

Atmospheric mercury deposition and its contribution of the regional atmospheric transport to mercury pollution at a national forest nature reserve, southwest China

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Received: 26 May 2015 / Accepted: 3 August 2015 / Published online: 23 August 2015
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Abstract Atmospheric mercury deposition by wet and dry processes contributes to the transformation of mercury from atmosphere to terrestrial and aquatic systems. Factors influencing the amount of mercury deposited to subtropical forests were identified in this study. Throughfall and open field precipitation samples were collected in 2012 and 2013 using precipitation collectors from forest sites located across Mt. Jinyun in southwest China. Samples were collected approximately every 2 weeks and analyzed for total (THg) and methyl mercury (MeHg). Forest canopy was the primary factor on THg and MeHg deposition. Simultaneously, continuous measurements of atmospheric gaseous elemental mercury (GEM) were carried out from March 2012 to February 2013 at the summit of Mt. Jinyun. Atmospheric GEM concentrations averaged $3.8 \pm 1.5 \text{ ng m}^{-3}$, which was elevated compared with global background values. Sources identification indicated that both regional industrial emissions and long-range transport of Hg from central, northeast, and southwest China were

corresponded to the elevated GEM levels. Precipitation deposition fluxes of THg and MeHg in Mt. Jinyun were slightly higher than those reported in Europe and North America, whereas total fluxes of MeHg and THg under forest canopy on Mt. Jinyun were 3 and 2.9 times of the fluxes of THg in wet deposition in the open. Highly elevated litterfall deposition fluxes suggest that even in remote forest areas of China, deposition of atmospheric Hg^0 via uptake by vegetation leaf may be a major pathway for the deposition of atmospheric Hg. The result illustrates that areas with greater atmospheric pollution can be expected to have greater fluxes of Hg to soils via throughfall and litterfall.

Keywords Mercury · Subtropical forest · Deposition fluxes · Gaseous elemental mercury · Source

Introduction

Mercury (Hg) is a highly toxic metal that can harm the environment and human health (Hylander 2001; Lindberg et al. 2002a, b; Feng et al. 2009a, b). Significant quantities of Hg primarily derived from the atmosphere are associated with vegetation in terrestrial ecosystems, and large pools of atmospheric Hg deposition are retained in surface litter and soil pools (Schroeder and Munthe 1998). As a consequence, terrestrial ecosystem is the main source of Hg to many aquatic ecosystems. The accumulation and retention of Hg in terrestrial compartments and the mobility of Hg within ecosystems are keys to understand how atmospheric Hg loadings ultimately affect aquatic ecosystems in remote pristine regions (Fitzgerald 1995; Lee et al. 1998; Munthe et al. 1995; Gustin 2000). Elevated levels of mercury in waters remote from the anthropogenic emission sources

Responsible editor: Philippe Garrigues

Highlights Higher GEM concentrations and deposition flux in southwest forest due to emission of atmospheric Hg in fast development areas of China.
Litterfall is the dominant input pathway.
Coal consumption is dominated by domestic use, and it often rises in summer causing the elevated atmospheric Hg.

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have also been documented (Bishop et al. 1998; Wang et al. 2006; Nguyen et al. 2007; Sigler et al. 2009; Zhang et al., 2009), indicating that atmospheric deposition is a major source of Hg contamination.

The forest ecosystem, which covers nearly 1/3 of the Earth's terrestrial surface, is very important in the global biogeochemical cycle of Hg and deserves further study to improve our understanding of Hg dynamics. Because of the large surface area associated with canopy foliage, atmospheric deposition of contaminants is elevated in forests compared with other types of ecosystems. Forest studies have indicated that total atmospheric Hg deposition may be estimated using fluxes of throughfall (precipitation that passes through the canopy) plus litterfall (plant material that falls to the forest floor; Rea et al. 2001). The quantification of the dry deposition of Hg to a forested ecosystem is difficult since several types of measurements have to be performed (Grigal et al. 2000; Fu et al. 2010a; Ma et al. 2013; Travníkov 2005; Kim et al. 2005; Valente et al. 2007). The important processes to be quantified include sorption on plant surfaces and/or direct uptake through stomata. Part of the dry deposited Hg and, possibly, some of wet deposited Hg will thus be retained in the canopy by an irreversible uptake, while the rest will be washed off by precipitation. Even though there are some uncertainties, it is at present reasonable to assume that the flux of Hg to the forest floor can be estimated by throughfall measurements and litterfall analysis.

China is considered to be an area exposed to atmospheric Hg contaminations due to regional anthropogenic emissions. Atmospheric Hg emissions in China are predicted to increase due to fast economic development (Wu et al. 2006). Large anthropogenic emissions have resulted in elevated atmospheric Hg concentrations and depositions in industrial and urban areas (Liu et al. 2002; Feng et al. 2008; Wan et al. 2006) and have the potential to cause Hg pollution in surrounding areas and even remote areas of China via long-range atmospheric transport (Wang et al. 2009). China is recognized as one of the biggest emitters of atmospheric Hg (Qiu et al. 2006; Fu et al. 2009). To date, only few studies in rural and semirural of China also showed extremely high Hg deposition fluxes (Guo et al. 2008; Fu et al. 2010a). Thus, the objective of this study was to quantify elevated atmospheric deposition and its potential sources at a national forest nature reserve in southeast China. Evergreen broad-leaf forest, the most representative vegetation type, was studied in this research. The GEM as well as deposition fluxes of Hg in south China were measured. Moreover, using the GEM and meteorological dataset, we summarized that the regional sources and long-range transport affected the GEM concentrations. Furthermore, we discussed the deposition and sink of atmospheric Hg in the forest ecosystem in China.

Materials and methods

Study area and sampling sites

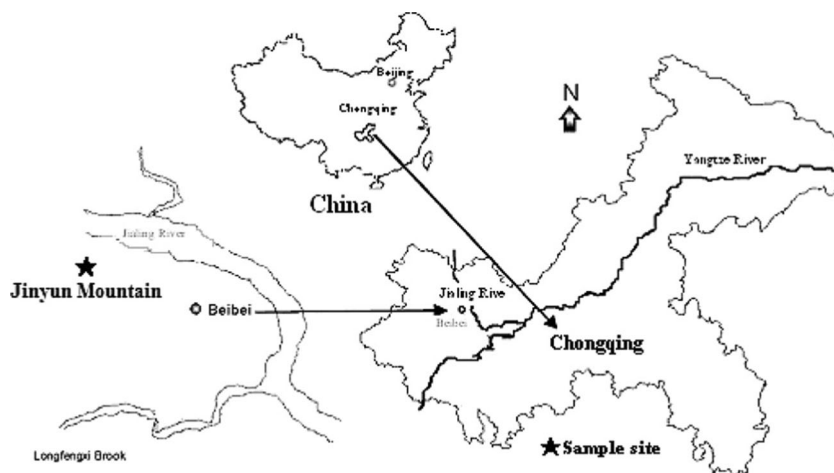
Chongqing is situated in the upper reaches of Yangtze River in the eastern Sichuan Basin, China. And environmental pollution of Chongqing is expected to be a major and long-term challenge as Chongqing's population may eventually exceed 33 million people. The study was conducted at the Jinyun Mountain, which is 50 km far from urban Chongqing (29°41'08" and 29°52'03" N; 106°17'43" and 106°24'50" E) (Fig. 1), occupying an area of 60.2 km². This region has a subtropical monsoon climate with abundant rainfall. The mean annual temperature is 18.6 °C with the highest recorded in August at an average of 34.5 °C and the lowest temperature in January at an average of -5.5 °C. The mean annual precipitation is 1541.3 mm with a daily maximum up to 146.5 mm. Evergreen broad-leaf forest is one of the most representative vegetation type preserved in Mt. Jinyun National Natural Reserve. Therefore, evergreen broad-leaf forest as the typical forest of subtropical zone was studied in this research.

Sampling methods and analysis

Measurements of atmospheric GEM

Real time continuous measurements of GEM were made from May 2012 to February 2013 using an automated Hg vapor analyzer (Tekran 2537X). Its technique is based on the collection of TGM (GEM + RGM) on gold traps, followed by thermal desorption and detection of Hg⁰ by cold vapor atomic fluorescence spectrometry. Two filter holders were installed separately at the Teflon tube inlet and the inlet of 2537X on its rear panel, with 47-mm-diameter Teflon membrane filters (pore size 0.2 μm). These filters, replaced weekly, prevented particular matters and droplets from entering the instrument. In this study, the measured TGM concentration was probably dominated by GEM because the concentration of GEM was generally at least two orders of magnitude higher than RGM, especially in remote areas (Fu et al. 2010b; Gustin et al. 2015). The sampling interval, sampling flow rate, and auto-calibrate interval of 2537X were programmed to 5 min, 1.5 L min⁻¹, and 23 h, respectively. The emission rate of internal permeation source was calibrated every 3 months by injecting Hg vapor from an external Hg source (Tekran 2505). The uncertainties of interval calibration between parallel gold cartridges during the sampling duration were lower than 10 %. The detect limit of Tekran 2537X is 0.1 ng m⁻³. During sampling, air was pulled into the analyzer from 6 m above ground.

Fig. 1 Schematic diagram of the monitoring site. Sample sites were located in Chongqing, China



Sampling method and analysis of precipitation and throughfall

The rain samples were collected by an automatic precipitation sampler (APS-3A, Changsha Xianglan Scientific Instruments Co., Hunan, China), which was situated on an unshadowed building roof at each sampling site. The sampler consisted of one tipping-bucket rain gauge, one moisture sensor, one automatic cover, one funnel, eight sampling borosilicate bottles, eight Teflon tubes connecting the funnel to the sampling bottles, and one portable fridge for cold storage (4 °C) of the rain samples. Each precipitation event was sampled from each site during the period between May 2012 and February 2013. In a precipitation event, we defined the period of rain as from the triggering of moisture sensor to 07:00 am the next day. Then the sampling borosilicate bottle was altered automatically for the next precipitation event. Throughfall samples (three per forest field) were collected by using a bulk precipitation collector with an acid-washed borosilicate glass bottle and a borosilicate glass wide-mouthed jar (15 cm in diameter) supported in a PVC housing system. Immediately after a precipitation event, throughfall collectors were sealed using polyethylene bags to prevent contamination of the collectors through Hg dry deposition.

The water samples were divided into two bottles, one filtered through 0.45 μm microfilters (Millipore, USA) for analyses of dissolved total mercury (DHg) and dissolved methylmercury (DMeHg); the other was unfiltered for analyses of THg and total methylmercury (MeHg). All the samples analyzed for species of Hg were acidified to 5 % (v/v) using trace-metal grade HCL. The rain samples were transported to the lab on ice and then stored in a refrigerator in the dark until analysis. The water samples were transferred from samplers to acid-cleaned borosilicate glass bottles. These bottles were initially soaked in 10 % (v/v) HNO₃ for at least 48 h, then rinsed with ultra-pure water, and baked for 1 hour in a muffle furnace at 500 °C. Finally, they were doubly bagged and stored in

wooden boxes until use. All operations were performed in accordance with ultraclean sample handling protocols.

Sampling method and analysis of litterfall

Fresh leaf litter was sampled at locations on Mt. Jinyun in late September 2012. Litter was collected using 0.25 m² litter traps that were deployed at four different locations within the subtropical evergreen forest field. The litter traps were made from treated lumber with a screen bottom. The accumulated litter was collected in brown paper bags and air dried in clean environment in the laboratory until analysis. THg concentrations in litterfall were determined by acid digestion followed by oxidation, purge and trap, and cold vapor atomic absorption spectrophotometry. Approximately 0.2 g sample was digested in 10 mL freshly mixed HNO₃/H₂SO₄ (4:1 v/v) for 6 h at 95 °C in a water bath. The digested solution was then diluted by adding Milli-Q water to a volume of 50 mL and analyzed for THg. For MeHg analysis, approximately 0.2 g ground sample was digested for 3 h at 75 °C in polyethylene bottles containing 5 mL 25 % KOH in methanol (US EPA, 2001). Then MeHg was extracted with methylene chloride and back-extracted from the solvent phase into water, and then the aqueous phase was ethylated for determination of MeHg (US EPA, 2001).

Sample analysis

For THg, DHg and RHg, and particulate Hg (PHg) (PHg = THg-DHg) determinations, the samples were analyzed (following the EPA Method 1631) by Cold Vapor Atomic Fluorescence Spectrometry (CVAFS, Brooks Rand model III, Brooks Rand Laboratories, Seattle, WA, USA) after oxidation, reduction, and trap (US EPA, 2002). RHg is defined as all Hg species that are readily available for reduction with SnCl₂ solution and volatile Hg species, which were measured on acidified and non-filtered water samples. Complying with the EPA Method 1630, samples for MeHg and DMeHg

(PMeHg = TMeHg-DMeHg) determinations went through distillation, ethylation, and gas chromatographic (GC) separation before CVAFS analyses (US EPA, 2001).

Quality control and statistical analysis

Quality controls for THg and MeHg determinations included method blank, blank spikes, duplicates, and matrix spikes. The method detection limits of THg and MeHg were 0.02 ng l^{-1} and 0.01 ng l^{-1} . The method blank was lower than the detection limits in all cases. The average relative standard deviation for the duplicate analyses of THg and MeHg were 5.2 and 5.4 %, respectively. Recoveries for matrix spikes ranged from 95 to 113 % for THg and 90 to 115 % for MeHg. The equipment blanks of automatic precipitation samplers for THg and MeHg were 0.04 ng L^{-1} and 0.02 ng L^{-1} , respectively.

Meteorological data and backward trajectory calculation

In this study, wind direction and wind speed were measured using a portable weather station located within 5 m from the TGM sampling site with a time resolution of 30 min. In order to identify the long-range transport of Hg and its influences on the atmospheric Hg distribution at the study site, 3-day back trajectories were calculated using Gridded Meteorological Data combined with the Geographic Information System (GIS) based software, Trajstat, from HYSPLIT (Fu et al. 2010a). All the back trajectories ended at the sampling site with an arrival height of 500 m above the ground. Hourly meteorological data were prepared using the Weather Research and Forecasting (WRF) model version 3.4 with the Noah Land Surface Model, WSM6 microphysics scheme, Kain-Fritsch cumulus scheme, and Dudhia radiation physics scheme. All back trajectories were generated using Gridded Meteorological Data archives of the Air Resource Laboratory, National Ocean and Atmospheric Administration (NOAA), which are available online at (<ftp://arlftp.arlhq.noaa.gov/pub/archives/gdas1/>), and were used as the input.

Results and discussion

General characteristics of Hg deposition fluxes (precipitation, throughfall, and litterfall)

The statistical summaries of the concentrations and fluxes of precipitation, throughfall, and litterfall measured at the peak of Mt. Junyun were listed in Table 1. Mean concentrations of THg ranged between 1.1 and 34 ng L^{-1} (Fig. 3), with an overall volume-weighted average of $11.9 \pm 7.6 \text{ ng L}^{-1}$ (Table 1) in precipitation. Concentrations of MeHg in direct wet deposition collected during 2012–2013 ranged between

0.01 and 0.66 ng L^{-1} (Fig. 3), with an overall volume-weighted average of $0.24 \pm 0.13 \text{ ng L}^{-1}$ (Table 1). Mean concentrations of MeHg in throughfall collected in 2012–2013 under forests ranged between 0.1 and 2.3 ng L^{-1} (Fig. 3), with an overall volume-weighted average of $0.55 \pm 0.24 \text{ ng L}^{-1}$ (Table 1). Mean concentrations of THg in throughfall ranged between 3.2 and 84 ng L^{-1} (Fig. 3), with an overall volume-weighted average of 17.7 ng L^{-1} (Table 1). The data indicated that canopy had the greatest influence on Hg concentrations and flux. Significant differences existed in THg and MeHg throughfall concentrations and flux based on the canopy cover.

As can be seen from Fig. 2, Hg concentrations in throughfall and precipitation were significantly different ($p < 0.001$). Fluxes of Hg in throughfall were $0.6 \mu\text{g of MeHg m}^{-2} \text{ year}^{-1}$ and $21.8 \mu\text{g of THg m}^{-2} \text{ year}^{-1}$ (Table 1). These fluxes of MeHg and THg were comparably higher than those in direct wet deposition, suggesting that dry deposition of Hg on Mt. Junyun was relatively high. The relatively high THg fluxes in throughfall at Mt. Junyun (more than 40 % enhancement) were different from results obtained at other sites. Some studies also showed that both stomatal and nonstomatal pathways were important ways for atmospheric Hg to enter vegetation leaves (Stamenkovic and Gustin 2009; Fu et al. 2010a). St. Louis et al. (2001) suggested that dry deposition of Hg at Experimental Lakes Area, northwestern Ontario, Canada, were relatively low. The relatively low THg fluxes of throughfall at Experimental Lakes Area, Canada (a 15 % enhancement) were different from data obtained at other more Hg contaminated sites. But some other studies showed that net throughfall was a good estimate of dry deposition of Hg to ecosystems (Lindberg et al. 2002a; Fu et al. 2010b), the reason perhaps was that not all atmospheric Hg deposited to the foliar surface was assimilated and fixed by the foliage. Rea et al. (2001) found that a large majority of PHg and RGM were probably washed off the surface of leaves or decreased and then reemitted to the atmosphere. They also found that dry deposition can readily wash off foliage by using foliar washing experiments. Therefore, elevated THg concentrations in throughfall mainly resulted from the dry deposition of PHg and RGM to vegetation, followed by washout of throughfall (Fig. 3). This was consensus with previous studies (Fu et al. 2010b; Rea et al. 2001).

During 2012 and 2013, for those events when wet deposition and throughfall were collected together, average volume-weighted concentrations of PHg (12.4 ng L^{-1}) and PMeTHg (0.25 ng L^{-1}) in throughfall were 2.6 and 1.8 times higher than average volume-weighted concentrations of PHg (4.87 ng L^{-1}) and PMeTHg (0.14 ng L^{-1}) in precipitation collected in the open (Fig. 3). As many researchers have shown, atmospheric deposition of Hg depends upon Hg speciation; highly soluble Hg^{2+} species are quickly stripped from the atmosphere and deposited locally, whereas PHg emissions

Table 1 Mean value of THg and MeHg concentrations and deposition fluxes in precipitation, throughfall, and litterfall

	THg concentration (ng L ⁻¹)				MeHg concentration (ng L ⁻¹)		
	THg	DHg	PHg	RHg	MeHg	DMeHg	PMeHg
Precipitation	11.9±7.6	7.1±5.6	4.9±2.4	4.5±3.6	0.20±0.013	0.14±0.05	0.10±0.08
Throughfall	20.1±12.3	7.8±8.4	12.4±6.2	4.9±9.6	0.55±0.24	0.25±0.12	0.31±0.14
Litterfall	THg concentration (ng g ⁻¹)				MeHg concentration (ng g ⁻¹)		
	104.5±23.5				0.84±0.12		
Annual deposition flux	THg (μg m ⁻² year ⁻¹)				MeHg (μg m ⁻² year ⁻¹)		
Precipitation (1337 mm)	15.9				0.26		
Throughfall (1084 mm)	21.8				0.60		
Litterfall (416 g m ⁻² year ⁻¹)	43.5				0.27		

are transported regionally, and elemental emissions are transported globally (Demers et al. 2007; Porvari and Verta 2003). On the issue of atmospheric transport and deposition at this study area, which are described in detail in “Potential source identification for transport of atmospheric Hg” section, RHg concentration in litterfall of the study area was slightly higher compared with other studies (Meng et al. 2011); no obvious Hg activation effect was observed.

It can be seen from Table 2 that precipitation and throughfall fluxes of THg in the sampling site were lower than those reported from several cities of Guizhou and Chongqing, southwestern China (precipitation 8.4–62.1 μg m⁻² year⁻¹, throughfall 15.6–292.1 μg m⁻² year⁻¹, Guo et al. 2008; Feng et al. 2009a, b; Wang et al. 2008). But results from measurement site were about 2–10 times higher than those observed in remote areas of North America and Europe (precipitation 3.1–10.0 μg m⁻² yr⁻¹, throughfall 6.7–23.0 μg m⁻² yr⁻¹, St. Louis et al. 2001; Keeler et al. 2005; US National atmospheric deposition program 2007). As

discussed above, large regional emissions of Hg from industrial activities and coal combustion might be responsible for the great loading of Hg to the upland forest.

Our data clearly showed that the forest canopy provided, primarily via litterfall, an important additional flux of THg to forest ecosystems. In fact, total flux of MeHg and THg under a standard 25-year-old forest canopy on Mt. Jiuyun was 3 and 2.9 times of the flux of THg in wet deposition in the open (Table 2). Litterfall deposition flux of THg in the forested areas of Mt. Jinyun was much higher than values observed from forests in North America and Europe (Grigal et al. 2000; Lee et al. 2000; Rea et al. 2001; Larsson et al. 2008). This may be caused by the current t high GEM concentrations in the study area. Previous studies indicated that atmospheric Hg⁰ is almost the exclusive source of Hg in vegetation leaf (Zhang et al. 2005; Fu et al. 2010a). GEM contacting leaf surfaces was either reemitted to the atmosphere or taken up by stomata and retained internally by the leaf tissue during events of elevated

Fig. 2 Concentration of THg and MeHg in precipitation and throughfall collected on Mt. Jinyun from March 2012 to February 2013

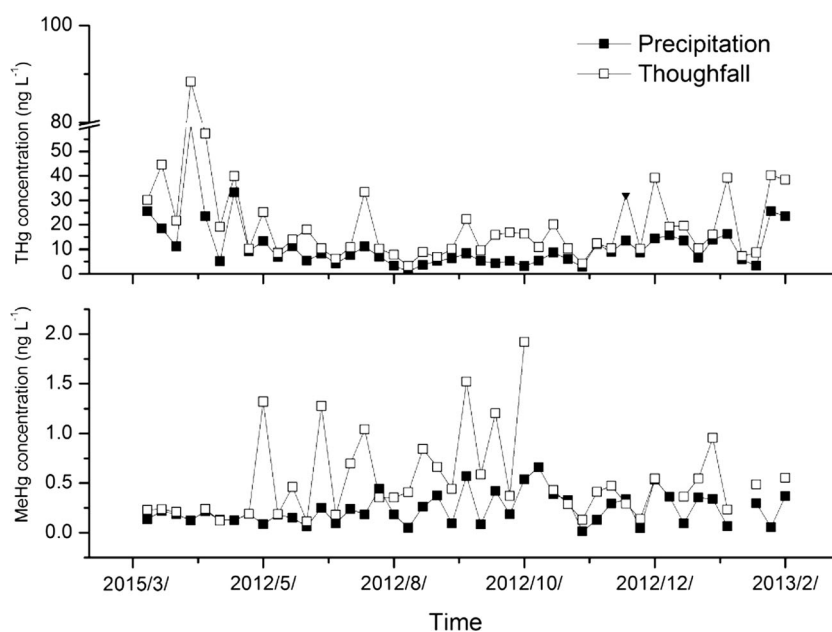
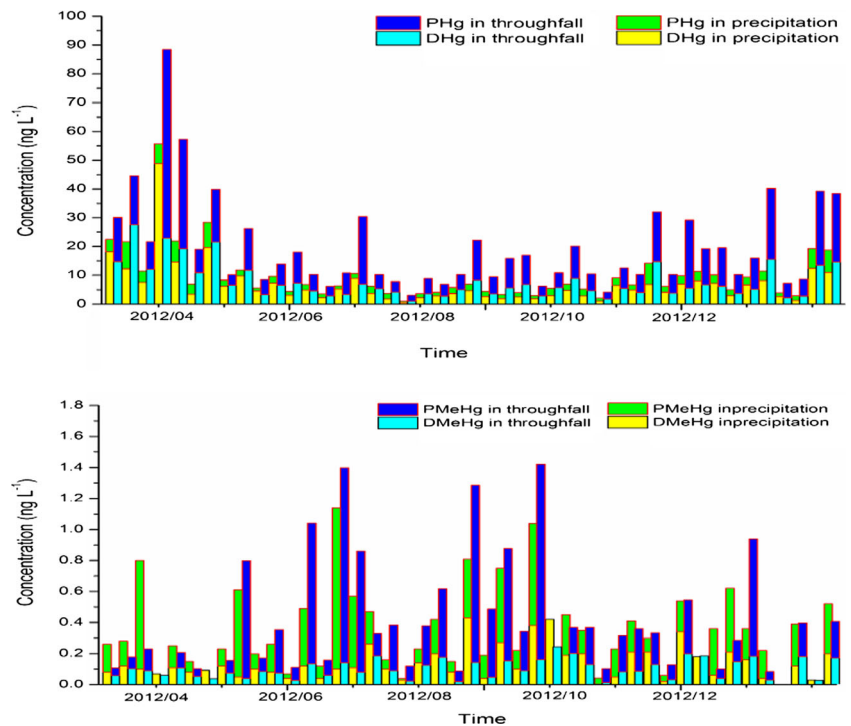


Fig. 3 THg and MeHg concentrations of different species in precipitation and throughfall collected on Mt. Jinyun from March 2012 to February 2013



atmospheric Hg deposition until deposited in litterfall (St. Louis et al. 2001). Another reason for the higher THg fluxes at the study area than other sites may due to the considerably more dense forest canopies in all the regions. As one of the best-preserved subtropical evergreen broad-leaved forests in China, the density of forest canopies in the catchment here can reach more than 90 %. Due to the high biomass and high ability to accumulate Hg, litterfall depositing is the major way of inputting Hg into forest soils.

GEM concentration and sources identification of atmospheric Hg at the study site

This research indicated that the deposition fluxes of THg in throughfall and litterfall in the forested area of Mt. Jinyun were much higher than those observed in the forests of North America and Europe. It may be because of the high GEM concentrations in the study site. Previous researchers had showed that atmospheric Hg⁰ was almost the exclusive source of Hg in vegetation leaves (Fu et al. 2010b; Zhang et al. 2005).

Table 2 Annual precipitation and throughfall flux of Hg in the study area and literatures

Area	Precipitation flux ($\mu\text{g m}^{-2} \text{ year}^{-1}$)		Throughfall flux ($\mu\text{g m}^{-2} \text{ year}^{-1}$)		Literatures
Svartberget, Norway	7.0	0.08	15.0	0.17	Larssen et al. 2008
Gårdsjön, Norway	10.0	0.12	23.0	0.16	Lee et al. 2000
Langtjem, Norway	4.8	0.06	6.7	0.18	Lee et al. 2000
Mt. Gongga, southwest China	26.1	0.30	57.6	0.54	Fu et al. 2010a
Mt. Leigong, southwest China	6.1	0.06	10.5	0.12	Fu et al. 2010b
Guizhou, China	35–112	0.30–0.44			Guo et al. 2008
Chongqing, China	36.8	0.36	45.2–291	0.30–0.65	Wang et al. 2008; Wang et al. 2014
Champlain, American	8.4	0.06			Scherbatakoy et al. 1998
Adirondack, USA			7.4		Demers et al. 2007
North American	3.1	0.04	6.8–15.8	0.10–0.16	US National atmospheric deposition program
Mt. Jinyun, southwest China	11.93±7.6	0.20±0.013	20.10±12.3	0.55±0.24	This study

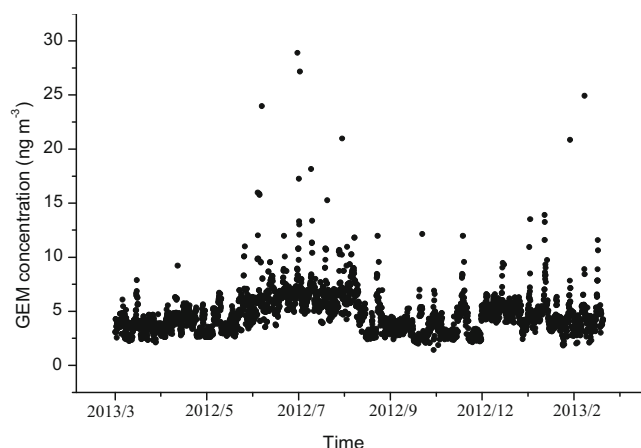


Fig. 4 Time series of gaseous elemental mercury (GEM) in Mt. Jinyun

The highly elevated litterfall deposition fluxes suggested that deposition of atmospheric Hg⁰ via uptake by vegetation leaves may be the major pathway for the depletion of atmospheric Hg in remote forests of China.

Figure 4 was the time series of 1-h averaged GEM concentrations in ambient air throughout the study period (from March 2012 to February 2013). The distribution of GEM was characterized by significant variations throughout the entire sampling campaign. It can be seen from Fig. 5 that GEM concentrations were lognormally distributed. GEM concentrations of 2.5–5.5 ng m⁻³ accounted for approximately 85 % of the total frequency, which was similar with results conducted in Mt. Leigong (Fu et al. 2010b).

The concentration began to rise in the morning in most of the days. Such a diurnal trend is somewhat similar to the morning pollutant accumulation in urban areas due to increased human activities. Episodes with extremely high GEM concentrations were abundant (0.5 % of values were greater than 10 ng m⁻³), and 65.4 % of these events were observed in the daytime. This phenomenon was also occurred in the research of Mt. Leigong (Fu et al. 2010b). The reasons probably were the following: (a) air masses from industrial and urbanized areas that probably related to heavy pollution

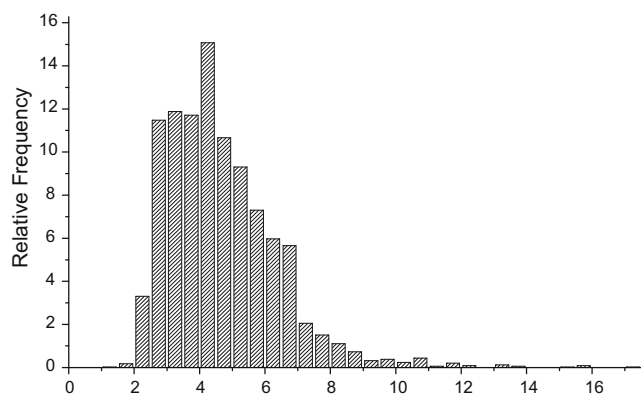


Fig. 5 Frequency distribution of GEM covered the whole period

of atmospheric Hg occurred in the sampling site (Feng et al. 2004; Valente et al. 2007), (b) solar radiation can temporally promote the reduction of previously deposited Hg to form Hg(0) and subsequently emitted to the surface atmosphere (Schroeder and Munthe 1998), and (c) atmospheric Hg released from industrial areas to Mt. Jinyun enriched during the night due to the shallow nocturnal boundary layer (Feng et al. 2004). After sunrise, the air mass was uplifted to the monitoring site.

The levels of GEM on Mt. Jinyun were comparable or slightly lower than the levels reported in a Global Atmospheric Watch (GAW) station located on An-Myun Island, Korea (4.6±2.2 ng m⁻³, Nguyen et al. 2007). The annual geometric mean of GEM concentrations at Mt. Jinyun was 4.2±2.6 ng m⁻³, ranging from 1.4 to 29.1 ng m⁻³, which were much higher than those observed from different remote areas of Europe and North America (generally lower than 2.0 ng m⁻³, Travníkov 2005; Kim et al. 2005; Valente et al. 2007) and still higher than those observed in remote areas of China (Table 3), such as Mt. Leigong of Guiyang, China (2.8±1.5 ng m⁻³, Fu et al. 2010b), Mt. Gongga in southwest China (3.9±1.6 ng m⁻³, Fu et al. 2010a) and Mt. Changbai in northeast China (3.6±1.8 ng m⁻³, Wan et al. 2009). Higher GEM levels on Mt. Jinyun were probably attributed to the large emissions of Hg in these densely populated and industrial areas. Although Mt. Jinyun was located in a national natural forest reserve, the study area still showed relatively high GEM concentrations compared with other background areas in China. The main reason for the discrepancy between regional GEM concentrations and Hg emission inventories was probably that the sampling site at Mt. Jinyun was affected by regional and local atmospheric Hg emissions (Fu et al. 2010a, b; Wan et al. 2009), which probably overestimated the regional backgrounds of atmospheric Hg. In Mt. Jinyun, the sampling site was affected by both domestic Hg emissions and Hg emissions from zinc and lead smelting factories in Simian town located within 80 km from the study site.

The seasonal diurnal variation of GEM concentration is shown in Table 4. We obtained a continuous data set of GEM concentrations from March 2012 to February 2013. The higher GEM concentrations in summer and lower levels in winter were not consistent with previous reports at sites influenced by local anthropogenic Hg emissions in China (Feng et al. 2004; Wang et al. 2007; Fu et al., 2008; Fu et al. 2010a). The highest mean GEM concentration was 4.99±0.6 ng m⁻³ in summer and the lower value was 4.68±1.8 ng m⁻³ in winter. The seasonal variation of GEM concentrations was in the descending order of summer, winter, spring, and fall (Table 4). A previous study in the Mt. Gongga area suggested that enhanced coal and biomass combustion played a significant role in elevated TGM concentrations in cold season (Fu et al. 2010a). Enhanced coal and biomass combustion in cold seasons is generally driven by the need

Table 3 Summary of GEM concentrations in other areas of China

Area		GEM concentration (ng m ⁻³)	Literatures
Remote area in China	Mt. Leigong	2.8±1.5	Fu et al. 2010b
	Mt. Gongga	3.9±1.6	Fu et al. 2010a
	Mt. Changbai	3.6±1.8	Wan et al. 2009
	Coastal/rural site of the Yellow Sea	2.31±0.74	Ci et al. 2011
	Mt. Waliguan	1.7±1.1	Wang et al. 2006
Cities in China	Beijing	12.6	Liu et al. 2002
	Guangzhou	13.5±7.1	Wang et al. 2006
	Guiyang	8.40	Feng et al. 2004

for residential heating in China. Although the sample site is located at a natural reserve, it is only just over 50 km far from Chongqing city. Unlike other places in China, Chongqing has an unusually hot summer; the highest temperatures can reach more than 40 °C and last for a long time. Since coal consumption is dominated by domestic use, it often rises in the summer because of the power needed for air conditioning and refrigeration systems, unlike in industrial areas, where coal consumption is evenly distributed through the year. On the other hand, the temperature of Chongqing in winter is much higher than elsewhere because of the subtropical climate. Average temperature in the winter of Chongqing is about 8 °C, which means less coal and biomass combustion for residential heating was needed in that season. According to government researches of the environmental protection bureau of Chongqing (Tao et al., 2003), air pollution mainly focuses on the summer, and coal pollution is still the key source of pollution, which accounts for 35 % of the city's total coal burning. This was probably one of the main reasons for the highly elevated GEM concentrations in Mt. Jinyun in summer. This is quite different from Hg wet deposition, which was not obviously elevated in summer. This result suggested that atmospheric GEM had a less immediate effect on direct wet deposition and throughfall compared with PHg and RGM. Since the study site was not a durably impacted receptor for direct anthropogenic Hg emission sources, the likelihood for steadily elevated RGM and PHg levels here was limited. GEM could undergo long-range transport from emission sources and

Table 4 Statistical summary of TGM concentration on Jinyun Mountain/ng·m⁻³

Season	N	Geomean	Min	Max	Sd
Spring	12,188	3.85	1.22	24.33	2.01
Summer	10,176	4.99	2.47	26.88	2.38
Fall	10,865	3.41	1.82	7.78	0.91
Winter	10,156	4.68	1.89	19.0	1.84

cause elevated levels at the sampling site. This may explain the low precipitation THg concentrations and high atmospheric GEM concentrations on Mt. Jinyun. The GEM concentrations in winter were higher than those in spring and autumn, which may partly because of several natural and anthropogenic factors, including (a) seasonal difference of meteorological conditions, such as reduced mixing height can enhance GEM levels in Mt. Jinyun in winter; and (b) Hg pollution tends to increase in China in winter as coal burning is still the main source of heat and energy (Feng et al. 2004).

Moreover, the seasonal variability may also be due to long-range transport of atmospheric Hg during monsoons. In order to gain an insight to the influence of long-range transport on distribution of GEM in Mt. Jinyun, we calculated 3-day air mass back trajectories using the initiate 48-h back trajectories (Wang et al. 2009). In warm seasons, the wind field in the study area was dominated by southeast monsoons, which originated from or passed through northeast and southeast central China (Fig. 6a), the two most severe Hg-polluted regions in China (Street et al. 2005; Wu et al. 2006). And, most importantly, the sampling site was located in the north of Chongqing city. The air masses would probably capture a large amount of Hg during transport. During these events, air parcels were transported mostly from the south or southeast to the sampling site, so most of the trajectories were passed over eastern Sichuan, Hebei, West Henan and Hubei where there were several major Hg sources including large coal-fired power plants, oil-fired power plants, and waste incinerators. In the cold season, air masses originating from the northwest inner land dominated, although the inland air masses occasionally affected the study site (Fig. 6b).

Potential source identification for transport of atmospheric Hg

Figure 7a showed that wind rose at the sampling site, which indicated that wind directions at Mt. Jinyun were dominantly from northeast, southeast, and southwest, possibly reflective of the three predominant monsoons in China including Southeast monsoon, Southwest monsoon, and Asian winter monsoon. We can also see from Fig. 7a that the distributions of GEM concentrations in each of the wind direction were quite different from each other, which was the same with results obtained from Mt. Leigong (Fu et al. 2010b). Generally speaking, southwest winds exhibited higher GEM events, while northwest winds showed lower GEM events. Similar with Mt. Leigong, the wind dependence of atmospheric GEM was probably attributed to an interplay of regional sources and long-range transport of Hg.

To gain a better understanding of the effects of regional sources on GEM distributions in Mt. Jinyun, daytime GEM dependence on wind direction was shown

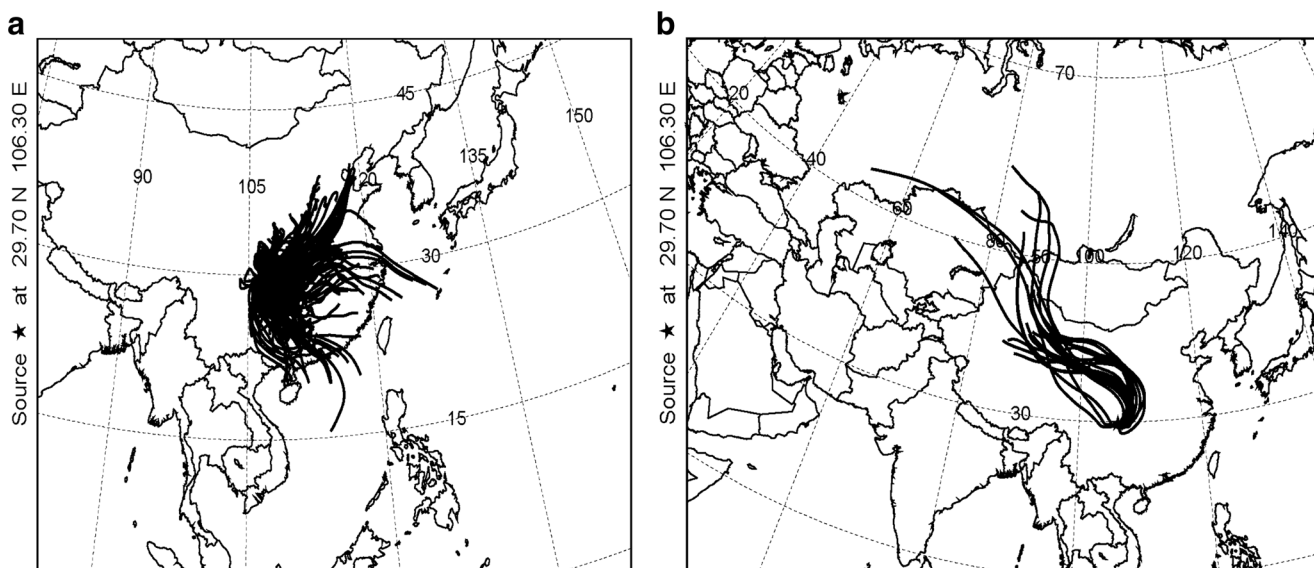


Fig. 6 Seventy-two-hour back trajectories of air masses on Mt. Jinyun in **a** cold seasons (October, November, December, and January) and **b** warm seasons (May, June, July, and August)

in Fig. 7b. It can be seen from Fig. 7b that high mean GEM concentrations were observed mostly from the north and east China, which indicated that the influence was from regional sources in these two directions. Due to high Hg content in coal, which is involved in non-ferrous smelting activities, the northeast is regarded as one of the highest atmospheric Hg source regions in China (Street et al. 2005; Wu et al. 2006; Feng and Qiu 2008; Li et al., 2009). There are many heavy industrial areas and large cities in the study area that may be affected by elevated Hg emissions. Moreover, this area is also prone to fog and haze, especially in the winter and spring (Liu et al. 2002; Feng et al. 2004). This may partly explains the high wet deposition fluxes

in the two seasons. Also, several smelting factories were located to the south of the study area, such as Bishan and Xiema counties. Chongqing city (located 50 km southwest of Mt. Jinyun) is the largest city in the study area and may be affected by elevated Hg emissions. Therefore, it is an important regional source for the study area. Beibei district (20 km southwest of Mt. Jinyun, urban fringe zone) is the nearest population center of the study site, which is also an important source region influencing the study site. Air flow from the west and north showed low GEM levels. The lowest mean GEM concentrations were observed from the northwest direction, which probably because this area was more naturally preserved and less populated.

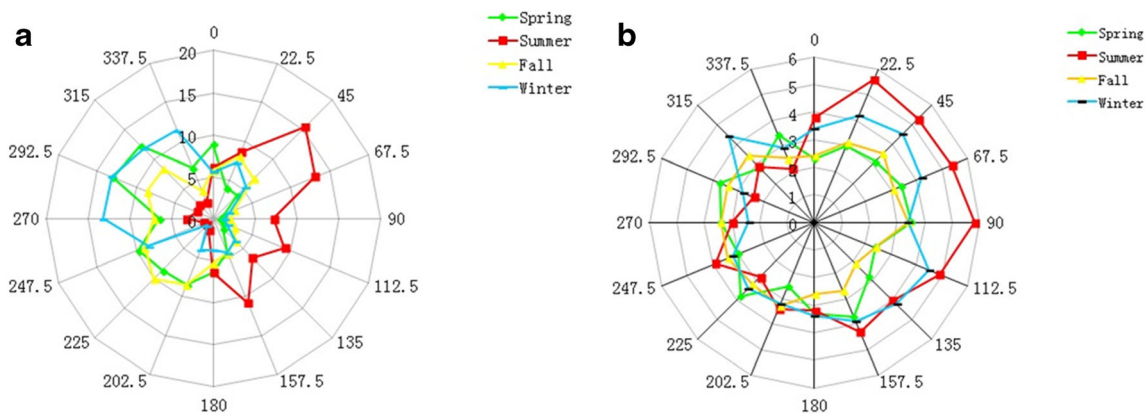


Fig. 7 Pollution roses showing **a** frequency of wind direction and **b** GEM concentrations during daytime

In order to gain insights into the effect of long-range transport on the distribution of GEM in Mt. Jinyun, 72-h air mass back trajectories were calculated by Hysplit software (Wang et al. 2009). It can be seen from Fig. 8 that there were totally four clusters arriving at the study site during our research period, showing with different colors. The red cluster (52 %) consists of air masses originating from the continental inland areas of central Asia, passing over the north and central China. The blue cluster (21 %) shows air masses originated from southwest China, passing over Guizhou province. Air masses in the green cluster (15 %) originated from southwest China and then passed over Guangxi province. The yellow cluster (13 %) shows air masses that originated from northwest China and then passed over Gansu and Xinjiang province. For the four types of air masses, the red cluster related to the highest GEM concentrations in this research. Air masses in the red cluster passed over the plain in central China, which is not only the most densely populated area but also the most heavily Hg-polluted area in China. Hg pollution in these areas was mainly from industrial and domestic coal combustion, smelting industries, cement production, biomass burning, etc. Since this highly GEM-polluted trajectory occurred most often, it may be a main source for the elevated GEM levels in Mt. Jinyun. This result was accorded with that conducted in Mt. Leigong (Fu et al. 2010b). Namely the higher GEM concentration in Mts. Jinyun and Leigong were both mainly from the long-range transportation of Hg from the central China. Mean GEM concentration in the blue cluster were remarkably lower than those in the red cluster. This is probably due to air masses originated or passed over the border areas of the provinces of Guangxi and Guizhou, both of which are generally less populated and developed in China. Air masses of the yellow cluster showed the lowest mean GEM concentration, which was due to the air masses

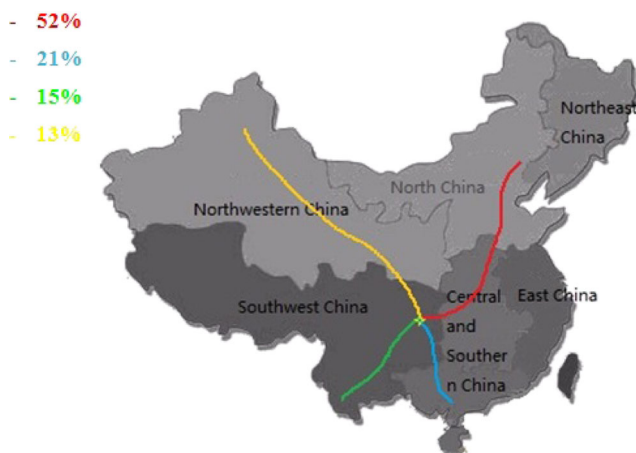


Fig. 8 Four types of 3-day back trajectories arriving at the study site

originated or passed over Gansu and Xinjiang, the two least underdeveloped provinces of China.

Conclusions

Measurements of THg and MeHg deposition in precipitation and throughfall were carried out at an upland forest catchment in Mt. Jinyun, southwest China from March 2012 to February 2013. GEM concentrations, THg and MeHg in litterfall, were also investigated. Annual means of THg and MeHg concentrations in precipitation were 11.9 ± 7.6 and 0.2 ± 0.13 ng L⁻¹ respectively. THg and MeHg concentrations in throughfall were more than two times higher than those in precipitation, with annual means of 20.1 ± 12.3 and 0.6 ± 0.24 ng L⁻¹, respectively. Precipitation deposition fluxes of THg and MeHg in Mt. Jinyun were $15.9 \mu\text{g m}^{-2} \text{yr}^{-1}$ and $0.26 \mu\text{g m}^{-2} \text{yr}^{-1}$, which were higher than those reported in Europe and North America. Deposition fluxes of THg and MeHg were 21.8 and $0.6 \mu\text{g m}^{-2} \text{yr}^{-1}$ for throughfall and 4.5 and $0.27 \mu\text{g m}^{-2} \text{yr}^{-1}$ for litterfall, respectively. Deposition flux of THg was higher than the value reported for forest at the background area or north American, and Europe indicated impacts of heavy regional Hg emissions from industrial and urban because highly PHg and Hg²⁺ species are easily stripped from the atmosphere and deposited locally; higher wet deposition illustrates that the local Hg emissions have obvious influence on the Hg accumulation on the regional forest field. GEM contacting leaf surfaces is either reemitted to the atmosphere or taken up by stomata and retained internally by the leaf tissue until deposited in litterfall, studies have shown, therefore, we can think of, the higher litterfall input flux and the elevated atmospheric Hg are direct and relevant, even in the nature reserve forest area. The study site was affected by both regional emissions and long-range transport of Hg. Regional emissions of Hg included coal combustion and smelting activities, which generally located south of Mt. Jinyun. Our results indicated that Mt. Jinyun may be affected by both the continental inland monsoon and southeast monsoon, which carried Hg-polluted air masses from central China and passed the northeast and Guizhou province, whereas air masses from northwest inner China generally related to low atmospheric Hg concentrations because of lower population and less development.

Acknowledgments This study was supported by the Natural Science Foundation of China (41103040), the National Basic Research Program of China (973 Program, 2013CB430003), the Natural Science Foundation of Chongqing city (No. cstc2011jjA20007), and the Fundamental Research Funds for the Central Universities (XDJK2013B044).

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