Contents lists available at ScienceDirect







journal homepage: www.elsevier.com/locate/atmos

Atmospheric mercury species measured in Guiyang, Guizhou province, southwest China

Na Liu^{a,b}, Guangle Qiu^{a,*}, Matthew S. Landis^c, Xinbin Feng^a, Xuewu Fu^a, Lihai Shang^a

^a State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, PR China

^b Graduate University of Chinese Academy of Sciences, Beijing 100049, PR China

^c US EPA, Office of Research and Development, Research Triangle Park, NC 27709, USA

ARTICLE INFO

Article history: Received 8 June 2010 Received in revised form 11 December 2010 Accepted 3 January 2011

Keywords: Atmospheric Hg Speciation Meteorological parameters Anthropogenic sources

ABSTRACT

Atmospheric mercury (Hg) species were measured in Guiyang City, the capital of Guizhou province, southwestern China at the Guiyang Monitoring Station Agency (GMSA) from September to November 2008 and at the Institute of Geochemistry, Chinese Academy of Sciences (IGCAS) during February, May, and July, 2009. Monitoring results found elevated concentrations of all three Hg species in ambient air in Guiyang. Large temporal and spatial variation patterns in the resulting data were also obtained. The overall average TGM concentrations at the GMSA and IGCAS sampling sites were 7.4 \pm 4.8 ng m⁻³ and 6.2 \pm 5.1 ng m⁻³, respectively. The average Hg(p) and RGM concentrations at GMSA were 1330 pg m⁻³ and 24 pg m⁻³, and at IGCAS were 250 pg m⁻³ and 19 pg m⁻³, respectively. It is hypothesized that local anthropogenic sources and the seasonal variability result in the high degree of spatial and temporal variability.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Mercury (Hg) is one of the most toxic environmental pollutants because of its methylation, easy uptake of its organic forms by biota, and ecological health impacts via bioaccumulation through the food chain in aquatic systems (Schroeder and Munthe, 1998). Both natural processes and anthropogenic activities release Hg into the atmosphere, where it can be transported on local, regional, and global scales (Munthe et al., 2001). Human activities, such as the combustion of fossil fuels, waste incineration, industrial processes, cement production, and metal ore treatment, currently have increased amounts of Hg cycling among the atmosphere, land, and ocean (Ebinghaus et al., 1999; Pacyna et al., 2006). Soil degassing, ocean surface emissions, volcanoes, and geothermal activities are all considered important natural sources of Hg emissions (Schroeder et al., 1989; Lindberg et al., 1992; Gustin et al., 1999). Once Hg is released into the

0169-8095/\$ – see front matter 0 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.atmosres.2011.01.002

atmosphere, its physical and chemical properties and transformation processes will determine its fate and transport (Lindberg and Stratton, 1998).

Generally, Hg in the atmosphere exists as gaseous elemental Hg (Hg⁰), divalent reactive gaseous Hg (RGM), and particlebound Hg (Hg(p)). Natural sources predominantly emit Hg⁰, while RGM and Hg(p) are emitted primarily from anthropogenic point sources (Moore and Carpi, 2005; Poissant et al., 2004; Gustin and Stamenkovic, 2005; Pacyna et al., 2006; Sillman et al., 2007). While in recent years, more and more studies have considered that the oxidation of Hg⁰ in the upper troposphere could be a significant source of RGM (Swartzendruber et al., 2006; Faïn et al., 2009; Sheu et al., 2010). Hg⁰ is the predominant form in the atmosphere (95%), with the rest being RGM and Hg (p) (Schroeder and Munthe, 1998). The residence time of Hg⁰ in the atmosphere is estimated to be about 0.5–2 years due to its high volatility, low solubility, and chemical stability, and can be transported far beyond the region while it was emitted (Schroeder and Munthe, 1998).

RGM can represent 1–3% of total Hg in the air of the urban continental sites, however, in remote rural areas its levels were documented in the range from below detection limits to

^{*} Corresponding author. Tel.: +86 851 5890446; fax: +86 851 5891609. *E-mail address*: qiuguangle@vip.skleg.cn (G. Qiu).

several hundreds of pg m⁻³ (Landis et al., 2002; Poissant et al., 2004). Recent studies have reported that RGM emitted from anthropogenic sources can represent more than 30% of the total Hg (Streets et al., 2005; Wu et al., 2006). Several events in which RGM comprised the total Hg over 60% in air have also been observed (Lindberg et al., 2001).

The form of Hg(p) presented in the atmosphere is also at low pg m⁻³ levels and generally represents less than 10% of the total Hg in the air (Lu and Schroeder, 2004), while it is crucial for understanding its cycling, transport, transformation, and deposition in the environment (Lu et al., 2001).

Guizhou province is an area in southwestern China now considered a hotspot regarding Hg pollution in the world. It is the most important Hg producing region in China with annual atmospheric emission from Hg mining and refining estimated at 11 t (Tan et al., 2000; Horvat et al., 2003). Guizhou also is one of the most important coal producing areas in China and the coal produced in the province contains relatively high Hg (Feng and Hong, 1999; Feng et al., 2002; Feng and Qiu, 2008). Hence, coal combustion in the province results in a substantial amount of atmospheric Hg emissions into the environment which have resulted in near field enhancements in the local environmental (Feng et al., 2003, 2004).

Several ambient total gaseous Hg (TGM) sampling campaigns were conducted in Guiyang showing an average annual TGM concentration in ambient air in Guiyang ranging between 8.4 and 9.1 ng m⁻³ (Feng et al., 2003, 2004; Zheng et al., 2007). However, there has not been a sufficient monitoring of Hg(p) and RGM to adequately characterize mercury impacts in the city. Even though RGM and Hg(p) represent a relatively small proportion of total Hg in the air, these species can dominate over all atmospheric deposition flux as a result of their high deposition velocities (Lindberg and Stratton, 1998).

To overcome the lack of information on these important atmospheric Hg species in Guiyang, a new study was undertaken to provide a high-time resolution measurement of TGM, RGM, and Hg(p) combined with meteorological measurements. The objective of this study was to characterize their temporal and spatial distributions in ambient air in areas of Guiyang impacted by anthropogenic activities.

2. Materials and methods

2.1. Study area and sampling sites

Guiyang, the capital of Guizhou province, is located in the center of the province (Fig. 1). Its climate represents a typical subtropical humid monsoon with an average annual temperature of 15.3 °C and an annual precipitation depth of 1100–1400 mm. The prevailing wind direction is from the northeast in winter and from the south in summer. In 2008, the city population was 3.7 million. Because of the abundant coal resources in Guiyang, residents utilize it for home heating. The main industries of Guiyang are tobacco products, nonferrous metal smelting and rolling, medicine, and rubber products accounting for more than 80% of the added value of the scale industrial enterprises. In addition, there are approximately 39,000 motor vehicles in Guiyang in 2009, and that number is expected to increase dramatically.

Two existing monitoring sites in Guiyang were selected for this study. One site is located in the southwest part of the city named Guiyang Monitoring Station Agency (GMSA) (E: 106°43'3", N: 26°33'56", Height: 1050 m) and the other site is located in the southeast part of the city, named Institute of Geochemistry, Chinese Academy of Science (IGCAS) (E: 106°43'23", N: 26°34'20", Height: 1080 m). Both sites are located in residential areas with a number of local industries including: a large coal-fired utility, Guiyang Power (1.5 km south); a cement plant (3.5 km south), and several non-ferrous metal smelters (Fig. 1). The GMSA site is located on a roof of an 8 story building adjacent to a city road, while the IGCAS site is on the roof of a 7 story building located on a college campus.

2.2. Experimental

The sampling campaign at GMSA was conducted from September to November in 2008, and at IGCAS during March, May, and July in 2009.

2.2.1. Sampling of TGM, Hg(p), and RGM

Measurements of TGM concentrations in ambient air were performed with a Tekran Instruments Corporation (Knoxville, TN) model 2537A automated Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) (Tekran, 2002). The model 2537A was configured to measure 5 min integrated samples at a flow rate of 1.0 L min⁻¹, and routine calibrations were automatically conducted on a daily basis using the internal permeation tube. The internal permeation tube was calibrated using a primary calibration system every 2 months. The precision of the Tekran Instruments Corporation model 2537A is less than 2% and the detection limit is less than 0.1 ng m⁻³.

The manual sampling system for RGM and Hg(p) includes an elutriator, a coupler/impactor, a KCl-coated annular denuder, a 47 mm Teflon filter holder (URG Inc.), a dry gas meter, a pump, and a sampling box maintained at 50 °C to prevent hydrolysis of KCl. Fresh denuders and clean particulate filters were installed prior to each sampling. The annular denuder used to sample RGM has a high adsorption efficiency while the air is passing through the KCl coated surfaces (Landis et al., 2002). The Hg(p) samples were collected on quartz fiber filters (0.45 µm, 47 mm diameter, Millipore) housed in quartz denuders (Landis et al., 2002). It is important to note that Hg(p) results reported here represent only the fine fraction (2.5 µm mass median aerodynamic diameter).

The denuders for RGM and Hg(p) traps were positioned vertically, and the inlets were located at 1.5 m above the ground. During sampling, denuders were maintained at 20–30 °C above the ambient air temperature using a heating tape in order to prevent condensation of water vapor on the inner surface of the denuder (Feng et al., 2000; Landis et al., 2002).

The total volumetric flow through the denuder and particulate filter assembly was $10 \text{ L} \text{min}^{-1}$ (Landis et al., 2002). During the sampling campaigns, 12 h Hg(p) and RGM samples were collected each day from 8:00 am/8:00 pm to 8:00 pm/8:00 am with a resulting sample volume of 6–7.2 m³. RGM and Hg(p) sampling train inlet components were acid cleaned and annular denuders and Hg(p) filters were pre-cleaned by pyrolysis at 500 °C for 15 min to obtain operational blanks.



Fig. 1. Location of sampling sites in Guiyang, China.

2.2.2. Hg(p) and RGM analysis

After sampling, the KCl-coated annular denuders and quartz filter units were thermally desorbed in a Thermo Scientific Lindberg/Blue tube furnace (Model 55035C) used at 525 °C and 800 °C for RGM and Hg(p) respectively. The resulting thermally decomposed Hg⁰ in zero air carrier gas was quantified using a Tekran model 2537A CVAFS instrument. The analysis procedures employed for RGM and Hg(p) via pyrolysis are described by Lu et al. (1998), Feng et al. (2000), and Landis et al. (2002). A detection limit of 0.89 pg m⁻³ was calculated for RGM and Hg(p) as three times the standard deviation of the average blank (0.97±2.1, n = 120) for the whole dataset collected during the sampling period. All RGM and Hg(p) concentrations presented are blank corrected.

2.2.3. Meteorological parameters

Meteorological parameters including wind direction (WD), wind speed (WS), air temperature (T), air pressure (P), and relative humidity (RH) were collected synchronously with TGM. All meteorological data were provided by the local weather station from the Guizhou Meteorological Administration (CAWS600-SE).

3. Results and discussion

3.1. TGM

The TGM concentrations measured at the GMSA and IGCAS sites are summarized in Table 1. At GMSA, the mean \pm standard

Table 1

Concentrations of Hg speciation (TGM, Hg(p), RGM) at two sampling sites in Guiyang, China.

Sampling sites	Hg speciation	Mean	Median	Max.	Min.	Variance	Ν
GMSA (Sept., Oct., and Nov., 2008)	TGM (ng m ⁻³)	7.4	6.7	440	2.1	0.66	25,633
	$Hg(p) (pg m^{-3})$	1330	910	7420	43	1	178
	RGM (pg m^{-3})	24	13	750	1.6	2.5	178
IGCAS (Feb., May., and July., 2009)	TGM (ng m ⁻³)	6.2	5.3	380	0.53	0.89	29,045
	Hg(p) (pg m ⁻³)	250	81	2350	6.9	1.8	192
	RGM (pg m ⁻³)	19	12	210	1.4	1.2	192



Fig. 2. The high-time resolution long-term data set of TGM concentrations in ambient air in Guiyang, China.

deviation TGM value in ambient air is 7.4 ± 4.8 ng m⁻³, with a range of 2.1–440 ng m⁻³. Large variability of the temporal TGM distribution pattern was observed at both sampling sites (Fig. 2). The highest TGM concentration of 440 ng m⁻³ was measured at 1:55 am, 29th September, 2008, and the lowest value of 2.1 ng m⁻³ was measured at 5:00 pm, 6th October, 2008, respectively (Fig. 2). The frequency distribution of TGM at GMSA followed a typical log normal pattern and the data for TGM dominantly fell in the range of 4.0–8.0 ng m⁻³, which accounted for 72% of the total frequency (Fig. 3).

At IGCAS, the mean TGM concentration is 6.2 ± 5.1 ng m⁻³, with a range of 0.53 to 380 ng m⁻³. The highest TGM concentration of 380 ng m⁻³ and the lowest value of 0.53 ng m⁻³ were measured at 10:05 pm, 17th July and at 6:05 pm, 31st July, 2009, respectively (Fig. 2). The frequency distribution of TGM at IGCAS also followed a typical log normal distribution pattern and TGM

dominantly fell in the range of 2.0–6.0 ng m⁻³, which accounted for 75% of the total frequency (Fig. 3).

Notable diurnal variations characterized by reduced concentrations during daytime were observed during sampling periods (Fig. 4). The variation coefficients (CVs) at the GMSA and IGCAS sites were 0.13 and 0.11, respectively. It is generally believed that on most nights shallow nocturnal boundary layers form, trapping TGM near the surface form, while thermal mixing during the day increases the boundary layer depth thus diluting the concentrations (Lee et al., 1998; Schmolke et al., 1999; Feng et al., 2003). The nighttime peaks of TGM concentrations were indicated to the fact that Hg⁰ emitted from the surface accumulated in the nocturnal inversion layer (Schmolke et al., 1999).

The higher concentrations of TGM at GMSA than that observed at IGCAS probably contributed to the domestic coal



Fig. 3. Relative frequency plot of TGM distribution data measured from the sampling site in Guiyang, China.



Fig. 4. Diurnal variations of TGM concentrations in different sites of Guiyang, China.

burning for house heating during the winter season. The other reason may be that the site GMSA was near a road and adjacent to industrial areas, which emit atmospheric Hg.

The TGM concentrations in ambient air in Guiyang during this study are compared with observations from other urban areas around the world in Table 2. Previous TGM measurements in the same study area, showed higher results than those reported here Feng et al. (2004) and Zheng (2007), which reported mean concentrations of 8.4 ng m⁻³ in 2001 and 9.1 ng m⁻³ in 2006, respectively. Compared to the global background value of 1.5–1.8 ng m⁻³ (Landis et al., 2004), the TGM concentrations in Guiyang were substantially high, reflecting the impact of local and regional sources in our study area including coal combustion, cement production, non-ferrous metals, and other industrial activities (Feng et al., 2003, 2008; Fu et al., 2008a).

3.2. Hg(p) distribution characteristics in the study sites

During our two sampling campaigns, elevated concentrations of Hg(p) were observed (Table 1). A mean Hg(p) concentration of 1330 pg m⁻³ was observed at the GMSA site, with values ranging from 43 to 7420 pg m⁻³. While at IGCAS, the mean concentration of Hg(p) was 250 pg m⁻³, and a seasonal analysis found significantly higher concentration in the winter (February), and lower concentrations in the spring/ summer (May and July). This seasonal variation may be the result of several factors: (i) the rainy season is between May and September in Guizhou, therefore, the lower Hg(p) levels observed in May and July may be due to the wet deposition, which can play an important role in removing Hg in the atmosphere (Mason et al., 1997; Abbott et al., 2002; Lin et al., 2006; Sakata and Asakura, 2007); and (ii) in winter the combination of increased coal combustion emissions from home heating and stronger nocturnal radiative inversions can lead to increased concentrations at the surface. Significant spatial variability of Hg(p) was observed between the two sampling sites (Fig. 5). High concentrations of Hg(p) observed in Guiyang might suggest high emissions of Hg(p) in the city. Studies showed that Hg(p) are emitted by various sources, and therefore, its concentrations in ambient air are largely varied and dependent on the direct emissions of local and regional sources and in situ formation in the atmosphere (Sakata and Asakura, 2007). Because of Guiyang as an important coal produced and utilized city, the local coal-fired power plants and residential coal-burning, especially during cold seasons might play an important role for measured high values of Hg(p).

Zheng et al. (2007) measured the concentration of total particulate Hg (TPM) in Guiyang and achieved an average value of 0.70 ± 0.57 ng m⁻³. The concentration of Hg(p) at IGCAS was similar to the study in Changchun City, northeastern China, which ranged between 145 and 1980 pg m⁻³ (Fang et al., 2004). While in the remote areas of China, such as Mt. Gongga, Sichuan province, and Mt. Changbai, Iilin province, the concentrations of Hg(p) were 31 and 77 pg m⁻³, respectively (Fu et al., 2008b; Wan et al., 2009b). Lynam and Keeler (2006) and Liu et al. (2007) found the concentrations of Hg(p) in Detroit, Michigan, USA ranged between 5.0 and 60 pg m^{-3} with a mean \pm standard deviation of $21 \pm 30 \text{ pg m}^{-3}$. Compared to the northern hemisphere background Hg(p) concentrations of <1.0-50 pg m⁻³ in the atmosphere (Jaffe et al., 2005), the concentrations of Hg(p) in Guiyang were significantly elevated.

3.3. RGM distribution characteristics in the study sites

The concentrations of RGM at GMSA ranged from 2 to 750 pg m⁻³, with a mean concentration of 24 pg m⁻³, and the RGM concentrations at IGCAS ranged from 2 to 210 pg m⁻³, and the mean concentration was 19 pg m⁻³ (Table 1). Fig. 6 shows the daily averages of RGM concentrations at the two sites, which exhibited a strong temporal variability. RGM concentrations

Table 2

Comparison of TGM concentrations measured in ambient air in various regions in the world.

Locations		TGM (ng m ^{-3})	Classification	Sampling duration	Sampling techniques	References
China	Guiyang	7.4	Urban	8 months	Tekran 2537 A	This study
		8.4	Urban	1 year	Tekran 2537 A	Feng et al., 2004
		9.1	Urban	126 days	Tekran 2537 A	Zheng et al., 2007
	Chongqing	6.7	Urban	1 year	Lumex RA-915 ⁺	Yang et al., 2009
		8.5	Urban	1 year	Lumex RA-915 ⁺	Wang et al., 2007b
	Changchun	11-18	Urban	1 year	Tekran 2537 A	Fang et al., 2004
	Guangzhou	5.4	Suburban	2 weeks	Lumex RA-915 ⁺	Wang et al., 2007a
	Mt. Changbai	3.6	Rural	1 year	Tekran 2537 A	Wan et al., 2009a
	Mt. Gongga	3.9 ± 1.2	Rural	1 year	Tekran 2537 A	Fu et al., 2009
Korea	Seoul	3.2 ± 2.1	Urban	1 year	Tekran 2537 A	Kim et al., 2009
USA	Nevada	3.0 ± 1.7	Urban	4 weeks	Tekran 2537 A	Lynam and Gustin, 2008
Canada	Alberta	1.6	Rural	1 year	Tekran 2537 A	Mazur et al., 2009



Fig. 5. The long-term data set of Hg(p) concentrations in ambient air in Guiyang, China.

were characterized by low variability at GMSA, however, high variability was observed at IGCAS. The variability of RGM concentration was similar as the Hg(p) variability at the site. It was suspected that the seasonal variability of rainy days occurring during May, and July, 2009 in Guiyang might be responsible for the large range concentrations of RGM and Hg(p)

measured at IGCAS. The prevalently highly elevated concentrations of Hg(p) and intermittent high peaks in RGM concentration suggested significant urban mercury sources in Guiyang. Anthropogenic point sources, such as the municipal coal-fired power plants as well as residential heating by means of coalburning are most likely to play an important role here. It is also



Fig. 6. The long-term data set of RGM concentrations in ambient air in Guiyang, China.

Table 3			
Relationships between Hg speciation	and meteorological	data at two	sampling sites.

Sampling sites	Hg speciation and parameters	TGM	Hg(p)	RGM	Т	RH	WS
GMSA (Sept., Oct., and Nov., 2008)	TGM	1	.15	.084	.047	.25 ^a	22 ^a
	Hg(p)	.15	1	.21 ^a	.18 ^a	18 ^b	—.29 ^a
	RGM	.084	.21*	1	.17 ^b	—.41 ^a	082
	Т	.047	.18 ^b	.17 ^b	1	—.32 ^a	.086
	RH	.25 ^a	—.18 ^b	41 ^b	—.32 ^a	1	013
	WS	—.22 ^a	—.29 ^a	082	.086	013	1
IGCAS (Feb., May., and July., 2009)	TGM	1	.22 ^a	.10	12	.055	45 ^a
	Hg(p)	.22	1	.15	16 ^b	24 ^a	.097
	RGM	.10	.15	1	.29 ^a	49 ^a	.049
	Т	12	16 ^b	.29 ^a	1	—.29 ^a	050
	RH	.055	—.24 ^a	—.49 ^a	—.29 ^a	1	13
	WS	45 ^a	.097	.049	050	13	1

^a Correlation is significant at the 0.01 level (2-tailed).

^b Correlation is significant at the 0.05 level (2-tailed).

viable that the RGM level measured to some extent is influenced by atmospheric oxidation (converting GEM to RGM) either by in-flux of RGM-rich air from higher stratum or by in-situ oxidation of GEM in polluted urban air (Swartzendruber et al., 2006; Faïn et al., 2009; Sheu et al., 2010).

Our results for RGM in Guiyang were comparable to the previous studies in the same region by Shang et al. (2003) and Zheng (2007), which reported an average concentration of

38 pg m⁻³ and a range of 16–387 pg m⁻³. In remote areas of China, however, Fu et al. (2008b) and Wan et al. (2009b) reported RGM values of 6.2 pg m⁻³ in Mt. Gongga and 65 pg m⁻³ in Mt. Changbai, respectively. Peterson et al. (2009) measured RGM values and achieved 26 pg m⁻³ in north of downtown Reno, Nevada, USA. Kim et al. (2009) measured RGM concentrations, which reached 27 ± 19 pg m⁻³ in Seoul, Korea. Those results for RGM were comparable to our study.



Fig. 7. TGM, Hg(p), and RGM concentrations during the daytime and nighttime in Guiyang, China.

3.4. Relationships among TGM, TPM, RGM, and meteorological parameters

The average percentage of Hg(p) to TGM was 15% at GMSA and 5.4% at IGCAS, while RGM percentage of TGM was 0.24% and 0.36%, respectively. The higher proportion of Hg(p) compared to RGM in the study is unique in the literature and may be due to gas to particle conversion facilitated by the relatively high concentrations of total PM_{2.5} mass at our sites (data not shown). The correlation of total PM_{2.5} to Hg(p) was strong ($r^2 = 0.253$, p<0.01). In addition, the low RGM may result from the precipitation scavenging owing to the high RH during this study. The percentages of RGM to TGM were similar to the findings in other study areas (Han et al., 2004; Fang et al., 2004; Gabriel et al., 2005; Kim et al., 2009). The correlations among Hg(p), RGM, TGM, as well as wind, humidity, and temperature were shown in Table 3.

Atmospheric Hg species concentrations at IGCAS showed more diurnal variability than at GMSA. Fig. 7 depicts the diurnal variability of atmospheric Hg species concentrations during the study period. A significant variation (p<0.05) was observed for TGM, and the trends were consistent between the two sites, while no significant differences were observed for Hg(p) and RGM. The average TGM concentration of daytime at GMSA and IGCAS, which was of 6.8 and 5.5 ng m⁻³, was significantly lower than that in nighttime, which was of 7.7 and 6.4 ng m⁻³, respectively. The daytime average concentration of Hg(p) was not significantly different from the nighttime average concentrations at either site. At GMSA, the average concentrations of Hg(p) were 1360 and 1290 pg m⁻³ for daytime and nighttime, and at IGCAS were 320 pg m⁻³ daytime, 320 pg m⁻³ nighttime, respectively.

The concentrations of RGM in daytime were significantly higher than that in nighttime at both sites. RGM concentrations were of 22.5 pg m⁻³ daytime and 16.3 pg m⁻³ nighttime at GMSA, and of 20.9 pg m⁻³ daytime and 18.9 pg m⁻³ nighttime at IGCAS, respectively. When the ambient temperatures decreased, the partitioning of gaseous Hg to the particulate phase would decrease RGM concentrations (Poissant et al., 2005; Lynam and Keeler, 2005).

Fig. 8A shows the frequency angular distribution of TGM segregated into five categories based on concentrations observed at GMSA per 6° bins of wind direction. Winds at GMSA were predominantly from the northeast (22.5°–67.5°). A significant relationship was found between the TGM concentration and wind direction at this site that was largely confined to the northeastern wind sector. Within this sector there are two small boilers operated for supplying heat during the colder seasons (Feng et al., 2003).

At IGCAS, the wind direction was mainly confined to two sectors: northeast (22.5°–67.5°) and south (202.5°–135°), with the frequency of 31.4% and 30.9%, respectively (Fig. 8B). In February, the predominant wind was from the northeast while from April to July, southerly winds were most prevalent. Elevated TGM concentrations were not significantly related to wind direction, suggesting that these observations were indicative of regional Hg emissions. Sources in the vicinity of IGCAS are mixed industrial complexes including two boilers located in the north, while two strong point sources, are located in the southwest of a distance of 300 m. At the south of the site, Guiyang Coal Fired Power Plant and



Fig. 8. Frequency increases of wind directions and TGM concentrations at wind directions at two sites in Guiyang, China.

Guizhou Cement Production Plant were the largest Hg emission point sources, which are located southwest of the study site with a distance of 20 km.

4. Conclusions

This study presents ambient Hg speciation concentrations in Guiyang city, Guizhou province. Large temporal and spatial variation patterns in the resulting data suggest local and regional anthropogenic activities impacted the sites. The concentration of TGM at GMSA was significantly higher than at IGCAS. Since sampling at GMSA occurred only in the winter the increased use of coal combustion for home heating during the cold seasons from late autumn through winter could explain this difference. The Hg(p) concentrations of our study were significantly elevated in comparison to values reported in North America, Europe, and the Arctic regions. The concentration of Hg(p) sampled at IGCAS are lower than those measured at GMSA. This occurred mainly due to an abrupt reduction in Hg(p) concentrations in May and July, 2009 during the rainy season. The reduction in Hg(p) and the similar abrupt decrease in RGM concentration were probably due to atmospheric washout. The concentrations of RGM in this study were comparable to a few previous smaller studies in Guiyang, and were also comparable to the studies in other urban areas in the U.S. and Europe. The relatively high concentrations of TGM and Hg(p) in Guiyang is attributable to local and regional atmospheric Hg emissions. Identification and quantification of the major atmospheric mercury sources in and around Guiyang and development of a detailed emission inventory in Guiyang is needed to further elucidate Hg distribution characteristics.

Acknowledgments

This research was performed while the authors held a U.S. National Research Council Associateship Award at U.S. EPA's National Exposure Research Laboratory (NERL). It has been reviewed by the Agency and approved for publication. It also was financially supported by the Natural Science Foundation of China (No. 40773067). We also acknowledge Dr. Jonas Sommar for his constructive suggestions on this manuscript and Kangdi Han for the field sampling assistance.

References

- Abbott, M.L., Susong, D.D., Krabbenhoft, D.P., Rood, A.S., 2002. Mercury deposition in snow near an industrial emission source in the western US and comparison to ISC3 model predictions. Water Air Soil Poll. 139, 95–114.
- Ebinghaus, R., Jennings, S.G., Schroeder, W.H., Berg, T., Donaghy, T., Guentzel, J., Kenny, C., Kock, H.H., Kvietkus, K., Landing, W., Mühleck, T., Munthe, J., Prestbo, E.M., Schneeberger, D., Slemr, F., Sommar, J., Urba, A., Wallschlakger, D., Xiao, Z., 1999. International field intercomparison measurements of atmospheric mercury species at Mace Head. Ireland. Atmos. Environ. 33, 3063–3073.
- Fang, F.M., Wang, Q.C., Li, J.F., 2004. Urban environmental mercury in Changchun, a metropolitan city in Northeastern China: source, cycle, and fate. Sci. Total Environ. 330, 159–170.
- Faïn, X., Obrist, D., Hallar, A.G., Mccubbin, I., Rahn, T., 2009. High levels of reactive gaseous mercury observed at a high elevation research laboratory in the Rocky Mountains. Atmos. Chem. Phys. 9, 8049–8060.
- Feng, X.B., Hong, Y., 1999. Modes of occurrence of mercury in coals from Guizhou. PR. China. Fuel 78, 1181–1188.
- Feng, X.B., Sommar, J., Gardfeldt, K., Lindqvist, O., 2000. Improved determination of gaseous divalent mercury in ambient air using KCl coated denuders. Fres. J. Anal. Chem. 366, 423–428.
- Feng, X.B., Sommar, J., Lindqvist, O., Hong, Y., 2002. Occurrence, emissions and deposition of mercury during coal combustion in the province Guizhou, China. Water Air Soil Poll. 139, 311–324.
- Feng, X.B., Tang, S.L., Shang, L.H., Yan, H.Y., Sommar, J., Lindqvist, O., 2003. Total gaseous mercury in the atmosphere of Guiyang. PR China. Sci. Total Environ. 304, 61–72.
- Feng, X.B., Tang, S.L., Shang, L.H., Yan, H.Y., Zheng, W., 2004. Temporal variation of total gaseous mercury in the air of Guiyang. China. J. Geophys. Res. 109, D03303.
- Feng, X.B., Qiu, G.L., 2008. Mercury pollution in Guizhou. China- an overview. Sci. Total Environ. 400, 227–237.
- Feng, X.B., Li, P., Qiu, G.L., Wang, S.F., Li, G.H., Shang, L.H., Meng, B., Jiang, H.M., Bai, W.Y., Li, Z.G., Fu, X.W., 2008. Human exposure to methylmercury through rice intake in mercury mining areas, Guizhou province. China. Environ. Sci. Technol. 42 (1), 326–332.
- Fu, X.W., Feng, X.B., Zhu, W.Z., Wang, S.F., Lu, J., 2008a. Total gaseous mercury concentrations in ambient air in the eastern slope of Mt. Gongga, South-Eastern fringe of the Tibetan plateau. China. Atmos. Environ. 42, 970–979.

- Fu, X.W., Feng, X.B., Zhu, W.Z., Zheng, W., Wang, S.F., Lu, J., 2008b. Total particulate and reactive gaseous mercury in ambient air on the eastern slope of the Mt. Gongga area. China. Appl. Geochem. 23, 408–418.
- Fu, X.W., Feng, X.B., Wang, S.F., Rothenberg, S., Shang, L.H., Li, Z.G., Qiu, G.L., 2009. Temporal and distributions of total gaseous mercury concentrations in ambient air in a mountainous area in southwestern China: implications for industrial and domestic mercury emissions in remote in China. Sci. Total Environ. 407, 2306–2314.
- Gabriel, M.C., Williamson, D.G., Brooks, S., Lindberg, S., 2005. Atmospheric speciation of mercury in two contrasting southeastern US airsheds. Atmos. Environ. 39, 4947–4958.
- Gustin, M.S., Lindberg, S.E., Marsik, F., Casimir, A., Ebinghaus, R., Edwards, G., Hubble-F, C., Kemp, R., Kock, H., Leonard, T., London, J., Majewski, M., Montecinos, C., Owens, J., Pilote, M., Poissant, L., Rasmussen, P., Schaedlich, F., Schneeberger, D., Schroeder, W., Sommar, J., Turner, R., Vette, A., Wallschlaeger, D., Xiao, Z., Zhang, H., 1999. Nevada STORMS project: Measurement of mercury emissions from naturally enriched surfaces. J. Geophys. Res. 104(D17), 21831-21844.
- Gustin, M.S., Stamenkovic, J., 2005. Effect of watering and soil moisture on mercury emission from soil. Biogeochemistry 76, 215–232.
- Han, Y.-J., Holsen, T.M., Hopke, P.K., Cheong, J.-P., Kim, H., Yi, S.-M., 2004. Identification of source locations for atmospheric dry deposition of heavy metals during yellow-sand events in Seoul, Korea in 1998 using hybrid receptor models. Atmos. Environ. 38, 5353–5361.
- Horvat, M., Nolde, N., Fajon, V., Jereb, V., Logar, S., Jacimovic, R., Falnoga, I., Liya, Q., Faganeli, J., Drobne, D., 2003. Total mercury, methylmercury and selenium in mercury polluted areas in the province Guizhou. China. Sci. Total Environ. 304, 231–256.
- Jaffe, D., Prestbo, E., Swartzendruber, P., Weiss-Penzias, P., Kato, S., Takami, S., Kajii, Y., 2005. Export of atmospheric mercury from Asia. Atmos. Environ. 39 (17), 3029–3038.
- Kim, S.H., Han, Y.J., Holsen, T.M., Yi, S.M., 2009. Characteristics of atmospheric speciated mercury concentrations (TGM, Hg(II) and Hg (p)) in Seoul. Korea. Atmos. Environ. 43, 3267–3274.
- Landis, M.S., Stevens, R.K., Schaedlich, F., Prestbo, E.M., 2002. Development and characterization of an annular denuder methodology for the measurement of divalent inorganic reactive gaseous mercury in ambient air. Environ. Sci. Technol. 36, 3000–3009.
- Landis, M.S., Keerler, G.J., Al-Wali, K.I., Stevens, R.K., 2004. Divalent inorganic reactive gaseous mercury emissions from a mercury cell chlor-alkali plant and its impact on near-field atmospheric dry deposition. Atmos. Environ. 38, 613–622.
- Lee, D.S., Dollard, G.J., Pepler, S., 1998. Gas-phase mercury in the atmosphere of the United Kingdom. Atmos. Environ. 32, 855–864.
- Liu, B., Keeler, G., Dovonch, J.T., Barres, J.A., Lynam, M.M., Marsik, F.J., Morgan, J.T., 2007. Temporal variability of mercury speciation in urban air. Atmos. Environ. 41, 1911–1923.
- Lin, C.J., Pongprueksa, P., Lindberg, S.E., Pehkonen, S.O., Byun, D., Jang, C., 2006. Scientific uncertainties in atmospheric mercury models: model science evaluation. Atmos. Environ. 40, 2911–2928.
- Lindberg, S.E., Meyers, T.P., Taylor, G.E., Turner, R.R., Schroeder, W.H., 1992. Atmosphere/surface exchange of mercury in a forest: results of modeling and gradient approaches. J. Geophys. Res. 97, 2519–2528.
- Lindberg, S.E., Stratton, W.J., 1998. Atmospheric speciation concentrations and behavior of reactive gaseous mercury in ambient air. Environ. Sci. Technol. 32, 49–57.
- Lindberg, S.E., Landis, M.S., Stevens, R.K., Brooks, S., 2001. Comments on atmospheric mercury species in the European Arctic: measurements and modeling. Atmos. Environ. 35, 5377–5378.
- Lu, J.Y., Schroeder, W.H., Berg, T., Munthe, J., Schneeberger, D., Schaedlich, F.A., 1998. Device for sampling and determination of total particulate mercury in ambient air. Anal. Chem. 70, 2403–2408.
- Lu, J.Y., Schroeder, W.H., Barrie, L.A., Steffen, A., Welch, E.H., Martin, K., Lockhart, W.L., Hunt, R.V., Boila, G., Richter, R., 2001. Magnification of atmospheric mercury deposition to polar regions in springtime: the link to tropospheric ozone depletion chemistry. Geophys. Res. Lett. 28, 3219–3222.
- Lu, J.Y., Schroeder, W.H., 2004. Annual time-series of total filterable atmospheric mercury concentrations in the Arctic. Tellus B. 56, 213–222.
- Lynam, M.M., Keeler, G.J., 2005. Automated speciated mercury measurements in Michigan. Environ. Sci. Technol. 39, 9253–9262.
- Lynam, M.M., Keeler, G.J., 2006. Source-receptor relationships for mercury in Urban Detroit. Michigan. Atmos. Environ. 39, 3144–3155.
- Lynam, S.N., Gustin, M.S., 2008. Speciation of atmospheric mercury at two sites in northern Nevada. USA. Atmos. Environ. 42, 927–939.
- Mason, R.P., Lawson, N.M., Sullivan, K.A., 1997. The concentration, speciation and sources of mercury in Chesapeake Bay precipitation. Atmos. Environ. 31, 354–3550.
- Mazur, M., Mintz, R., Lapalme, M., Wiens, B., 2009. Ambient air total gaseous mercury concentrations in the vicinity of coal-fired power plants in Alberta. Canada. Sci. Total Environ. 408 (2), 373–381.

- Moore, C., Carpi, A., 2005. Mechanisms of the emission of mercury from soil: role of UV radiation. J. Geophys. Res. 110, 1–9.
- Munthe, J., Kindbom, K., Kruger, O., Petersen, G., Pacyna, J., Iverfeld, A., 2001. Examining source-receptor relationships for mercury in Scandinavia, modeled and empirical evidence. Water Air Soil Poll. 1 (3–4), 299–310.
- Pacyna, E.G., Pacyna, J.M., Steenhuisen, F., Wilson, S., 2006. Global anthropogenic mercury emission inventory for 2000. Atmos. Environ. 40 (22), 4048–4063.
- Peterson, C., Gustin, M., Lyman, S., 2009. Atmospheric mercury concentrations and speciation measured from 2004 to 2007 in Reno, Nevada. USA. Atmos. Environ. 43, 4646–4654.
- Poissant, L., Pilote, M., Constant, P., Beauvais, C., Zhang, H.H., Xu, X.H., 2004. Mercury gas exchanges over selected bare soil and flooded sites in the bay St. François wetlands (Québec, Canada). Atmos. Environ. 38, 4205–4214.
- Poissant, L., Pilote, M., Beauvais, C., Constant, P., Zhang, H.H., 2005. A year of continuous measurements of three atmospheric mercury species (GEM, RGM and Hg-P) in southern Québec. Canada. Atmos. Environ. 39, 1275–1287.
- Sakata, M., Asakura, K., 2007. Estimating contribution of precipitation scavenging of atmospheric particulate mercury to mercury wet deposition in Japan. Atmos. Environ. 41, 1669–1680.
- Schmolke, S.R., Schroeder, W.H., Kock, H.H., Schneeberger, D., Munthe, J., Ebinghaus, R., 1999. Simultaneous measurements of total gaseous mercury at four sites on a 800 km transect: spatial distribution and short-time variability of total gaseous mercury over central Europe. Atmos. Environ. 33, 1725–1733.
- Schroeder, W.H., Munthe, J., Lindqvist, O., 1989. Cycling of mercury between water, air and soil compartments of the environment. Water Air Soil Poll. 48, 337–347.
- Schroeder, W.H., Munthe, J., 1998. Atmospheric mercury—an overview. Atmos. Environ. 32, 809–822.
- Sillman, S., Marsik, F.J., Al-Wali, K.I., Keeler, G.J., Landis, M.S., 2007. Reactive mercury in the troposphere: model formation and results for Florida, the northeastern United States, and the Atlantic Ocean. J. Geophys. Res. 112, D23305.
- Streets, D.G., Hao, J., Wu, Y., Jiang, J., Chan, M., Tian, H., Feng, X.B., 2005. Anthropogenic mercury emissions in China. Atmos. Environ. 39, 7789–7806.
- Shang, L.H., Feng, X.B., Zheng, W., Yan, H.Y., 2003. Preliminary study of the distribution of gaseous mercury species in the air of Guiyang City. China. Bull. Mineral. Petrol. Geochem. 22 (2), 157–158.

- Swartzendruber, P.C., Jaffe, D.A., Prestbo, E.M., Weiss-Penzias, P., Selin, N.E., Park, R., Jacob, D.J., Strode, S., Jaeglé, L., 2006. Observations of reactive gaseous mercury in the free troposphere at the Mount Bachelor Observatory. J. Geophys. Res. 111, D24301. doi:10.1029/2006JD007415.
- Sheu, G.R., Lin, N.H., Wang, J.L., Lee, C.T., Yang, C.F.O., Wang, S.H., 2010. Temporal distribution and potential sources of atmospheric mercury measured at a high-elevation background station in Taiwan. Atmos. Environ. 44, 2393–2400.
- Tan, H., He, J.L., Liang, L., Lazoff, S., Sommer, J., Xiao, Z.F., Lindqvist, O., 2000. Atmospheric mercury deposition in Guizhou. China. Sci. Total Environ. 259, 223–230.
- Tekran, 2002. Model 2537A Mercury Vapour Analyzer User Manual. Canada, Toronto.
- Wang, Z.W., Chen, Z.S., Duan, N., Zhang, X.S., 2007a. Gaseous elemental mercury concentration in atmosphere at urban and remote sites in China. J. Environ. Sci. 19, 176–180.
- Wang, P.A., Zhang, C., Wang, C.X., Wang, D.Y., 2007b. Research of spatial temporal variation of atmospheric mercury in Beibei District of Chongqing. J. Southwest Univ. 29, 125–129.
- Wan, Q., Feng, X.B., Lu, J.L., Zheng, W., Song, X.J., Li, P., Han, S.J., Xu, H., 2009a. Atmospheric mercury in Changbai Mountain area, northeastern China I: the season distribution pattern of total gaseous mercury and its potential sources. Environ. Res. 109, 201–206.
- Wan, Q., Feng, X.B., Lu, J.L., Zheng, W., Song, X.J., Li, P., Han, S.J., Xu, H., 2009b. Atmospheric mercury in Changbai Mountain area, northeastern China II: the distribution of reactive gaseous mercury and particulate mercury and mercury deposition fluxes. Environ. Res. 109, 721–727.
- Wu, Y., Wang, S., Streets, D.G., Hao, J., Chan, M., Jiang, J., 2006. Trends in anthropogenic mercury emissions in China from 1995 to 2003. Environ. Sci. Technol. 40 (17), 5312–5318.
- Yang, Y., Chen, H., Wang, D.Y., 2009. Spatial and temporal distribution of gaseous elemental mercury in Chongqing. China. Environ. Monit. Assess. 156, 479–489.
- Zheng, W., Feng, X.B., Yan, H.Y., 2007. Characteristics of total particulate mercury pollution in the atmosphere of a residential area in the city of Guiyang, PR China. Earth Environ. 35 (2), 154–157.
- Zheng, W., 2007. Atmospheric Mercury Species in the Central Urban Area of Guiyang. Dissertation submitted to Institute of Geochemistry Chinese Academy of Sciences.