Distribution and elevated soil pools of mercury in an acidic subtropical forest of southwestern China

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ABSTRACT

Tieshanping catchment in southwest China was supposed to a large pool of atmospheric mercury. This work was aimed to examine THg (total mercury) concentrations, pools and influence factors in the acidic forest. THg concentrations were highly elevated in the study area, which was significantly depended on TOM (total organic matter) concentrations and altitudinal elevation, whereas negatively correlated with soil pH. The pools of mercury accumulated in soils were correlated strongly with the stocks of TOM and altitude, ranged from 5.9 to 32 mg m⁻² and averaged 14.5 mg m⁻², indicating that the acidic forest was a great sink of atmospheric mercury in southwest China. THg concentrations in stream waters decreased with altitude increasing and regression analyses showed that soil/air exchange flux would be increased with the decrease of altitude. Present results suggest that elevation increasing decreases THg losses as low THg concentrations in runoffs and volatilization from soils.

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1. Introduction

Mercury is a highly toxic heavy metal and is well-known global contaminant that can affect the health of people and ecosystems (Depew et al., 2013; Li et al., 2013). Unlike other heavy metals, mercury can be emitted to the atmosphere in vapor form by both natural and anthropogenic sources. Archives of historical mercury deposition recorded from peat bog and lake sediments have provided evidence that elevated mercury deposition over the past century is directly related to the emissions of human industrial activities (Zhou et al., 2013; Liu et al., 2003). Studies in southwestern China, have estimated litterfall to be surpassing precipitation and throughfall and responsible for close to 70% of the mercury flux to a forested watershed, indicated that litterfall play a crucial role in mercury cycling in forest ecosystems (Fu et al., 2010b; Zhou et al., 2013).

Soils of forested watershed is a large reservoir of atmospherically deposited mercury, accounting for up to 90% of mercury in forests, which is predominantly bound with soil total organic matter (TOM) and more than 95% of the mercury resides in the organic soil (Grigal, 2003; Juillerat et al., 2012). Average

concentrations of mercury in the surface levels of forest soils in remote areas reported by recent studies were much higher than a few decades ago (Zhou et al., 2013; Wang et al., 2013; Jin, 1993). However, by contrast, the data reported in the 1990s of Europe much higher than that in the 2000s (Schwesig et al., 1999; FOREGS, 2005; Szopka et al., 2011).

China is the largest developing country worldwide. With the rapid economic development during the past three decades, the amount of mercury emitted in China has increased significantly. Previous studies demonstrated that the concentration of total gaseous mercury (TGM) is elevated in the urban and suburban areas in Chongqing due to regional industrial and coal combustion emissions (Yang et al., 2009). Our previous studies demonstrated that atmospheric deposition was significantly elevated in Tieshanping National Forest Park (TNFP) area (Wang et al., 2009), which was several or even dozens of times compared to estimates obtained in North America and Europe (Johnson and Haines, 2007; Larssen et al., 2008). Therefore, it can be deduced that the subtropical forest in TNFP has become a massive atmospheric mercury sink. In this paper, we present a study on the mercury pools and effective factors of distribution in an upland forest located in the TNFP forested catchment. From January to November 2014, we undertook comprehensive field measurements on the distribution of mercury in litter, soils, soil solutions, stream water and air/soil fluxes. The main objective of this study was: (1) to examine the

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concentrations and pools of THg accumulated in soils, and their dependence on soil properties and altitude; and (2) to investigate the mercury output by stream water and soil/air flux influence on THg accumulation in different altitudes at the catchment.

2. Materials and methods

2.1. Study area

Tieshanping National Forest Park (29°38'N, 104°41'E), one of the Sino-Norwegian multidisciplinary Integrated Monitoring Program on Acidification of Chinese Terrestrial Systems (IMPACTS) project monitoring sites, is located on a sandstone ridge, 20 km in the northeast of the metropolitan Chongqing City and on the side of the Yangtze River. The forest stand in TNFP is a Masson Pine dominated, coniferous-broad leaf mixed subtropical forest and trees were planted in the 1960s (Wang et al., 2009). The soil is typically mountain yellow earth and its texture is haplic Acrisol/Alisol, which is severely acidified with an acidic pH 3.79 and TOM 12.7% in the organic horizon (Table 1).

2.2. THg in litter and soils

Litter and soil samples were collected at 66 sites inside the park and surrounding forest (Fig. 1) in March, 2014. Sampling sites represented various altitudes in the range 200–600 m a.s.l. In each sampling site, representative samples were collected in triplicates from the litter (ectohumus, 1–4 cm) and from the correspondingly organic layers (unequal depth, 2–4 cm) and mineral topsoil layers (4 cm), which were collected within a 2 m × 2 m plot and mixed together. Litter samples were stored into paper bags, and soils into a polyethylene zip-type bags. The sampling sites were chosen randomly and located at least 100 m away from roads and buildings. Soil samples were air-dried in a clean environment and litter samples dried at 60 °C by an oven. Subsequently, plant samples from each site were completely ground to a fine powder in a pre-cleaned stainless steel blender and the air-dried soil samples were homogenized to a size of 150 meshes per inch with a mortar before chemical analysis.

A DMA-80 direct mercury analyzer (Milestone Ltd., Italy) was used for measuring THg concentrations in plant and soil samples. Instrument detection limit for THg was 0.005 ng and the method detection limit was 0.34 ng g⁻¹. Each sample was measured in duplicate and analyses were repeated when the coefficient of variability of samples exceeded 5%. Quality assurance and quality control of the analytical processes were addressed with blind

duplicates, matrix spikes, and certified reference materials. Instrument calibration curves covering the appropriate concentrations were confirmed by soil standards (IGGE IRMA China, 590 ± 80 ng g⁻¹) and citrus leaf standards (GBW10020, 150 ± 20 ng g⁻¹), and checked by the control standard samples every six samples. The precisions, obtained from ten duplicated measurements of samples, were 3.5% for soil and 5.7% for plant. An average THg concentration of 596 ± 28 ng g⁻¹ was obtained from IGGE IRMA and 148 ± 7 ng g⁻¹ citrus leaf.

2.3. THg in stream water and soil solution

Stream water samples were collected in the study area at the same time with soil (Fig. 1). The soil solution was sampled by tension lysimeters using ceramic suction cups (type P80, Staatliche Porzellan-Manufaktur, Berlin) which were installed more than two years, repeatedly at 5 cm (L1) and 25 cm (L2) depth in the soil of 4 sites (A–D) along a hill slope in the forest. Site A was located on the top of slope; site B was in the middle; site C was in the low-lying land and site D was in the wetland. All the water samples were poured into rigorously pre-cleaned 350 ml PET bottles. For sample collection, bottles were rinsed three times with the water samples before being filled and preserved by adding trace-metal grade HCl (to 0.5% of total sample volume). Polyethylene gloves were used throughout the whole sampling campaign. PET bottles with samples were individually sealed into double successive polyethylene bags and packed in black plastic bags to avoid light, then shipped to the laboratory and frozen until analysis.

THg concentrations in water samples were determined following US EPA Method 1631 (US EPA, 1999). Samples were analyzed via BrCl oxidation followed by SnCl₂ reduction, and dual amalgamation combined with CVAFS detector. The spike recoveries for THg were in the range of 97–110%.

2.4. Evasion flux of mercury from soil

The soil/air mercury fluxes from forest soil were determined by using a coupling method of dynamic flux chamber and manual pure gold quartz trap. A semi-cylinder and open-bottom flux chamber made of quartz glass, which designed according to Fu et al. (2008), had been used throughout the sampling campaign. At the outlet of the chamber, an orifice was connected to two exits, one was connected a regulated suction pump, whereas the other exit was connected to a gold trap for trapping outlet TGM. On the two opposite section of the chamber, out of the inlet, another gold trap was placed to trap inlet TGM in the surrounding air.

Table 1

The effect of altitudinal zone on the mean concentrations of THg and soil parameters in various layers, and on the mean pools of THg and TOM.

Layer (depth)	Altitude (m)	pH	TOM (%)	THg (ng g ⁻¹)		TOM pool (g m ⁻²)	THg pool (mg m ⁻²)	
				Range	Mean ± SD		Range	Mean ± SD
Organic (2–4 cm)	200–400	3.9 ± 0.21ab	11 ± 2.8c	54–263	167 ± 54bc	5.1 ± 0.34a	3.5–10	8.1 ± 2.1a
	400–500	3.8 ± 0.12c	13 ± 4.2bc	83–371	181 ± 57abc	5.2 ± 0.35a	5.2–12	7.8 ± 1.5ab
	500–600	3.8 ± 0.17c	14 ± 4.7b	144–462	224 ± 75a	5.4 ± 0.19a	6.0–24	8.9 ± 3.9a
	Avg.	3.8 ± 0.16bc	13 ± 4.3bc	54–462	191 ± 65ab	5.3 ± 0.31a	3.5–24	8.2 ± 2.6a
Mineral top (4 cm)	200–400	4.0 ± 0.11a	4.1 ± 1.0d	23–99	65 ± 24e	3.2 ± 0.54b	2.0–7.6	5.1 ± 1.7c
	400–500	3.9 ± 0.09ab	4.7 ± 0.72d	37–159	73 ± 26de	3.6 ± 0.36b	2.9–11	5.5 ± 1.8c
	500–600	3.9 ± 0.10ab	5.4 ± 1.2d	50–160	101 ± 30d	3.9 ± 0.53b	4.1–12	7.3 ± 2.1c
	Avg.	3.9 ± 0.11a	4.8 ± 1.0d	23–160	80 ± 31de	3.6 ± 0.50b	2.0–12	6.0 ± 2.1c
Litter (1–4 cm)	200–400		87 ± 2.7a	110–180	150 ± 21c	2.3 ± 0.14c	0.30–0.48	0.39 ± 0.050d
	400–500		86 ± 5.1a	109–208	157 ± 23bc	2.3 ± 0.25c	0.31–0.51	0.41 ± 0.050d
	500–600		85 ± 5.8a	113–201	160 ± 26bc	2.2 ± 0.29c	0.31–0.49	0.41 ± 0.060d
	Avg.		86 ± 5.0a	109–208	157 ± 24bc	0.77 ± 0.080c	0.30–0.51	0.14 ± 0.020d
All	Avg.					9.4 ± 0.32	5.90–32	15 ± 3.9

Mean values for zones marked with different letters differ significantly (ANOVA, Tukey test, P = 0.05).

Fig. 1. The location of the study site.

To detect the collection efficiency of our gold quartz traps before sampling in field, two traps were connected in sequence and ambient lab air was sampled for 24 h. Sampling flow rate was maintained $0.4\text{--}0.5\text{ L min}^{-1}$ by a rotameter and the air volume passing through each trap was accurately measured by an integrating flow meter. For all the traps, there was a small quantity of detectable mercury on the second traps (penetration $< 1.0\%$), which can be ignored. The mercury flux was calculated using the following equation:

$$F = (C_0 - C_i) \times Q/A \quad (1)$$

where F is the mercury flux ($\text{ng m}^{-2} \text{h}^{-1}$); C_0 and C_i are the steady state mercury concentration (ng m^{-3}) of the outlet and inlet air stream, respectively; A is the surface area (0.06 m^2) enclosed by the chamber; Q is the flushing flow rate (10 L min^{-1}). In this work, mercury fluxes were measured from soils at two different altitudes (220 m and 512 m) through semi-in situ experiment. One of the soils (including litterfall) was shipped up from lower elevations (220 m a.s.l.) to the higher elevations (512 m a.s.l.), and replaced the original surface soil about 10 cm. The other one was the undisturbed soil in 512 m a.s.l. The shipped soil was equilibrated for one month before the measurement of flux by two chambers side by side simultaneously. The fluxes were continuous monitoring for a week, including gold traps were sampled every half an hour for 1 day (24 h) and collected at 8:00 am and 6:00 pm in the remaining 6 days, represented daytime and night, respectively. All the gold traps were brought back to TNFP Forestry Station for mercury quantification by CVAFS detector (Brooks Rand III, US EPA, 1999) using dual gold trap amalgamation procedure after every sampling.

2.5. THg pools, soil pH and TOM

Soil pH was measured with a glass electrode pH meter in a 1:5 soil: water suspension. TOM content in forest soils and litter were determined by using the sequential loss on ignition (LOI) (Heiri et al., 2001; Fu et al., 2010a, b; Zhou et al., 2013). Air-dried soil

samples (WS) were dried at $105\text{ }^\circ\text{C}$ by an oven for about 12–24 h to obtain the dry weight of the samples (DW_{105}). The heated dry sample was then burned at $550\text{ }^\circ\text{C}$ for 4 h to obtain the DW_{550} . Then, the TOM content (LOI_{550}) was calculated according to the following formula (2):

$$\text{LOI}_{550} = 100(\text{DW}_{105} - \text{DW}_{550})/\text{WS} \quad (2)$$

On the basis of measured mercury and TOM concentrations in the three layers, the pools of mercury and TOM accumulated in soil were calculated for each sampling site on the soil bulk density (ρ_i) and concentrations (c_i) according to the method of Zhou et al. (2013) as the following formula:

$$M_{\text{THg/TOM}} = \sum_{i=1}^n c_i \times \rho_i = \sum_{i=1}^n c_i \times s_i/v_i \quad (3)$$

Part of samples collected by a cutting ring sampler, and v_i was the known volume of the cutting ring sampler and s_i was the constant weight of the samples dried in an oven at $105\text{ }^\circ\text{C}$. For this purpose, some other soil bulk density was assessed by the model proposed by Prevost (2004).

3. Results and discussion

3.1. THg concentrations in litter and soils

The concentrations of THg in the layers of litter and surface soils in the TNFP, varied in a broad range: $23\text{--}462\text{ ng g}^{-1}$ (Table 1). High values of standard deviation (SD) and variability coefficient proved a high diversity of THg concentrations, particularly in the organic soil layers. Higher THg concentrations in the organic layer compared to forest litter result partly from natural processes of litterfall decomposition and transformation, in which organic matter binding mercury compounds are usually more stabilized via complexing, humification and adsorption to clay minerals (Schlüter, 2000; Gunda and Scanlon, 2013). This result was

consistent well with observations reported by other studies which stressed the affinity of atmospheric mercury to accumulate in the surface layers of soils (Wang et al., 2013; Pena-Rodriguez et al., 2014).

Generally, THg concentrations in surface soils in the TNFP were comparable to mercury levels from other forest soils in China (Lin et al., 2012; Fu et al., 2010a; Liu et al., 2003). But THg concentrations in the soils of our study area were slight lower than THg levels from some remote areas of Eastern Europe which were generally more than 200 ng g^{-1} for organic layers, primarily due to much higher atmospheric deposition to the forest (Szopka et al., 2011; Gunda and Scanlon, 2013; Navrátil et al., 2014). However, THg concentrations in surface soils and litter in the study area were much higher (1.5–2.0 folds higher) than those observed in mountain areas of North America and northeastern China, which were generally less than 150 ng g^{-1} for surface soils and 100 ng g^{-1} for litterfall (Larsen et al., 2008; Juillerat et al., 2012; Tabatchnick, 2012; Luo et al., 2014). We may attribute the elevated concentrations in litter and soils to the elevated TGM concentrations (3.8 ng m^{-3} in March, our unpublished data) in ambient air in the study area, which was from regional industrial and coal combustion emissions (Yang et al., 2009) and given rise to high THg in foliage and throughfall and resulted in elevated loading of THg in the study forest.

Basic physical and chemical characteristics of soil, especially TOM and pH, play the most important role in regulating soil mercury concentration and transformation. Enrichment in mercury observed in the litter layer and organic layer compared with mineral topsoil layer, undoubtedly demonstrates the crucial role of TOM in the accumulation of air-borne mercury. Regression analysis based on Pearson correlation coefficient, indicated that the concentrations of THg in the organic and mineral topsoil layers were linearly dependent on the content of TOM in soil (Fig. 2). Like other soft acid metal, mercury preferentially binds to ligands of sulfur, but the main form in which it accumulates in soils, is the compounds with TOM (Yang et al., 2007). Soil TOM and THg interact strongly with each other and the interactions can greatly influence the transport, transformation, and mobility (Grigal, 2003). Thus this physical-chemical bond helps stabilize mercury in the soil system and inhibits dissolution to the stream water (Schwesig et al., 1999) and volatilization into the atmosphere (Schlüter, 2000).

Changes in soil pH alter not only the fractions of mercury in soil solution but can also change mercury speciation in soils (Gunda and Scanlon, 2013). Higher THg concentrations but lower pH observed in the organic layer compared with mineral topsoil layer, undoubtedly indicated the crucial role of pH in the accumulation of mercury in soils. The scatterplot in the Fig. 2 illustrates the significantly negative relationships between THg and pH concentrations in both soil layers. As pH of the soil increases, more affinity of mercury binding groups in the organic matter is decreased, therefore more mercury is released from the soil (Gunda and Scanlon, 2013).

THg concentrations in three layers under different altitude are presented in Table 1. In general, the litter collected from TNFP was comparable in terms of leaf types, with Masson Pine varieties being the most dominant species. Litter mercury concentrations were not found to be significantly different and correlated with altitudes (Tables 1 and 2). This relatively homogenous distribution of mercury in litter is possibly due to TGM involved in leaf-level accumulation, while TGM may be well mixed and abundant in the atmosphere. Therefore litter mercury distribution varied a little with respect to aspect and litterfall mercury deposition was similar in the study area.

Interestingly, altitudinal distribution of mercury concentrations in the organic and mineral topsoil layer differed from those in the

litter, which significantly correlated with altitude (Table 2). In previous studies, Zechmeister (1995) and Evans and Hutchinson (1996) have shown that surface soils at higher altitudes received higher annual precipitation, and simultaneously higher loadings of pollutants, including mercury. As well as the increasing of altitude reduced turnover rates in soil TOM pools and lower pH, which allows a greater opportunity for mercury accumulation and suppression of mercury release from organic layers (Schlüter, 2000). Moreover, lower temperature at higher altitude also restrained mercury evasion from soils as discussed in section 3.3. For the mineral topsoil in the areas endangered by acid deposition, the THg content correlated with altitude and corresponding organic soil layers, probably because the level of THg concentrations and leaching of base constituents from organic soils was increased at higher altitudes due to higher precipitation and THg in organic soils. Therefore, the significant correlation of THg concentration with TOM and pH in organic and mineral topsoil (Fig. 2) demonstrated the relation of all these parameters to altitude or terrain influence. However, Fu et al. (2010a) and Mohammad et al. (2014) have found the opposite relationships, of which THg in surface soils and foliage decreased with altitudinal elevation.

3.2. THg pools in litter and soils

THg pools (down to mineral topsoil) in the TNFP subtropical forest remain in a broad range, from 5.9 to 32 mg m^{-2} and with the mean value of 14.5 mg m^{-2} (Table 1) and should be considered as relatively high compared with the values reported by other literature (Table 3). However, it should be stressed that the attempts to compare our results with the data from other studies are facing some difficulties, because the other studies either reported the amounts of THg accumulated in various horizons which were inconsistent with our research, or calculated THg pools accumulated within soil profiles of various depths. We have found that the largest amounts of THg were present in the organic layer (44–75% of the total pool) due to significantly higher concentrations (Table 1). The contributions of THg present in forest litter were the lowest with mean of 2.8% and the remaining 41% was stored in the mineral topsoil layer (Fig. 3a). Additionally, we found the correlation coefficient of THg and TOM pools was particularly strong (Fig. 4a).

In order to assess the quantity ratio of THg to TOM pools, the mean values of THg/TOM ratio were calculated for separate soil layers. The THg/TOM ratio determined for the litter was in the range of 0.11 – $0.29 \text{ } \mu\text{g g}^{-1}$ (mean $0.18 \text{ } \mu\text{g g}^{-1}$) and corresponding values for the organic and mineral topsoil layers were $1.56 \text{ } \mu\text{g g}^{-1}$ (ranges of 0.78 – $4.6 \text{ } \mu\text{g g}^{-1}$) and $1.66 \text{ } \mu\text{g g}^{-1}$ (ranges of 0.83 – $43 \text{ } \mu\text{g g}^{-1}$), respectively. Some studies reported much lower values of THg/OM (approximate to $0.22 \text{ } \mu\text{g g}^{-1}$) in organic horizons in North American and European forests of the last century (Låg and Steinnes, 1978). The data from central and eastern Europe and were higher, ranging from 0.70 to $0.90 \text{ } \mu\text{g g}^{-1}$ (Godbold, 1994) and averaged $0.77 \text{ } \mu\text{g g}^{-1}$ in top 10 cm soils (Szopka et al., 2011). Our results referring to the organic soil layer are almost 2–7-fold as high as those given by most authors. The reason may be related to ten to thirty times air-borne mercury input in our study areas compared forest areas of North America and Europe according our previous study (Wang et al., 2009).

The tendency of increasing THg concentrations in soils with growing altitudes as described above, was also reflected by the increase of THg pools accumulated in the corresponding layers down to the depth of mineral topsoil (Fig. 4b). The dependence was significant but much lower compared to the correlation between TOM with THg pools in soils and the results of a two-way factorial ANOVA analysis indicated that there were no significant differences

Fig. 2. The correlation and distribution THg concentrations vs. TOM concentrations and pH in organic (a) and mineral top (b) soil layers respectively. Auxiliary graphs illustrate the data distribution interval.

($P > 0.05$) between the pools of mercury accumulated in soils in various altitudinal zones (Fig. 3b). A similar relationship also referred to the stocks of TOM which were significant enrichment with the increase of elevations (Table 2). It turns out that the pool of

stored TOM is a key factor governing the amounts of THg accumulated in soils of the TNFP forest. Such dependence was corresponded with our inference, as severe environmental conditions at higher altitudes were supposed to receive higher mercury wet deposition and suppress organic matter decomposition to make for TOM and THg enrichment in the organic layer.

Table 2
Correlation coefficients of Altitude (m a.s.l.) with soil THg and parameters in TNFP.

	pH	TOM	THg	TOM pool	THg pool
Litter layer		−0.070	0.050	−0.070	0.020
Organic layer	−0.34 ^a	0.27 ^b	0.34 ^a	0.27 ^b	0.18
Mineral topsoil layer	−0.38 ^a	0.45 ^a	0.46 ^a	0.46 ^a	0.43 ^a
Total layers				0.42 ^a	0.35 ^a

^a Correlation is significant at the 0.01 level (two-tailed).

^b Correlation is significant at the 0.05 level (two-tailed).

3.3. Mercury in stream water and evasion from forest soil: possible effects on mercury distribution in forest soils

Variation of un-filtered THg concentrations in stream water in the TNFP is shown in Fig. 5a. THg concentrations varied between 1.5 and 5.0 ng L^{−1}, with an overall average concentration of 3.1 ± 1.2 ng L^{−1}. THg concentrations in stream water were obviously

Table 3

THg pools and output flux of THg in the study area and literature.

Site localities	THg pools		Stream water concentrations (ng L ⁻¹)	References
	Depth (cm), horizon	Pools, mg m ⁻²		
Riparian wetland, USA	0–90	30		Selvendiran et al., 2008
Beaver meadow, USA	0–90	20		
Upland, USA	0–90	64		
Lehstenbach, Germany	0–60	89	13	Schwesig and Matzner, 2000
Steinkreuz, Germany	0–60	19	10	
Five forests, Czech	Organic	5.3–10		Navrátil et al., 2014
Langtjern, Norway	0–B	17	4.0 ^a	Larssen et al., 2008
Karkonosze, Polish–Czech	Litter to 20	17		Szopka et al., 2011
Marcell, USA	0–50	48	12.5	Grigal et al., 2000
PANP young stand, Canada	Organic	1.0		Friedli et al., 2007
PANP old stand, Canada	Organic	2.9		
Vermont, USA	A	7.5		Juillerat et al., 2012
LGS, south China	0–60	109	4.3	Wang et al., 2009
TNFP, southwest China	Litter to mineral topsoil	15	3.1	This study

^a concentration was estimated from figures.

higher than those reported from some natural forest (Table 3), which was probable attributed to the great soil mercury sequestration. In addition, soil erosion and runoff were also important sources to stream water. Number of the sampling sites was increased with elevation and No 1 to 7 were under an altitude of 300 m a.s.l., which seems to be higher concentrations than that in high elevation areas (Fig. 5a). Linear regression analysis showed that altitude significantly negatively correlated with THg in stream waters ($r = -0.49$, $p < 0.05$). The reasons may be that, firstly, mercury in stream water was probably derived from increased soil

erosion and volume of runoff during stream transport in lower altitude with larger slopes. Secondly, lower TOM content and pH in soils of low altitude areas increased THg loss. These, in turn, indicated that more mercury output by runoff led to low concentrations in soil at low altitudes. Therefore, this may be another reason of mercury concentrations and pools increased with the increase of elevations.

Concentrations of THg in the soil solution tended to increase with soil depth for the site A–C and decreased from top to down of the hill slope in the TNFP (Fig. 5b). However, in contrast, our

Fig. 3. THg pools in three layers (a) and three altitudinal gradients vs. corresponding TOM pools (b) (error bars represent standard error of total pools in three layers) in the TNFP. **Fig. 4.** Dependence of THg pools accumulated in soils on TOM pools for all soil samples (a) and altitude for all sampling sites (b).

Fig. 5. Distribution of THg in stream waters (a) and soil solutions (b) in TNFP.

previous study (Wang et al., 2009) reported that concentrations of THg in the soil solution strongly decreased with increasing depth, which in top soils ($60 \pm 40 \text{ ng L}^{-1}$) were much higher than that in deep soils ($10.1 \pm 7.9 \text{ ng L}^{-1}$) and this phenomenon was also found by Rieder et al. (2014) in five Swiss forests. Thus it should be noted that our sampling was carried out during a heavy rain and the large amount of rainfall may dilute the THg concentrations in top soil solutions. Similarly, along with the hill slope, dilute strength was greater by surface runoff, thus result in highest THg in the soil solution on the top and lowest in the wetland. Significantly higher soil THg concentrations was observed in top soils compared to deep soils, but THg in soil solutions was the opposite, therefore, the question should be asked now, to what extent, THg deposited to the soil surface has been translocated or leached down to deep soils. Some authors reported high mobility of THg in acidic forest soils, attributed to the strong coupling of mercury to dissolved or colloidal organic matter (Akerblom et al., 2008). To our previous results, THg concentrations in deep soil solutions were comparable, but these in top soil were much lower. We may suppose that heavy rainfall in the acidic forest diluted THg concentration in surface soils but not deep ones and THg leaching amount from surface soils directly related to rainfall, even if we have not measured dissolved organic matter.

Mercury fluxes was obtained from 24 consecutive hours and 7 days of field sampling as shown in Fig. 6 and Fig. 7. Overall, all net evasions were observed during the sampling period, and the average fluxes of mercury emission was $6.3 \text{ ng m}^{-2} \text{ h}^{-1}$ for the soil collected from altitude 220 m and $6.4 \text{ ng m}^{-2} \text{ h}^{-1}$ for the soil in altitude 512 m during sampling time (7 days). Within natural forest ecosystems, soil/air exchange flux of mercury is an important

pathway for mercury deposition or losses from landscapes. However, it is still difficult to accurately quantify the magnitude of the emission of mercury from the study area because mercury emission from soil was controlled by multiple interacting factors, such as experimental methods (Eckley et al., 2010), soil physical-chemical factors (soil temperature and humidity, soil gas mercury, soil TOM, pH etc.) (Choi and Holsen, 2009; Yang et al., 2007) and meteorological parameters (e.g. UV radiation, air temperature, rainfall) (Gabriela et al., 2011; Corbett-Hains et al., 2012), etc. Diurnal variation trends of 24 h of mercury exchange flux are presented in Fig. 6, which showed a significant correlation with air temperature, soil temperature and solar radiation for both soils ($p < 0.01$ for all) and these observations round out the research results of many years (Ericksen et al., 2006; Fu et al., 2012; Mazur et al., 2014).

Altitude position is considered as a major soil forming factor (Jenny, 1941). In this study, the pH of surface organic soils and up mineral soils had a significant negative correlation with elevation (Table 2). This indicated stronger acidification at higher altitudes, probably owing to high precipitation and strong soil leaching. Instead, TOM was significant positive correlated with elevation in both soil layers (Table 2). Soils at lower altitude have higher pH and lower TOM, which was supposed to increase opportunity for mercury evasion. However, based on our continuous observation of 7 days, there was no obvious fluxes difference between the two kinds of soils (Fig. 6). Previous studies showed that soil/air mercury fluxes

Fig. 6. Effect of ambient air and soil temperature and solar radiation on mercury emission fluxes of soils collected from Altitude 220 m (Altitude 1) and Altitude 512 m (Altitude 2).

Fig. 7. Comparisons of mercury emission fluxes between soils collected from Altitude 220 m and Altitude 512 m for 7-day sampling.

Fig. 8. Regression plots between temperature and mercury emission fluxes of soil collected from Altitude 220 m (a) and Altitude 512 m (b).

were significantly correlated with air temperature in subtropical forests in China (Fu et al., 2010a; Ma et al., 2013). Regression analyses also showed that mercury emission fluxes (F) of the two kinds of soils were statistically significant with air temperature (T) in our studies ($F_{220} = 0.66T - 9.7$, $F_{512} = 0.72T - 11$, $r = 0.72$ and 0.77 , $p < 0.01$ for both, respectively) (Fig. 8a and b), which may imply that temperature can be used to predict the soil emission of mercury in the study area (Fu et al., 2010a). As the average temperature is $21\text{ }^{\circ}\text{C}$ in the 24hr-sampling day, the corresponding fluxes are 4.2 and $4.1\text{ ng m}^{-2}\text{ h}^{-1}$ calculated by linear equations, which was comparable with the directly measured value of 4.1 and 4.2 for the soils collected from Altitude 220 m and Altitude 512 m, respectively. However, it is known as the altitude increases 100 m , the temperature may gradually reduce $0.6\text{ }^{\circ}\text{C}$. Thus, the temperature may be 22.8 at the elevation of 220 m and the corresponding flux is $5.4\text{ ng m}^{-2}\text{ h}^{-1}$ calculated by linear equations. Evasion fluxes of the kinds of the soils was comparable at the same meteorological conditions and elevation, but if we considered the temperature affected by elevation, the fluxes would be increased in lower elevations. Therefore, this may be also an important reason for the soil mercury concentrations and pools distribution along with the altitude.

Therefore, the possible factor of effects on mercury distribution in this acidic forest soils primarily come from two aspects: input and output. Actually, we have not directly measured the input of mercury in various altitudes, but higher altitudes were supposed to receive higher mercury deposition (Zechmeister, 1995). However, we have directly measured THg in the stream water and soil evasion flux by a semi-in situ experiment in different altitudes, which were the two major output pathways from forest soil. The result indicated that the output by runoff and evasion flux were both higher at low altitude. Thus, our observation suggested that the characters of mercury distribution in the forest soil was driven primarily by higher mercury input and lower output at higher altitude.

4. Conclusions

Measurements of THg concentration and pool in litter, organic and mineral top soils were carried out at an acidic forest catchment in Tieshanping National Forest Park, southwest China. Soil emission flux, stream water and soil solutions were also investigated. Undoubtedly, Air-borne depositions are the main source of mercury in soils. The mean THg concentrations in litter, organic and mineral top soils were 157 , 191 and 80 ng g^{-1} , respectively, which were strongly influence soil TOM and pH, as well as altitude. THg pool from litter to mineral topsoil was 14.53 mg m^{-2} , which were strongly dependent on the amounts of TOM stored. Pools of THg indicated that the acidic forest in southwest China was a great sink

of atmospheric mercury. THg concentrations in stream waters and soil/air exchange flux of mercury would be increased along with the decrease of the altitude. Therefore, elevated mercury concentrations in runoffs and volatilization from soil were identified as the major pathway for increasing THg losses gradually along with the down of the elevation height.

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