

# 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  $\mu\text{g m}^{-2} \text{yr}^{-1}$ , respectively, which were remarkably higher than those observed from other forest fields in the background of North America and Europe. Hg fluxes across the soil/air interface (18.6  $\text{mg m}^{-2} \text{yr}^{-1}$ ) and runoff/stream flow (7.2  $\mu\text{g m}^{-2} \text{yr}^{-1}$ ) 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 is estimated to 25341  $\mu\text{g m}^2$ . 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.

**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 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, 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 (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

45 wet areas. Thus the release of Hg compounds from the forest field can be considered as an initial  
46 step of Hg mobilization in forested catchments, and seems to be of high importance for its  
47 mobility.

48

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

## 65 **2 Materials and methods**

### 66 **2.1 Site description**

67 We conducted this research at Mt. Simian National Natural Reserve (106° 22' ~106° 25' E, 28°  
68 35'~28° 39' N), which is situated about 200 km away from Chongqing city (Fig. 1). Chongqing is  
69 the largest industrial city in southwest China, where combustion of coal accounted for more than  
70 75% of the regional energy supplies in recent years. The study area has a subtropical monsoon  
71 climate, with abundant rainfall every year. The mean annual temperature is 13.7 °C, with the  
72 highest and lowest records in August (average: 31.5 °C) and January (averages: -5.5 °C)  
73 respectively. The mean annual precipitation in the study area is 1,522.3 mm with a daily  
74 maximum up to 160.5 mm (Lv et al, 2014). There are four seasons in Chongqing, spring (March  
75 to May), summer (June to August), autumn (September to November), and winter (December to  
76 February), with a well-defined wet/warm season from June to October. The study area is typical of  
77 the region with hills of 1394 m and watersheds of about 100.1 km<sup>2</sup>. The evergreen broad-leaf  
78 forest selected in our research is believed to be one of the most representative vegetation types  
79 preserved in the study reserve due to the following reasons. First, it is one of the most complete  
80 forest located in the place between Chongqing and Guizhou. Second, it is almost all subtropical  
81 forest and until recent decades is one of Asia's least populated and most inaccessible areas. Third,  
82 it is the only largest and intact forest in the same latitude of the earth. Therefore, the evergreen  
83 broad-leaf forest was selected as the representative forest of subtropical vegetation in this  
84 research.

### 85 **2.2 Sampling methods and analysis**

#### 86 **2.2.1 Sampling method of throughfall and precipitation**

87 The throughfall samples were obtained from the evergreen broad-leaf forest where Hg dynamics  
88 have been investigated for one year, from March 2012 to February 2013. The precipitation

89 samples were collected by automatic precipitation samplers (APS-3A, Changsha Xianglan  
90 Scientific Instruments Co., Hunan, China), which were placed on the forest field of the sampling  
91 site. The throughfall was collected and measured using the same rain gauges (APS-3A, Ma et al.,  
92 2015). Four rain gauges were randomly placed in each of the three 20×20 m<sup>2</sup> permanent  
93 observation plots in each plantation, resulting in 12 throughfall sampling points for each plantation.  
94 The containers were pre-washed with dilute (5%) HCl and thoroughly rinsed with deionized water  
95 after each sampling. Moreover, the throughfall and precipitation samples were collected after each  
96 precipitation event from each site during the sampling period.

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

$$99 \quad \text{VWM} = (X_1 \times V_1 + X_2 \times V_2 + \dots + X_t \times V_t) / (V_1 + V_2 + \dots + V_t) = \sum (X_t \times V_t) / \sum V_t$$

100 where,  $X_t$  means the ion concentration in each precipitation event (ng L<sup>-1</sup>),  $V_t$  means the volume of  
101 each rainfall (mm).

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

$$105 \quad F_w = \frac{1}{1000} \sum_{i=1}^{i=n} (C_R^i p^i)$$

106 where,  $F_w$  is the annual THg or MeHg wet deposition flux (mg m<sup>-2</sup> yr<sup>-1</sup>),  $C_i$  is the VWM (ng L<sup>-1</sup>) of  
107 each rain sample, and  $P_i$  (mm) is the precipitation or throughfall amount.

### 108 **2.2.2 Sampling method of the stream**

109 The stream/runoff was collected at the edge of the forest catchment. For the water yield of the  
110 stream/runoff, it was monitored in the outlets of the forest catchment by the local hydrological  
111 departments. Stream water samples for analysis were collected in 7 sampling sites every two  
112 weeks from March 2012 to February 2013. The 250 ml Teflon bottles were used to collect the  
113 stream water samples. All Teflon bottles were cleaned with detergent, thoroughly rinsed with tap  
114 water, boiled in a 30% HNO<sub>3</sub> solution (v/v) for 1.5 h, rinsed and filled with Milli-Q water.  
115 Trace-metal grade HCl was immediately treated to the samples to acidify them. It should be noted  
116 that the water samples were not filtered and thus represented the stream load of THg. The  
117 subtropical forest field in the study area is 100.1 km<sup>2</sup>. Annual water discharge of the study site is  
118 1.86×10<sup>8</sup> m<sup>3</sup> (hydrological departments of Jiangjin district). The annual precipitation (Table 1) of  
119 the sampling site is slightly lower than the annual discharge. Therefore, it can be assumed that the  
120 calculation has certain representativeness. Volume weighted concentrations were computed by the  
121 stream/runoff collected during the study period. The fluxes were achieved by multiplying the  
122 average Hg concentration by the total amount of runoff during the study period.

### 123 **2.2.3 Sampling method of litterfall and soil pool**

124 The litter samples were collected by self-made litter collectors (0.5 m×0.5 m), which were made  
125 from treated lumber with a screen bottom. During the study period, the collectors were placed at  
126 four different sites within the study field. The litter collected was saved in brown paper bags and  
127 transported to the laboratory under 4°C, and then air-dried in clean environment in the laboratory  
128 until analysis. Soil samples were collected at five different sites in each field using polyvinyl  
129 chloride pipes (2.54 cm). Soil samples were obtained from 5 soil profiles. Three layers ( $O_i$ ,  $O_e$ ,  
130 and  $O_a$  horizons) were collected from each profile according to diagnostic horizons. The average

131 thickness of the organic soil horizon (O horizon) was ~98 cm. The  $O_i$  and  $O_e$  combined were ~38  
132 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  
133 floor were based on two replicate soil cores from each of the five litter decomposition plots in  
134 each forest stand. After freeze-dried, the samples were preserved in acid-cleaned polypropylene  
135 containers at room temperature until further analysis. Litter and soil collections were done  
136 monthly from March 2012 to February 2013.

#### 137 **2.2.4 Hg volatilization from the forest field**

138 A dynamic flux chamber (DFC) in series with Tekran 1110 synchronized dual-port sampling unit  
139 and Tekran automated Hg analyzer (2537X) were used to measure the emission rates of  $Hg^0$  (Fu et  
140 al., 2010). The special DFC method was described in detail at Ma et al. (2013). Hg emission  
141 fluxes were calculated by the equation below (Ma et al., 2013):

$$142 \quad F = (C_{out} - C_{in}) \times Q / A$$

143 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  
144 analyzer ( $ng\ m^3$ );  $Q$  is the flushing flow rate through the chamber ( $m^3\ h^{-1}$ ); and  $A$  is the surface  
145 area of the soil exposed in the chamber ( $m^2$ ).

146 Hg emission fluxes across the air/soil interface were monitored seasonally during eight intensive  
147 field campaigns from spring 2012 to winter 2013 (Spring: March 4<sup>th</sup>-16<sup>th</sup>, May 8<sup>th</sup> -15<sup>th</sup>, 2012;  
148 Summer: July 5<sup>th</sup> -12<sup>th</sup>, August 15<sup>th</sup> -22<sup>rd</sup>, 2012; Autumn: September 15<sup>th</sup> -22<sup>rd</sup>, October 20<sup>th</sup> -27<sup>th</sup>,  
149 2012; Winter: December 24<sup>th</sup> -31<sup>st</sup>, 2012; February 6<sup>th</sup> -13<sup>th</sup>, 2013). Hg emission flux were  
150 monitored at three sampling sites in the evergreen broadleaved forest of Mt. Simian. Hg emission  
151 fluxes were measured continuously for 7 days for each sampling. Quality assurance was  
152 conducted by manually injected Hg to the ambient air and soil vapor of the Tekran analyzer before  
153 and after data collection. At the beginning and end of each measurement date, the Hg fluxes over a  
154 clean Teflon<sup>TM</sup> sheet in the field was measured and regarded as the chamber blanks. The  
155 chamber blanks in our research ranged from 0.48 to 0.64  $ng\ m^{-2}\ h^{-1}$ , with an average of  $0.54 \pm$   
156  $0.07\ ng\ m^{-2}\ h^{-1}$  ( $n=12$ ). No blank value was needed to be subtracted from the flux due to no  
157 significant difference found.

#### 158 **2.3 Sample analysis and quality control**

159 For THg and MeHg in water samples, the special method was described at Ma et al. (2015).  
160 Detailed introduction of the measurement of THg and MeHg in soil and litter samples can also be  
161 found at Ma et al (2015). The detection limits of THg and MeHg in this research were  $0.02\ ng\ L^{-1}$   
162 and  $0.01\ ng\ L^{-1}$  respectively. The dissolved total mercury (DHg), dissolved methylmercury  
163 (DMeHg), particulate Hg (PHg) and particulate MeHg (PMeHg) were analyzed following the  
164 EPA Method 1631 (US EPA, 1999). The method blank was lower than detection limits in all cases.  
165 And the equipment blanks for THg and MeHg were  $0.04\ ng\ L^{-1}$  and  $0.02\ ng\ L^{-1}$ , respectively. The  
166 detection limits of Tekran 2537X was  $0.1\ ng\ L^{-1}$  for GEM. The average relative standard deviation  
167 for the duplicate analyses of THg and MeHg were 5.2% and 5.4%, respectively. Matrix spikes  
168 recoveries for THg and MeHg were both within acceptable range, 89% to 115% for THg, and 91%  
169 to 117% for MeHg. Precision was determined by relative standard deviations. For duplicate  
170 samples, the precision were 5% for THg in water samples, 9% for MeHg in water samples, 8% for  
171 THg in soil samples, and 4.1% for THg in leaf tissues.

### 172 **3. Results and discussion**

#### 173 **3.1 Hg concentrations and deposition fluxes in throughfall and litterfall**

174 THg concentrations in the throughfall ranged from 3.2 to 62.5  $ng\ L^{-1}$  for the individual samples,

175 and the average level of throughfall was  $24.1 \pm 7.9 \text{ ng L}^{-1}$ . Canopy density did have an effect on  
176 THg and MeHg concentrations (the forest cover is more than 90% and the canopy density is 0.9).  
177 THg concentrations measured in the throughfall of the subtropical evergreen broad-leaved forest  
178 ( $24.1 \pm 7.9 \text{ ng L}^{-1}$ ) were significantly higher than those measured in the open field ( $10.9 \pm 3.1 \text{ ng}$   
179  $\text{L}^{-1}$ ). Similar to THg concentrations, MeHg concentrations in the throughfall were nearly 2.5 times  
180 higher than that in precipitation ( $p=0.004$ ,  $n=49$ ).

181

182 THg concentrations in the throughfall were consistently at their highest in the cold season (Fig.1),  
183 which was probably due to the lower rainfall but elevated atmospheric Hg in this season. In the  
184 subtropical region of China, the monsoon-driven climate of northwest China doesn't bring much  
185 precipitation in cold season. At the same time, atmospheric stability is high during the cold period,  
186 and pollutants like atmospheric Hg do not spread easily, which contributes to the higher  
187 scavenging ability of Hg in the atmosphere. While the warm season (from April to September) is  
188 influenced by the southeast monsoon, and the rainfall increases greatly, which leads to lower  
189 concentration of Hg (Fig.1). The study station has obscure seasons and clear rainy and dry seasons.  
190 The deposition fluxes of THg through throughfall also showed the seasonal variation  
191 characteristics, with higher fluxes appearing in wet-season (June to August). The deposition fluxes  
192 of THg through throughfall in summer at Mt. Simian accounted more than 40% of total annual Hg  
193 deposition. However, it is still in September and October that a higher throughfall flux is observed.  
194 This may be because that the rainfall in the two months is mainly effected by Indian Monsoon,  
195 contributing to a higher rainfall (Fu et al., 2008a) comparing with other months. The minimum  
196 values for THg deposition occurred in the cold season.

197

198 During the surveillance, THg in the throughfall was evaluated to be  $32.2 \mu\text{g m}^{-2} \text{ yr}^{-1}$ . The  
199 deposition fluxes of THg through throughfall in Mt. Simian were lower than those investigated in  
200 the southwestern cities of China, such as Guizhou and Chongqing (Precipitation:  $8.4\text{--}62.1 \mu\text{g m}^{-2}$   
201  $\text{yr}^{-1}$ , throughfall:  $15.6\text{--}292.1 \mu\text{g m}^{-2} \text{ yr}^{-1}$ , Guo et al., 2008; Feng et al., 2009a,b; Wang et al., 2007).  
202 However, the deposition fluxes of THg through throughfall in Mt. Simian were approximately  
203 2–10 times higher than those reported in remote areas of North America and Europe (Precipitation:  
204  $3.1\text{--}10.0 \mu\text{g m}^{-2} \text{ yr}^{-1}$ , throughfall:  $6.7\text{--}23.0 \mu\text{g m}^{-2} \text{ yr}^{-1}$ , St. Louis et al., 2001; Keeler et al., 2005).  
205 Obviously, the THg fluxes at Mt. Simian were higher than other sites abroad. The reason perhaps  
206 was that Mt. Simian had considerably more dense forest canopies. As one of the National Natural  
207 Reserves of China, it has preserved the best subtropical evergreen broad-leaved forest of China.  
208 The forest cover in the reserves reaches over 90%. The increased THg concentrations in  
209 throughfall mainly resulted from the dry deposition of Hg on the vegetation, followed by the  
210 washout of throughfall. Another possible reason for the elevated deposition fluxes, which may be  
211 the most important one, probably related with the increased atmospheric Hg concentrations in the  
212 past 30 years due to China's fast economic development. This area, especially Chongqing city, has  
213 a large demand for energy consumption, and about 70% of which is from coal combustion. The  
214 annual mean gaseous elemental Hg (GEM) concentration in the middle of Chongqing city  
215 ( $9.6\text{--}31.9 \text{ ng m}^{-3}$ , Wang et al., 2006), more than 200 km away from the study site, tripled  
216 comparing with global background level (Lindberg et al., 2002a, b), which corresponded to the  
217 high annual deposition flux of Hg in the study area. It is also reported that the GEM concentration  
218 in the study area is as high as  $3.8 \pm 1.5 \text{ ng m}^{-3}$  (Ma et al., 2015), even if it is situated in a natural

219 subtropical forest reserve. The MeHg flux was  $0.45 \mu\text{g m}^{-2} \text{yr}^{-1}$ , which was higher than those  
220 measured in other areas. While MeHg/THg in the throughfall samples was 1.3 %, which was a  
221 relatively high value compared with other studies (0.4%-0.8%, Lee et al., 2000; Demers et al.,  
222 2007; Choi et al., 2008; Fu et al., 2008a; Guo et al., 2008; Larssen et al., 2008). Here, the higher  
223 ratio of MeHg to THg in throughfall samples may suggest that the contribution of MeHg from  
224 throughfall cannot be ignored and should be taken care of in future studies. After all,  
225 accumulation of MeHg in the soil might have caused serious risks in the functioning of natural  
226 downstream ecosystems.

227

228 The deposition fluxes of THg through litterfall are shown in Table 1. The average concentrations  
229 of THg and MeHg in leaf litter were  $106.7 \pm 8.3 \text{ ng g}^{-1}$  (SE = 2.6, N=60) and  $0.8 \pm 0.4 \text{ ng g}^{-1}$  (SE =  
230 0.2, N=60), respectively. The deposition flux of THg through litterfall was estimated to be  $42.9 \mu\text{g}$   
231  $\text{m}^{-2} \text{yr}^{-1}$  in the measurement field, which was remarkably higher than the input flux through  
232 throughfall. It is also considerably higher than litterfall fluxes reported from other regions (St.  
233 Louis et al., 2001; Demers et al., 2007). GEM can be absorbed by stomata and detained in the leaf  
234 tissue (Ericksen et al., 2003; Fu et al., 2008a, b). Therefore, we believed that the elevated litterfall  
235 input fluxes directly related to the increased GEM concentrations, even in remote areas.

### 236 **3.2 Mercury emission from soils under the canopy**

237 The emission characteristics and air-surface exchange of GEM from the subtropical forest field  
238 have been investigated during eight intensive field campaigns from 2012 to 2013. At the forest  
239 field, GEM released from soils had the characteristic of obvious diurnal and seasonal variations.  
240 Day and night GEM fluxes were statistically different (t-test,  $p < 0.001$ ), with nighttime emissions  
241 considerably lower than that in daytime in all seasons (Fig.2). Average fluxes of Hg in spring,  
242 summer, autumn and winter were  $12.2 \pm 5.1 \text{ ng m}^{-2} \text{h}^{-1}$ ,  $14.2 \pm 4.7 \text{ ng m}^{-2} \text{h}^{-1}$ ,  $9.9 \pm 2.5 \text{ ng m}^{-2} \text{h}^{-1}$ ,  
243 and  $3.1 \pm 1.1 \text{ ng m}^{-2} \text{h}^{-1}$ , respectively. It can be seen that the highest value occurred in summer,  
244 followed by spring and fall, while the lowest value was observed in winter. The average fluxes of  
245 Hg in spring ( $12.2 \pm 5.1 \text{ ng m}^{-2} \text{h}^{-1}$ ) were slightly lower than that in summer ( $14.2 \pm 4.7 \text{ ng m}^{-2}$   
246  $\text{h}^{-1}$ ), which was different from other studies (Larssen et al., 2008; Fu et al., 2010). It appeared that  
247 warm temperature with low canopy density in spring at the mid subtropical forest were more  
248 likely to release GEM. Perhaps the primary reason lies that the forest canopies are lushly and well  
249 spaced in spring, and thus the forest can receive more sunlight. Therefore, the reduction rate of  
250  $\text{Hg}^{2+}$  by photochemical, thermal and biogenic processes probably increased.

251 This research indicated that Hg fluxes of forest field were far lower than those observed from  
252 contaminated areas such as heavily air-polluted areas in eastern Guizhou ( $33\text{--}3638 \text{ ng m}^{-2} \text{h}^{-1}$ )  
253 (Wang et al., 2007), some cities in southwest China ( $15.0\text{--}44.4 \text{ ng m}^{-2} \text{h}^{-1}$ ) (Qiu et al., 2006), dry  
254 landfills ( $46.5\text{--}22.8 \text{ ng m}^{-2} \text{h}^{-1}$ ) (Zhu et al., 2010) and wetlands ( $20\text{--}500 \text{ ng m}^{-2} \text{h}^{-1}$ ) (Lindberg et  
255 al., 2002b). But the emission of GEM elevated in comparison with those reported from other  
256 places ( $-5.4\text{--}4.2 \text{ ng m}^3$ , Lindberg et al., 2002a, b;  $1.7\text{--}8.4 \text{ ng m}^3$ , Travnikov, 2005). At Mt. Simian,  
257 the estimated net GEM fluxes were released from soils during the warm season and slightly  
258 volatilized during the cold season. Hg deposition was only observed in several nights of the cold  
259 season during the study period. Hg released from the snow/air interface was extremely low  
260 comparing with the soil/air interface. It was supposed that the  $\text{Hg}^0$  flux was zero from  
261 snow-covered surface (Huang et al., 2012). At most subtropical areas, especially mid-subtropical  
262 forests, however, there were short winter seasons with unstable snow cover, and the snow cover

263 season only tended to occur in January. So we assumed that there still existed Hg<sup>0</sup> emission in  
264 December and February in winter. Therefore, the annual total net Hg emission flux was 18.6 mg  
265 m<sup>-2</sup> yr<sup>-1</sup>.

### 266 **3.3 Hg concentrations and out-flux in stream water**

267 Annual volume-weighted concentrations of THg and MeHg were measured at the outlet stream of  
268 the forest field of Mt. Simian. The mean concentrations of THg and MeHg in the outflow stream  
269 were 3.9 ±2.0 and 0.2±0.08 ng L<sup>-1</sup>, respectively. THg and MeHg concentrations in stream water  
270 draining the upland in our research were slightly higher than those reported in literature (Fu et al.,  
271 2008a, b; Larssen et al., 2008). THg concentrations in runoff/stream water in rainy seasons  
272 (4.6±2.0ng L<sup>-1</sup>) were significantly higher than those in dry seasons (3.3±1.8 ng L<sup>-1</sup>), which can  
273 probably be attributed to the soil erosion and runoff (Ma et al., 2015). It is known that if a remote  
274 forest field does not have other obvious Hg pollution sources, Hg concentrations in the  
275 runoff/stream water can represent risks from a solitary watershed. Numerous studies showed that  
276 the catchments of remote forest were regarded as filters between atmosphere and hydrosphere  
277 (Lee et al., 2000; Larssen et al., 2008; Ericksen et al., 2003). The fate of Hg stored in the forest  
278 soils can be divided into three parts. One part of them transfers through food webs, threatening the  
279 balance of forest ecosystems; the second part of them is released into the atmosphere again; the  
280 third part of them probably transfers with the runoff/stream, becoming one of the Hg sources of  
281 downstream aquatic ecosystem. Therefore, to a certain extent, the role of forested catchments as  
282 Hg filters can be characterized by Hg output (runoff/stream) from the forest field.

283 This study showed that, even though Hg deposition fluxes in throughfall was high, THg  
284 concentration in stream/runoff was lower than that in contaminated sites under the same  
285 geological background. This indicated that subtropical forest field had the filtering effect of Hg in  
286 precipitation and throughfall. On the other hand, the lower concentration in stream/runoff  
287 indicated that the study area did not suffer from severe anthropogenic Hg pollution. Steam output  
288 of THg was calculated by multiplying the average THg concentration in stream water (3.9 ±2.03  
289 ng L<sup>-1</sup>) by the water discharge rate in the forest field of the study site (annual water discharge:  
290 1.86×10<sup>8</sup> m<sup>3</sup>, from hydrological departments of Jiangjin district). The export flux of THg via  
291 runoff/stream was 0.73 kg yr<sup>-1</sup>. The subtropical forest field in the study area is 100.1 km<sup>2</sup>. So the  
292 export flux of THg through stream water was 7.23 μg m<sup>-2</sup> yr<sup>-1</sup>, which tripled the values reported  
293 in the catchments of Sweden (1.6–1.8 μg m<sup>-2</sup> yr<sup>-1</sup>, Lee et al., 2000; 2.4 μg m<sup>-2</sup> yr<sup>-1</sup>, Larssen et al.,  
294 2008). Our results indicated that the output fluxes of MeHg via stream water were 0.08 μg m<sup>-2</sup>  
295 yr<sup>-1</sup>, which was similar to or slightly larger than other results (0.03–0.07 μg m<sup>-2</sup> yr<sup>-1</sup>, Lee et al.,  
296 2000; 0.05 μg m<sup>-2</sup> yr<sup>-1</sup>, Schwesig and Matzner, 2001). As we mentioned above that Mt. Simian  
297 was one of the most complete forest and until recent decades was one of Asia's  
298 least populated and most inaccessible areas. Average Hg concentration in the soil detected in  
299 previous research was 0.28 mg kg<sup>-1</sup> (Ma et al., 2013), which indicated that it was not an obvious  
300 geological Hg hotspot. Therefore, the elevated Hg fluxes in stream water were probably attributed  
301 to the great atmospheric Hg depositions. At the same time, our preliminary research results also  
302 illustrated that forest runoff and soil erosion could increase Hg output from subtropical forest  
303 catchments (Ma et al., 2013). But the total output fluxes of THg and MeHg were far lower than  
304 the input fluxes via wet deposition (32.2 μg m<sup>-2</sup> yr<sup>-1</sup> for THg and 0.5 μg m<sup>-2</sup> yr<sup>-1</sup> for MeHg). This  
305 study showed that the subtropical forest was able to exert purification effect of filtration, even  
306 under the condition of elevated deposition of Hg.

### 307 3.4. Dynamics and transport of Hg based on forest field

308 THg content in the forest field (forest floor and soil profiles) of Mt. Simian was shown in Table 2.  
309 The THg stocked in the forest soil was approximately  $20192 \mu\text{g m}^{-2}$  (average soil depth is 98 cm),  
310 while that in the organic floor was  $5148 \mu\text{g m}^{-2}$  (average litter depth is 19 cm). THg content in soil  
311 profile were three times more than the organic horizon in the subtropical forest field. The active  
312 pool (the upper 22 cm,  $O_i$ ) of THg represented 41 % of the total storage of the study area. In the  
313 soil profile, THg content in the organic horizon ( $O_i$ ) is obviously higher than those in the other  
314 horizons. At the same time, the organic matter is well decomposed under warm and rainy  
315 subtropical climate, which has high affinity to Hg in soil.  
316 Due to the good adsorption and reduction of organic matter, the organically bound contents of Hg  
317 could be released into the environment again during the decomposition of organic matter.

318 The ultimate fate of Hg in the terrestrial ecosystem may depend upon its delivery and  
319 incorporation into the forest floor. And the average Hg fluxes were also estimated. Input of THg to  
320 the forest field of Mt. Simian included net throughfall and litterfall depositions (St. Louis et al.,  
321 2001; Fu et al., 2010). Annual throughfall and litterfall deposition fluxes of THg in Mt. Simian  
322 were  $32.2$  and  $42.9 \text{ mg m}^{-2} \text{ y}^{-1}$ , respectively (Fig.3). Litterfall deposition inputs were estimated to  
323 134% of the throughfall deposition at the forest field. In the study forest field, the predominant  
324 pathway of Hg fluxes to the forest floor was via litterfall (57.1%). A majority of atmospherically  
325 deposited THg was released through  $\text{Hg}^0$  at a rate of  $18.6 \mu\text{g m}^{-2} \text{ y}^{-1}$ . Steam outflow of THg from  
326 the wetland was  $7.2 \mu\text{g m}^{-2} \text{ yr}^{-1}$ . The ratio between output and input of THg was 0.34 at the  
327 subtropical forest field of Mt. Simian, which was significantly higher than others (0.02-0.04, Lee  
328 et al., 2000; 0.16, Larssen et al., 2008; 0.30, Fu et al., 2010). The apparently higher ratio between  
329 the output/input fluxes of THg may represent an important ecological risk.

330 The THg stored in the forest field was 982 times larger than the annual THg output by  
331 stream/runoff outflow and soil volatilization, and 338 times larger than the input estimated from  
332 wet and dry depositions (Fig.3). The estimates of the deposition flux of THg in this study were  
333 much higher than values reported from the northeastern American ( $3.8\text{--}12.6 \mu\text{g m}^{-2} \text{ yr}^{-1}$ ; Driscoll  
334 et al., 2007) and Norway ( $7 \mu\text{g m}^{-2} \text{ yr}^{-1}$ ; Larssen et al., 2008), probably indicating a significant  
335 impact of heavy regional Hg emissions from industry and urban on local Hg deposition. The  
336 reason perhaps was that highly soluble  $\text{Hg}^{2+}$  was easily stripped from the atmosphere and  
337 deposited locally. Higher wet deposition can illustrate the remarkable influence of local Hg  
338 emissions on Hg accumulation in the regional forest field. The THg flux through litterfall was 1.5  
339 times larger than that through throughfall due to greater input of litter mass and higher Hg  
340 concentrations in the litter. Annual exports of THg in stream water of the study area ( $3.2\text{--}9.5 \mu\text{g}$   
341  $\text{m}^{-2}\text{yr}^{-1}$ ) were not accorded with those reported from northern forest catchments ( $1.0\text{--}3.4 \mu\text{g m}^{-2}$   
342  $\text{yr}^{-1}$ ; St. Louis et al., 2001; Grigal et al., 2000). An amount of the atmospherically deposited THg  
343 was lost via emissions at a rate of  $18.6 \mu\text{g m}^{-2} \text{ yr}^{-1}$ . Compared with stream outflow, the evasion of  
344 Hg from forest soil played a more essential role in THg outputs.

345 Compared the ratios of output to input flux with other places (Larssen et al., 2008; Fu et al., 2010),  
346 the higher ratio may be greatly affected by the elevated deposition. Therefore, regional emission  
347 of Hg may have stronger influence on forest ecosystems, in which the deposition of THg through  
348 litterfall and throughfall, being affected more by local and regional changes of Hg emissions and  
349 cycling, were the main paths for Hg entering into soil surface (Demers et al., 2007). However, in  
350 this study, the outflow of Hg via runoff output and the soil-air interface accounted for a small



351 fraction of Hg budget in the study area. And the accumulation pattern of Hg in forest floor and soil  
352 profiles was seasonal. As we mentioned above that Mt. Simian was one of the most typical  
353 subtropical forest systems and the least accessed area, average Hg concentrations in all soil  
354 surfaces of this area were below  $0.30 \text{ mg kg}^{-1}$  (Fu et al., 2010; Ma et al., 2013). Therefore, the  
355 accumulation of Hg in soil would be enhanced with time. At the same time, the ultimate fate of  
356 deposited Hg depends upon the biogeochemical processes that have not been well quantified  
357 within the ecosystem. Hg dynamics during litter decomposition, for instance, need to be  
358 considered as a whole so that we can better understand controls on long-term accumulation of Hg  
359 in the forest ecosystem and its delayed release to surface water.

#### 360 **4. Conclusions**

361 In this study, the mass balance and transport of Hg in southwestern China were first measured at a  
362 subtropical forest, Chongqing, China. Results revealed that litterfall deposition inputs were the  
363 predominant pathway ( $42.9 \text{ mg m}^{-2} \text{ y}^{-1}$ , account for 57.1%) of Hg flux to the forest floor. Annual  
364 deposition fluxes of Hg through throughfall were  $32.2 \text{ m}^{-2} \text{ y}^{-1}$ , accounting for 42.9% of the Hg  
365 inputs. Researchers should pay more attention to the higher ratio of MeHg to THg in the  
366 throughfall deposition when they model the biogeochemical cycling in a typical local forest  
367 watershed. For the output process, the exchange of Hg ( $18.6 \text{ } \mu\text{g m}^{-2} \text{ y}^{-1}$ ) across the forest field-air  
368 interface was an essential part of the biogeochemical cycle of Hg. The runoff/steam outflow of  
369 THg from the wetland was  $7.2 \text{ mg m}^{-2} \text{ yr}^{-1}$ , which was lower than that in contaminated sites under  
370 the same geological background. Therefore, we may conclude that: 1) the study area does not  
371 suffer from severe anthropogenic Hg pollution; 2) the forested field has the filtering effect of Hg  
372 in precipitation and throughfall, even in the elevated atmospheric Hg area.

373 The forest field (forest floor and soil profiles) plays an important role in the cycling of THg and  
374 MeHg. In reality, it is just another problem created by the accumulation of Hg,  
375 which would be a potential risk affecting the output of Hg in the long term. Terrestrial ecosystems  
376 that have accumulated more Hg may ultimately emit them to the wetlands and surface water,  
377 finally affecting the entire aquatic ecosystems. Therefore, it is a signal that we should not ignore.  
378 In this case, however, any changes in the forest floor like deforestation or forestland degradation  
379 may strongly affect Hg budget of the region.

#### 380 **Data availability**

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

#### 383 **Author contribution**

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

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 492 2010.

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## Tables

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

	THg Concentration (ng L <sup>-1</sup> )			MeHg Concentration (ng L <sup>-1</sup> )		
	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 <sup>-1</sup> )			MeHg Concentration (ng g <sup>-1</sup> )		
	106.7±18.3			0.79±0.36		
Annual deposition flux	THg (µg m <sup>-2</sup> yr <sup>-1</sup> )			MeHg (µg m <sup>-2</sup> yr <sup>-1</sup> )		
Precipitation (1508mm)	15.45			0.36		
Throughfall (1336mm)	32.17			0.45		
Litterfall (402g m <sup>-2</sup> yr <sup>-1</sup> )	42.89			0.32		

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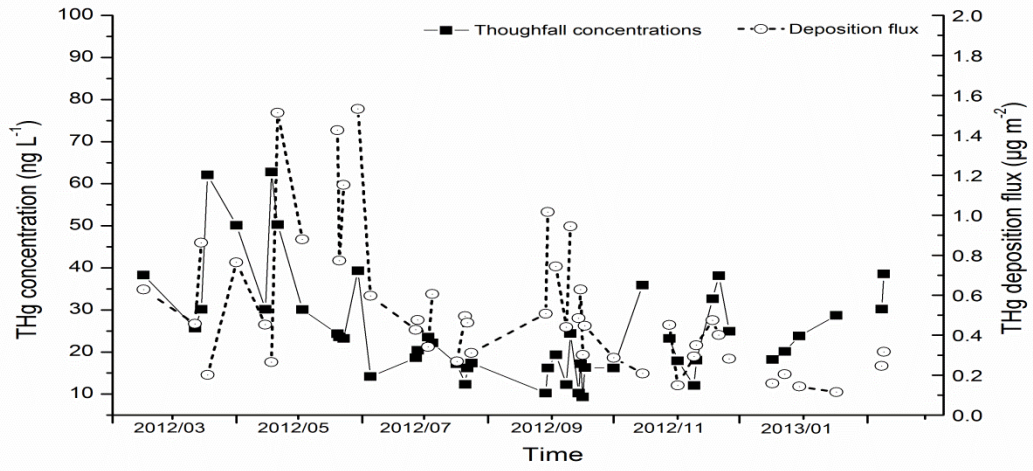
Table 2 The concentrations and contents of THg in forest floor and different soil layers

		THg (ng g <sup>-1</sup> )	Density (g cm <sup>-3</sup> )	Thickness (m)	THg content(µg m <sup>-2</sup> )	Total contents
	Initial leaf litter	46.30±14.2	0.28±6.2	0.06±0.02	774.8	
Forest floor	Half decomposition	51.22±9.4	0.49±18.1	0.08±0.03	2000.8	5148.7
	decomposition	57.88±10.3	0.82±9.9	0.05±0.02	2373.1	
	<i>O<sub>i</sub></i>	297.8±15.2	1.27±2.1	0.22±0.10	8320.5	
Soil profile	<i>O<sub>e</sub></i>	117.4±32.3	1.65±16.2	0.34±0.08	6586.1	20192.6
	<i>O<sub>a</sub></i>	68.4±13.6	1.84±20.7	0.42±0.06	5286.0	

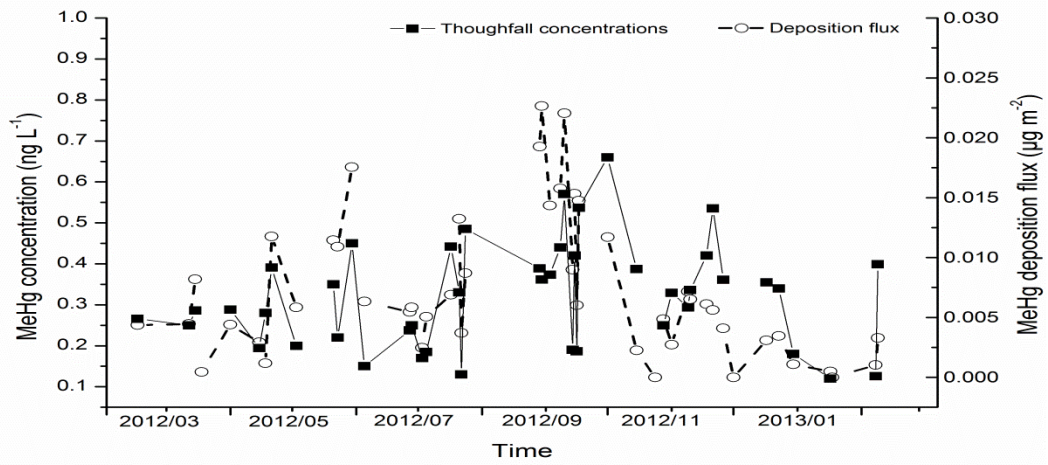
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### Figures



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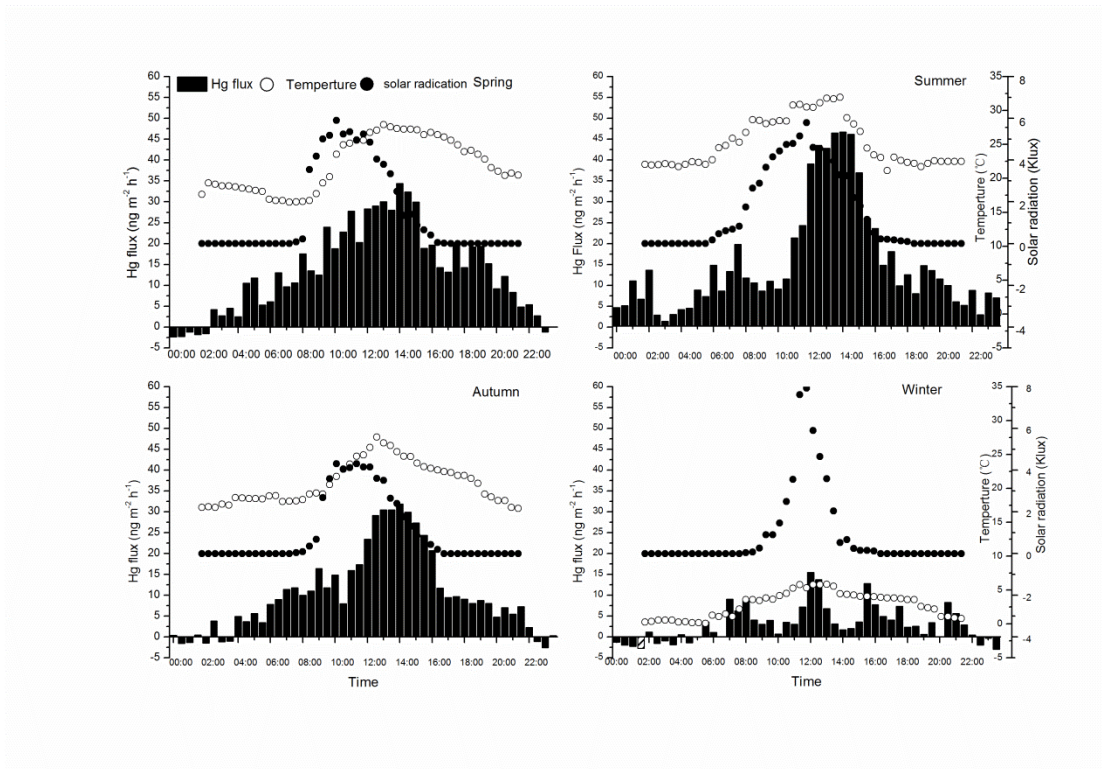


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Fig. 1. Volume-weighted mean concentrations of THg and MeHg and deposition fluxes of throughfall in the evergreen broad-leaf forest from March 2012 to February 2013



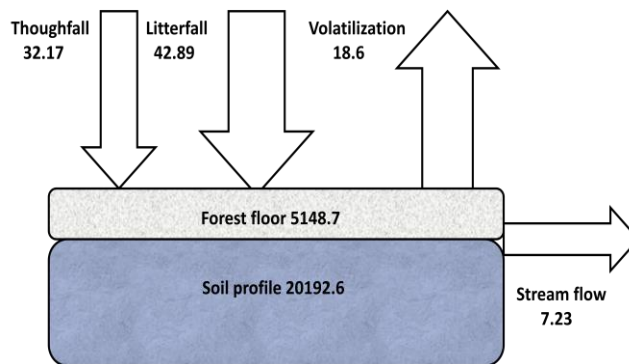
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511 Fig. 2. Soil emission fluxes of Hg and air temperature in the evergreen broad-leaf forest field.  
 512 Spring: March 4<sup>th</sup>-16<sup>th</sup>, May 8<sup>th</sup>-15<sup>th</sup>, 2012; Summer: July 5<sup>th</sup>-12<sup>th</sup>, August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

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

## 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  $\mu\text{g m}^{-2} \text{yr}^{-1}$ , 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  $\text{mg m}^{-2} \text{yr}^{-1}$ ) and runoff/stream flow (7.2  $\mu\text{g m}^{-2} \text{yr}^{-1}$ ) 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 25341  $\mu\text{g m}^2$ . 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.

**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 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,

45 Hg in the forest soil and decomposed litterfall can transfer into MeHg, resulting in increased  
46 MeHg levels in downstream wet areas. Thus the release of Hg compounds from the forest field  
47 can be considered as an initial step of Hg mobilization in forested catchments, and seems to be of  
48 high importance for its mobility.

49

50 Biogeochemical mass balance studies quantifying Hg pools and fluxes in the ~~whole~~-forest  
51 ecosystem are essential for assessing current rates of Hg inputs to, retention within, and release  
52 from terrestrial ecosystems. Major research initiatives have improved our understanding of current  
53 Hg pools and fluxes (Grigal et al., 2000; Schwesig and Matzner, 2001), however, knowledge of  
54 the internal cycling dynamics controlling retention within and release from these ecosystems  
55 which are located in the elevated Hg emitting regions is still limited (Demers et al., 2007).  
56 China's rapid economic development is predicted to increase the emission of atmospheric Hg (Fu  
57 et al., 2008a, b). The coal burning leads to Hg pollution in industrial and urban areas, as well as  
58 remote areas due to the long-range atmospheric transport of Hg (Feng and Qiu., 2008; Fu et al.,  
59 2009). In this study, we conducted a full-scale investigation on the distribution of Hg in the  
60 throughfall, litterfall and precipitation for a ~~whole~~-year. At the same time, we calculated the output  
61 and input of Hg during the study period. Thus, the objectives of this study were to: 1) evaluate the  
62 deposition and output fluxes of Hg in the forest field and the accumulation of THg in a subtropical  
63 forest soil pool of southwest China, 2) discuss Hg import and export characteristics via deposition  
64 and runoff/stream flow in the study field, and 3) explore the main factors affecting Hg deposition,  
65 retention within and output fluxes in the subtropical forest ecosystem.

## 66 2 Materials and methods

### 67 2.1 Site description

68 We conducted this research at Mt. Simian National Natural Reserve (106° 22' ~106° 25' E, 28°  
69 35'~28° 39' N), which is situated about 200 km away from Chongqing city (Fig. 1). Chongqing is  
70 the largest industrial city in southwest China, where combustion of coal accounted for more than  
71 75% of the regional energy supplies in recent years. The study area has a subtropical monsoon  
72 climate, ~~which means that this area has with~~ abundant rainfall every year. The mean annual  
73 temperature is 13.7 °C, with the highest and lowest records in August (average: 31.5 °C) and  
74 January (averages: -5.5 °C) respectively. The mean annual precipitation in the study area is  
75 1,522.3 mm with a daily maximum up to 160.5 mm (Lv et al., 2014). There are four seasons in  
76 Chongqing, spring (March to May), summer (June to August), autumn (September to November),  
77 and winter (December to February), with a well-defined wet/warm season from June to October.

78 The study area is typical of the region with hills of 1394 m and watersheds of about 100.1 km<sup>2</sup>.  
79 The evergreen broad-leaf forest selected in our research is believed to be one of the most  
80 representative vegetation types preserved in the study reserve due to the following reasons. First, it  
81 is one of the most complete forest located in the place between Chongqing and Guizhou. Second,  
82 it is almost all subtropical forest and until recent decades is one of Asia's least populated and most  
83 inaccessible areas. Third, it is the only largest and intact forest in the same latitude of the earth.  
84 ~~And it is also the only largest and intact forest in the same latitude of the earth.~~ Therefore, the  
85 evergreen broad-leaf forest was selected as the representative forest of subtropical vegetation in  
86 this research.

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89 **2.2 Sampling methods and analysis**

90 **2.2.1 Sampling method of throughfall and precipitation**

91 The throughfall samples were obtained from the evergreen broad-leaf forest where Hg dynamics  
92 have been investigated for one ~~whole~~ year, from March 2012 to February 2013. The precipitation  
93 samples were collected by ~~self-made~~ automatic precipitation samplers (APS-3A, Changsha  
94 Xianglan Scientific Instruments Co., Hunan, China), which were placed on the forest field of the  
95 sampling site. The throughfall was collected and measured using the same rain gauges (APS-3A,  
96 Ma et al., 2015). Four rain gauges were randomly placed in each of the three 20×20 m<sup>2</sup>  
97 permanent observation plots in each plantation, resulting in 12 throughfall sampling points for  
98 each plantation. The containers were pre-washed with dilute (5%) HCl and thoroughly rinsed with  
99 deionized water after each sampling. Moreover, the throughfall and precipitation samples were  
100 collected after each precipitation event from each site during the ~~whole~~ sampling period.

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

103 
$$VWM = (X_1 \times V_1 + X_2 \times V_2 + \dots + X_i \times V_i) / (V_1 + V_2 + \dots + V_i) = \sum (X_i \times V_i) / \sum V_i$$

104 where,  $X_i$  means the ion concentration in each precipitation event (ng L<sup>-1</sup>),  $V_i$  means the volume of  
105 each rainfall (mm).

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

109 
$$F_w = \frac{1}{1000} \sum_{i=1}^{i=n} (C_i^i p^i)$$

110 where,  $F_w$  is the annual THg or MeHg wet deposition flux (mg m<sup>-2</sup> yr<sup>-1</sup>),  $C_i$  is the VWM (ng L<sup>-1</sup>) of  
111 each rain sample, and  $P_i$  (mm) is the precipitation or throughfall amount.

112 **2.2.2 Sampling method of the stream**

113 The stream/runoff was ~~carried out~~ collected at the edge of the forest catchment. ~~For the water~~  
114 ~~yield of the stream/runoff, it was monitored in the outlets of the forest catchment~~ ~~The measured~~  
115 ~~data of the stream/runoff for calculating flow rate were collected~~ by the local hydrological  
116 departments ~~in the outlets~~. Stream water samples for analysis were collected in 7 sampling sites  
117 every two weeks from March 2012 to February 2013. The 250 ml Teflon bottles were used to  
118 collect the stream water samples. All Teflon bottles were cleaned with detergent, thoroughly  
119 rinsed with tap water, boiled in a 30% HNO<sub>3</sub> solution (v/v) for 1.5 h, rinsed and filled with  
120 Milli-Q water. ~~The bottles were rinsed by the water samples for three times before collection.~~  
121 Trace-metal grade HCl was immediately treated to the samples to acidify them. It should be noted  
122 that the water samples were not filtered and thus represented the stream load of THg. The  
123 subtropical forest field in the study area is 100.1 km<sup>2</sup>. Annual water discharge of the study site is  
124 1.86×10<sup>8</sup> m<sup>3</sup> (hydrological departments of Jiangjin district). The annual precipitation (Table 1) of  
125 the sampling site is slightly lower than the annual discharge. ~~The annual precipitation of the~~  
126 ~~sampling site is slightly lower than the annual discharge.~~ Therefore, it can be assumed that the  
127 calculation has a certain representativeness. Volume weighted concentrations were computed by  
128 the stream/runoff collected during the ~~whole~~ study period. The fluxes were achieved by  
129 multiplying the average Hg concentration by the total amount of runoff during the ~~whole~~  
130 ~~year~~ study period. ~~The robustness of the approach for THg and MeHg was 5 % and 9 %~~

131 ~~respectively.~~

### 132 2.2.3 Sampling method of litterfall and soil pool

133 The litter samples were collected by self-made litter collectors (0.5 m×0.5 m~~0.25 m<sup>2</sup>~~), which were  
134 made from treated lumber with a screen bottom. During the study period, the collectors were  
135 placed at four different sites within the study field. The litter collected was saved in brown paper  
136 bags and transported to the laboratory under 4°C, and then air-dried in clean environment in the  
137 laboratory until analysis. Soil samples were collected at five different sites in each field using  
138 polyvinyl chloride pipes (2.54 cm). Soil samples were obtained from 5 soil profiles. Three layers  
139 (O<sub>i</sub>, O<sub>e</sub>, and O<sub>a</sub> horizons) were collected from each profile according to diagnostic horizons. The  
140 average thickness of the organic soil horizon (O horizon) was ~98 cm. The O<sub>i</sub> and O<sub>e</sub> combined  
141 were ~38 cm in thickness, and the O<sub>a</sub> horizon was ~60 cm. THg in the O<sub>i</sub>, O<sub>e</sub>, and O<sub>a</sub> horizons of  
142 the forest floor were based on two replicate soil cores from each of the five litter decomposition  
143 plots in each forest stand. After freeze-dried, the samples were preserved in acid-cleaned  
144 polypropylene containers at room temperature until further analysis. Litter and soil collections  
145 were done monthly from March 2012 to February 2013.

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

### 154 2.2.4 Hg volatilization from the forest field

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

$$164 F = (C_{out} - C_{in}) \times Q / A$$

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

168 Hg emission fluxes across the air/soil interface were monitored seasonally during eight intensive  
169 field campaigns from spring 2012 to winter 2013 (Spring: March 4<sup>th</sup>-16<sup>th</sup>, May 8<sup>th</sup>-15<sup>th</sup>, 2012;  
170 Summer: July 5<sup>th</sup>-12<sup>th</sup>, August 15<sup>th</sup>-22<sup>rd</sup>, 2012; Autumn: September 15<sup>th</sup>-22<sup>rd</sup>, October 20<sup>th</sup>-27<sup>th</sup>,  
171 2012; Winter: December 24<sup>th</sup>-31<sup>st</sup>, 2012; February 6<sup>th</sup>-13<sup>th</sup>, 2013). Hg emission flux were  
172 monitored at three sampling sites in the evergreen broadleaved forest of Mt. Simian. ~~And the~~ Hg  
173 emission fluxes were measured continuously for 7 days for each sampling. Quality assurance was  
174 conducted by manually injected Hg to the ambient air and soil vapor of the Tekran analyzer before

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175 and after data collection. At the beginning and end of each measurement date, the Hg fluxes over a  
176 clean Teflon<sup>TM</sup> sheet in the field was measured and regarded as the chamber blanks. The  
177 chamber blanks in our research ranged from 0.48 to 0.64 ng m<sup>-2</sup> h<sup>-1</sup>, with an average of 0.54 ±  
178 0.07 ng m<sup>-2</sup> h<sup>-1</sup> (n=12). No blank value was needed to be subtracted from the flux ~~results~~ due to no  
179 significant difference found.

### 180 2.3 Sample analysis and quality control

181 For THg and MeHg in water samples, the special method was described at Ma et al. (2015).  
182 Detailed introduction of the measurement of THg and MeHg in soil and litter samples can also be  
183 found at Ma et al (2015). The detection limits of THg and MeHg in this research were 0.02 ng L<sup>-1</sup>  
184 and 0.01 ng L<sup>-1</sup> respectively. The dissolved total mercury (DHg), dissolved methylmercury  
185 (DMeHg), particulate Hg (PHg) and particulate MeHg (PMeHg) were analyzed following the  
186 EPA Method 1631 (US EPA, 1999). The method blank was lower than detection limits in all cases.  
187 And the equipment blanks for THg and MeHg were 0.04 ng L<sup>-1</sup> and 0.02 ng L<sup>-1</sup>, respectively. The  
188 detection limits of Tekran 2537X was 0.1 ng L<sup>-1</sup> for GEM. The average relative standard deviation  
189 for the duplicate analyses of THg and MeHg were 5.2% and 5.4%, respectively. Matrix spikes  
190 recoveries for THg and MeHg were both within acceptable range, 89% to 115% for THg, and 91%  
191 to 117% for MeHg. Precision was determined by relative standard deviations. For duplicate  
192 samples, the precision were 5% for THg in water samples, 9% for MeHg in water samples, 8% for  
193 THg in soil samples, and 4.1% for THg in leaf tissues.

## 194 3. Results and discussion

### 195 3.1 Hg concentrations and deposition fluxes in throughfall and litterfall

196 THg concentrations in the throughfall ranged from 3.2 to 62.5 ng L<sup>-1</sup> for the individual samples,  
197 and the average level of throughfall was 24.1 ±7.9 ng L<sup>-1</sup>. Canopy density did have an effect on  
198 THg and MeHg concentrations (the forest cover is more than 90% and the canopy density is 0.9).  
199 THg concentrations measured in the throughfall of the subtropical evergreen broad-leaved forest  
200 (24.1 ±7.9 ng L<sup>-1</sup>) were significantly higher than those measured in the open field (10.9 ± 3.1 ng  
201 L<sup>-1</sup>). Similar to THg concentrations, MeHg concentrations in the throughfall were nearly 2.5 times  
202 higher than that in precipitation ( $p=0.004$ ,  $n=49$ ).

203  
204 THg concentrations in the throughfall were consistently at their highest in the cold season (Fig.1),  
205 which was probably due to the lower rainfall but elevated atmospheric Hg in this season. In the  
206 subtropical region of China, the monsoon-driven climate of northwest China doesn't bring much  
207 precipitation in cold season. At the same time, atmospheric stability is high during the cold period,  
208 and pollutants like atmospheric Hg do not spread easily, which contributes to the higher  
209 scavenging ability of Hg ~~in~~ the atmosphere. While the warm season (from April to September)  
210 is influenced by the southeast monsoon, and the rainfall increases greatly, which leads to lower  
211 concentration of Hg (Fig.1). The study station has obscure seasons and clear rainy and dry seasons.  
212 The deposition fluxes of THg through throughfall also showed the seasonal variation  
213 characteristics, with higher ~~data fluxes~~ appearing in wet-season (June to August). The deposition  
214 fluxes of THg through throughfall in summer at Mt. Simian accounting ~~ed~~ more than 40% of total  
215 annual Hg deposition. ~~It is,~~ However, ~~it is~~ still in September and October that a higher  
216 throughfall flux is observed. This may because that the rainfall in the two months is mainly  
217 effected by Indian Monsoon, contributing to a higher rainfall (Fu et al., 2008a) comparing with  
218 other months. The minimum values for THg deposition occurred in the cold season.

219

220 During the surveillance, THg in the throughfall was evaluated to be  $32.2 \mu\text{g m}^{-2} \text{yr}^{-1}$ . The  
221 deposition fluxes of THg through throughfall in Mt. Simian were lower than those investigated in  
222 the southwestern cities of China, such as Guizhou and Chongqing (Precipitation:  $8.4\text{--}62.1 \mu\text{g m}^{-2}$   
223  $\text{yr}^{-1}$ , throughfall:  $15.6\text{--}292.1 \mu\text{g m}^{-2} \text{yr}^{-1}$ , Guo et al., 2008; Feng et al., 2009a,b; Wang et al., 2007).  
224 However, the deposition fluxes of THg through throughfall in Mt. Simian were approximately  
225 2–10 times higher than those reported in remote areas of North America and Europe (Precipitation:  
226  $3.1\text{--}10.0 \mu\text{g m}^{-2} \text{yr}^{-1}$ , throughfall:  $6.7\text{--}23.0 \mu\text{g m}^{-2} \text{yr}^{-1}$ , St. Louis et al., 2001; Keeler et al., 2005).  
227 ~~Obviously, it was obviously that~~ the THg fluxes at Mt. Simian were higher than other sites ~~at home~~  
228 ~~and~~ abroad. The reason perhaps was that Mt. Simian had considerably more dense forest canopies.  
229 As one of the National Natural Reserves of China, it has preserved the best subtropical evergreen  
230 broad-leaved forest of China. The forest cover in the reserves reaches over 90%. The increased  
231 THg concentrations in throughfall mainly resulted from the dry deposition of Hg on the vegetation,  
232 followed by the washout of throughfall. Another possible reason, ~~which may be the most~~  
233 ~~important one,~~ for the elevated deposition fluxes, ~~which may be the most important one,~~ ~~were~~  
234 probably ~~bound up~~ related with the increased atmospheric Hg concentrations in the past 30 years  
235 due to China's fast economic development. This area, especially Chongqing city, has a large  
236 demand for energy consumption, ~~and~~ about 70% of which is from coal combustion. The annual  
237 mean gaseous elemental Hg (GEM) concentration in the middle of Chongqing city (~~9.6-31.9 ng~~  
238 ~~m<sup>3</sup>~~, Wang et al., 2006), more than 200 km away from the study site, ~~;) tripled~~ comparing with  
239 global background level (Lindberg et al., 2002a, b; Yang et al., 2009), which corresponded to the  
240 high annual deposition flux of Hg in the study area. It is also reported that the GEM concentration  
241 in the study area is as high as  $3.8 \pm 1.5 \text{ ng m}^{-3}$  (Ma et al., 2015), even if it is situated in a natural  
242 subtropical forest reserve. The MeHg flux was  $0.45 \mu\text{g m}^{-2} \text{yr}^{-1}$ , which was higher than those  
243 measured in other areas. While MeHg/THg in the throughfall samples was 1.3 %, which was a  
244 relatively high value compared with other studies (~~0.4%-0.8%~~, Lee et al., 2000; Demers et al.,  
245 2007; Choi et al., 2008; Fu et al., 2008a; Guo et al., 2008; Larssen et al., 2008). Here, the higher  
246 ratio of MeHg to THg in throughfall samples may suggest that the contribution of MeHg from  
247 throughfall cannot be ignored and should be taken care of in future studies. After all,  
248 accumulation of MeHg in the soil might have caused serious risks in the functioning of natural  
249 downstream ecosystems.

250

251 The deposition fluxes of THg through litterfall ~~were~~ ~~are~~ shown in Table 1. The average  
252 concentrations of THg and MeHg in leaf litter were  $106.7 \pm 18.3 \text{ ng g}^{-1}$  (SE = 2.6, N=60) and  
253  $0.8 \pm 0.4 \text{ ng g}^{-1}$  (SE = 0.2, N=60), respectively. The deposition flux of THg through litterfall was  
254 estimated to be  $42.9 \mu\text{g m}^{-2} \text{yr}^{-1}$  in the measurement field, which was ~~obvious~~ ~~remarkably~~ higher  
255 than the input flux through throughfall. ~~And~~ ~~it~~ is also considerably higher than litterfall fluxes  
256 reported from other regions (St. Louis et al., 2001; Demers et al., 2007;). GEM can be absorbed by  
257 stomata and detained in the leaf tissue (Eriksen et al., 2003; Fu et al., 2008a\_b). Therefore, we  
258 believed that the elevated litterfall input fluxes ~~were~~ directly related to the increased GEM  
259 concentrations, even in remote areas.

### 260 3.2 Mercury emission from soils under the canopy

261 The emission characteristics and air–surface exchange of GEM from the subtropical forest field  
262 have been investigated during eight intensive field campaigns from 2012 to 2013. At the forest

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263 field, GEM released from soils had the characteristic of obvious diurnal and seasonal variations.  
264 Day and night GEM fluxes were statistically different (t-test,  $p < 0.001$ ), with nighttime emissions  
265 considerably lower than ~~that in~~ daytime ~~fluxes~~ in all seasons (Fig.2). Average fluxes of Hg in  
266 spring, summer, autumn and winter were  $12.2 \pm 5.1 \text{ ng m}^{-2} \text{ h}^{-1}$ ,  $14.2 \pm 4.7 \text{ ng m}^{-2} \text{ h}^{-1}$ ,  $9.9 \pm 2.5 \text{ ng}$   
267  $\text{m}^{-2} \text{ h}^{-1}$ , and  $3.1 \pm 1.1 \text{ ng m}^{-2} \text{ h}^{-1}$ , respectively. It can be seen that the highest value occurred in  
268 summer, followed by spring and fall, while the lowest value was observed in winter. ~~Unlike some~~  
269 ~~other studies, in which~~The average fluxes of Hg in spring ( $12.2 \pm 5.1 \text{ ng m}^{-2} \text{ h}^{-1}$ ) were slightly  
270 lower than that in summer ( $14.2 \pm 4.7 \text{ ng m}^{-2} \text{ h}^{-1}$ ), ~~which was different from other studies (Larssen~~  
271 ~~et al., 2008; Fu et al., 2010).~~ It appeared that warm temperature with low canopy density in spring  
272 at the mid subtropical forest were more likely to release GEM. ~~Perhaps the primary reason lies~~  
273 ~~that~~One of the possible reasons ~~perhaps was that~~ the forest canopies ~~were~~ are lushly and well  
274 spaced in spring, and thus the forest can receive more sunlight. Therefore, the reduction rate of  
275  $\text{Hg}^{2+}$  by photochemical, thermal and biogenic processes probably increased.

276 This research indicated that Hg fluxes of forest field were far lower than those observed from  
277 contaminated areas such as heavily air-polluted areas in eastern Guizhou ( $33\text{--}3638 \text{ ng m}^{-2} \text{ h}^{-1}$ )  
278 (Wang et al., 2007), some cities in southwest China ( $15.0\text{--}44.4 \text{ ng m}^{-2} \text{ h}^{-1}$ ) (Qiu et al., 2006), dry  
279 landfills ( $46.5\text{--}22.8 \text{ ng m}^{-2} \text{ h}^{-1}$ ) (Zhu et al., 2010) and wetlands ( $20\text{--}500 \text{ ng m}^{-2} \text{ h}^{-1}$ ) (Lindberg et  
280 al., 2002b). But the emission of GEM elevated in comparison with those reported from other  
281 places ( ~~$5.4\text{--}4.2 \text{ ng m}^{-3}$~~ , Lindberg et al., 2002a, b;  ~~$1.7\text{--}8.4 \text{ ng m}^{-3}$~~ , Travnikov, 2005). At Mt. Simian,  
282 the estimated net GEM fluxes were released from soils during the warm season (~~spring, summer~~  
283 ~~and fall~~) and slightly volatilized during the cold season (~~winter~~). ~~Hg deposition was only observed~~  
284 ~~in several nights of the cold season during the study period,-- and thus only several data were~~  
285 ~~observed with Hg deposition in the night.~~ Hg released from the snow/air interface was extremely  
286 low comparing with the soil/air interface. ~~Normally it~~ was supposed that the  $\text{Hg}^0$  flux was zero  
287 from snow-covered surface (Huang et al., 2012). At most subtropical areas, especially  
288 mid-subtropical forests, however, there were short winter seasons with unstable snow cover, and  
289 the snow cover season only tended to occur in January. So we assumed that there still existed  $\text{Hg}^0$   
290 emission in December and February in winter. Therefore, the annual total net Hg emission flux  
291 was  $18.6 \text{ mg m}^{-2} \text{ yr}^{-1}$ .

### 292 3.3 Hg concentrations and out-flux in stream water

293 Annual volume-weighted concentrations of THg and MeHg were measured at the outlet stream of  
294 the forest field of Mt. Simian. The mean concentrations of THg and MeHg in the outflow stream  
295 were  $3.9 \pm 2.0$  and  $0.2 \pm 0.08 \text{ ng L}^{-1}$ , respectively. THg and MeHg concentrations in stream water  
296 draining the upland in our research were slightly higher than those reported in literature (Fu et al.,  
297 2008a,b; Larssen et al., 2008). THg concentrations in runoff/stream water in rainy seasons  
298 ( $4.6 \pm 2.0 \text{ ng L}^{-1}$ ) were significantly higher than those in dry seasons ( $3.3 \pm 1.8 \text{ ng L}^{-1}$ ), which can  
299 probably be attributed to the soil erosion and runoff (Ma et al., 2015). It is known that if a remote  
300 forest field does not have other obvious Hg pollution sources, Hg concentrations in the  
301 runoff/stream water can represent risks from a solitary watershed. Numerous studies showed that  
302 ~~the catchments of the~~ remote forest ~~already considered the forested catchments were regarded~~ as  
303 filters between atmosphere and hydrosphere (Lee et al., 2000; Larssen et al., 2008; Ericksen et al.,  
304 2003). The fate of Hg stored in the forest soils can be divided into three parts. One part of them  
305 transfers through food webs, threatening the balance of forest ecosystems; the second part of them  
306 is released into the atmosphere again; the third part of them probably transfers with the

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307 runoff/stream, becoming one of the Hg sources of downstream aquatic ecosystem. Therefore, to a  
308 certain extent, the role of forested catchments as Hg filters can be characterized by Hg output  
309 (runoff/stream) from the forest field.

310 This study ~~shows~~ showed that, even though Hg deposition fluxes in throughfall ~~was~~ high, THg  
311 concentration in stream/runoff ~~was~~ lower than that in contaminated sites under the same  
312 geological background. This indicated that subtropical forest field had the filtering effect of Hg in  
313 precipitation and throughfall. On the other hand, the lower concentration in stream/runoff  
314 indicated that the study area did not suffer from severe anthropogenic Hg pollution. Steam output  
315 of THg was calculated by multiplying the average THg concentration in stream water ( $3.9 \pm 2.03$   
316  $\text{ng L}^{-1}$ ) by the water discharge rate in the forest field of the study site (annual water discharge:  
317  $1.86 \times 10^8 \text{ m}^3$ , from hydrological departments of Jiangjin district). The export ~~mass~~ flux of THg via  
318 runoff/stream was  $0.73 \text{ kg yr}^{-1}$ . The subtropical forest field in the study area is  $100.1 \text{ km}^2$ . So the  
319 export ~~mass-flux~~ of THg through stream water was  $7.23 \mu\text{g m}^{-2} \text{ yr}^{-1}$ , which tripled the values  
320 reported in the catchments of Sweden ( $1.6\text{--}1.8 \mu\text{g m}^{-2} \text{ yr}^{-1}$ , Lee et al., 2000;  $2.4 \mu\text{g m}^{-2} \text{ yr}^{-1}$ ,  
321 Larssen et al., 2008). Our results indicated that the output fluxes of MeHg via stream water were  
322  $0.08 \mu\text{g m}^{-2} \text{ yr}^{-1}$ , which was similar to or slightly larger than other results ( $0.03\text{--}0.07 \mu\text{g m}^{-2} \text{ yr}^{-1}$ ,  
323 Lee et al., 2000;  $0.05 \mu\text{g m}^{-2} \text{ yr}^{-1}$ , Schwesig and Matzner, 2001). ~~Here the elevated Hg fluxes in~~  
324 ~~stream water were probably attributed to the great atmospheric Hg depositions. As we mentioned~~  
325 ~~above that Mt. Simian was one of the most complete forest and until recent decades was~~  
326 ~~one of Asia's least populated and most inaccessible areas. Average Hg concentration in the soil~~  
327 ~~detected in previous research was  $0.28 \text{ mg kg}^{-1}$  (Ma et al., 2013), which indicated that it was not~~  
328 ~~an obvious geological Hg hotspot. Therefore, the elevated Hg fluxes in stream water were~~  
329 ~~probably attributed to the great atmospheric Hg depositions.~~ At the same time, our preliminary  
330 research results also illustrated that forest runoff and soil erosion could increase Hg output from  
331 subtropical forest catchments (Ma et al., 2013). But the total output fluxes of THg and MeHg were  
332 far lower than the input fluxes via wet deposition ( $32.2 \mu\text{g m}^{-2} \text{ yr}^{-1}$  for THg and  $0.5 \mu\text{g m}^{-2} \text{ yr}^{-1}$   
333 for MeHg). This study showed that the subtropical forest was able to exert purification effect of  
334 filtration, even ~~with~~ under the condition of elevated deposition of Hg.

#### 335 3.4. Dynamics and transport of Hg based on forest field

336 THg content in the forest field (forest floor and soil profiles) of Mt. Simian was shown in Table 2.  
337 The THg stocked in the forest soil was approximately  $20192 \mu\text{g m}^{-2}$  (~~mean~~ average soil depth is  
338  $98 \text{ cm}$ ), while that in the organic floor was  $5148 \mu\text{g m}^{-2}$  (~~mean~~ average litter depth is  $19 \text{ cm}$ ). THg  
339 content in soil profile were three times more than the organic horizon in the subtropical forest field.  
340 The active pool (the upper  $22 \text{ cm}$ ,  $O_i$ ) of THg represented  $41 \%$  of the total storage of the study  
341 area. In the soil profile, THg content in the organic horizon ( $O_i$ ) is obviously higher than those in  
342 the other horizons. At the same time, the organic matter is well decomposed under warm and rainy  
343 subtropical climate, which has high affinity to Hg in soil.  
344 Due to the good adsorption and reduction of organic matter, the organically bound contents of Hg  
345 could be released into the environment again during ~~the~~ decomposition of organic matter.

346 The ultimate fate of Hg in the terrestrial ecosystem may depend upon ~~the means of its~~ delivery and  
347 incorporation ~~of Hg~~ into the forest floor. And the average Hg fluxes were also estimated. Input of  
348 THg to the forest field of Mt. Simian included net throughfall and litterfall depositions (St. Louis  
349 et al., 2001; Fu et al., 2010). Annual throughfall and litterfall deposition fluxes of THg in Mt.  
350 Simian were  $32.2$  and  $42.9 \text{ mg m}^{-2} \text{ yr}^{-1}$ , respectively (Fig.3). Litterfall deposition inputs were

351 estimated ~~as to~~ 134% of ~~the~~ throughfall deposition at the forest field. In the ~~studied-study~~ forest  
352 field, the predominant pathway of Hg fluxes to the forest floor was via litterfall (57.1%). ~~A~~  
353 ~~majority of~~~~An amount of the~~ atmospherically deposited THg was released through Hg<sup>0</sup> ~~emission~~  
354 at a rate of 18.6  $\mu\text{g m}^{-2} \text{yr}^{-1}$ . Steam outflow of THg from the wetland was 7.2  $\mu\text{g m}^{-2} \text{yr}^{-1}$ . The ratio  
355 between output and input of THg was 0.34 at the subtropical forest field of Mt. Simian, which was  
356 significantly higher than others (~~0.02-0.04~~, Lee et al., 2000; ~~0.16~~, Larssen et al., 2008; ~~0.30~~, Fu et  
357 al., 2010). The apparently higher ratio between the output/input fluxes of THg may represent an  
358 important ecological risk.

359 The THg stored in the forest field was 982-~~2~~ times larger than the annual THg output by  
360 stream/runoff outflow and soil volatilization, and 33~~87-6~~ times larger than the input estimated  
361 from wet and dry depositions (Fig.3). The estimates of the deposition flux of THg in this study  
362 were much higher than values reported from the northeastern American (3.8–12.6  $\mu\text{g m}^{-2} \text{yr}^{-1}$ ;  
363 Driscoll et al., 2007) and Norway (7  $\mu\text{g m}^{-2} \text{yr}^{-1}$ ; Larssen et al., 2008), probably indicating a  
364 significant impact of heavy regional Hg emissions from industry and urban on local Hg deposition.  
365 The reason perhaps was that highly soluble Hg<sup>2+</sup> was easily stripped from the atmosphere and  
366 deposited locally. ~~H~~~~And~~ higher wet deposition can illustrate the ~~obvious-remarkable~~ influence of  
367 local Hg emissions on Hg accumulation in the regional forest field. The THg flux through litterfall  
368 was 1.5 times larger than that through throughfall due to greater input of litter mass and higher Hg  
369 concentrations in the litter. Annual exports of THg in stream water of the study area (3.2–9.5  
370  $\mu\text{g m}^{-2} \text{yr}^{-1}$ ) were not accorded with those reported from northern forest catchments (1.0–3.4  
371  $\mu\text{g m}^{-2} \text{yr}^{-1}$ ; St. Louis et al., 2001; Grigal et al., 2000). An amount of the atmospherically deposited THg  
372 was lost via emissions at a rate of 18.6  $\mu\text{g m}^{-2} \text{yr}^{-1}$ . Compared with stream outflow, the evasion of  
373 Hg from forest soil played a more essential role in THg outputs.

374 Compared the ratios of output ~~to input~~ flux with other places (Larssen et al., 2008; Fu et al., 2010),  
375 the higher ~~output flux ratio~~ may be greatly affected by the elevated deposition. Therefore, regional  
376 emission of Hg may have stronger influence on forest ecosystems, in which the deposition of THg  
377 through litterfall and throughfall, being affected more by local and regional changes of Hg  
378 emissions and cycling, were the main paths for Hg entering into soil surface (Demers et al., 2007).  
379 However, in this study, the outflow of Hg via runoff output and the soil-air interface accounted for  
380 a small fraction of Hg budget in the study area. And the accumulation pattern of Hg in forest floor  
381 and soil profiles was seasonal. ~~As we mentioned above that Mt. Simian was one of the most~~  
382 ~~typical subtropical forest systems and the least accessed area, average Hg concentrations in all soil~~  
383 ~~surfaces of this area were below 0.30 mg kg<sup>-1</sup>(Fu et al., 2010; Ma et al., 2013).~~ Therefore, the  
384 accumulation of Hg in soil would be enhanced with time. At the same time, the ultimate fate of  
385 deposited Hg depends upon the biogeochemical processes that have not been well quantified  
386 within the ecosystem. Hg dynamics during litter decomposition, for instance, need to be  
387 considered as a whole so that we can better understand controls on long-term accumulation of Hg  
388 in the forest ecosystem and its delayed release to surface water.

#### 389 4. Conclusions

390 In this study, the mass balance and transport of Hg in southwestern China were first measured at a  
391 subtropical forest, Chongqing, China. Results revealed that litterfall deposition inputs were the  
392 predominant pathway (42.9  $\text{mg m}^{-2} \text{yr}^{-1}$ , account for 57.1%) of Hg flux to the forest floor. Annual  
393 deposition fluxes of Hg through throughfall were 32.2  $\text{mg m}^{-2} \text{yr}^{-1}$ , accounting for ~~42.90~~% of the Hg  
394 inputs. Researchers should pay more attention to the higher ratio of MeHg to THg in the

395 throughfall deposition when they model the biogeochemical cycling in a typical local forest  
396 watershed. For the output process, the exchange of Hg ( $18.6 \mu\text{g m}^{-2} \text{y}^{-1}$ ) across the forest field-air  
397 interface ~~is~~ was an essential part of the biogeochemical cycle of Hg. ~~The R~~unoff/~~S~~steam outflow  
398 of THg from the wetland was  $7.2 \text{ mg m}^{-2} \text{ yr}^{-1}$ , ~~which was lower than that in contaminated sites~~  
399 ~~under the same geological background. Therefore, we may conclude that: 1) the study area does~~  
400 ~~not suffer from severe anthropogenic Hg pollution; 2) the forested field has the filtering effect of~~  
401 ~~Hg in precipitation and throughfall, even in the elevated atmospheric Hg area.~~

402 The forest field (forest floor and soil profiles) plays an important role in the cycling of THg and  
403 MeHg. In reality, it is just another problem created by the accumulation of Hg,  
404 which would be a potential risk affecting the output of Hg in the long term. Terrestrial ecosystems  
405 that have accumulated more Hg may ultimately emit them to ~~the~~ wetlands and surface water,  
406 finally affecting the entire aquatic ecosystems. Therefore, it is a signal that we should not ignore.  
407 In this case, however, any changes in the forest floor like deforestation or forestland degradation  
408 may strongly affect Hg budget of the region.

#### 409 Data availability

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

#### 412 Author contribution

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

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## Tables

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

	THg Concentration (ng L <sup>-1</sup> )			MeHg Concentration (ng L <sup>-1</sup> )		
	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 <sup>-1</sup> )			MeHg Concentration (ng g <sup>-1</sup> )		
	106.7±18.3			0.79±0.36		
Annual deposition flux	THg (µg m <sup>-2</sup> yr <sup>-1</sup> )			MeHg (µg m <sup>-2</sup> yr <sup>-1</sup> )		
Precipitation (1508mm)	15.45			0.36		
Throughfall (1336mm)	32.17			0.45		
Litterfall (402g m <sup>-2</sup> yr <sup>-1</sup> )	42.89			0.32		

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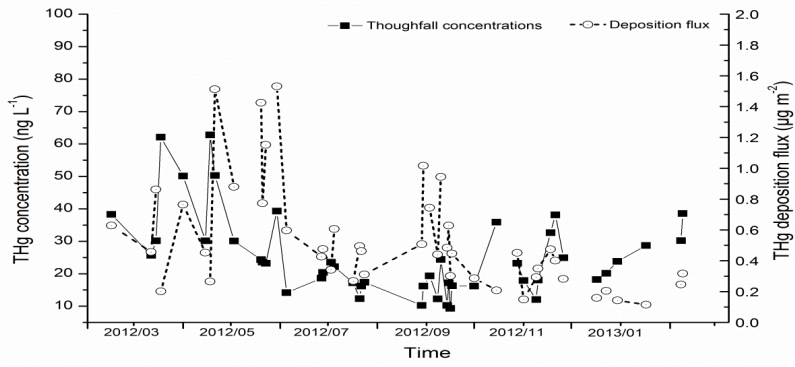
540 Table 2 The concentrations and contents of THg in forest floor and different soil layers

	THg (ng g <sup>-1</sup> )	Density (g cm <sup>-3</sup> )	Thickness (m)	THg content—(µg m <sup>-2</sup> )	Total contents
Initial leaf litter	46.30±14.2	0.28±6.2	0.06±0.02	774.8	
Forest floor					
Half decomposition	51.22±9.4	0.49±18.1	0.08±0.03	2000.8	5148.7
decomposition	57.88±10.3	0.82±9.9	0.05±0.02	2373.1	
<i>O<sub>i</sub></i>	297.8±15.2	1.27±2.1	0.22±0.10	8320.5	
Soil profile					
<i>O<sub>e</sub></i>	117.4±32.3	1.65±16.2	0.34±0.08	6586.1	20192.6
<i>O<sub>a</sub></i>	68.4±13.6	1.84±20.7	0.42±0.06	5286.0	

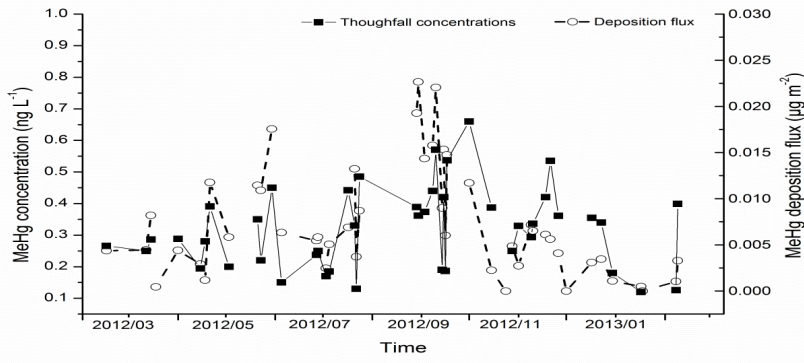
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## Figures



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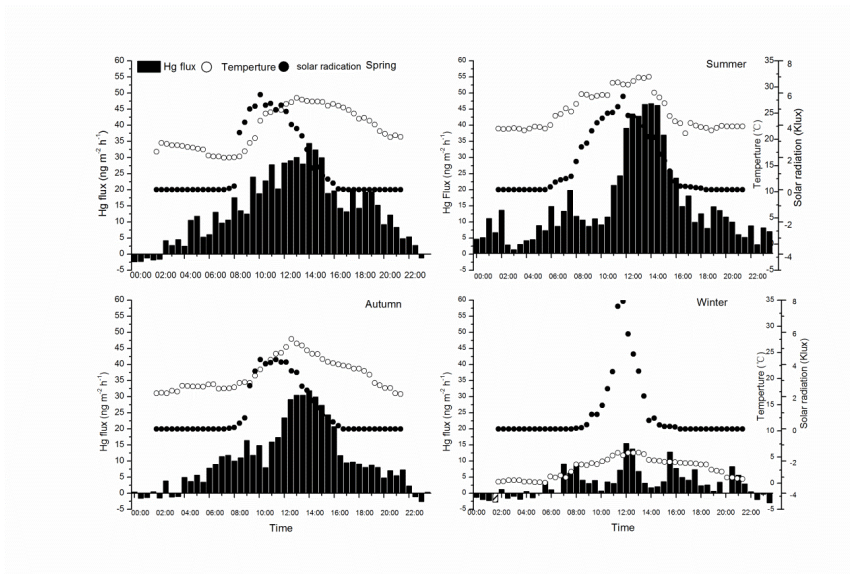


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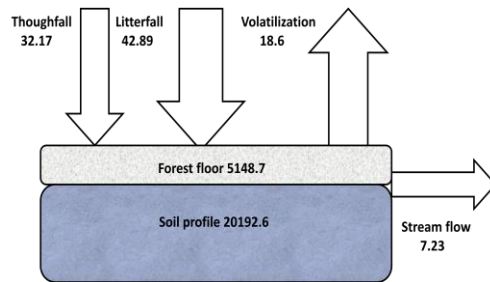
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Fig. 1. Volume-weighted mean concentrations of THg and MeHg and deposition fluxes of throughfall in the evergreen broad-leaf forest from March 2012 to February 2013



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



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