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Spatial distribution of mercury deposition fluxes in Wanshan Hg mining area, Guizhou, China

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

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

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Abstract

A long-term mining history introduced a series of environmental problems in Wanshan Hg mining area, Guizhou, China. The spatial distribution of gaseous elemental Hg (Hg^0) concentrations in ambient air were investigated using RA-915$^+$ Zeeman Mercury Analyzer during day time and night time in May 2010, which showed 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 Wanshan Hg mining area. Meanwhile, both precipitation and throughfall samples were collected weekly at Shenchong, Dashuixi, and Supeng from May 2010 to May 2011, respectively. Our data showed that the concentrations of different Hg species varied with a large range, and the annual volume-weighted mean total mercury (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. Besides, THg concentrations in all throughfall samples were 1–7 folds higher than those in precipitation samples. 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 Wanshan Hg mining area 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 Wanshan Hg mining area.

1 Introduction

Determining the primary source of mercury to terrestrial ecosystems is critical to understand the biogeochemical cycling of mercury in the environment (Landis and Keeler, 2002; Rolfhus et al., 2003; Wiener et al., 2003). A series of seriously environmental

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problems to the global environment are generated by the deposition of atmospheric Hg because of its deposition, bioaccumulation and the enrichment of highly toxic methylmercury (MeHg) compounds in the aquatic food chain, even in remote areas (Lindberg et al., 2001; Miller et al., 2005). There are three species of mercury in atmosphere, including gaseous elemental mercury, semivolatile oxidized form Hg (II) 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 is the main form (>95 %) and has a long residence time (from 0.5 to 2 yr) in the atmosphere. Compared with Hg^0, PHg and Hg (II) are more reactive and readily scavenged via wet and dry deposition because Hg^0 must firstly be oxidized before it is efficiently deposited by wet and dry depositional processes (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; Sigler et al., 2009; Rutter et al., 2009). More than 100 sites cross North America called Mercury Deposition Network (MDN) sites have been developed to monitor mercury wet deposition flux (National Atmospheric Deposition Program, 2007). Furthermore, dry deposition of atmospheric Hg to forest canopies is increasingly recognized as an important sink for atmospheric Hg. Foliage can both take up and emit Hg^0 and Hg^0 may be oxidized to form other Hg species which may adsorb to or wash off from the leaf surface (Browne and Fang, 1978; Lindberg, 1996). It was estimated that fluxes of Hg in throughfall exceeded wet deposition fluxes by 60–90 % (Iverfeldt et al., 1991; Munthe et al.,1995; Rea et al., 1996).

China is regarded as one of the largest atmospheric mercury emission sources in the world, especially in central, east and south China (Jiang et al., 2006; Zhang and Wong, 2007). Up to now, however, only a few studies reported a long-term measurement of atmospheric Hg and deposition fluxes in semi-rural and urban/industrial areas in China. The results suggest that most urbanized areas in China are exposed to a

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certain degree of atmospheric Hg contamination (Fu et al., 2011). Atmospheric Hg concentrations in Mt. Gongga in southwest China and Mt. Changbai in northeast China were approximately two times higher than the values commonly observed at remote sites in North America and Europe (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, data with regard to Hg distribution in ambient air in China are still limited to fully understand impact of Hg emission in China on both the local and regional scale. Therefore, it is a great need to conduct long-term measurements of atmospheric Hg and deposition fluxes in China.

Wanshan Hg mining area in Guizhou, the largest Hg mine in the China, was an important mercury production center in China (Qiu et al., 2006). Wanshan Hg mine is located in the circum-Pacific mercuriferous belt (Gustinet al., 1999), and consists of three Hg ore fields and twenty Hg mineral deposits (Zhou and Li, 1958). A long term of about 3000 years of Hg mining activities has experienced in Wanshan Hg mining area and the Hg mining activities have introduced significant quantities of gangues and mine tailings (calcines) stockpiled near the abandoned Hg processing sites and retorts. Between 1949 and 1990s, there were 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 large-scale state owned Hg mining activities were completely shut down in 2004, large quantities of illegal artisanal Hg mining activities are still operating in Wanshan. A long-term large scale Hg mining and the on-going artisanal Hg mining activities resulted in serious Hg contamination in the local environment. A number of studies were carried out to investigate Hg distribution in surface water, soil compartment and crop in this area and it is demonstrated that both soil and surface water compartments in Wanshan Hg mining area were seriously contaminated with Hg (Horvat et al., 2003; Qiu et al., 2005, 2008; Li et al., 2009b; Zhang et al., 2010a, b, c; Feng and Qiu, 2008). Among all crops cultivated in Wanshan Hg mining area, it is found that only rice has a strong ability to bioaccumulate MeHg in its seeds (Zhang et al., 2010c; Meng et al., 2010, 2011). Rice consumption is proven

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to be the main MeHg exposure pathway to the local inhabitants in Wanshan Hg mining area (Feng et al., 2008; Zhang et al., 2010d). However, the information on mercury distribution in ambient air and mercury deposition fluxes in Wanshan Hg mining area is still lacking, which prevents our fully understanding of Hg biogeochemical cycling in Wanshan Hg mining area, and especially of the contribution of Hg contamination to the ecosystem from both historical large scale Hg mining and on-going artisanal Hg mining activities.

In this study, we investigated the spatial distribution of Hg^0 in ambient air in Wanshan Hg mining area to identify the major sources of atmospheric mercury. In the meantime, as an important part of the mass balance study in Wanshan area, both precipitation and throughfall samples were collected weekly from May 2010 to May 2011 at Shenchong, Dashuixi and Supeng sites. The dry and wet deposition fluxes of THg are discussed. 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

Wanshan Hg mining area is located in eastern Wuling mountain area of Guizhou province. We selected a catchment with an area of 169.47 km^2 which is composed by Wanshan town, Aozhai ethnic town and Xiaxi ethnic town with a population of 32 000 as our study area as shown in Fig. 1. The rice paddy fields in the catchment occupy 15.59 km^2, 25.7 % of which are irrigated by streams and creeks. The study area has a sub-tropical climate, and the annual precipitation is about 1200–1400 mm with 75 % rainfall occurred between April and October. Elevation of the catchment ranges from 1149 to 270 m a.s.l.

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2.2 Sampling procedures

To decipher the spatial distribution of Hg^0 concentrations in ambient air within the study area, two sampling campaigns were performed using a portable RA-915$^+$ Zeeman Mercury Analyzer during daytime and nighttime of May 2010. The operation of the instrument is based on Zeeman cold vapor atomic absorption spectrometry using high-frequency modulation of light polarization. The detection limit of the instrument for ambient air monitoring is 0.3 ng m^{-3} at a sampling flow rate of 18 L min^{-1} (Sholupov et al., 2004; Rodriguez et al., 2007). We installed the Hg detector on a car with a travel speed of 10 km h^{-1} and Hg^0 concentrations and geographical coordinates were recorded by a portable computer through appropriate software by every 5 s. Hg concentrations recorded at individual points were smoothed into a geochemical map using a computer software (GIS). 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 open-air sites. To study the dry deposition of Hg to the forest canopy, throughfall samples were simultaneously collected from a cuculidae forest, which is the preponderant tree in the study area, located within 30 m from the precipitation sampling site. Precipitation and throughfall samples were collected by a weekly-integrated bulk sampler designed based on the version of the collector used by European countries (Oslo and Paris Commission, 1998, Guo et al., 2008). The sampling train consisted of three borosilicated glass components: (1) a funnel (15 cm diameter), (2) a connecting tube, acting as capillary to prevent the diffusion of Hg^0 into the precipitation sample as well as the volatilization of mercury from sample, and (3) a sampling bottle (800 ml volume). The sample collector was mounted on the trestle about 1.5 m above the ground to avoid contamination from soil particles by splashing during heavy rainfall (Landing et al., 1998). The connecting tube and the sampling bottlewere placed inside a PVC column which was filled with sponge to be shielded from sunlight (Guo et al., 2008).

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Cleaning procedure was conducted using trace metal clean protocols. All funnels, tubes and bottles were cleaned rigorously by dipping in dilute acid (10 % HNO_3), rinsing with ultrapure deionized water (18 MQ cm) and baking for one hour in a muffle furnace at 500°, and then doubled bagged, stored in a plastic boxes until use. Just prior to deployment, 5 mL trace-metal grade HCl (12 N) was added into the sampling bottle to prevent adsorption and volatilization of mercury after collection. Samples collected at each site were poured into two 100 mL borosilicate glass bottles, then shipped to the laboratoryand stored in a refrigerator (0–4°) until analysis. A new clean sampling collection bottle was replaced when the precipitation sample was collected. The losses after sub-sampling are assumed to be insignificant (Guo et al., 2008).

2.3 Sample analyses

Total mercury (non-filtered), and dissolved mercury (DHg, filtered water, passed through a 0.45 µm microfilter) concentrations were determined by Cold Vapor Atomic Fluorescence Spectrophotometer (CVAFS) detection following US EPA Method 1631 (US EPA, 2001a) and Method 1630 (US EPA, 2001b). Samples were analyzed for THg and DHg with the addition of 0.5 ml 0.2 N BrCl, and shaken and allowed to oxidize at room temperature for 24 h. Prior to measurement, 0.2 ml 20 % $NH_2OH{\cdot}HCl$ were added to remove the residual BrCl. 0.3 ml 20 % $SnCl_2$ were used for reducing Hg (II) to Hg^0 (Horvat et al., 2003; Kotnik et al., 2007; Guo et al., 2008). PHg was obtained by subtracting DHg from THg.

Quality control included reagent blanks, field blanks, blind duplicates and matrix spikes to assess contamination and precision of Hg analysis. Reagent blanks were under 0.07 ng L^{-1} in all experiments. The THg concentrations of field blanks were from 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 percentages of recovery on spiked samples 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. Beside, rainfall data were supplied by nearby

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meteorological stations. The statistical method was performed based on Excel and SPSS 18.

2.4 Preprocessing of vegetation index

Normalized difference vegetation index (NDVI) was used to extract vegetation coverage for calculating the area of forest. 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 spatial resolution was 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. Then the true value of NDVI transform from Digital Number (DN) of every pixel according to the formula (1) was conducted (Carlson and Ripley, 1997).

$$\mathrm{NDVI} = \mathrm{DN} \times 0.004 - 0.1 \quad (1)$$

2.5 Calculation of the wet/dry deposition flux

Kocman et al. (2011) described the following Eq. (2) for calculating the deposition flux in the Idrijca River catchment, Slovenia, and it is modified in our study:

$$D_{Hg} = \frac{\sum M_{Hg}}{A_{sam}} \quad (2)$$

where, D_{Hg} is the monthly mercury deposition flux (ng m^{-2}), M_{Hg} is the mass of Hg per sample in one month (ng), and A_{sam} is the collector area (m^{-2}).

According to previous studies, the wash-off of dry deposition, the incoming rain and internal foliar leaching are sources of Hg species in throughfall samples (Lindberg and

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Harriss, 1985; Iverfeldt, 1991; Lindberg et al., 1992; Choi et al., 2008). The following assumptions are necessary for calculating the dry deposition fluxes: (1) there is no Hg (II) reducing to Hg^0 on leaf surface and degassing prior to the next rain event, and (2) the stomatal plant 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 areas of each subunit were calculated based on the software of GIS.

Net throughfall deposition, which has been suggested to be a good 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; Graydon et al., 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 Hick et al. (1987) and modified by Lindberg et al. (1992) is used to determine depositional flux in a forest canopy as shown in Eq. (3):

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

where, F_{Hg} is the dry deposition flux ($\mu g\, m^{-2}\, yr^{-1}$), C_T is THg in throughfall ($ng\, L^{-1}$), C_R is THg in precipitation ($ng\, L^{-1}$), P_{Tf}^i is the precipitation associated with each sample, and τ is dry deposition time (h).

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3 Results and discussion

3.1 Mercury concentrations in ambient air

The concentrations of Hg^0 in ambient air in the study area showed a large variation, ranging from 17 to 5679 ng m^{-3}. According to the spatial distribution pattern of Hg^0 concentrations in air as shown in Fig. 2, it is revealed that the highest Hg^0 concentrations occurred at the districts of stockpiles of calcines and mine wastes at Dashuixi, large residential areas with large energy consumption at Xiaxi and Wanshan town, and the artisanal Hg mining site at Supeng during day time. However, during nighttime period, Hg^0 concentrations in ambient air were much lower compared to those observed during day time, and only much elevated concentrations were observed around Wanshan town. The elevation of Hg^0 concentrations in ambient air at Supeng site was resulted from Hg emission from artisanal Hg mining activities (Li et al., 2008, 2009a, b). Since artisanal Hg mining activities at Supeng only occurred during day time when our measurement campaign was conducted, Hg^0 concentrations in air dropped significantly during night when Hg mining operations stopped. 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 significantly positively correlated to ambient air temperature and solar radiation (Wang et al., 2005; Qiu, 2005; Feng and Qiu, 2008). During day time, the intensity of solar radiation and temperature increased, and Hg emission fluxes from the calcine heaps were much higher than those during night time, which can explain the difference of Hg^0 concentrations between daytime and nighttime. The elevation of Hg^0 concentrations in residential areas of Wanshan town and Xiaxi during day time was probably resulted from both emission of Hg from contaminated soil and coal burning for cooking during day time. The Hg^0 concentrations in ambient air at Shenchong site was still higher than the value observed at Mt. Leigong which is a background site of

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Guizhou Province and the average Hg^0 concentration was 2.80±1.51 ng m^{-3} (Fu et al., 2010). This demonstrated that both calcine heaps generated from historical large scale Hg mining activities and current on-going artisanal Hg mining activities have resulted in Hg pollution to the ambient air of Wanshan Hg mining area.

3.2 Concentrations of Hg species in precipitation and throughfall samples

Table 1 shows the statistical summary of Hg concentrations in precipitation and throughfall samples during the whole sampling campaign (17 May 2010 to 23 May 2011). We intended to collect samples weekly, however, interruptions were inevitable because during dry season we were not able to collect enough rain samples. 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 are enhanced as atmospheric Hg concentrations increased (Erichsen et al., 2003; Bushey et al., 2008; Zhang et al., 2005; Poissant et al., 2008). When atmospheric Hg deposit to the foliar surface, actually, most of the PHg and Hg(II) are probably washed off from the leaf surface or reduced and then reemitted to the atmosphere (Rea et al., 2001). Therefore, elevated THg concentration in throughfall was mostly attributed to the deposition of PHg and Hg(II) to foliar followed by washout of throughfall (Iverfeldt, 1991; Munthe et al., 1995; Schwesig and Matzner, 2000; Wu et al., 2006).

Compared to the concentrations of Hg species among three sites, Supeng presented the highest Hg concentrations among three sites. In Wanshan Hg mining area, artisanal Hg mining activities have been operated at Supeng site for a long time, and the

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elevated Hg^0 concentration in ambient air was the main cause of the elevated concentration of Hg species in rainfall. Furthermore, a lot of coarse aerosols containing cinnabar may also be emitted to ambient air during the on-going artisanal mining activity (Guentzel et al., 2001; Moreno et al., 2005), and therefore, even a single cinnabar particle could result in a significant elevation of Hg concentrations in precipitation and throughfall samples. The lowest concentrations of Hg species were observed at Shenchong, the control site of the study area. However, the values were still much higher than those observed in Changchun, urban city of northeastern China (354 ng L^{-1}), heavily polluted with respect to atmospheric Hg, as well as at remote areas in Europe and North America (Fang et al., 2004; Hall et al., 2005; Witt et al., 2009).

Figure 4 shows that there are significantly positive correlations between monthly mean concentrations of THg and PHg in precipitation and throughfall at 3 sites. As a whole, elevated THg concentrations in all samples are found to be associated with elevated PHg concentrations which account for approximately 64.5 %–76.7 % of THg. Lee et al. (2001) demonstrated PHg concentration was a crucial factor controlling the THg concentration in precipitation. Our data also indicate that particles are effectively scavenged from the atmosphere directly by precipitation. On the other hand, a series of homogeneous and heterogeneous oxidation of Hg^0 reactions occurring in the air may also contribute to elevated THg concentrations in precipitation because Hg^0 concentrations in ambient air in Wanshan Hg mining area are elevated as discussed in Sect. 3.1 (Lindqvist et al., 1991).

We only observed a significantly negative correlation between THg concentrations in both precipitation and throughfall and rainfall volume 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, 2011). 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

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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 impacted by the intensities of artisanal Hg mining activities. At these two sites, THg concentrations in precipitation is governed by the oxidation of Hg^0 by atmospheric oxidants (e.g. OH, Br, O_3 etc.). The variation of THg concentrations in precipitation may reflect the variation of Hg^0 concentrations in ambient air.

3.3 THg deposition fluxes in Wanshan Hg mining area

Wet and dry Hg deposition fluxes and annual total Hg deposition at Shenchong, Dashuixi and Supeng are listed in Table 2. The total annual Hg deposition in the study area is estimated to be 189.1 kg yr^{-1}, and the dry deposition contributed 88.6 % of total deposition. Our data demonstrated that THg deposition fluxes in Wanshan Hg mining area still maintained at persistently high levels even though the large scale Hg mining activities have completely stopped for a few years. Our data also showed that the dry deposition processes played a dominant role in atmospheric Hg deposition in Wanshan Hg mining area. A large amount of Hg emission from on-going 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 shown in Fig. 5. The monthly wet and dry deposition fluxes at each site varied 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 would be much more easily transformed to MeHg in rice paddy field and bioaccumulated in rice seeds. Therefore, the consistently observed elevated MeHg concentrations in rice cultivated in Wanshan Hg mining area

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(Horvat et al., 2003; Qiu et al., 2008; Feng et al., 2008; Zhang et al., 2010d) may be resulted from the elevated THg deposition fluxes. In order to reduce bioaccumulation of MeHg in rice in Wanshan Hg mining area, measures needs to be taken to reduce Hg deposition fluxes in the area. First of all, 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 Wanshan Hg mining area 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 Idrijca 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 Wanshan Hg mining area was similar with the values reported in Idrijca in 1999. However, the annual Hg deposition fluxes measured in Wanshan Hg mining area were 2–45 and 12–200 folds higher for wet and dry deposition than those observed in Idrijca area, respectively (Kocman, 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 $\mu g\,m^{-2}\,yr^{-1}$, 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, 2011). THg wet deposition fluxes in remote areas in China were also higher than the values reported from the analogous studies in other countries ($<10\,\mu g\,m^{-2}\,yr^{-1}$), except for the case from Lehstenbach, Germany ($35\,\mu g\,m^{-2}\,yr^{-1}$) which were impacted by air pollution from Eastern Europe (Schwesig and Matzner,

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1999). 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 Wanshan Hg mining area were much higher than THg wet deposition fluxes reported in urban areas in 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. The Hg^0 concentrations ranged from 17 to 5679 $ng\,m^{-3}$, and from the spatial distribution of Hg^0 concentrations in ambient air in the study area, it shows that calcines and mine wastes piles located in Dashuixi and on-going artisanal Hg mining activities at Supeng are the major sources of atmospheric mercury in Wanshan Hg mining area. The concentrations of Hg species in precipitation and throughfall varied spatially and temporally, and the average THg concentration 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, which accounted for 64.5 %-76.7 % of THg. 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 Wanshan Hg mining area were much higher than data reported in urban areas in China, and other sites in North America, Europe and other countries. Atmospheric Hg deposition is still an important pathway

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of Hg contamination to the local environment in Wanshan Hg mining areas.

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

		Precipitation			Througfall		
		THg	DHg	PHg	THg	DHg	PHg
Shenchong ($n = 21$)	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
Dashuixi ($n = 28$)	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
Supeng ($n = 24$)	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	54 936.0	19 925.0	50 485.4
	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	11 239.2

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Table 2. The THg deposition fluxes and annual THg deposition at Supeng, Dashuixi and Shenchong sites.

	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

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Table 3. Comparison of THg deposition fluxes measured in Wanshan mercury mining area and those at other sites.

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	This study
Wanshan, China (Dashuixi)	May 2010 to May 2012	Contaminated site	68.1	2606.9	
Wanshan, China (Supeng)	May 2010 to May 2013	Contaminated site	592.6	6174.4	
Idrijca, Slovenia	Oct 2006 to Sep 2007	Contaminated site	13.1	29.7	Kocman (2010)
Steubenville, USA	2004	urban	19.7		Gerald 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. (2010c)
Mt.Gongga, China	May 2005 to Apr 2007	Remote	26.1	57	Fu et al. (2010d)
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 September 1993	Remote	10	14	Lindber 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 et al. (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)

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Fig. 1. The locations of study area and sampling sites.

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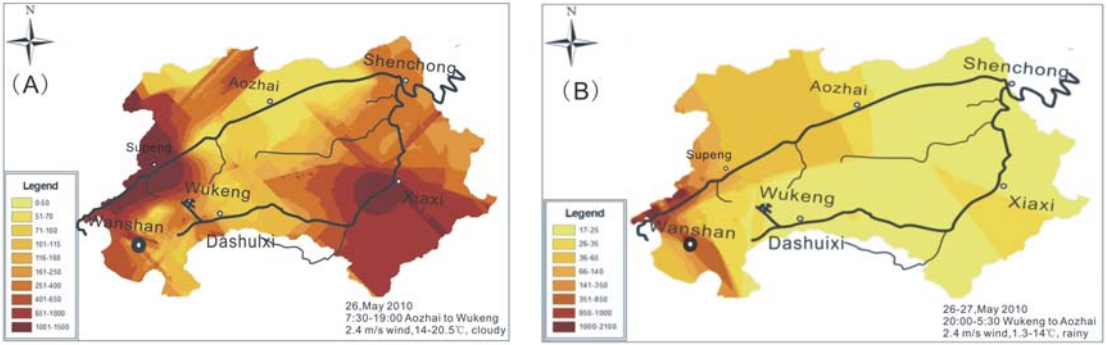

Fig. 2. Distribution of atmospheric mercury concentration in Wanshan mining area.

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Spatial distribution of mercury deposition fluxes in Wanshan Hg mining area

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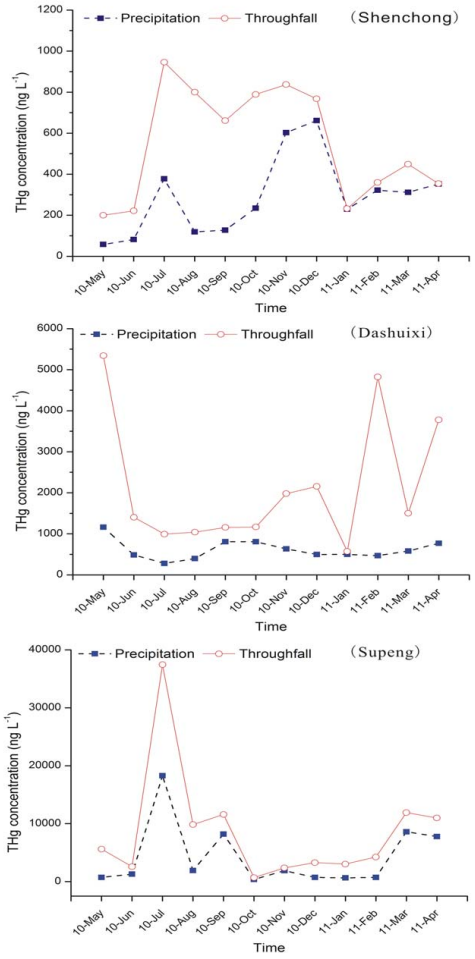

Fig. 3. Comparison with monthly mean THg concentrations in precipitation and throughfall at 3 sites.

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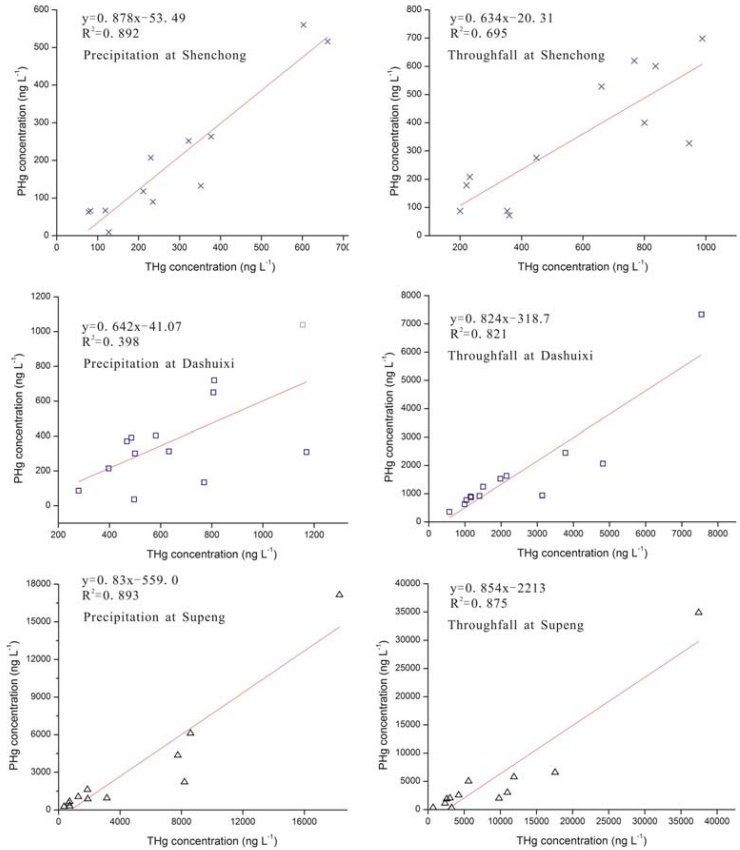

Fig. 4. Relationship between PHg concentrations and THg concentrations in precipitation and throughfall.

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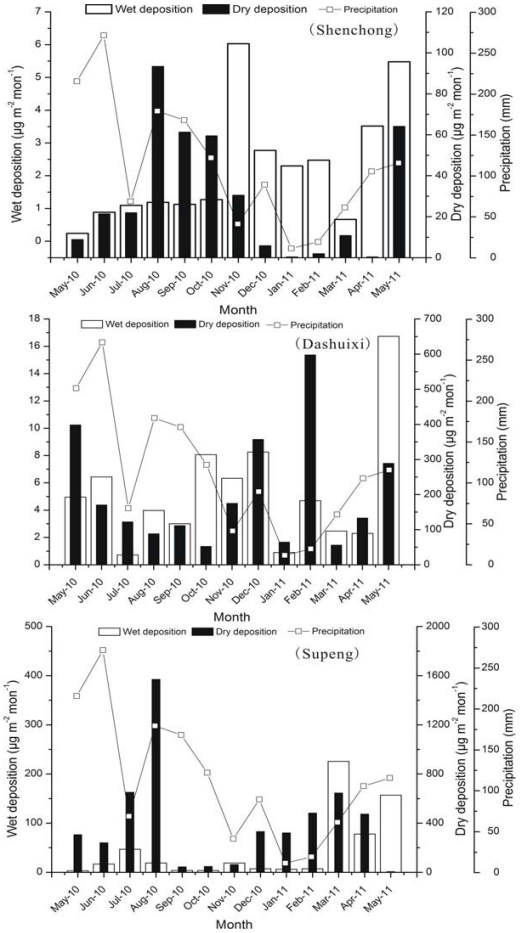

Fig. 5. Monthly changes in deposition fluxes of THg and the amount of rainfall at 3 sites in Wanshan.

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Spatial distribution of mercury deposition fluxes in Wanshan Hg mining area

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