**Atmospheric
Chemistry
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# Spatial distribution of mercury deposition fluxes in Wanshan Hg mining area, Guizhou province, China

**Z. H. Dai[1,2], X. B. Feng[1], J. Sommar[1], P. Li[1], and X. W. Fu[1]**

[1]State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China
[2]Graduate University of the Chinese Academy of Sciences, Beijing 100049, China

*Correspondence to:* X. B. Feng (fengxinbin@vip.skleg.cn)

**Abstract.** The legacy of long-term mining activities in Wanshan mercury (Hg) mining area (WMMA), Guizhou, China including a series of environmental issues related to Hg pollution. The spatial distribution of gaseous elemental mercury ($Hg^0$) concentrations in ambient air were monitored using a mobile RA-915$^+$ Zeeman Mercury Analyzer during daytime and night time in May 2010. The data imply that calcines and mine wastes piles located at Dashuixi and on-going artisanal Hg mining activities at Supeng were major sources of atmospheric mercury in WMMA. For a full year (May 2010 to May 2011), sampling of precipitation and throughfall were conducted on a weekly basis at three sites (Shenchong, Dashuixi, and Supeng) within WMMA. Hg in deposition was characterized by analysis of total Hg (THg) and dissolved Hg (DHg) concentrations. The corresponding data exhibit a high degree of variability, both temporarily and spatially. The volume-weighted mean THg concentrations in precipitation and throughfall samples were 502.6 ng l$^{-1}$ and 977.8 ng l$^{-1}$ at Shenchong, 814.1 ng l$^{-1}$ and 3392.1 ng l$^{-1}$ at Dashuixi, 7490.1 ng l$^{-1}$ and 9641.5 ng l$^{-1}$ at Supeng, respectively. THg was enhanced in throughfall compared to wet deposition samples by up to a factor of 7. The annual wet Hg deposition fluxes were 29.1, 68.8 and 593.1 µg m$^{-2}$ yr$^{-1}$ at Shenchong, Dashuixi and Supeng, respectively, while the annual dry Hg deposition fluxes were estimated to be 378.9, 2613.6 and 6178 µg m$^{-2}$ yr$^{-1}$ at these sites, respectively. Dry deposition played a dominant role in total atmospheric Hg deposition in WMMA since the dry deposition fluxes were 10.4–37.9 times higher than the wet deposition fluxes during the whole sample period. Our data showed that air deposition was still an important pathway of Hg contamination to the local environment in WMMA.

## 1 Introduction

An assessment of the primary mercury (Hg) sources to terrestrial ecosystems is imperative to evaluate its biogeochemical cycling (Landis and Keeler, 2002; Rolfhus et al., 2003; Wiener et al., 2003). Atmospheric transport and transformation and its eventual deposition constitutes an important source of mercury to pristine areas. Deposition is in-turn linked to the levels of bioavailable and neurotoxic form methylmercury (MeHg) in the aquatic food-web (Lindberg et al., 2001; Miller et al., 2005). There are three species of mercury in atmosphere, including gaseous elemental mercury, semi-volatile oxidized species (acronym: GOM) and non-volatile particulate form (PHg, Schroeder and Munthe, 1998). Unlike other heavy metals, which tend to exist in the atmosphere in the particulate phase, $Hg^0$ vapour is a ubiquitous constituent ($> 95\%$) of tropospheric airborne mercury due to a long residence time (from 0.5 to 2 yr). Compared with $Hg^0$, PHg and GOM fractions are more prone to undergo physical removal and are readily scavenged via wet and dry deposition (Guentzel et al., 2001).

To understand the regional budget of atmospheric Hg, it is important to determine spatial and long-term variability of atmospheric Hg concentrations and deposition fluxes. In North America and Europe, monitoring of atmospheric Hg has been carried out by a number of studies (e.g. Valente et al., 2007; Munthe et al., 2003; Wängberg et al., 2008; Sigler et al., 2009; Rutter et al., 2009). More than 100 sites cross North America called Mercury Deposition Network (MDN) sites have been set-up to monitor mercury wet deposition flux (National Atmospheric Deposition Program, 2007). Furthermore, dry deposition of atmospheric Hg to forest canopies
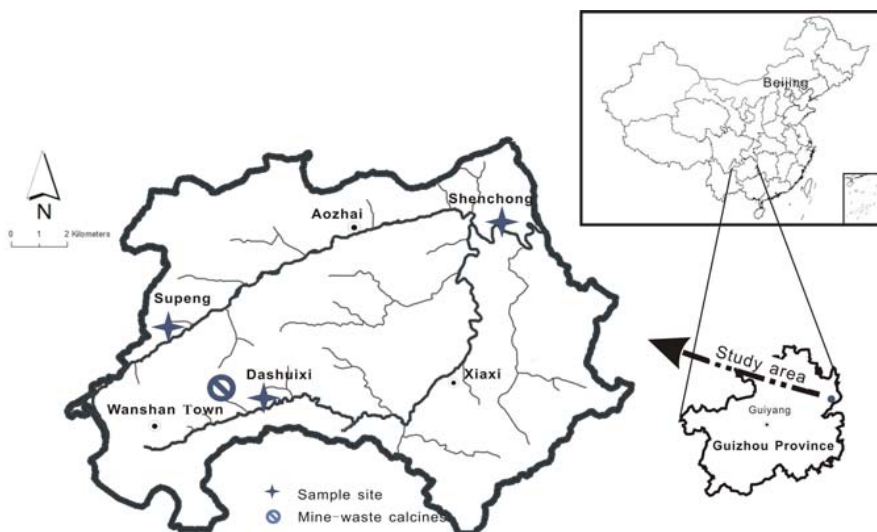
**Fig. 1.** Map of the study area and sampling sites.

has been recognized as an important sink for atmospheric Hg. Foliage can both take up and emit $Hg^0$ and $Hg^0$ may in-turn be oxidized to form other Hg species which may adsorb to or wash off from the leaf surface (Browne and Fang, 1978; Lindberg, 1996). For locations in Scandinavia and North America, it has been reported that fluxes of Hg in throughfall exceeded those of wet deposition by 60–90 % (Iverfeldt et al., 1991; Munthe et al., 1995; Rea et al., 1996).

East Asia has emerged as the world's largest source region of atmospheric mercury mainly due to a rapid expansion in fossil fuel combustion and increased industrialization in China and surrounding countries in contrast to significant reduction in anthropogenic emissions from Europe and North America (Jiang et al., 2006; Zhang and Wong, 2007). Up to now, however, only a few studies have been oriented towards long-term measurement of atmospheric Hg and deposition fluxes in semi-rural and urban/industrial areas in China. The results are in favour that most urbanized areas in China are exposed to a significant degree of atmospheric Hg pollution (Fu et al., 2012). Long-term monitoring of atmospheric Hg at the remote Chinese sites (Mt. Gongga, Mt. Leigong and Mt. Changbai) has revealed annual mean concentrations significantly above the North hemispheric background level ($1.5–2.0\,\mathrm{ng\,m^{-3}}$) (Fu et al., 2008; Wan et al., 2009a; Travnikov, 2005; Kim et al., 2005; Valente et al., 2007; Guo et al., 2008; Wang et al., 2008). However, observations of airborne Hg in China are spatially insufficient to fully understand the impact of Hg emission in China on both the local and regional scales. Therefore, there is impetus to conduct further long-term measurements of atmospheric Hg and deposition fluxes in China.

Wanshan Hg mining area (WMMA; $27°24'29''$–$27°37'22''$ N, $109°07'17''$–$109°23'12''$ E in Guizhou province, the largest Hg mine in the China, was an important mercury production centre in China (Qiu et al., 2006). Wanshan Hg mine is located in the circum-Pacific mercuriferous belt (Gustin et al., 1999), and consists of three Hg ore fields and twenty Hg mineral deposits (Zhou and Li, 1958). Hg mining operations in the area, which go down in history to tenth century BC, have generated significant quantities of gangues and mine tailings (calcines) stockpiled near the abandoned Hg processing sites and retorts. Between 1949 and 1990s, approximately 125.8 million tons of calcines and 20.2 billion cubic meters of Hg-contained exhaust gas had been dispersed into the adjacent ecosystems (Liu, 1998). Although the large-scale state owned Hg mining enterprise was completely shut down in 2004, artisanal (small-scale) Hg production is still deployed in WMMA. Hg mining and production activities have resulted in serious Hg contamination in the local environment, including surface waters, alluvial soils and agricultural crops (Horvat et al., 2003; Qiu et al., 2005, 2008; Li et al., 2009b; Zhang et al., 2010a, b, c; Feng and Qiu, 2008). Among crops cultivated in WMMA, solelyrice (*Oryza sativa*) has been identified to exhibit a significant ability to bioaccumulate MeHg in its seeds (Zhang et al., 2010c; Meng et al., 2010, 2011). Rice consumption has in-turn been identified as the main MeHg exposure pathway to the local inhabitants in WMMA (Feng et al., 2008; Zhang et al., 2010d). The distribution of Hg in ambient air has previously been studied in WMMA mainly within connection with air-soil $Hg^0$ gas exchange studies using enclosure method (Wang et al., 2007). However, a more comprehensive investigation of Hg in ambient air and in atmospheric deposition to WMMA is still lacking, which prevents a broader understanding of Hg biogeochemical cycling in WMMA.
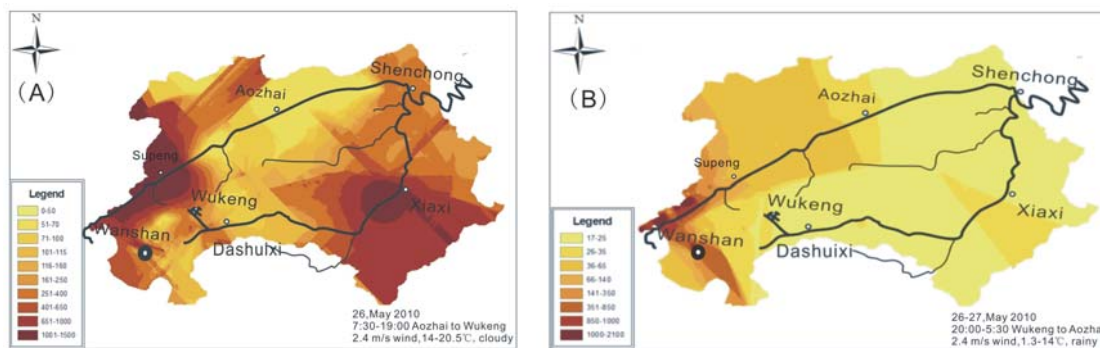
**Fig. 2.** Contour chart of the spatial distribution of atmospheric mercury concentration in Wanshan mining area.

In this study, we investigated the spatial distribution of $Hg^0$ in ambient air of WMMA in order to track the major sources down. In the meantime, as an important part of the mass balance study in Wanshan area, both precipitation and throughfall samples were collected on a weekly basis from May 2010 to May 2011 at three sites Shenchong, Dashuixi and Supeng. The samples was subsequently processed for Hg analysis and the data obtained was utilized for determine dry and wet deposition fluxes. The deployed methods are presented and further discussed below. The major goals of this study are (1) to identify source regions of atmospheric mercury in the area, (2) to evaluate temporal and spatial variations of both the dry and wet deposition fluxes in the region, and (3) to provide important information on the status of the atmospheric mercury pollution in this Hg mining area.

## 2 Experimental

### 2.1 Site description

WMMA is located in the eastern Wuling mountain range of Guizhou province. For our study, a catchment area of $\sim 170\,km^2$ was selected. There are three major settlements in study area (cf. Fig. 1), namely Wanshan town and the villages of Aozhai and Xiaxi with a total population of 32 000. Rice paddy fields occupy $15.59\,km^2$ in the catchment, of which 25.7 % are irrigated by streams and creeks. The study area has a humid sub-tropical climate with mild temperatures (annual mean temperature $17\,°C$). The annual precipitation totaling 1200–1400 mm, where of 75 % of the amount occurs between April and October. The catchment has a typical karstic terrain with elevations from 270 to 1149 m a.s.l.

### 2.2 Sampling procedures

To decipher the spatial distribution of $Hg^0$ in ambient air within the study area, sampling campaigns were performed using a portable RA-915^{+} Zeeman Mercury Analyzer (Lumex Ltd. Co., St. Petersburg, Russia) during May 2010. The Lumex instrument is portable atomic absorption spectrometer operating on the Zeeman principle to monitor $Hg^0$ in air, with a detection limit of $0.3\,ng\,m^{-3}$ at a sampling flow rate of $18\,l\,min^{-1}$ (Sholupov et al., 2004; Rodriguez et al., 2007). The instrument was installed in a car and air was brought to RA-915^{+} through a reinforced tube with inlet positioned well outside the vehicle perimeter. A series of road trips was conducted in the WMMA at a travelling speed of $\sim 10\,km\,h^{-1}$, whereby $Hg^0$ concentration and geographical position were recorded every 5 s and collected on a portable computer by using appropriate softwares. Hg concentrations recorded at individual points were smoothed into a geochemical map using a computer software (Arc/Info 9.3). We used the ordinary kriging method to generate maps of spatial distribution pattern of $Hg^0$ in ambient air in the study area (Yamamoto, 2000).

Precipitation samples were collected from May 2010 to May 2011 at three sites under open sky. Coevally throughfall samples were collected below the canopy of an adjacent ($< 30\,m$ distance) grove. Both precipitation and throughfall were collected by a weekly-integrated bulk sampler with a design based on a type of collectors used in European countries (Oslo and Paris Commission, 1998; Guo et al., 2008). The sampling train consisted of three borosilicate glass components: a funnel (15 cm diameter) connected via a capillary tube to a 800 ml collection bottle. The set-up was housed in an opaque plastic cylinder to protect it from sunlight (Guo et al., 2008). Furthermore, the bulk sampler was mounted on a trestle table at $\sim 1.5\,m$ above the ground to avoid contamination from soil particles by splashing during heavy rainfall (Landing et al., 1998).

Cleaning procedure was conducted using trace metal clean protocols. Funnels, tubes and bottles were cleaned rigorously by dipping in diluted oxidizing acid (10 % $HNO_3$), rinsing with ultrapure deionized water (Milli-Q, $18.2\,M\Omega\,cm$) and baking for one hour in a muffle furnace at $500°$, and then doubled bagged, stored in a plastic box until use. Immediately before deployment, 5 ml trace-metal grade HCl (12 N) was added into the sample collection bottle to prevent adsorption

**Table 1.** Statistical summary of observed concentrations of mercury species in precipitation and throughfall samples collected at the three sites Supeng, Dashuixi and Shenchong from May 2010 to May 2011.

| | | Precipitation | | | Througfall | | |
|---|---|---|---|---|---|---|---|
| | | THg | DHg | PHg | THg | DHg | PHg |
| Shen chong ($n = 21$) | Min($ng\,l^{-1}$) | 24.4 | 9.7 | 10.0 | 110.3 | 16.6 | 16.0 |
| | Max($ng\,l^{-1}$) | 683.4 | 294.0 | 623.4 | 2062.0 | 1590.0 | 811.0 |
| | Volume-weighted mean($ng\,l^{-1}$) | 502.6 | 178.3 | 324.3 | 977.8 | 601.0 | 376.8 |
| | Standard deviation($ng\,l^{-1}$) | 178.9 | 79.4 | 164.9 | 455.2 | 380.2 | 235.5 |
| Da shuixi ($n = 28$) | Min($ng\,l^{-1}$) | 147.8 | 16.8 | 5.0 | 167.3 | 40.0 | 32.0 |
| | Max($ng\,l^{-1}$) | 2122.0 | 1665.0 | 1114.6 | 7886.3 | 3310.0 | 7802.7 |
| | Volume-weighted mean($ng\,l^{-1}$) | 814.1 | 510.8 | 496.3 | 3392.1 | 1199.4 | 2192.7 |
| | Standard deviation($ng\,l^{-1}$) | 413.3 | 338.9 | 304.6 | 1933.5 | 957.7 | 1772.8 |
| Su peng ($n = 24$) | Min($ng\,l^{-1}$) | 301.0 | 9.4 | 198.0 | 645.0 | 147.5 | 200.0 |
| | Max($ng\,l^{-1}$) | 9685.0 | 4116.0 | 8065.0 | 54936.0 | 19925.0 | 50485.4 |
| | Volume-weighted mean($ng\,l^{-1}$) | 7490.1 | 1742.0 | 5748.1 | 9641.5 | 3189.9 | 6107.0 |
| | Standard deviation($ng\,l^{-1}$) | 3091.8 | 1163.4 | 2215.8 | 12644.1 | 5774.8 | 11239.2 |

**Table 2.** Estimated THg deposition fluxes and annual THg deposition at Supeng, Dashuixi and Shenchong sites of WMMA.

| | Wet deposition | | | Dry deposition | | |
|---|---|---|---|---|---|---|
| | Deposition flux ($ng\,m^{-2}\,day^{-1}$) | Annual deposition ($kg\,yr^{-1}$) | Area ($km^2$) | Deposition flux ($ng\,m^{-2}\,day^{-1}$) | Annual deposition ($kg\,yr^{-1}$) | Area ($km^2$) |
| Shenchong | 79.7 | 1.2 | 40.1 | 1038.1 | 9.3 | 24.6 |
| Dashuixi | 188.5 | 2.8 | 41.1 | 7161.1 | 37.8 | 14.5 |
| Supeng | 1624.9 | 17.6 | 29.7 | 16 926.0 | 120.4 | 19.5 |

and volatilization of mercury after collection. Samples collected at each site were poured into two 100 ml borosilicate glass bottles, then shipped to the laboratory and stored in a refrigerator (0–4°) prior to analysis. A new clean sampling collection bottle was replaced when the precipitation sample was collected. Losses after sub-sampling were assumed to be insignificant (Guo et al., 2008).

## 2.3 Sample analyses

Total mercury (non-filtered), and dissolved mercury (DHg, filtered through a 0.45 µm microfilter) concentrations were determined by Cold Vapour Atomic Fluorescence Spectrophotometry (CVAFS) following US EPA Method 1631 (US EPA, 2001). Samples were initially allowed to oxidize at room temperature for 24 h after the addition of 0.5 ml 0.2 N BrCl. Prior to measurement, 0.2 ml 20 % $NH_2OH\cdot HCl$ solution were added to remove the residual BrCl. Finally, $Hg^{II}$ in the sample was reduced to $Hg^0$ by the addition of 0.3 ml 20 % $SnCl_2$ (Horvat et al., 2003; Kotnik et al., 2007; Guo et al., 2008). An estimate of mercury attached to particulate matter (PHg) was obtained by subtracting DHg from THg in a sample.

Quality control measures included reagent blanks, field blanks, blind duplicates and matrix spikes to assess contamination and precision of Hg analysis. Reagent blanks were consistently below $0.07\,ng\,l^{-1}$ in the experiments. The THg concentration of field blanks was present in the range $0.03$–$0.24\,ng\,l^{-1}$. The average relative standard deviation was found to be less than 7.3 %. The difference of sample duplicates was below 6 %. The recoveries for matrix spikes ranged between 85 % and 110 % for THg and DHg analysis.

The calculation of Hg deposition flux was based on the monthly Hg concentration data in precipitation and throughfall. Precipitation depth data were supplied by a nearby meteorological station. Statistical analysis of data was performed using Microsoft Excel and SPSS 18 softwares.

## 2.4 Pre-processing of vegetation index

Normalized difference vegetation index (NDVI) was used to extract vegetation coverage for calculating the forested area. Digital cartographic generalization was a result of remote sense images scanned in September 2009 and March 2010 by the thematic mapper (TM) of Landsat 4–5, and available with a spatial resolution of 30 m. The process is based on ENVI 4.3 and Arc/Info 9.3. It mainly included atmospheric

correction, radiometric correction and geometric correction of imagery. The following two operations were performed before analysis. First of all, the image rectification involving of rectification of longitude and latitude, and definition of projection, was performed. WGS 1984 was applied to raster and vector data. Subsequently, the true value of NDVI was calculated from Digital Number (DN) of each pixel according to Eq. (1) (Carlson and Ripley, 1997).

$$NDVI = DN \times 0.004 - 0.1 \tag{1}$$

## 2.5 Calculation of wet and dry deposition flux

The monthly deposition flux was calculated using the following equation:

$$D_{Hg} = \frac{4 \cdot \sum_i M_{Hg, i}}{\pi d^2} \tag{2}$$

where $D_{Hg}$ is the monthly mercury deposition flux (ng m$^{-2}$ month$^{-1}$), $M_{Hg, i}$ is the mass of Hg in weekly sample (ng), and $d$ is the diameter of the collector area (m).

There are a number of methods employed to quantify atmospheric dry deposition (Zhang et al., 2009). In the past, throughfall and litterfall based methods have been used to estimate dry deposition in forested landscape (Lindberg and Harriss, 1985; Iverfeldt, 1991; Choi et al., 2008). Accordingly, Hg species in throughfall samples have been suggested to derive from wash-off of dry deposition onto foliage, internal foliar leaching and, of course, the incoming rain. In this study, the following assumptions were applied in order to calculate dry deposition fluxes: (1) reduction of Hg$^{II}$→Hg$^0$ on the leaf surface is negligible and (2) stomatal uptake of Hg is limited. Theissen polygon method was used to divide the catchment into three subunits, and the centers of three subunits were placed at the sites where precipitation samples were collected (Owens and Norton, 1989; Milner et al., 1996; Gibson et al., 2006). The area of each subunit was calculated based on the GIS software.

Net throughfall deposition, which has been suggested to be a viable pathway to estimate dry deposition of atmospheric Hg, is used to quantify the portion originating from the canopy (total throughfall deposition minus precipitation deposition) (St. Louis et al., 2001; Rea et al., 2001; Graydon et al., 2006, 2008). However, the contribution of foliar leaching to dry deposition was not investigated in the present work. Therefore, dry depositional fluxes can be obtained by direct determination and estimation using theoretical models. A multiple resistance model developed by Hicks et al. (1987) and applied by Wan et al. (2009b) to calculate the dry depositional flux of atmospheric Hg in Mt. Changbai is used to determine depositional flux in a forest canopy as shown in Eq. (3):

$$F_{Hg} = \frac{1}{1000} \sum_{i=1}^{i=12} [(C_T^i - C_R^i) \frac{P_{Tf}^i}{\tau^i}] \tag{3}$$
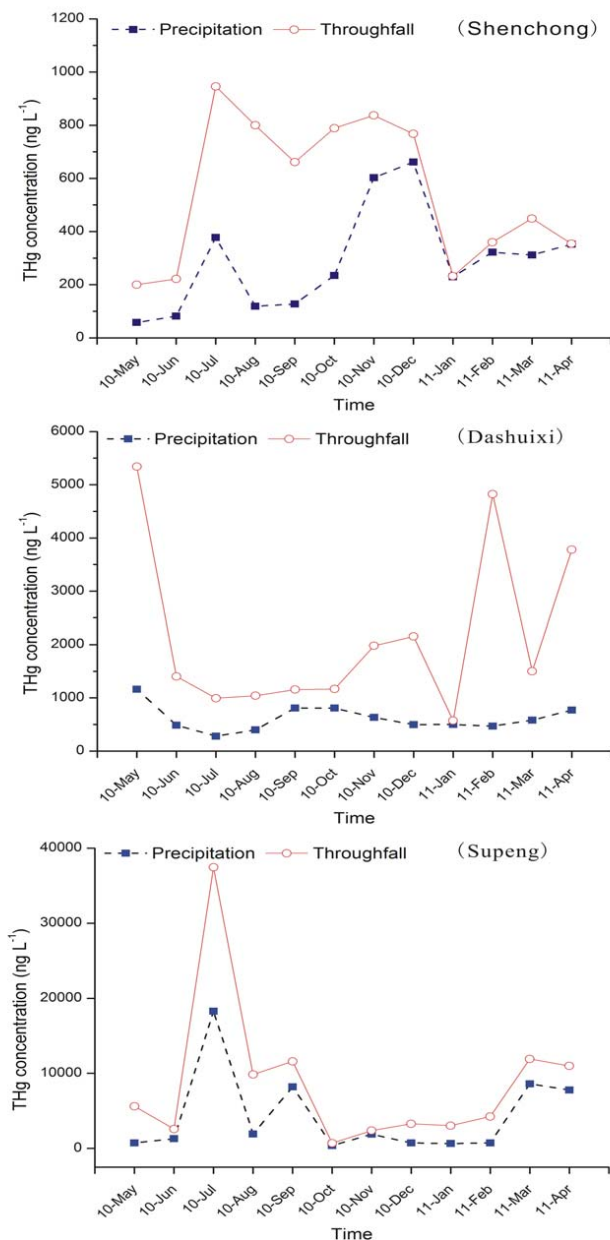


**Fig. 3.** Monthly mean THg concentrations in precipitation and throughfall during the period May 2010–May 2011 (Shenchong upper panel, Dashuixi mid panel and Supeng site lower panel).

where, $F_{Hg}$ is the dry deposition flux (µg m$^{-2}$ yr$^{-1}$), $C_T$ is THg in throughfall (ng l$^{-1}$), $C_R$ is THg in precipitation (ng l$^{-1}$), $P_{Tf}^i$ is the precipitation depth associated with each sample, and $\tau$ is dry deposition time (h).
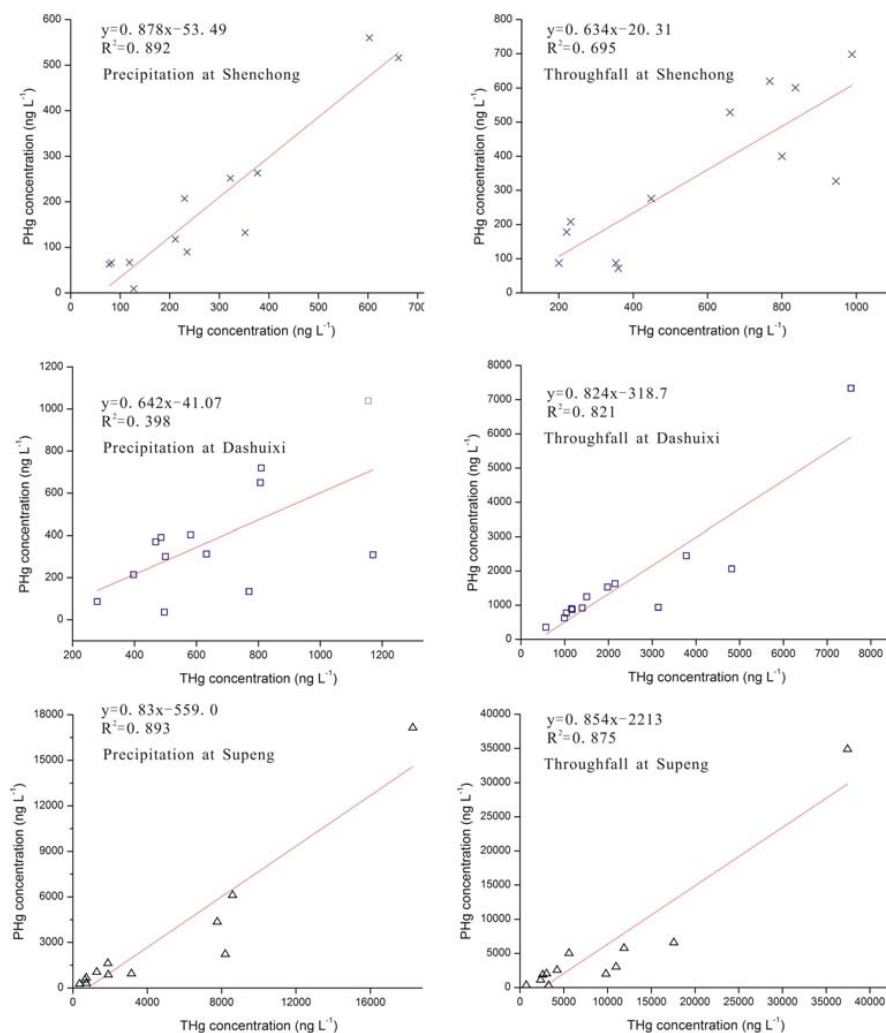
**Fig. 4.** Scatter plots of PHg vs. THg concentrations in precipitation and throughfall.

# 3   Results and discussion

## 3.1   Mercury concentrations in ambient air

The concentration span of $Hg^0$ observations in ambient air of WMMA ranged over two orders of magnitude (17–2100 ng m$^{-3}$). The spatial distribution pattern of $Hg^0$ concentrations in air (Fig. 2) indicates the highest level in connection with stockpiles of calcines and mine wastes at Dashuixi, residential areas with large energy consumption at Xiaxi and Wanshan town, and the artisanal Hg mining site at Supeng during day time. However, during night-time period, surface level $Hg^0$ concentrations dropped significantly with only a tendency of elevated levels around Wanshan town. The highly enhanced $Hg^0$ levels in ambient air at Supeng site during daytime are related to nearby artisanal Hg smelting activities by indigenous techniques described in Li et al. (2008, 2009a, b). At Dashuixi, $Hg^0$ concentrations in ambient air

during day time were also elevated compared to night time. A long term of large scale Hg mining activities in the region introduced significant quantities of piles and spoils heaps of calcine, which were dumped along the stream banks at Dashuixi. It is demonstrated that the calcine heaps continued to release $Hg^0$ to ambient air and Hg emission fluxes were significantly positively correlated to ambient air temperature and solar radiation (Wang et al., 2005; Qiu, 2005; Feng and Qiu, 2008), which may explain the diurnal variations in $Hg^0$ observations. On the whole, the $Hg^0$ concentration data from WMMA is evidently higher than long-term atmospheric observations made on a mountain peak ∼ 70 km in SSW (Fu et al., 2010).

**Table 3.** Comparison of THg deposition fluxes measured in this study with those measured in some related studies globally.

| Location | Time | Classification | THg deposition flux ($\mu g\,m^{-2}\,yr^{-1}$) | | Reference |
|---|---|---|---|---|---|
| | | | Wet deposition | Dry deposition | |
| Wanshan, China (Shenchong) | May 2010 to May 2011 | Contaminated site | 29.9 | 378 | |
| Wanshan, China (Dashuixi) | May 2010 to May 2011 | Contaminated site | 68.1 | 2606.9 | This study |
| Wanshan, China (Supeng) | May 2010 to May 2011 | Contaminated site | 592.6 | 6174.4 | |
| Idrija, Slovenia | Oct 2006 to Sep 2007 | Contaminated site | 13.1 | 29.7 | Kocman (2011) |
| Steubenville, USA | 2004 | urban | 19.7 | | Keeler et al. (2006) |
| Fakahatchee Strand, USA | 1993 to 1996 | urban | 23 | | Guentzel et al. (2001) |
| Japan | Dec 2002 to Nov 2003 | urban | 12.8 | 8 | Sakata and Marumoto (2005) |
| Chongqing, China | Mar 2003 to Feb 2006 | Suburban | 77.6 | 113 | Wang et al. (2008) |
| Luchongguan, China | Jan to Dec 2005 | Suburban | | 77.7 | Wang et al. (2008) |
| Wujiang , China | Jan to Dec 2006 | Semi-remote | 34.7 | | Guo et al. (2008) |
| Mt.Leigong, China | May 2008 to May 2009 | Remote | 6.1 | 10.5 | Fu et al. (2010) |
| Mt.Gongga, China | May 2005 to Apr 2007 | Remote | 26.1 | 57 | Fu et al. (2010) |
| Mt.Changbai, China | Aug 2005 to Jul 2006 | Remote | 8.4 | | Wan et al. (2009b) |
| Ontario, Canada | 2005 to 2006 | Remote | 3.1 | 5.1 | Graydon et al. (2008) |
| Walker Branch, USA | Jul to Sep 1993 | Remote | 10 | 14 | Lindberg et al. (1996) |
| Lake Huron, USA | Jun 1996 to Jun 1997 | Remote | 4.9 | 6.7 | Rea et al. (2001) |
| Lake Champlain Basin, USA | Aug to Sep 1994 | Remote | 7.9 | 11.7 | Rea et al. (1996) |
| Uraani, Finland | 1994 to 1995 | Remote | 5.1 | 15.8 | Porvari and Verta ( 2003) |
| Svartberget, Sweden | 1993 to 1994 | Remote | 7 | 15 | Lee et al. (2000) |
| Lehstenbach, Germany | Apr 1998 to Apr 1999 | Remote | 35 | 38.4 | Schwesig and Matzner (2000) |

## 3.2 Concentrations of Hg species in precipitation and throughfall samples

Table 1 shows a statistical summary of Hg concentrations in precipitation and throughfall samples during the sampling period (17 May 2010 to 23 May 2011). We intended to collect samples weekly, however, interruptions were inevitable due to drought periods. The concentrations of Hg species varied with a large range at three sites, especially at Supeng site, whereas Hg concentrations exhibited a relatively stable level at Shenchong site. Mean concentrations of THg in precipitation and throughfall were 502.6 and 977.8 ng l$^{-1}$ at Shenchong, 814.1 and 3392.1 ng l$^{-1}$ at Dashuixi, 7490.1 and 9641.5 ng l$^{-1}$ at Supeng, respectively. In general, THg concentrations in throughfall samples throughout the sampling period were 1–7 folds higher than the corresponding Hg concentrations in precipitation (Fig. 3). In general, foliage is a sink of atmospheric Hg species, and deposition of atmospheric Hg to foliar surfaces is enhanced as atmospheric Hg concentrations increased (Erichsen et al., 2003; Bushey et al., 2008; Zhang et al., 2005; Poissant et al., 2008).

In a comparison, Supeng exhibited the highest Hg deposition fluxes among three sites. The site is within the reach of the source plume from artisanal Hg smelting operations, which exhibits a very high emission factor of Hg$^0$ (Li et al., 2009). Furthermore, it could be speculated that this type of operations acts as source of mercury (e.g. cinnabar) containing particulate matter (Guentzel et al., 2001; Moreno et al., 2005), which in-turn will positively influence the Hg concentrations in precipitation and throughfall samples. The lowest deposition fluxes in this study were observed at Shen-

chong. site. Nevertheless, the volume-weighted mean THg concentrations at Shenchong are still elevated compared to observations made in polluted Chinese urban areas (such as Changchun, north-eastern China, Fang et al., 2004).

Figure 4 shows that there are significantly positive correlations between monthly mean concentrations of THg and PHg in precipitation as well as throughfall at the three sites. Lee et al. (2000) demonstrated PHg concentration was a crucial factor controlling the THg concentration in precipitation. Our data also may imply that particles are effectively scavenged from the atmosphere directly by precipitation. On the other hand, Hg$^0$ in the surface air of WMMA may to some degree become oxidized to GOM species, which are easily scavenging by precipitation (Lindqvist et al., 1991).

A significantly negative correlation was observed between THg concentrations in both precipitation and throughfall and precipitation depth at Shenchong site ($r = -0.47$, $p < 0.05$ in precipitation; $r = -0.43$, $p < 0.05$ in throughfall; $n = 26$), which is consistent with the previous observations conducted in the southwest of China (Feng et al., 2002, 2004; Fu et al., 2008, 2010, 2012). At this site, we also found a clear seasonal variation of THg concentrations in both precipitation and throughfall with elevated THg in cold seasons and low THg in warm seasons. Nevertheless, there are no obviously seasonal variations of THg concentrations in precipitation and throughfall at Dashuixi and Supeng sites. At Dashuixi site, the calcine piles continued to release Hg$^0$ to ambient air and the emission fluxes correlated to ambient air temperature and solar radiation (Wang et al., 2007). At Supeng site, Hg$^0$ concentrations in ambient air were strongly impacted by the intensities of artisanal Hg mining activities.
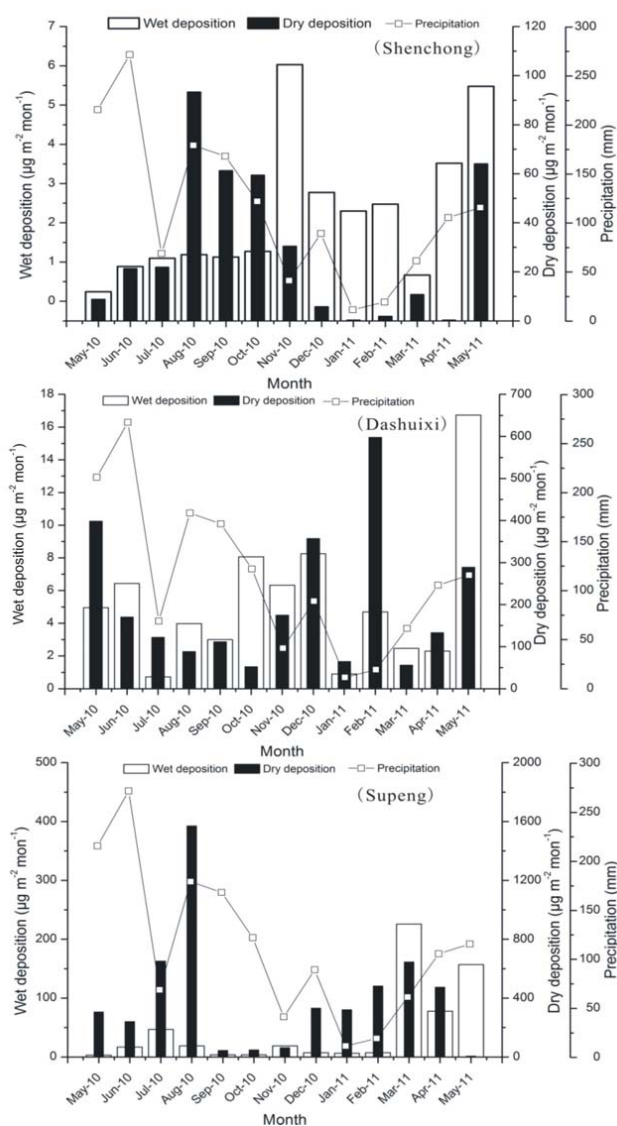
**Fig. 5.** Time series of monthly deposition fluxes and corresponding precipitation depth.

## 3.3 THg deposition fluxes in WMMA

Estimated wet and dry Hg deposition fluxes and annual total Hg deposition at Shenchong, Dashuixi and Supeng sites are listed in Table 2. The total annual Hg deposition to the study area is estimated to be 189.1 kg yr$^{-1}$, whereof dry deposition contributed 88.6 % of the total deposition. Our data demonstrated that THg deposition fluxes to WMMA are still at an elevated level in spite of the fact that large scale Hg mining activities have been completely shut-down for several years. Our data also indicated that the dry deposition processes played a dominant role in atmospheric Hg deposition to WMMA. A large amount of Hg emission from ongoing artisanal Hg mining activities could explain the much

elevated annual Hg deposition flux observed at Supeng site compared to the other two sampling sites.

The monthly wet and dry deposition fluxes of THg at three sampling sites are plotted together with precipitation depth in Fig. 5. The monthly wet and dry deposition fluxes at each site changed with the volume of rainfall, but the correlations were not significant during the rainy season. Recent studies have demonstrated that an increase in Hg atmospheric deposition fluxes resulted in an increase in MeHg production in aquatic systems and subsequently an increase of MeHg concentrations in fish (e.g. Harris et al., 2007). Meng et al. (2010) also showed that newly deposited Hg appears to be more labile towards transformation to MeHg in rice paddies, a species being bioaccumulated in rice seeds. Therefore, elevated MeHg concentrations in rice cultivated in WMMA (Horvat et al., 2003; Qiu et al., 2008; Feng et al., 2008; Zhang et al., 2010d) may indirectly stem from the elevated THg deposition fluxes. In order to reduce bioaccumulation of MeHg in rice in WMMA, measures need to be taken to reduce Hg deposition fluxes to the area. First of all, artisanal Hg mining activities should be appropriately regulated so that Hg emission from this category can be significantly reduced. Moreover, mercury emission from the calcine and tailing piles and contaminated soil in WMMA needs to be controlled.

## 3.4 Comparison with deposition flux observed in other areas

A comparison of THg deposition fluxes in urban, suburban, remote areas of China, North America, Europe and other sites is showed in Table 3. In comparison with the Idrijca catchment of Idrija Hg mining area in Slovenia, which is the second largest Hg mine in the world, we found that the concentration of Hg$^0$ in ambient air in WMMA was similar with the values reported in Idrija in 1999 (Kotnik et al., 2005). However, the annual Hg deposition fluxes measured in WMMA were 2–45 and 12–200 folds higher for wet and dry deposition than those observed in Idrijca area, respectively (Kocman et al., 2011).

Huge emissions of Hg will not only result in high Hg deposition fluxes at the local scale, but also have a strong impact on Hg deposition in a regional scale. THg wet deposition fluxes reported for urban and industrial areas of China were in the range of 77.6–152 µg m$^{-2}$ yr$^{-1}$, which were much higher than the values reported from North America and Europe (Carpi and Chen, 2002; Dommergue et al., 2002; Lynam and Keeler, 2005). For urban areas of China, relatively high THg deposition fluxes were observed at inland cities, which are generally co-located with large point sources (e.g. coal-fired power plants, non-ferrous metal smelters, etc.) and residential coal burning (Fu et al., 2009, 2012). THg wet deposition fluxes in remote areas in China were also higher than the values reported from the analogous studies in other countries ($<$ 10 µg m$^{-2}$ yr$^{-1}$), except for the case from Lehstenbach, Germany (35 µg m$^{-2}$ yr$^{-1}$) which were

impacted by air pollution from Eastern Europe (Schwesig and Matzner, 2000). In general, THg wet deposition fluxes in semi-remote and remote areas in China fall in the range of $6.0$–$34.7\,\mu g\,m^{-2}\,yr^{-1}$, which were significantly lower than those in the urban areas. However, the THg wet deposition fluxes in WMMA were elevated compared to observations made in urban areas of China.

## 4 Conclusions

Measurements of $Hg^0$ in ambient air and atmospheric Hg deposition fluxes were carried out in Wanshan mining area from May 2010 to May 2011. Observations of $Hg^0$ concentrations in air showed large temporal and spatial variability. Emissions of mercury from calcines and mine wastes piles located in Dashuixi and on-going artisanal Hg mining activities at Supeng were identified as the major sources of atmospheric mercury in WMMA. The concentrations of Hg species in precipitation and throughfall varied spatially and temporally, and the average THg concentrations in precipitation and throughfall were $502.6\,ng\,l^{-1}$ and $977.8\,ng\,l^{-1}$ at Shenchong, $814.1\,ng\,l^{-1}$ and $3392.1\,ng\,l^{-1}$ at Dashuixi, $7490.1\,ng\,l^{-1}$ and $9641.5\,ng\,l^{-1}$ at Supeng, respectively. PHg is the major form of Hg species in precipitation and throughfall. THg concentrations in throughfall samples were 1–7 folds higher than THg concentrations in the corresponding precipitation. The elevation of THg concentrations in both precipitation and throughfall samples at Supeng site is related to Hg emission from on-going artisanal Hg mining activities. The concentrations of Hg species in both precipitation and throughfall samples collected at Supeng were also elevated compared to data obtained from other sites in Wanshan. The annual THg wet deposition fluxes at Shenchong, Dashuixi and Supeng were 29.1, 68.8 and $593.1\,\mu g\,m^{-2}\,yr^{-1}$, and the annual dry deposition fluxes at these sites were 378.9, 2613.8 and $6178.0\,\mu g\,m^{-2}\,yr^{-1}$, respectively. The Hg deposition fluxes observed in WMMA were elevated compared to urban areas in China, and other sites in North America, Europe and other countries. Atmospheric Hg deposition remains to be an important pathway of Hg contamination to the local environment of WMMA.

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