other studies, in which average fluxes of Hg in spring (12.24 ± 5.1 ng m^{-2} h^{-1}) was slightly lower than that in summer (14.24 ± 4.7 ng m^{-2} h^{-1}), it appeared that warm temperature with low canopy density in spring at mid subtropical forest were more likely to release GEM. Because the branches and leaves were not so luxuriant but well spaced in spring and received more sunlight, which increased the rate of reduction of Hg^{2+} by photochemical and thermal processes and biological activities.” in 3.2.

No change in the manuscript.

2. It is uncommon that the forest field (defined by land cover) and watershed (defined by hydrological features) under investigation had the same size, “The study area is typical of the region with hills of 1394m

and watersheds of about 100.1 km-2." (pg_60, L12) "The subtropical forest field in the study area is 100.1km-2" (pg_68, L18). This could be one of the reasons an annual water discharge rate (1.86X 10+8 m3, from hydrological departments of Jiangjin district, pg_68, L16) greater than the water input rate (annual precipitation of 1508 mm in Table 1 times 100.1km2 = 1.52X 10+8 m3) was reported and used in the Hg flux calculation. This implies a negative evapotranspiration flux from a subtropical forest (assume the net water flow to/from the groundwater reservoirs is negligible), which is almost absent from the literature. Therefore, the representativeness of the Hg mass balance as presented could be challenged due to a large discrepancy in the water balance. In that case, the Hg mass balance may need to be reconsidered.

We appreciate very much for this question of the referee. The steam outflow of THg was estimated by multiplying the mean THg concentration in stream water and the water discharge rate in the forest field of Mt. Simian. The export flux of THg via runoff/stream was 0.73 kg yr^{-1}, and subtropical forest field in the study area is 100.1 km^{-2}. So the export mass of THg via stream water was 7.23 μg m^{-2} yr^{-1}. The referee is right that choosing smaller catchment or using soil water Hg leaching instead may be better, so we will pay attention to it in future research. But now, this area is still the ideal area considering all aspects.

No change in the manuscript.

3. Volume-weighted average Hg concentrations of precipitation, throughfall, and output stream water should be used in flux calculation. Please include those in Table 1 and the main body, in addition to (arithmetic) means as the table caption and standard deviation imply. If the values presented are indeed volume-weighted average Hg concentrations, please provide the method of standard deviation calculation.

Yes, you are right.

According to the advice of the referee, we made the following changes in 2.2.1:

"The volume-weighted mean concentration (VWM) is obtained with the formula introduced in Acid Deposition Monitoring Network in East Asia, 2012:

$$\text{VWM} = (X_1 \times V_1 + X_2 \times V_2 + \cdots + X_t \times V_t) / (V_1 + V_2 + \cdots + V_t) = \sum (X_t \times V_t) / \sum V_t$$

where, X_t means the ion concentration in each precipitation event (ng L^{-1}), V_t means the volume of each rainfall (mm).

Hg flux was determined by multiplying Hg concentrations by the volume of precipitation collected. Wet deposition fluxes of THg and MeHg were calculated according to the following equation:

$$F_W = \frac{1}{1000} \sum_{i=1}^{i=n} (C_R^i \, p^i)$$

where, F_w is the annual THg or MeHg wet deposition flux (mg m^{-2} yr^{-1}), C_i is the VWM (ng L^{-1}) of each rain sample, and P_i (mm) is the precipitation or throughfall amount."

4. The comparison with other studies was at times hard to follow due to the use of general statements of higher/lower, e.g. "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"; "The MeHg flux was 0.45 μgm-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."; "And it is also considerably higher than litterfall fluxes reported from other regions."; "But the emission of GEM elevated in comparison with those reported from other places."; "THg and MeHg concentrations in stream water draining the upland in our research were slightly higher than those reported in

literature."; "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." The authors may want to provide data support of others' results in tables as in Ma et al. (2013) and Ma et al. (2015) or provide the values or ranges in the main body."

We appreciate very much for this advice of the referee. The suggestions will benefit the improvement of the paper. We've modified the ambiguous sentence in the coming manuscript (provide data support).

According to the advice of the referee, we made the following changes:

Section 3.1: Add the data and reference "*(9.6-31.9 ng m^3, Wang et al., 2006)*":

The annual mean gaseous elemental Hg (GEM) concentration in the middle of Chongqing city (9.6-31.9 ng m^3, Wang et al., 2006), more than 200 km away from the study site, tripled comparing with global background level (Lindberg et al., 2002a,b), which corresponded to the high annual deposition flux of Hg in the study area.

Add this reference to the list:

Wang, D., He, L., Shi, X., Wei, S., and Feng, X.: Release flux of mercury from different environmental surfaces in Chongqing, China, Chemosphere, 64(11), 1845-1854, doi:10.1016/j.chemosphere.2006.01.054, 2006.

Section 3.1: Add the data "*0.4%-0.8%,*":

While MeHg/THg in the throughfall samples was 1.3 %, which was a relatively high value compared with other studies (0.4%-0.8%, Lee et al., 2000; Demers et al., 2007; Choi et al., 2008; Fu et al., 2008a; Guo et al., 2008; Larssen et al., 2008).

Section 3.2, last paragraph: Add the data "*(-5.4-4.2 ng m^3, Lindberg et al., 2002a,b; 1.7-8.4 ng m^3, Travnikov, 2005).*":

But the emission of GEM elevated in comparison with those reported from other places (-5.4-4.2 ng m^3, Lindberg et al., 2002a,b; 1.7-8.4 ng m^3, Travnikov, 2005).

Section 3.4, second paragraph: add the data "*(0.02-0.04, Lee et al., 2000; 0.16, Larssen et al., 2008; 0.30, Fu et al., 2010)*":

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 (0.02-0.04, Lee et al., 2000; 0.16, Larssen et al., 2008; 0.30, Fu et al., 2010).

5. Nearly identical methodology was employed in this study and that reported by Fu et al. (2010a: Elevated atmospheric deposition and dynamics of mercury in a remote upland forest of southwestern China), and both are in southwest China. The authors may want to compare the soil profiles, mass balance, and seasonal variations of the two studies, instead of just a comparison of the output to input ratio as presented. In addition to the study by Feng et al. (2009a: Mercury mass balance study in Wujiangdu and Dongfeng Reservoirs, Guizhou, China), another recent Hg mass balance study in south/southwest China is by Wang et al. (2009, Mercury fluxes and pools in three subtropical forested catchments, southwest China. Environmental Pollution 157, 801–808), see Table 4 in Fu et al. (2010). Inclusion of these studies in your mass balance discussion would highlight anything new that we have learned from this study.

Thanks for the referee's question. We know that atmospheric Hg emissions in China are predicted to increase due to fast economic development. The huge emissions have resulted in elevated atmospheric Hg depositions in industrial and urban areas, and have the potential to cause Hg pollution in surrounding areas and even remote

areas of China via long-range atmospheric transport. Some Studies already showed extremely high Hg deposition fluxes. These results suggested that many urbanized areas of China were exposed to atmospheric Hg contaminations due to regional anthropogenic emissions. However, there are still limitations to fully describe temporal and spatial distributions of Hg in China. Hence, there is a great need to conduct long-term continuous measurements of Hg and deposition fluxes in remote areas of China.

At the sometime, research in recent years showed that if there is no other obvious mercury pollution sources, mercury levels in its runoff/stream water can reflect the characteristics of mercury inputs and risks of a remote forest. Studies in remote areas of forest already emphasized the role of forested catchments as filters between atmosphere and hydrosphere. As for Hg accumulated in the forest soils, one part of them transfers through food webs, threatening the balance of forest ecosystems; one part of them releases into the atmosphere again; the other parts of them probably transfer 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 forest field. Therefore, even the higher Hg deposition fluxes in throughfall, it can be concluded that "THg concentration in stream/runoff was lower than that in contaminated sites under the same geological background, indicating that the study area did not suffer from severe anthropogenic Hg pollution." On one hand, this means that forested field has the filtering effect of Hg in precipitation and throughfall, even in the elevated atmospheric Hg area.

According to the advice of the referee, we added the following sentences in Conclusion:

"The runoff/Steam outflow of THg from the wetland was 7.2 mg m^{-2} yr^{-1}, which was lower than that in contaminated sites under the same geological background. Therefore, we may conclude that: 1) the study area did not suffer from severe anthropogenic Hg pollution; 2) the forested field has the filtering effect of Hg in precipitation and throughfall, even in the elevated atmospheric Hg area."

6. Some statements are not supported by data presented in this manuscript, e.g. "The annual precipitation of the sampling site is slightly lower than the annual discharge."; "The robustness of the approach for THg and MeHg was 5 and 9% respectively."; "There may be very few errors of estimates of Hg output from the soil pool."

According to the advice of the referee, we made the following changes:

"The annual precipitation of the sampling site is slightly lower than the annual discharge."; changed to:

"The subtropical forest field in the study area is 100.1 km^{-2}. Annual water discharge of the study site is 1.86×10^{8} m^{3} (hydrological departments of Jiangjin district). The annual precipitation (Table 1) of the sampling site is slightly lower than the annual discharge." (see section 2.2.2, P35861, L13-14)

"The robustness of the approach for THg and MeHg was 5 and 9% respectively." was cancelled and add the following sentences in 2.3 "Quality control":

"The precision was determined by relative standard deviations. For duplicate samples, which were 5% for THg analysis in water samples, 9% for MeHg analysis in water samples, 8% for THg analysis in soil samples, and 4.1% for THg analysis in leaf tissues."

"There may be very few errors of estimates of Hg output from the soil pool." No change.

7. Please reference your sources when presenting data/results from others work, e.g.pg _60, L6-16; pg _67, L27; pg _68, L1-3.

According to the advice of the referee, we made the following changes:

P35860, L6-16, add the reference: (Lv et al., 2014)

Add the following reference in the reference list:

Lv, W., Zhang, H., Wang, W., Du, S., Wu, Y., He, P., and Xiao, L.: Characteristics of soil aggregates in different forestlands in Simian mountains, Chongqing, J. Soil Water Conserv., 24(4):193-197, doi:10.13870/j.cnki.stbcxb.2010.04.048, 2014.

P35867, L27, add the reference: (Ma et al., 2015)

P35868, L1-3, add the reference: (Lee et al., 2000; Larssen et al., 2008; Ericksen et al., 2003)

Clarification issues

1. Please provide the division of the 12 months into the four seasons, and the dry and rainy seasons.

According to the advice of the referee, we made the following changes in 2.1:

"There are four seasons in Chongqing, spring (March to May), summer (June to August), autumn (September to November), and winter (December to February), with a well-defined wet/warm season from June to October."

See modifications in P35860, L11, section 2.1.

2. Section 2.2.4 could be condensed by referencing Ma et al., 2013, because the method employed is identical.

Section 2.2.4 had been condensed as follows according to the suggestion.

*"*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., 2010). The special DFC method was described in detail at Ma et al (2013). Hg emission fluxes were calculated by the equation below (Ma et al., 2013):*..."*

See modifications in P35862, L18-25, section 2.2.4.

3. Pg _62, L6-14, suggest removing this passage because it is not related to sampling method of litterfall and soil.

P35862, L6-14: *According to the advice of the referee, we removed the second paragraph in section 2.2.3.*

4. Pg _63, L12, "No blank value was needed to be subtracted from the flux results due to no significant difference found." Please clarify.

*This issue is also proposed by the referee #1 (**P35863, L12).***

We are sure that it is no problem based on the following reasons.

Blanks of the flux sampling system were routinely measured by placing the chamber on a Quartz glass surface. Here we thought the blanks were small based on the background values of TGM of China. And we did not need to make blank correction for measured flux.

5. Pg _64, L4, "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)." The reviewer could not find any density levels or any ranges of canopy density to support the association or a lack of association between canopy density and Hg concentrations.

Higher canopy density may be one of the reasons of higher THg and MeHg concentrations in throughfall. We believed it was one of the important reasons and proposed it in the manuscript.

So, we made no change in the coming version for this question.

6. Pg _65, L23, "GEM concentration in the study area is as high as 3.8_1.5 ng m-3 (Ma et al. (2015)." In Ma

et al. (2015), this value was reported as mean concentration in another study. Furthermore, please comment on the distance between the monitoring site in this study and that in Ma et al. (2015).

The precipitation samples were collected at an open-air site near a meteorological station, which belong to the Simian Mountain Alpine Ecosystem station of the Southwest University. Precipitation was taken from the nearest meteorological station (1318 m from the sample site in Ma et al., 2015) at an catchment of Mt. Simian with an elevation of 1427 m, which can be fully representative of the study area. Precipitation samples were collected by automatic APS-3A rain collectors installed in an unshadowed field at the sampling sites.

7. Pg _67, L16, "So we assumed that there still existed Hg^0 emission in December and February in winter." Please provide in Fig 2 the month when each seasonal sampling (pg _63, L4) was conducted. Similarly, in the main body please provide the month when each of the "eight intensive field campaigns" (pg _66, L16) was conducted.

Thanks for the good suggestion. We'll add the detailed month in fig.2 and the main text in the coming version.

According to the advice of the referee, we add the following sentences in Material and Method, section 2.2.4:

Hg emission fluxes across the air/soil interface were monitored seasonally during eight intensive field campaigns from spring 2012 to winter 2013 (Spring: March 4^{th}-16^{th}, May 8^{th} -15^{th}, 2012; Summer: July 5^{th} -12^{th}, August 15^{th} -22^{rd}, 2012; Autumn: September 15^{th} -22^{rd}, October 20^{th} -27^{th}, 2012; Winter: December 24^{th} -31^{st}, 2012; February 6^{th} -13^{th}, 2013).

The title of Fig.2 had been changed as follows:

Fig. 2. Soil emission fluxes of Hg and air temperature in the evergreen broad-leaf forest field. Spring: March 4^{th}-16^{th}, May 8^{th} -15^{th}, 2012; Summer: July 5^{th} -12^{th}, August 15^{th} -22^{rd}, 2012; Autumn: September 15^{th} -22^{rd}, October 20^{th} -27^{th}, 2012; Winter: December 24^{th} -31^{st}, 2012; February 6^{th} -13^{th}, 2013.

8. Pg _71, L7-9, the total input as presented (57.1% plus 40%) is less than 100%.

Here we want to say that the input fluxes through throughfall accounted for nearly 40% (exactly 42.9%) of the total Hg inputs, which is lower than that through litterfall. We will use the exact number (42.9%) or add the word "nearly" before 40% in the coming version.

See the modification in Conclusion.

9. The second part (pg _71, L14-21) of the Conclusions, those general statements could be better placed in the Introduction or Results and discussion section.

Thanks for your suggestion, but we discussed this question and believed that not changing the place was better.

10. Table 1, please define DHg, PHg, DMgHg, PMeHg and provide methods of analytical analyses in the main body.

Good suggestion! We'll add the definitions and analytical methods of DHg, PHg, DMgHg and PMeHg in Material and Methods.

See the modification in 2.3.

"The dissolved total mercury (DHg), dissolved methylmercury (DMeHg), particulate Hg (PHg) and particulate MeHg (PMeHg) were analyzed following the EPA Method 1631 (US EPA,1999)."

11. Table 2, please provide a column header for the last two values (5148.7, 20 192.6).

Very good suggestion! We'll add a column header, "total", for the last two values (5148.7, 20 192.6) in table 2 in the coming version.

We added "Total contents" in Table 2.

12. The meaning of the three *Os* in Table 2 and in the main body should be defined.

Very good suggestion! We'll add the meaning of the three Os in Table 2 and the main body (Materials and Methods) in the coming version.

According to the advice of the referee, we made the following changes in 2.2.3:

"Soil samples were obtained from 5 soil profiles. Three layers (O_i, O_e, and O_a horizons) were collected from each profile according to diagnostic horizons. The average thickness of the organic soil horizon (O horizon) was ~98 cm. The O_i and O_e combined were ~38 cm in thickness, and the O_a horizon was ~60 cm."

13. Fig 2 caption, "Volume-weighted mean concentrations. . ." Did you mean "Sample concentrations"? If not, please provide method to calculate volume-weighted mean concentrations for each sample.

Very good suggestion! The method to calculate "Volume-weighted mean concentrations" was introduced in "A3" of the referee 2. And we'll add this introduction in the coming version.

According to the advice of the referee, we added the method to calculate volume-weighted mean concentrations for each sample in 2.2.1. See the answer to the third question of reviewer #2.

14. The redundancy in the presentation should be eliminated, e.g. pg _69, L5-8, L8-11, L18-22.

Very good suggestion! Combing with the question 12, we will delete the introduction of Os here and define it in Materials and Methods. But we do think Line 18-22 is reasonable, so we think it should not be deleted.

Please see the modifications in 2.2.3.

Editorial comments/suggestions:

The use of English language is overall satisfactory. However, there is much room for improvement. There are quite a few awkward word choices, phrases and sentences. The authors may want to enlist the help of a native English speaker to improve the readability.

Some of my suggestions are listed below.

1. Examples of awkward word choices: obvious, obviously, formerly, fishes, whole (one whole year, whole sampling period, need to be considered as a whole, the whole forest ecosystem).

The awkward word choices, such as obvious, obviously, formerly, fishes, whole etc. had been modified.

P35858, Line 7, obviously→ remarkably; "formerly" is deleted; "fishes" → "fish".

P35859, Line 11, "whole" is deleted; Line 22, "whole" is deleted;

P35860, Line 20, "whole" is deleted;

P35861, Line 4, "whole" is deleted; Line 16, "whole" is deleted; line 17: "during the whole year" → "during the study period"

P35865, Line 9, "It was obviously that" → "Obviously,"

2. Examples of awkward phrases: Hg as a gas phase can travel; higher data; bound up; One of the possible reasons perhaps was; Normally it was supposed; mean average.

The awkward phrases, such as "Hg as a gas phase can travel; higher data; bound up; One of the possible reasons perhaps was; Normally it was supposed; mean average, and so on had been modified.

P35858, line 17: "Hg as a gas phase" → "gaseous Hg"
P35864, line 21, "with higher data appearing in wet-season" → "with higher fluxes appearing in wet-season"
P35865, line 15-17, "were probably bound up with" → "probably related with"
P35866, line 26-27, "One of the possible reasons perhaps was" → "Perhaps the primary reason lies that"
P35867, line 13, "Normally it was supposed that" → "It was supposed that"

P35869, line 5-7: "mean average" → "average".

3. Examples of awkward sentences, "Hg transformation processes in the forest is considered as a vital part of global Hg cycling and possible climate changes."; "The study area has . . .., which means that this area has . . ."; "The stream/runoff was carried out at the edge of the forest catchment. "; "The measured data of . . .were collected by the local hydrological departments in the outlets"; "It is, however, still in September and October that a higher throughfall flux is observed."; "thus only several data were observed with Hg deposition in the night"; "Numerous studies showed that the remote forest already considered the forested catchments as filters between. . ."; "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."; "An amount of the atmospherically deposited THg was released through Hg0 emission at a rate of 18.6 μgm-2 yr-1."

Awkward sentences:

P35858, line 24-26: "Hg transformation processes in the forest is considered as a vital part of global Hg cycling and possible climate changes." →
"Hg transformation processes in the forest is considered as a vital part of global Hg cycling."

P35860, line 7-8: "The study area has . . .., which means that this area has . . ."; →
"The study area has a subtropical monsoon climate, with abundant rainfall every year."

P35861, line 6-8: "The stream/runoff was carried out at the edge of the forest catchment. The measured data of . . ....were collected by the local hydrological departments in the outlets." →
"The stream/runoff was collected at the edge of the forest catchment. For the water yield of the stream/runoff, it was monitored in the outlets of the forest catchment by the local hydrological departments."

P35864, Line 23-24:
"It is, however, still in September and October that a higher throughfall flux is observed." →
"However, it is still in September and October that a higher throughfall flux is observed."

P35867, Line 11-12:
"and thus only several data were observed with Hg deposition in the night" →
"At Mt. Simian, the estimated net GEM fluxes were released from soils during the warm season and slightly volatilized during the cold season. Hg deposition was only observed in several nights of the cold season during the study period."

P35868, Line 1-2:
"Numerous studies showed that the remote forest already considered the forested catchments as filters between atmosphere and hydrosphere." →

"Numerous studies showed that the catchments of remote forest were regarded as filters between atmosphere and hydrosphere."

P35869, Line 15-16:
"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." →
"The ultimate fate of Hg in the terrestrial ecosystem may depend upon its delivery and incorporation into the forest floor."

P35869, Line 22-23:
"An amount of the atmospherically deposited THg was released through Hg0 emission at a rate of 18.6 μgm-2 yr-1." →
"A majority of atmospherically deposited THg was released through Hg^0 *at a rate of 18.6 μg* m^{-2} y^{-1}*."*

4. Example of contradicting statements, "The deposition fluxes of THg through throughfall in Mt. Simian were lower than those investigated in the southwestern cities of China, . . . approximately 2–10 times higher than those reported in remote areas of North America and Europe. . . It was obviously that the THg fluxes at Mt. Simian were higher than other sites at home and abroad." (pg _65, L2-10)
For contradicting statements:
P35865, Line 2-10:
"The deposition fluxes of THg through throughfall in Mt. Simian were lower than those investigated in the southwestern cities of China, . . . approximately 2–10 times higher than those reported in remote areas of North America and Europe. . . It was obviously that the THg fluxes at Mt. Simian were higher than other sites at home and abroad."
Yes, it is contradicted. We are sorry for the clerical error! "It was obviously that the THg fluxes at Mt. Simian were higher than other sites at home and abroad." will be changed to "Obviously, the THg fluxes at Mt. Simian were higher than other sites abroad." in the coming version.

5. Example of incorrect statements, "Unlike some other studies, in which average fluxes of Hg in spring (12.25.1 ngm-2 h-1) were slightly lower than that in summer (14.24.7 ngm-2 h-1)"; the seasonal fluxes reported here seem to be yours.
Yes, it is an incorrect use of clause. It will be changed to "The average fluxes of Hg in spring (12.25.1 ngm-2 h-1) were slightly lower than that in summer (14.24.7 ngm-2 h-1), which was different from other studies (Larssen et al., 2008; Fu et al., 2010)." (P35866, Line 23-26)

6. The word "and" may not be used to start a sentence.
We made the following changes:
P35860, Line 14, "And it is also……"→ "Third, it is the only…."
P35863, Line 6, "And the Hg emission fluxes……"→ "Hg emission fluxes…."
P35866, Line 8: "And it is also…" → *"It is also…"*
P35870, Line 11: "And higher wet deposition…" → *"Higher wet deposition…"*

7. Pg _61, L3, "through" could be replaced by "throughfall".
P35861, L3, "through" had been replaced by "throughfall". Thanks a lot!

8. Pg _66, L4, “are shown in Table 1”.
P35866, L4, “were shown in Table 1”. → “are shown in Table 1”.

9. Pg _68, L19, “export mass of THg through stream water was 7.23 μgm^{-2} yr^{-1}”. Either change to “export flux” or report total mass.
P35868, L19, “export mass of THg through stream water was 7.23 μgm^{-2} yr^{-1}”. → “export flux of THg through stream water was 7.23 μgm^{-2} yr^{-1}”

10. Pg _70, L19, “Compared the ratios of output flux with other places”, it should read “the ratios of output to input flux”, or “the output flux”.
P35870, L19, “Compared the ratios of output flux with other places, the higher output flux may be greatly…” → “Compared the ratios of output to input flux with other places, the higher ratios may be greatly...”

11. The significant figures seem to be a bit excessive at times, e.g. “982.2 times”, “337.6 times”, suggest using integers in those two incidents.
P35870, Line 3-4: “982.2 times” → “982 times”; “337.6 times” → “338 times”

12. The readability of sections 3.3 and 3.4 could be improved by avoiding long paragraphs and eliminating redundancy with sections 3.1 and 3.2, e.g. comparison of individual concentration/flux with other studies.
Thanks a lot for this suggestion. We had separate 3.3 to two paragraphs, and 3.4 to three paragraphs based on the logical relationship.

In addition, we also made other changes to the use of English language. Under the help of an English teacher from the USA in our university, the English in this paper has changed a lot and we think it can meet the requirement of ACP.

Thanks very much!
Ma Ming

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

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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 μg m^{-2} yr^{-1}, respectively, which were remarkably~~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 mg m^{-2} yr^{-1}) and runoff/stream flow (7.2 μg 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~~is estimated to 25341 μg 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.

Keywords: Mercury; flux; output/input ratio; deposition; subtropical forest

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1. Introduction

Mercury (Hg) can cause damage to the environment and human health due to its extreme toxicity. It is well established that gaseous Hg~~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 fish~~es~~, 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., 2008a, b). 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.

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~~with abundant rainfall every year. The mean annual temperature is 13.7 ℃, with the highest and lowest records in August (average: 31.5 ℃) and January (averages: –5.5 ℃) respectively. The mean annual precipitation in the study area is 1,522.3 mm with a daily maximum up to 160.5 mm (Lv et al, 2014). There are four seasons in Chongqing, spring (March to May), summer (June to August), autumn (September to November), and winter (December to February), with a well-defined wet/warm season from June to October. 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 due to the following reasons. First, it is one of the most complete forest located in the place between Chongqing and Guizhou. Second, it is almost all subtropical forest and until recent decades is one of Asia's least populated and most inaccessible areas. Third, it is the only largest and intact forest in the same latitude of the earth.~~ 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.

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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 20×20 m^2 permanent observation plots in 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 throughfall and precipitation samples were collected after each precipitation event from each site during the ~~whole~~ sampling period.

The volume-weighted mean concentration (VWM) is obtained with the formula introduced in Acid Deposition Monitoring Network in East Asia, 2012:

$$VWM = (X_1 \times V_1 + X_2 \times V_2 + \cdots + X_i \times V_i)/(V_1 + V_2 + \cdots + V_i) = \sum (X_t \times V_t)/\sum V_t$$

where, X_t means the ion concentration in each precipitation event (ng L^{-1}), V_t means the volume of each rainfall (mm).

Hg flux was determined by multiplying Hg concentrations by the volume of precipitation collected. Wet deposition fluxes of THg and MeHg were calculated according to the following equation:

$$F_W = \frac{1}{1000} \sum_{i=1}^{i=n} (C_R^i p^i)$$

where, F_w is the annual THg or MeHg wet deposition flux (mg m^{-2} yr^{-1}), C_i is the VWM (ng L^{-1}) of each rain sample, and P_i (mm) is the precipitation or throughfall amount.

2.2.2 Sampling method of the stream

The stream/runoff was c~~arried out~~ollected at the edge of the forest catchment. For the water yield of the stream/runoff, it was monitored in the outlets 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. All Teflon bottles were cleaned with detergent, thoroughly rinsed with tap water, boiled in a 30% HNO_3 solution (v/v) for 1.5 h, rinsed and filled with Milli-Q water.~~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 subtropical forest field in the study area is 100.1 km^{-2}. Annual water discharge of the study site is 1.86×10^8 m^3 (hydrological departments of Jiangjin district). The annual precipitation (Table 1) of the sampling site is slightly lower than the annual discharge.~~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~~study period. ~~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 (0.5 m ×0.5 m~~0.25 m²~~), 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). Soil samples were obtained from 5 soil profiles. Three layers (O_i, O_e, and O_a horizons) were collected from each profile according to diagnostic horizons. The average thickness of the organic soil horizon (O horizon) was ~98 cm. The O_i and O_e combined were ~38 cm in thickness, and the O_a horizon was ~60 cm. THg in the O_i, O_e, 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., 2010). The special DFC method was described in detail at Ma et al. (2013). ~~The DFC used here can measure 20 cm × 20 cm × 60 cm. The volume of the DFC is 0.024 m³. 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):

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

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 during eight intensive field campaigns from spring 2012 to winter 2013 (Spring: March 4th-16th, May 8th -15th, 2012; Summer: July 5th -12th, August 15th -22rd, 2012; Autumn: September 15th -22rd, October 20th -27th, 2012; Winter: December 24th -31st, 2012; February 6th -13th, 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

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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 ng L^{-1} and 0.01 ng L^{-1} respectively. The dissolved total mercury (DHg), dissolved methylmercury (DMeHg), particulate Hg (PHg) and particulate MeHg (PMeHg) were analyzed following the EPA Method 1631 (US EPA,1999).The method blank was lower than detection limits in all cases. And the equipment blanks for THg and MeHg were 0.04 ng $L^{-1}$and 0.02 ng L^{-1}, respectively. The detection limits of Tekran 2537X was 0.1 ng L^{-1} for GEM. 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. Precision was determined by relative standard deviations. For duplicate samples, the precision were 5% for THg in water samples, 9% for MeHg in water samples, 8% for THg in soil samples, and 4.1% for THg in leaf tissues.

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 doesn't 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~~in 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~~ fluxes appearing in wet-season (June to August). The deposition fluxes of THg through throughfall in summer at Mt. Simian account~~ing~~ed more than 40% of total annual Hg deposition. ~~It is, H~~However, it is 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., 2008a) comparing with other months. The minimum values for THg deposition occurred in the cold season.

During the surveillance, THg in the throughfall was evaluated to be 32.2 μg 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 μg m^{-2} yr^{-1}, throughfall: 15.6–292.1 μg 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 μg m^{-2} yr^{-1}, throughfall: 6.7–23.0 μg m^{-2} yr^{-1}, St. Louis et al., 2001; Keeler et al., 2005). Obviously,~~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, which may be the most important one, ~~were~~ probably ~~bound up~~related 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, and about 70% of which is from coal combustion. The annual mean gaseous elemental Hg (GEM) concentration in the middle of Chongqing city (9.6-31.9 ng m^3, Wang et al., 2006), more than 200 km away from the study site,~~)~~ tripled comparing with global background level (Lindberg et al., 2002a, b~~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 ±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 μg 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 (0.4%-0.8%, Lee et al., 2000; Demers et al., 2007; Choi et al., 2008; Fu et al., 2008a; 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 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~~ are shown in Table 1. The average concentrations of THg and MeHg in leaf litter were 106.7±18.3 ng g^{-1} (SE = 2.6, N=60) and 0.8±0.4 ng g^{-1}(SE = 0.2, N=60), respectively. The deposition flux of THg through litterfall was estimated to be 42.9 μg m^{-2} yr^{-1} in the measurement field, which was ~~obvious~~remarkably higher than the input flux through throughfall. ~~And i~~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., 2008a, b). 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

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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 that in daytime ~~fluxes~~ in all seasons (Fig.2). Average fluxes of Hg in spring, summer, autumn and winter were 12.2 ±5.1 ng m^{-2} h^{-1}, 14.2 ±4.7 ng m^{-2} h^{-1}, 9.9 ±2.5 ng m^{-2} h^{-1}, and 3.1 ± 1.1 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~~The average fluxes of Hg in spring (12.2 ± 5.1 ng m^{-2} h^{-1}) were slightly lower than that in summer (14.2 ±4.7 ng m^{-2} h^{-1}), which was different from other studies (Larssen et al., 2008; Fu et al., 2010). ~~I~~it appeared that warm temperature with low canopy density in spring at the mid subtropical forest were more likely to release GEM. Perhaps the primary reason lies that~~One of the possible reasons perhaps was that~~ the forest canopies ~~were~~ are 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 (-5.4-4.2 ng m^3, Lindberg et al., 2002a, b; 1.7-8.4 ng m^3, 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)~~. Hg deposition was only observed in several nights of the cold season during the study period, ~~, 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. I~~Normally i~~t 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 mg 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 ±2.0 and 0.2±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., 2008a,b; Larssen et al., 2008). THg concentrations in runoff/stream water in rainy seasons (4.6±2.0ng L^{-1}) were significantly higher than those in dry seasons (3.3±1.8 ng L^{-1}), which can probably be attributed to the soil erosion and runoff (Ma et al., 2015). 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 catchments of~~the~~ remote forest ~~already considered the forested catchments~~were regarded as filters between atmosphere and hydrosphere (Lee et al., 2000; Larssen et al., 2008; Ericksen et al., 2003). 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

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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~~ showed that, even though Hg deposition fluxes in throughfall ~~i~~was high, THg concentration in stream/runoff wa~~i~~s 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 ±2.03 ng L^{-1}) by the water discharge rate in the forest field of the study site (annual water discharge: 1.86×10^8 m^3, from hydrological departments of Jiangjin district). The export ~~mass~~ flux of THg via runoff/stream was 0.73 kg yr^{-1}. The subtropical forest field in the study area is 100.1 km^{-2}. So the export ~~mass~~ flux of THg through stream water was 7.23 μg m^{-2} yr^{-1}, which tripled the values reported in the catchments of Sweden (1.6–1.8 μg m^{-2} yr^{-1}, Lee et al., 2000; 2.4 μg m^{-2} yr^{-1}, Larssen et al., 2008). Our results indicated that the output fluxes of MeHg via stream water were 0.08 μg m^{-2} yr^{-1}, which was similar to or slightly larger than other results (0.03–0.07 μg m^{-2} yr^{-1}, Lee et al., 2000; 0.05 μg 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.~~ As we mentioned above that Mt. Simian was one of the most complete forest and until recent decades was one of Asia's least populated and most inaccessible areas. Average Hg concentration in the soil detected in previous research was 0.28 mg kg^{-1} (Ma et al., 2013), which indicated that it was not an obvious geological Hg hotspot. Therefore, 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 μg m^{-2} yr^{-1} 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~~ under the condition of 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 20192 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 the decomposition of organic matter.

The ultimate fate of Hg in the terrestrial ecosystem may depend upon ~~the means of~~its 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., 2010). Annual throughfall and litterfall deposition fluxes of THg in Mt. Simian were 32.2 and 42.9 mg m^{-2} y^{-1}, respectively (Fig.3). Litterfall deposition inputs were

estimated ~~as~~to 134% of the throughfall deposition at the forest field. In the ~~studied~~ study forest field, the predominant pathway of Hg fluxes to the forest floor was via ltterfall (57.1%). A majority of~~An amount of the~~ atmospherically deposited THg was released through Hg^0 ~~emission~~ at a rate of 18.6 μg m^{-2} y^{-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 (0.02-0.04, Lee et al., 2000; 0.16, Larssen et al., 2008; 0.30, Fu et al., 2010). The apparently 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 338~~7.6~~ 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 μg m^{-2} yr^{-1}; Driscoll et al., 2007) and Norway (7 μg 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. H~~And h~~igher wet deposition can illustrate the ~~obvious~~ remarkable 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 μg $m^{-2}yr^{-1}$) were not accorded with those reported from northern forest catchments (1.0–3.4 μg 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 μg 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 to input flux with other places (Larrsen et al., 2008; Fu et al., 2010), the higher ~~output flux~~ratio 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. As we mentioned above that Mt. Simian was one of the most typical subtropical forest systems and the least accessed area, average Hg concentrations in all soil surfaces of this area were below 0.30 mg kg^{-1}(Fu et al., 2010; Ma et al., 2013). 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 ecosystem. 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 mg m^{-2} y^{-1}, account for 57.1%) of Hg flux to the forest floor. Annual deposition fluxes of Hg through throughfall were 32.2 m^{-2} y^{-1}, accounting for 42.9~~0~~% 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 μg m^{-2} y^{-1}) across the forest field-air interface ~~is~~ was an essential part of the biogeochemical cycle of Hg. The ~~R~~runoff/~~S~~steam outflow of THg from the wetland was 7.2 mg m^{-2} yr^{-1}~~.~~, which was lower than that in contaminated sites under the same geological background. Therefore, we may conclude that: 1) the study area does not suffer from severe anthropogenic Hg pollution; 2) the forested field has the filtering effect of Hg in precipitation and throughfall, even in the elevated atmospheric Hg area.

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 the 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.

Author contribution

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.

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References

Choi, H. D., Sharac, T. J., and Holsen, T. M.: Mercury deposition in the Adirondacks: A comparison between precipitation and throughfall, Atmos. Environ., 42(8), 1818–1827, doi:10.1016/j.atmosenv.2007.11.036, 2008.

Demers, J. D., Driscoll, C. T., Fahey, T. J., and Yavitti, J. B.: Mercury cycling in litter and soil in different forest types in the Adirondack region, New York, USA, Ecol. Appl., 17(5), 1341–1351, doi:10.1890/06-1697.1, 2007.

Driscoll, C. T., Han Y. J., Chen, C.Y., Evers, D. C., Lambert, K. F., Holsen, T. M., Kamman, N. C., and Munson, R.K.: Mercury contamination in forest and freshwater ecosystems in the northeastern United States. BioScience, 57, 17–28, doi:10.1641/B570106, 2007.

Ericksen, J. A., Gustin, M. S., Schorran, D. E., Johnson, D. W., Lindberg, S. E., and Coleman, J. S.: Accumulation of atmospheric mercury in forest foliage, Atmos. Environ., 37(12), 1613–1622, doi:10.1016/S1352-2310(03)00008-6, 2003.

Feng, X., and Qiu, G.: Mercury pollution in Guizhou, Southwestern China– an overview~~.~~, Sci.

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Total Environ., 400, 227–237, doi:10.1016/j.scitotenv.2008.05.040, 2008.
Feng, X., Jiang, H., Qiu, G., Yan, H., Li, G., and Li, Z.: Mercury mass balance study in Wujiangdu and Dongfeng reservoirs, Guizhou, China, Environ. Pollut., 157, 2594–2603, doi:10.1016/j.envpol.2009.05.024, 2009a.
Feng, X., Jiang, H., Qiu, G., Yan, H., Li, G., and Li, Z.: Geochemical processes of mercury in Wujiangdu and Dongfeng reservoirs, Guizhou, China, Environ. Pollut., 157, 2970–2984, doi:10.1016/j.envpol.2009.06.002, 2009b.
Fu, X., Feng, X., Dong, Z., Yin, R., Wang, J., Yang, Z., and Zhang, H.: Atmospheric gaseous elemental mercury (GEM) concentrations and mercury depositions at a high-altitude mountain peak in south China, Atmos. Chem. Phys., 10, 2425–2437, doi:10.5194/acp-10-2425-2010, 2008a.
Fu, X., Feng, X., Zhu, W., Wang, S., and Lu, J.: Total gaseous mercury concentrations in ambient air in the eastern slope of Mt. Gongga, South-Eastern fringe of the Tibetan plateau, China, Atmos. Environ., 42, 70–979, doi:10.1016/j.atmosenv.2007.10.018, 2008b.
Fu, X., Feng, X., Wang, S., Rothenberg, S., Shang, L., Li, Z., and Qiu, G.: Temporal and spatial distributions of total gaseous mercury concentrations in ambient air in a mountainous area in southwestern China: Implications for industrial and domestic mercury emissions in remote areas in China, Sci. Total Environ., 407, 2306–2314, doi:10.1016/j.scitotenv.2008.11.053, 2009.
Fu, X., Feng, X., Zhu, W., Rothenberg, S., Yao, H., and Zhang, H.: Elevated atmospheric deposition and dynamics of mercury in a remote upland forest of Southwestern China, Environ. Pollut., 158, 2324–2333, doi:10.1016/j.envpol.2010.01.032, 2010.
Grigal, J. A., Kolka, R. K., Fleck, J. A., and Nater, E. A.: Mercury budget of an upland-peatland watershed, Biogeochemistry, 50(1), 95–109, doi: 10.1023/A:1006322705566, 2000.
Guo, Y., Feng, X., Li, Z., He, T., Yan, H., Meng, B., Zhang, J., and Qiu, G.: Distribution and wet deposition fluxes of total and methyl mercury in Wujiang reservoir Basin, Guizhou, China, Atmos. Environ., 42, 7096–7103, doi:10.1016/j.atmosenv.2008.06.006, 2008.
Huang, J., Kang, S., Zhang, Q., Jenkins, M., Guo, J., Zhang, G., and Wang, K.: Spatial distribution and magnification processes of mercury in snow from high-elevation glaciers in the Tibetan Plateau, Atmos. Environ., 46 (1), 140–146, doi:10.1016/j.atmosenv.2011.10.008, 2012.
Keeler, G. J., Gratz, L. E., and Al-wali, K.: Long-term atmospheric mercury wet deposition at Underhill, Vermont, Ecotoxicology, 14(1–2), 71–83, doi:10.1007/s10646-004-6260-3, 2005.
Larssen, T., De Wit, H. A., Wiker, M., and Halse, K.: Mercury budget of a small forested boreal catchment in southeast Norway, Sci. Total Environ., 404(2–3), 290–296, doi:10.1016/j.scitotenv.2008.03.013, 2008.
Lee, Y. H., Bishop, K. H., and Munthe, J.: Do concepts about catchment cycling of methylmercury and mercury in boreal catchments stand the test of time? Six years of atmospheric inputs and runoff export at Svartberget, northern Sweden, Sci. Total Environ., 260, 11–20, doi:10.1016/S0048-9697(00)00538-6, 2000.
Lindberg, S. E., Zhang, H., Vette, A. F., Gustin, M. S., Barnett, M. O., and Kuiken, T.: Dynamic flux chamber measurement of gaseous mercury emission fluxes over soils, Part 2: effect of flushing flow rate and verification of a two-resistance exchange interface simulation model. Atmos. Environ, 36, 847–859, doi:10.1016/S1352-2310(01)00502-7, 2002a.
Lindberg, S. E., Dong, W., and Meyers, T.: Transpiration of gaseous elemental mercury through vegetation in a subtropical wetland in Florida. Atmos. Environ., 36, 5207–5219, doi: 10.1016/S1352-2310(02)00586-1, 2002b.

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Lv, W., Zhang, H., Wang, W., Du, S., Wu, Y., He, P., and Xiao, L.: Characteristics of soil aggregates in different forestlands in Simian mountains, Chongqing, J. Soil Water Conserv., 24(4):193-197, doi:10.13870/j.cnki.stbcxb.2010.04.048, 2014.

Ma, M., Wang, D., Du H, Sun, R., Zhao Z., and Wei S.: Gaseous mercury emissions from subtropical forested and open field soils in a national nature reserve, southwest China, Atmos. Environ., 64,116–123, doi:10.1016/j.atmosenv.2012.09.038, 2013.

Ma, M., Wang, D., Sun, R., Shen, Y., and Huang L.: Atmospheric mercury deposition and its contribution of the regional atmospheric transport to mercury pollution at a national forest nature reserve, southwest China,- Environ. Sci. Pollut. Res., online, doi: 10.1007/s11356-015-5152-9, 2015.

Qiu, G., Feng, X., Wang, S., and Shang, L.: Environmental contamination of mercury from Hg-mining areas in Wuchuan, northeastern Guizhou, China, Environ. Pollut., 142 (3), 549–558, doi:10.1016/j.envpol.2005.10.015, 2006.

Schwesig, D., and Matzner, E.: Dynamics of mercury and methylmercury in forest floor and runoff of a forested watershed in Central Europe, Biogeochemistry, 53(2), 181–200, doi: 10.1023/A:1010600600099, 2001.

Sigler, J. M., Mao, H., and Talbot, R.: Gaseous elemental and reactive mercury in Southern New Hampshire, Atmos. Chem. Phys., 9, 1929–1942, doi:10.5194/acp-9-1929-2009, 2009.

St. Louis, V. L., Rudd, W. M, Kelly, C. A., Hall, B. D., Rolfhus, K. R., Scott, K. J., Lindberg, S. E., and Dong, W.: Importance of the forest canopy to flux of methylmercury and total mercury to boreal ecosystems, Environ. Sci. Technol., 35, 3089–3098, doi: 10.1021/es001924p, 2001.

Stamenkovic, J., and Gustin, M. S.: Nonstomatal versus Stomatal uptake of atmospheric mercury, Environ. Sci. Technol., 43,1367–1372, doi: 10.1021/es801583a, 2009.

Travnikov, O.: Contribution of the intercontinental atmospheric transport to mercury pollution in the Northern Hemisphere, Atmos. Environ., 39, 7541–7548, doi:10.1016/j.atmosenv.2005.07.066, 2005.

US EPA: Method 1631: Revision B, Mercury in water by Oxidation, Purge and Trap, and Cold Vapor atomic Fluorescence Spectrometry, United States Environmental Protection Agency, 1–33, 1999.

~~US EPA: Method 1630: Methyl mercury in water by distillation, aqueous ethylation, purge and trap, and CVAFS. U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology Engineering and Analysis Division (4303), 1200 Pennsylvania Avenue NW, Washington, DC 20460, 1–41, 2001.~~

Wang, D., He, L., Shi, X., Wei, S., and Feng, X.: Release flux of mercury from different environmental surfaces in Chongqing, China, Chemosphere, 64(11), 1845-1854, doi:10.1016/j.chemosphere.2006.01.054, 2006.

Wang, S., Feng, X., Qiu, G., Fu, X., and Wei, Z.: Characteristics of mercury exchange flux between soil and air in the heavily air-polluted area, eastern Guizhou, China, Atmos. Environ., 41(27), 5584–5594, doi:10.1016/j.atmosenv.2007.03.002, 2007.

Zhu, J., Wang, D., Liu, X., and Zhang, Y.: Mercury fluxes from air/surface interfaces in paddy field and dry land, Appl. Geochemistry, 26(2), 249–255, doi:10.1016/j.apgeochem.2010.11.025, 2010.

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Tables

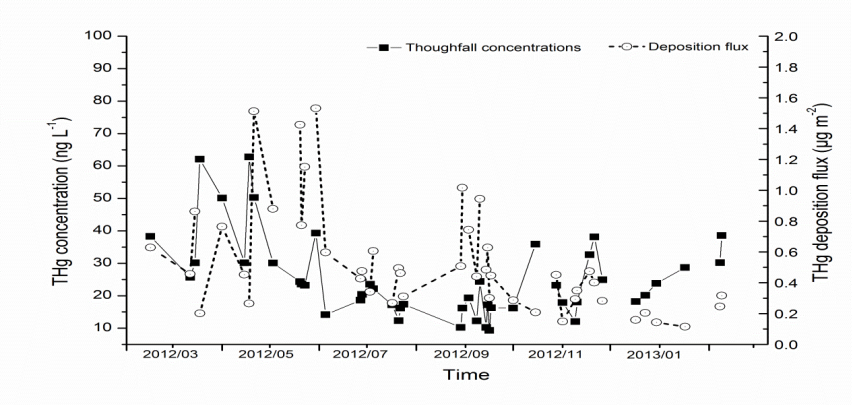
Table 1 Mean values of THg and MeHg concentrations and deposition fluxes in throughfall and litterfall

	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 (μg m^{-2} yr^{-1})			MeHg (μg m^{-2} yr^{-1})		
Precipitation (1508mm)	15.45			0.36		
Throughfall (1336mm)	32.17			0.45		
Litterfall (402g m^{-2} yr^{-1})	42.89			0.32		

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 (μg m^{-2})	Total contents
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	20192.6
	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	

Figures



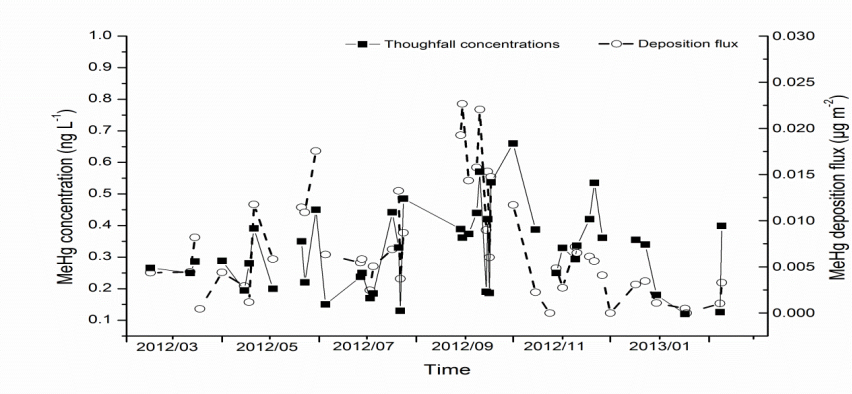


Fig. 1. Volume-weighted mean concentrations of THg and MeHg and deposition fluxes of throughfall in the evergreen broad-leaf forest from March 2012 to February 2013

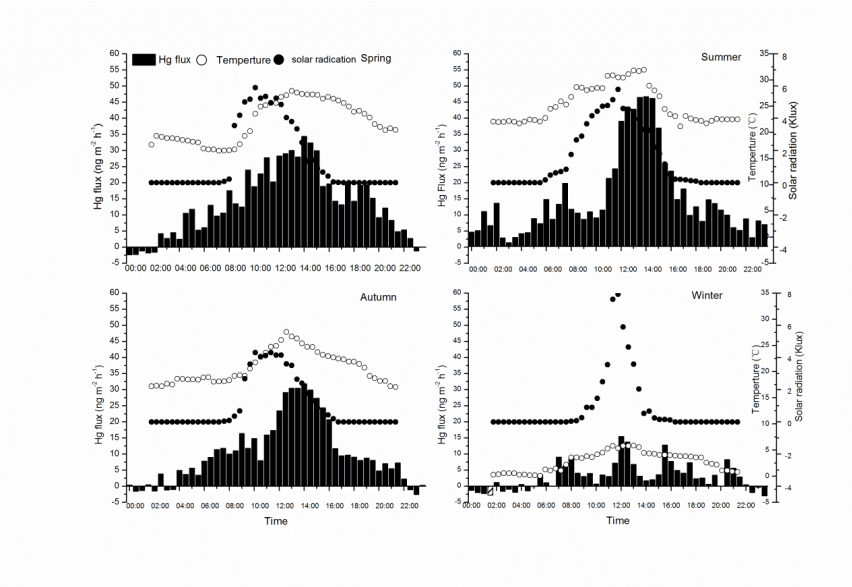


Fig. 2. Soil emission fluxes of Hg and air temperature in the evergreen broad-leaf forest field. Spring: March 4th-16th, May 8th -15th, 2012; Summer: July 5th -12th, August 15th -22rd, 2012; Autumn: September 15th -22rd, October 20th -27th, 2012; Winter: December 24th -31st, 2012; February 6th -13th, 2013.

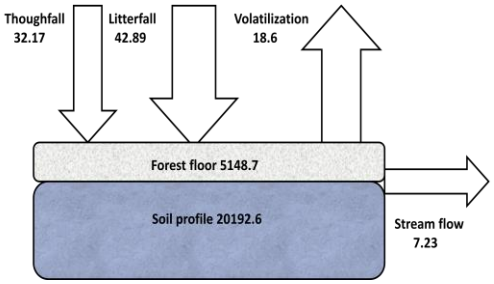


Fig.3. Annual ecosystem Hg fluxes and pools in the evergreen broad-leaf forest field. Fluxes (μg m^{-2} yr^{-1}) were represented by arrows, while pools (μg m^2) by boxes.