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ORIGINAL ARTICLE

Characteristics and distributions of atmospheric mercury emitted from anthropogenic sources in Guiyang, southwestern China

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Abstract Continuous measurements of speciated atmospheric mercury (Hg), including gaseous elemental mercury (GEM), particulate mercury (PHg), and reactive gaseous mercury (RGM) were conducted in Guizhou Province, southwestern China. Guiyang Power Plant (GPP), Guiyang Wujiang Cement Plant, Guizhou Aluminum Plant (GAP), and Guiyang Forest Park (GFP) in Guiyang were selected as study sites. Automatic Atmospheric Mercury Speciation Analyzers (Tekran 2537A) were used for GEM analysis. PHg and RGM were simultaneously collected by a manual sampling system, including elutriator, coupler/impactor, KCl-coated annular denuder, and a filter holder. Results show that different emission sources dominate different species of Hg. The highest average GEM value was 22.2 ± 28.3 ng·m^{-3} and the lowest 6.1 ± 3.9 ng·m^{-3}, from samples collected at GPP and GAP, respectively. The maximum average PHg was 1984.9 pg·m^{-3} and the minimum average 55.9 pg·m^{-3}, also from GPP and GAP, respectively. Similarly, the highest average RGM of 68.8 pg·m^{-3} was measured at GPP, and the lowest level of 20.5 pg·m^{-3} was found at GAP. We conclude that coal combustion sources are still playing a key role in GEM; traffic contributes significantly to PHg; and domestic pollution dominates RGM.

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1 Introduction

Mercury (Hg) is a persistent hazardous pollutant with adverse effects on human health and wildlife due mainly to bioaccumulation and biomagnification in aquatic food webs (Lindqvist et al. 1991; Schroeder and Munthe 1998). Mercury is also regarded as a global pollutant for its tendency to migrate through the atmosphere to oceanic systems and remote regions, where it tends to be converted to methylmercury, a more toxic and bioavailable form (Wängberg et al. 2001; Poissant et al. 2005; Aspmo et al. 2006).

Atmospheric Hg can be operationally categorized into three forms: gaseous elemental mercury (GEM) (Fu et al. 2008), particulate mercury (PHg), and reactive gaseous mercury (RGM). GEM has a long residence time of 0.5–2 years in the atmosphere due to its high volatility and low solubility in water, and thus can be transported from the regions where it was released to more remote areas (Schroeder and Munthe 1998). In contrast, RGM and PHg have a short lifetime (several hours to several weeks) and can be quickly incorporated into surroundings via dry and wet deposition (Schroeder and Munthe 1998). GEM is sometimes converted to RGM and PHg, and settles onto the ground surface (Poissant et al. 2005).

Natural processes and anthropogenic activities are both sources of Hg emissions into the atmosphere (Munthe et al. 2001). Major natural sources include soil degassing, water evaporation, vegetation transpiration, wild fires, volcanoes, and geothermal sources. The major anthropogenic sources include agricultural materials combustion, fossil-fuel

combustion, mining, metal smelting, refining and manufacturing, chlor-alkali plants, and waste incineration, with most atmospheric Hg traced to anthropogenic activities (Feng et al. 2003; Pacyna et al. 2006). Asia is the largest emitter to global Hg emissions, contributing approximately 54 % of the total (Pacyna et al. 2010). Global anthropogenic emissions of Hg were estimated to be 2319.7 tons in 2010, of which approximately 26.2 % were from China (Pirrone et al. 2010).

The major anthropogenic Hg emission sources in China are industrial burning of coal, coal-fired plants, nonferrous smelting, and cement production (Zhang et al. 2015). These activities are concentrated in urban areas. Numerous studies have been conducted (e.g. Feng et al. 2003; Fu et al. 2011; Landis et al. 2014); however, Hg levels, especially the species emitted from the anthropogenic sources mentioned above, have not been extensively investigated in China. Guizhou province, southwestern China, has been considered a hotspot owing to its high level of Hg in the atmosphere (Feng et al. 2003, 2004). Previous studies in Guiyang reported average values of annual atmospheric Hg ranging between 6.4 and 9.1 $ng \cdot m^{-3}$. Fu et al. (2011) and Liu et al. (2011) measured speciated atmospheric Hg in ambient air in Guiyang. However, a detailed description of atmospheric Hg pollution from anthropogenic sources in Guiyang is still lacking.

Our study was carried out to obtain continuous measurements of GEM, PHg, and RGM from anthropogenic sources in order to elucidate temporal and spatial distribution patterns caused by anthropogenic Hg sources in urban and suburban areas of Guiyang. In this study, a power plant and a cement plant in urban areas, and an aluminum plant and a forest park in suburban areas were chosen to investigate and evaluate their individual and collective impacts on atmospheric Hg and its species in ambient air.

2 Materials and methods

2.1 Study areas and sampling sites

The climate of Guiyang represents a typical subtropical humid monsoon with an average annual rainfall of 1100 to 1400 mm. Dominant wind directions are northeast in winter and south in summer. In 2014, the population of Guiyang was about 4.32 million according to The People's Government of Guiyang Municipality (2014). Industry is the pillar of the Guiyang economy, including coal-fired power plants, nonferrous metal smelting and further processing, cement, tobacco products, medicine, and rubber products. Guiyang is abundant in coal resources; coal is widely used by local residents.

Field measurements in this study were conducted at 2 km downstream of prevailing winds of selected typical Hg emission sources in Guiyang (Fig. 1): Guiyang coal-fired Power Plant (GPP; 106.692°E, 26.549°N), Guiyang Wujiang Cement Plant (GWCP; 106.677°E, 26.523°N), Guizhou Aluminum Plant (GAP; 106.66°E, 26.678°N),and Guiyang Forest Park (GFP; 106.766°E, 26.557°N). GPP and GWCP are situated about 2.5 km apart in the southwest quadrant of the urban district of Guiyang, while GAP and GFP are located in suburban areas. GFP lies to the east of GPP, in the southeast of Guiyang. GAP is in the northwest of Guiyang, more than 15 km away from the other three sites. Although GPP (recently closed) was equipped with a cold-side electrostatic precipitator (ESP) and wet-type flue gas desulfurization (FGD) system, it was a big industrial emission source due to its large coal consumption (Zhang et al. 2012a, b). A recreation area of Guiyang, GFP is located on the east edge of main city.

2.2 Sample collection and analysis

2.2.1 Sampling of GEM, PHg, and RGM

In 2011, field measurements were conducted at GPP from October 5 to 13, at GWCP from October 20 to 25, at GFP from November 1 to 7, and at GAP from November 12 to 17.

GEM monitoring was conducted using a Tekran 2537A automated mercury Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) (model 2537A Tekran, 2002). The model 2537A was programed to measure GEM at an air sampling flow rate of 1.5 $L \cdot min^{-1}$ using a 5min sampling duration. The Tekran 2537A conducted automatic calibration on a daily basis using the internal permeation tube. The relative measurements error of the Tekran 2537A is estimated to be less than 2 %, and the detection limit in this model is less than 0.1 $ng \cdot m^{-3}$.

The manual operation sampling system of RGM and PHg consists of an elutriator, a coupler/impactor, a 47 mm Teflon filter holder (URG Inc), a KCl-coated annular denuder, a dry gas meter, a pump, and a sampling kit maintained at 50 °C to avoid hydrolysis of KCl. The installations of clean particulate filters and fresh denuder were set prior to the sampling. The PHg samples were captured on quartz fiber filters (0.45 μm, 47 mm diameter, Millipore) prior to RGM sampling.

The denuders and a 47 mm-Teflon filter holder for RGM and PHg taps were placed perpendicularly, and the inlets were set at 1.5 m above the ground. At the sampling periods, denuders were maintained at 20 to 30 °C above the surrounding air temperature with a heating tape to avoid condensation of water vapor on the inner surface (Feng et al. 2000; Landis et al. 2002). The total flow rate through

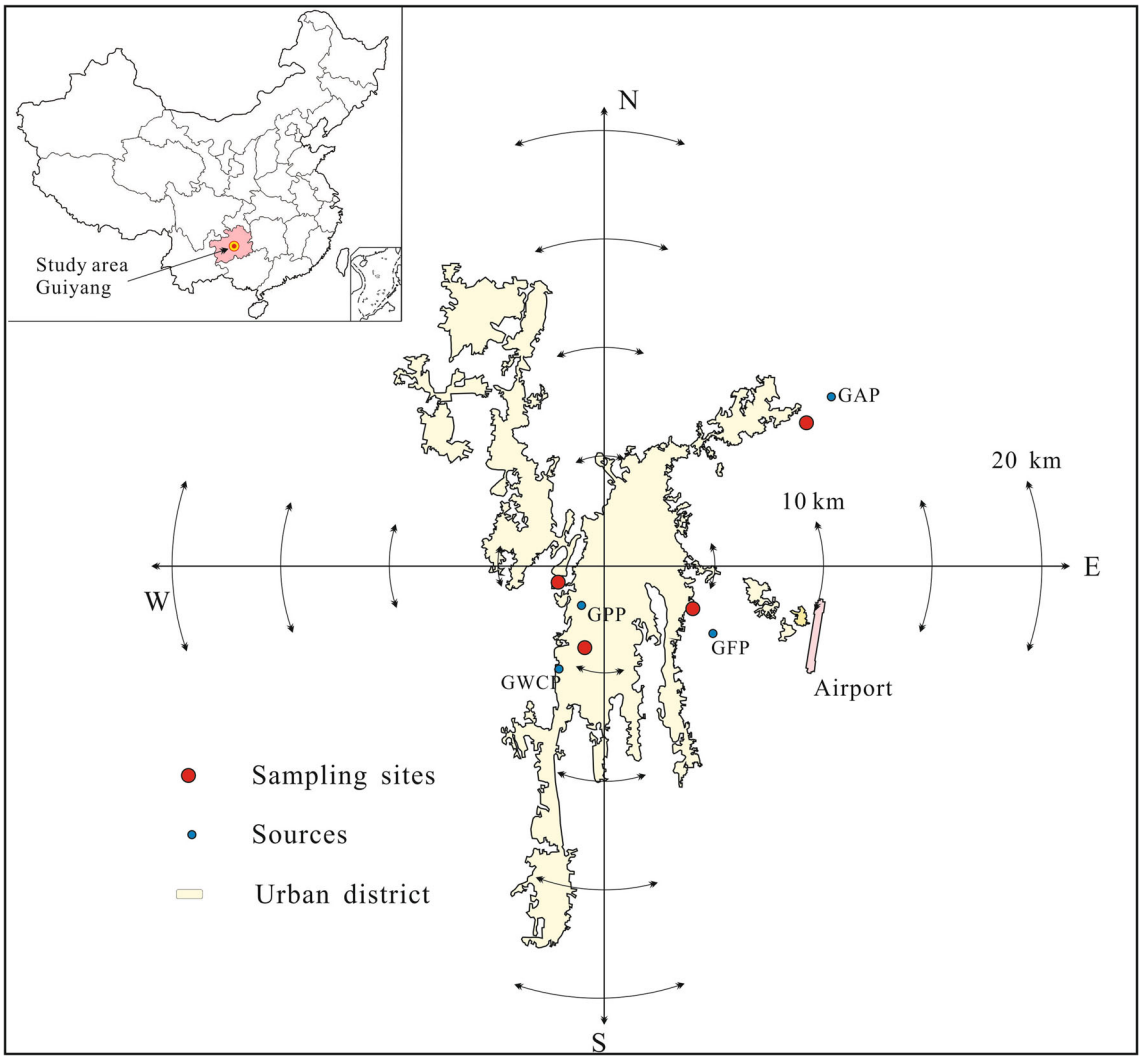

Fig. 1 Map of sampling sites in Guiyang, China

the denuder and particulate filter units was 10 $L \cdot min^{-1}$ (Landis et al. 2002). During the sampling campaigns, the sampling period of each PHg and RGM sample was 12 h—every day from 8:00 am to 8:00 pm with a final sample volume of 6 to 7.2 m^3. The inlet components of the PHg and RGM dredge were acid-cleaned. Annular denuders and PHg filters were pyrolyzed at 500 °C for about 30 min to produce operation blanks.

2.3 PHg and RGM analysis

Upon fulfillment of the sampling process, KCl-coated annular denuders and quartz filter assemblies were thermally decomposed in a Thermo Scientific Lindberg/Blue tube furnace (Model 55035C) at 525 °C for RGM and 800 °C for PHg. Then the Tekran 2537A CVAFS instrument was used to detect the thermally released Hg(0) in zero air gas. Further information about the analysis processes of RGM and Hg(0) via pyrolysis are described by previous studies (Lu et al. 1998; Feng et al. 2000; Landis et al. 2002). During the period of sampling, we calculated a detection limit of 0.89 $pg \cdot m^{-3}$ for RGM and PHg as three times the standard deviation of the average blank (0.97 ± 2.1 $pg \cdot m^{-3}$, $n = 120$) for the data collected. All the concentrations of RGM and PHg were blank calibrated.

2.3.1 Meteorological parameters

In this study, meteorological parameters of ambient air temperature, air pressure, relative humidity, wind direction, and wind speed were measured simultaneously with Hg species by the Guizhou Meteorological Administration (CAWS600-SE).

3 Results and discussion

3.1 GEM

Results for data obtained over the measurement periods at four sampling sites are summarized in Table 1. All dates mentioned in this section are 2011.

For the GPP site, concentrations of GEM in ambient air exhibited a wide range of 1.5 to 226 ng·m^{-3}, with an average value of 22 ng·m^{-3}. The maximum value was measured at 12:30 pm and the minimum value at 7:10 pm, both on October 12. As shown in Fig. 2, GEM exhibited elevated values during the day, with the highest values around noon, which is consistent with previous reports (Mazur et al. 2009; Song et al. 2009; Friedli et al. 2011).Three episodes of high GEM concentration were observed between October 4 and October 7; five-minute mean GEM levels reached or exceeded 80 ng·m^{-3} during each episode. The range of 8 to 16 ng·m^{-3} dominated the distribution, accounting for more than 66 % of all data (Fig. 3). The frequency of GEM concentrations was close to a lognormal distribution, which is similar to the study from Zhang et al. (2012a, b).

GEM levels remained below 20 ng·m^{-3} except for two episodes. The average GEM result at GPP was higher than those obtained at Shanghai, China; Alberta, Canada; and Alabama and New York; USA (Friedli et al. 2009; Mazur et al. 2009; Engle et al. 2010; Choi et al. 2013), reflecting an elevated contribution from local and regional sources in this study (Fu et al. 2011; Liu et al. 2011). These high GEM levels existed prior to October 8 and might be attributable to the shutdown of dust removal equipment; in China most of the dust removal equipment is artificially controlled (Li et al. 2014). During the Chinese national holiday period, which fell in the first 7 days of October in the study year, nearly all of the workers and regulators were not at work. If the dust removal equipment was indeed shut down, this implies it played a key role in the production process and that there were some control measures yet to be taken at the power plant (Wang et al. 2012).

For the GWCP site, the GEM in ambient air ranged from 3.58 to 55.28 ng·m^{-3}, with an average value of 13.2 ng·m^{-3}. The highest value was observed at 1:50 pm, October 23, and the lowest value at 5:45 am, October 20. The range of 5 to 12 ng·m^{-3} dominated the distribution, accounting for more than 60 % of all samples. The frequency of GEM concentrations displayed an approximately normal distribution. Similar to the study at GPP, the GEM diurnal pattern includes peak values at mid-day. During the sampling period, from October 19 to 24, there were four peaks in GEM (Fig. 2).

Few studies on environmental impacts of Hg emission caused by cement plants have been performed. The average value observed in this study at GWCP is much higher than the established global background mean values (1.5 to 1.8 ng·m^{-3}, Landis et al. 2002). The average GEM value is higher than those measured in New Jersey (Goodrow et al. 2005) and San Francisco (Rothenberg et al. 2010), USA; and in Seoul, Korea (Kim et al. 2009).

For the GAP site, the GEM concentrations ranged from 1.7 to 56.7 ng·m^{-3} with an average value of 5.1 ng·m^{-3}. The highest GEM concentration of 56.7 ng·m^{-3} was observed at 4:55 pm, September 18, and the lowest concentration at 11:00 am, September 15 (Fig. 2). The range of 3.0 to 8.0 ng·m^{-3} dominated the distribution, accounting for 79 % of all samples (Fig. 3). The frequency of GEM levels obeyed a typical normal distribution pattern. At GAP, the mean GEM value was lower than the average value obtained near an aluminum plant in the Slovak Republic (Haldíková et al. 2001); however, it was comparable to mean concentrations previously observed in Beijing and in other studies in Guiyang (Liu et al. 2002, 2011; Fu et al. 2012a, b).

Table 1 Summary of GEM, PHg, and RGM concentrations measured at four sampling sites in Guiyang, China

Samplings	Hg speciation	Mean	Median	Max	Min	SD	N
GPP	GEM (ng·m^{-3})	22	14	226	1.5	28	2645
	PHg (pg·m^{-3})	2000	1400	7100	600	1600	16
	RGM (pg·m^{-3})	68	42	300	12	76	16
GWCP	GEM (ng·m^{-3})	13	10	55	3.6	9.3	1664
	PHg (pg·m^{-3})	1100	800	3000	300	810	11
	RGM (pg·m^{-3})	41	34	76	12	19	11
GAP	GEM (ng·m^{-3})	6.1	5.1	57	1.7	3.9	1930
	PHg (pg·m^{-3})	56	57	73	36	11	11
	RGM (pg·m^{-3})	21	14	56	5.5	15	11
GFP	GEM (ng·m^{-3})	13	6.4	47	1.9	12	2323
	PHg (pg·m^{-3})	1700	1000	4900	480	1500	12
	RGM (pg·m^{-3})	39	30	140	15	34	12

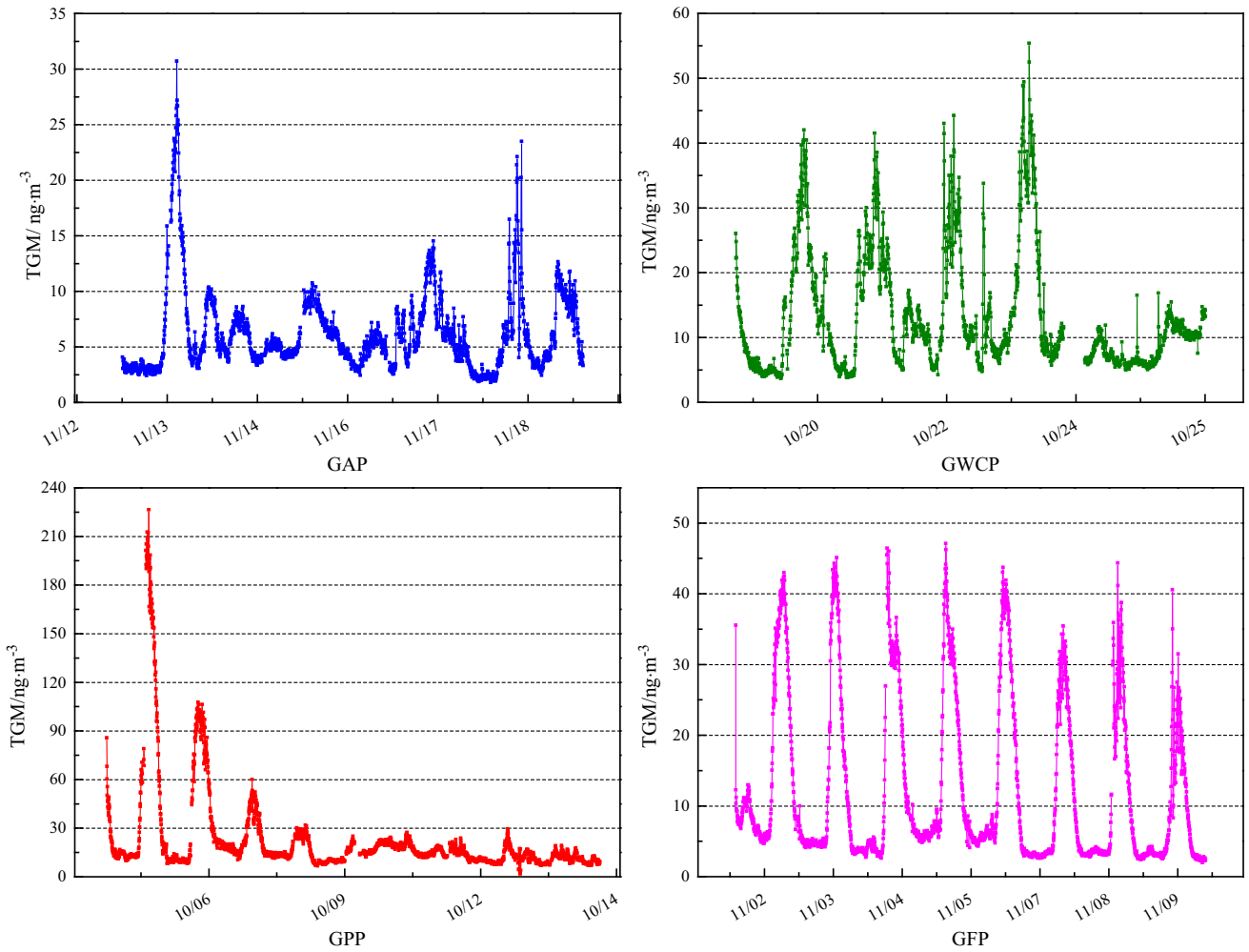

Fig. 2 The time sequence of 5minute mean GEM concentration in ambient air at sampling sites

At the GFP site, the GEM varied from 1.9 to 47 ng·m^{-3} with a mean value of 12.58 ng·m^{-3}. Most data fell in the range of 3 to 11 ng·m^{-3}, which accounts for 91.8 % of measurements. The highest concentration of 47 ng·m^{-3} was measured at 9:50 am November 5, and the lowest concentration of 1.88 ng·m^{-3} at 10:35 pm November 9. Being a scenic area, at first GFP was chosen as a background site. Interestingly, daily peaks in GEM were observed during the sampling campaign at GFP, which did not conformed to the expected results. As one of a "by-product" emission, an iron/steel production factory was found situated in the northwest of the sampling site of GFP, which may contribute a lot to the elevated results obtained at GFP (Streets et al. 2005; Pacyna et al. 2010). Also, a lot of barbecue activities were being held at GFP, with charcoal used as the main fuel. Biomass burning is an important source of Hg in the atmosphere (Hall et al. 2014) which might be related to the large number of barbecue activities with coal combustion in the immediate vicinity (Wan et al. 2009). The average GEM level was higher than results previously reported in Guiyang (Feng et al. 2003; Fu et al. 2008; Liu et al. 2011). Considering GFP as a background site in an urban area, the average concentration is comparable to results achieved in Changchun (Fang et al. 2004), but much higher than a study conducted in Canada (Sigler et al. 2003).

The GEM concentrations in the air of the four sites displayed similar periodic changes. A 24-hour time series is illustrated in Fig. 4, reflecting the emission characteristics of GEM from four anthropogenic sites. The GEM concentrations of all four sites presented an early-to-mid morning increase and a later declining trend, with peak values usually recorded at mid-day (10:00 am to 2:00 pm).

The mean concentrations of GEM decreased in the order GPP>GWCP>GFP>GAP. The concentration of GEM at GPP was nearly twice the concentration of GEM at the other three sites. As the second largest anthropogenic Hg sources in Guiyang, cement plants, represented here by

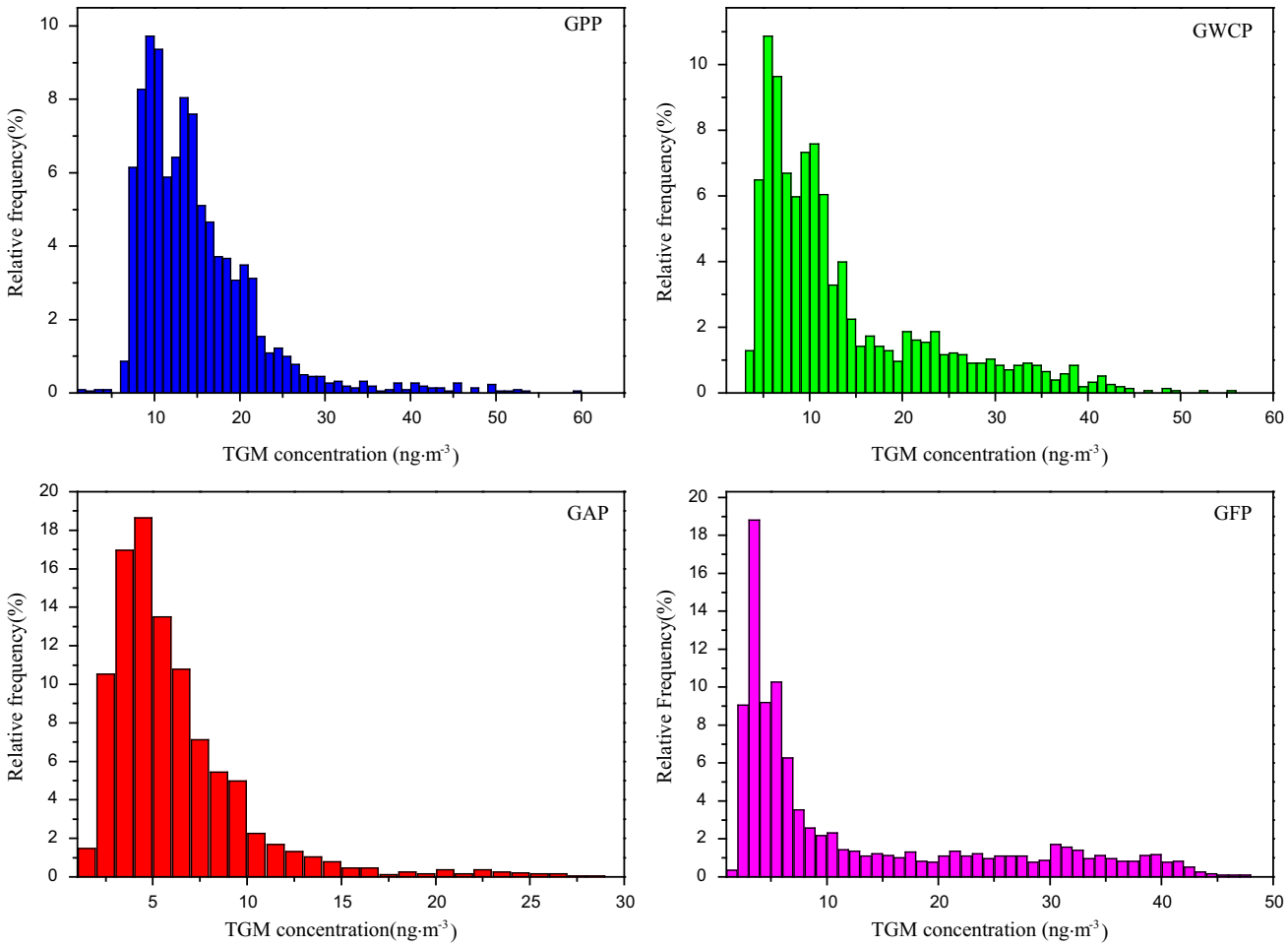

Fig. 3 Relative frequency plot of GEM distribution data obtained at sampling sites

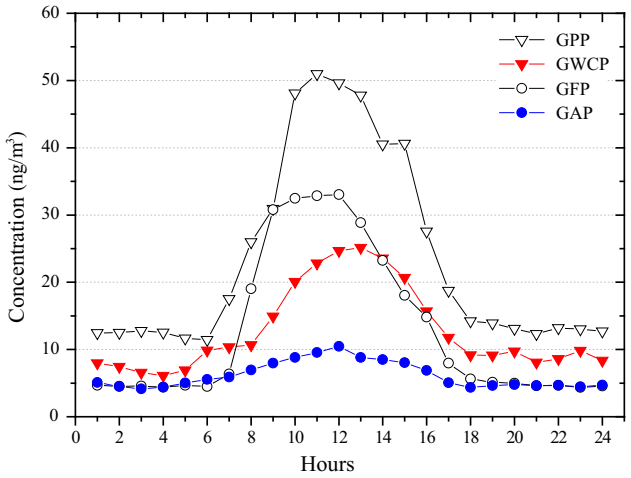

Fig. 4 Time series for GEM at four sampling sites

GWCP, are characterized by highly concentrated alkaline solids containing sodium and potassium oxides; high concentrations of CaO contribute to an environment that effectively captures gaseous species (Zheng et al. 2012). Interestingly, GAP, as a non-ferrous metal plant, was not contributing as much as the other sites. Compared to the other sites, the low average GEM at GAP may be due to the typical procedure of primary smelting, in which Hg removal efficiency was over 99 % (Zhang et al. 2012a, b).

Except at GAP, the average GEM values in this study are comparable to the average reported in Changchun, China (Fang et al. 2004), but much higher than the data from the other urban areas in Table 2. Previous GEM observations in the same research area were higher than those reported here; Feng et al. (2004), Fu et al. (2011), and Liu et al. (2011) reported mean values of 8.4 $ng \cdot m^{-3}$ in 2001, 9.72 $ng \cdot m^{-3}$ in 2009, and 7.4 $ng \cdot m^{-3}$ in 2009, respectively. In comparison with the global background concentration of 1.5 to 1.8 $ng \cdot m^{-3}$ (Landis et al. 2004), the GEM concentrations obtained in this study are all notably high. Elevated GEM in this study verified previous studies in this area, which have suggested that GEM in ambient air is influenced by coal combustion, cement production, non-

Table 2 Atmospheric Hg speciation in Guiyang compared to other cities worldwide

Locations	GEM ($ng \cdot m^{-3}$)	PHg ($pg \cdot m^{-3}$)	RGM ($pg \cdot m^{-3}$)	Time	References
China					
Guiyang	9.14 ± 4.64			Nov 2009	Feng et al. (2003)
	7.09		37.5		Shang et al. (2003)
	10.54 ± 10.26			Nov 2002	Feng et al. (2004)
	9.72 ± 10.2	368 ± 676	35.7 ± 43.9	Aug–Dec 2009	Fu et al. (2011)
	7.4	1330	24	Sep–Nov 2009	Liu et al. (2011)
	6.2	250	19	Feb, May, Jul, 2009	
Shanghai		330–560		Mar 2002–Sep 2003	Xiu et al. 2009
Shanghai	2.7 ± 1.7			Aug–Sep 2009	Friedli et al. (2011)
Changchun	18.4	276		Jul 1999–Jan 2000	Fang et al. (2004)
Canada					
Toronto	4.5 ± 3.1	21.5 ± 16.4	14.2 ± 13.2	Dec 2003–Nov 2004	Song et al. (2009')
USA					
Tuscaloosa	4.05 ± 1.28	16.4 ± 19.5	13.6 ± 20.4	Jun–Jul 2003	Gabriel et al. (2005)
Milwaukee	2.48 ± 1.67	11.8 ± 0.3	10.3 ± 0.2	Jun 2004–May 2005	Rutter et al. (2010)
East St. Louis	4.6 ± 6	483 ± 1954	737 ± 2862	Oct–Dec 2002	Manolopoulos et al. (2007)
Detroit	2.2 ± 1.3	20.8 ± 30.0	17.7 ± 28.9	2003	Liu et al. (2007)
Korea					
Seoul	3.22 ± 2.10	23.9 ± 19.6	27.2 ± 19.3	Feb 2005–Feb 2006	Kim et al. (2009)
China					
Miyun, Beijing	3.23	98.2	10.1	Dec 2008–Nov 2009	Zhang et al. 2013
Beijing	5.3–9			Jan, Feb, and Sep 1998	Liu et al. (2002)
The Slovak republic					
Krompachy	14.2	1560		1996–1997	Haldíková et al. (2001)
USA					
San Francisco	2.2 ± 1.39	25.2 ± 52.8	80.8 ± 283	2008	Rothenberg et al. 2010
Alabama	1.64	2.83	3.8	Spring, Summer, Winter	Engle et al. (2010)
New York	1.6	8.7	5.6	Dec 2007–Nov 2009	Choi et al. (2013)
Canada					
Alberta	1.57 ± 0.29			2005–2007	Mazur et al. (2009)

ferrous metals, and other industrial activity (Feng et al. 2003, 2008; Fu et al. 2011; Liu et al. 2011).

3.2 PHg and RGM

High PHg concentrations and notable diurnal variations were observed at all four sites in Guiyang (Table 1).The highest average PHg concentration of 1984.9 $pg \cdot m^{-3}$ was found at GPP, with a range of 600–7067.8 $pg \cdot m^{-3}$, while the lowest average of 55.9 $pg \cdot m^{-3}$ was at GAP, with a range of 36.3–73.2 $pg \cdot m^{-3}$. At GFP, the average PHg concentration was 1651.8 $pg \cdot m^{-3}$, with a range of 474–4891.5 $pg \cdot m^{-3}$, and at GWCP the average PHg concentration was 1082.8 $pg \cdot m^{-3}$, with a range of 297.4–2966.5 $pg \cdot m^{-3}$. The average percentage of PHg relative to GEM at the four study sites was 9.02 %, 8.20 %, 0.91 %, and 13.13 % at GPP, GWCP, GAP, and GFP, respectively.

The PHg values at GPP, GFP, and GWCP were comparable to the study at Guiyang Monitoring Station Agency (GMSA), but higher than those observed at IGCAS, a residential area in Guiyang (Liu et al. 2011). Results observed at GPP, GWCP, and GFP were much higher than those in other cities in China, such as Beijing, Shanghai, and Changchun (Fang et al. 2004; Xiu et al. 2009; Zhang et al. 2013). Fu et al. (2008) and Wan et al. (2009) obtained PHg concentrations of 31 and 77 $pg \cdot m^{-3}$ at Mt. Gongga, Sichuan Province, and Mt. Changbai, Jilin Province, respectively. The data collected at GAP are comparable to background values of 1–86 $pg \cdot m^{-3}$ (Keeler et al. 1995); the levels at GPP, GFP, and GWCP were considerably higher than northern hemisphere background values of <1.0–86 $pg \cdot m^{-3}$ (Keeler et al. 1995; Jaffe et al. 2005). Compared to locations in North America, Europe, and Asia, such as Detroit (Liu et al. 2007), Tuscaloosa (Gabriel et al. 2005), Milwaukee (Rutter et al. 2010), San

Francisco (Rothenberg et al. 2010), Alabama (Engle et al. 2010), New York (Choi et al. 2013), East St. Louis (Manolopoulos et al. 2007), and Toronto (Song et al. 2009) in North America, Krompachy in the Slovak Republic, Europe (Haldíková et al. 2001), and Seoul in Korea (Kim et al. 2009), PHg concentrations in Guiyang were much higher and showed different patterns.

The RGM levels at the four research sites showed different distribution characteristics (Table 2). The highest average RGM concentration of 68.22 pg·m^{-3} (and ranging from 12.07 to 302.53 pg·m^{-3}) was documented at GPP. The lowest average RGM concentration of 20.5 pg·m^{-3} (and ranging from 5.48 to 56.48 pg·m^{-3}) was observed at GAP. At GWCP and GFP, similar average RGM values of 40.90 and 38.68 pg·m^{-3} were obtained, with ranges of 12.40–76.1 pg·m^{-3} and 14.90–143.28 pg·m^{-3}, respectively.

3.3 Day- and night-time distributions

The daily average values of RGM concentrations at the four sites showed a temporal change (Fig. 5). At GPP and GWCP, the concentrations of RGM were symbolized by large variability; however, low variability was obtained at GFP and GAP. The mean GEM values in the daytime at GPP, GFP, and GAP (17.19, 23.03, and 7.53 ng·m^{-3}, respectively,) were notably higher than nighttime values (12.52, 5.35, and 4.72 ng·m^{-3}, respectively). In contrast, the average GEM concentration of 10.67 ng·m^{-3} at GWCP in the daytime was lower than the 17.98 ng·m^{-3} nighttime average. The average PHg concentrations at GPP, GWCP, and GFP also exhibited diurnal variability. The daytime mean concentrations at GWCP and GFP, which were

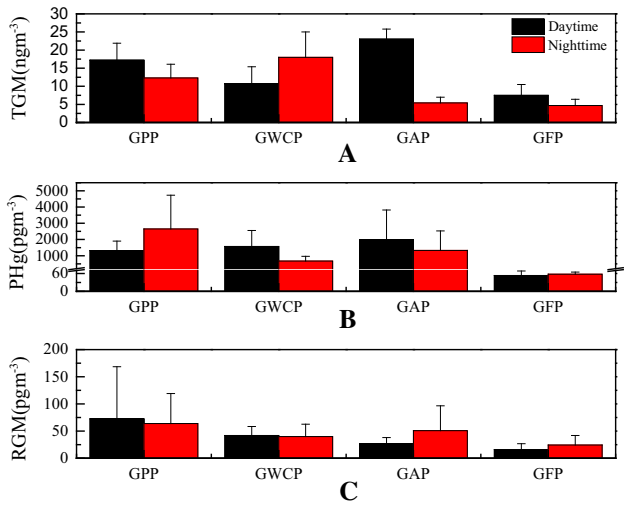

Fig. 5 Average GEM, PHg, and RGM daytime and nighttime values at four sites in Guiyang, China

1571.6 and 1978.5 pg·m^{-3}, were significantly higher than nighttime means of 675.5 and 1325 ng·m^{-3}. However, the average daytime PHg concentration at GPP, 1317.6 pg·m^{-3}, was much lower than that measured during the night—2652.2 pg·m^{-3}. With regard to GAP, the mean concentration of PHg was less variable: 53.55 pg·m^{-3} in daytime, 57.88 pg·m^{-3} in nighttime. The daytime levels of RGM were not significantly different from nighttime. The average RGM levels in daytime at GPP and GWCP were 72.60 and 41.93 pg·m^{-3}, roughly comparable to those in nighttime, 63.85 and 40.04 pg·m^{-3}, respectively. However, the mean values at GFP and GAP of 26.52 and 15.96 pg·m^{-3} during the daytime were significantly lower than those at nighttime (50.83 and 24.28 pg·m^{-3}). The conversion rate from GEM to RGM would be expected to decrease with ambient temperature, as would RGM concentrations (Lynam and Keeler 2005; Poissant et al. 2005).

A similar variability between RGM and PHg has been demonstrated in previous studies (Wan et al. 2009; Liu et al. 2011). For GWCP, the RGM value is quite similar to the results achieved at a cement plant in San Francisco (Rothenberg et al. 2010). The ratio of RGM to GEM was around 0.3 %, which was significantly lower than the corresponding PHg ratio of around 10 %. Similar to the previous study in the area, the lower RGM ratios may be due to the gas to particle conversion facilitated by the relatively high concentrations of total $PM_{2.5}$ mass (Liu et al. 2011). The high levels of PHg were in parallel to occasional high peaks of RGM, demonstrating the effect of predominant home heating or other combustion mercury sources in Guiyang (Kim and Kim 2000). It is feasible that RGM concentrations obtained may be affected by input of RGM-containing air from a higher layer, solar radiation, or in situ photochemical processes and oxidation of GEM (Swartzendruber et al. 2006; Fain et al. 2009; Liu et al. 2010; Sheu et al. 2010). Further research on atmospheric Hg speciation is necessary in order to understand the pollutant's fate after being released.

Our results are quite different from previous studies in several respects; the collected RGM values at GPP, GWCP, and GFP were much higher than GAP in our research, and only GAP was at the same level reported in previous studies in Guiyang (Shang et al. 2003; Zheng 2007; Liu et al. 2010, 2011; Fu et al. 2011; Gratz et al. 2013). However, the RGM average value of 20.50 pg·m^{-3} at GAP was comparable to the value reported by Liu et al. (2010) in Guiyang. In suburban, rural, and remote areas of China, Fu et al. (2008, 2012a), Wan et al. (2009), and Xu et al. (2015) reported RGM levels of 6.2 pg·m^{-3} in Mt Gongga, 7.4 ± 4.8 pg·m^{-3} in Mt. Waliguan, 65 pg·m^{-3} in Mt. Changbai, and 61.05 pg·m^{-3} in Xiamen.

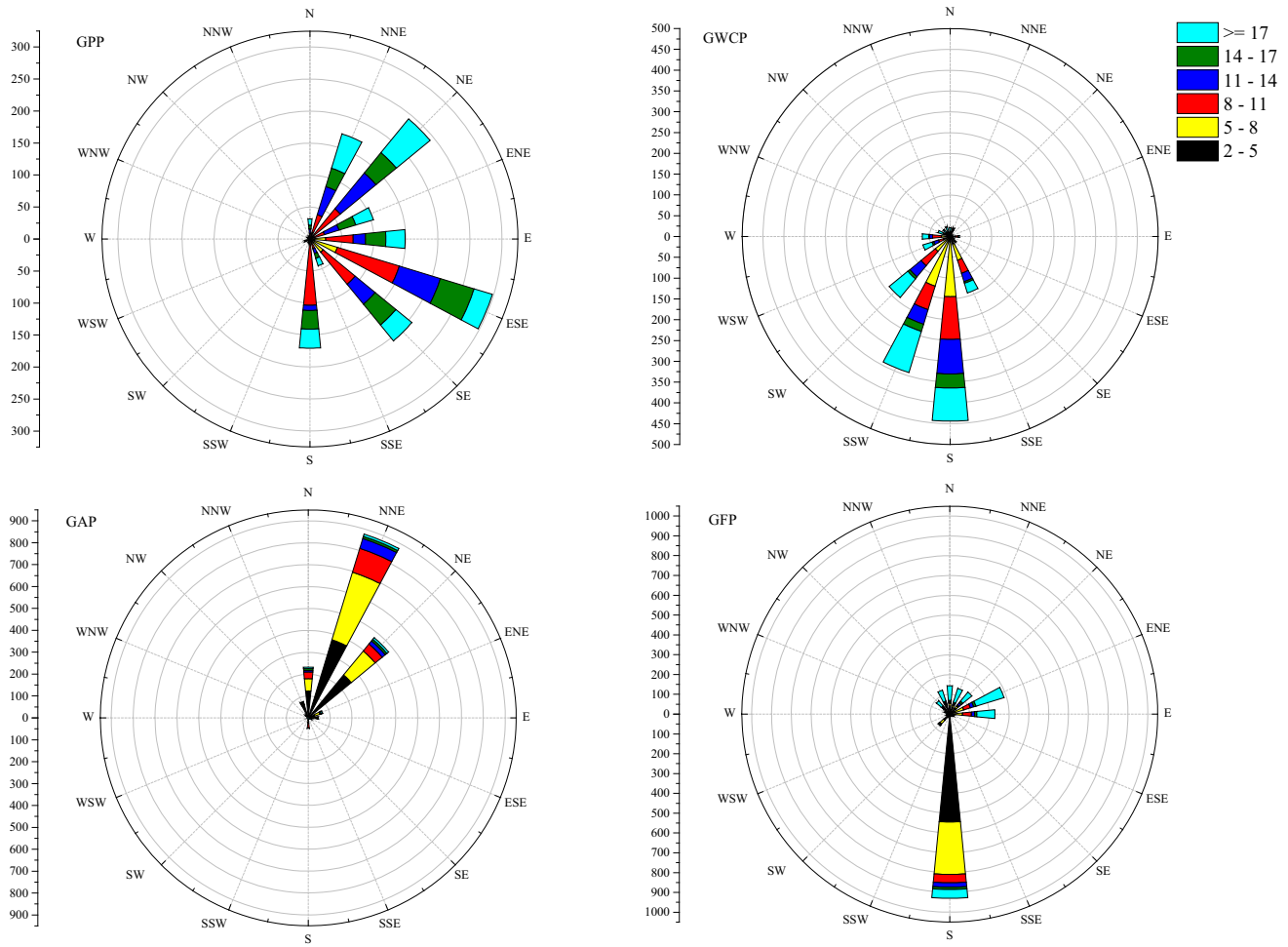

Fig. 6 Frequency of wind directions and GEM concentrations in wind directions at four sites in Guiyang, China

3.4 Potential atmospheric Hg contribution in Guiyang

The frequency angular distributions of GEM classified into six levels at four sites are depicted in Fig. 6. At GPP, the prevailing wind directions were from the southeast, east, and northeast (22.5°–180°). The dominant winds obtained at GWCP were from the southwest and south (180°–225°); downwind were the main urban areas of Guiyang (Liu et al. 2011). At GFP, the wind directions were confined to the southern sector, indicating that during the sampling period, GEM from GFP would have been the main source of pollution for areas in Guiyang. At GAP, winds were dominantly in the northern and northeastern sector (0°–65°), with a frequency of 87.1 %, which would also have contributed GEM to the main urban areas. The previous study conducted at IGCAS suggested two main emissions from GWCP and GPP play a key role in elevated GEM in IGCAS (Fu et al. 2011; Liu et al. 2011). Though all the sources except for GAP can release Hg into the ambient air constantly, all the data collected at the other three sites were higher than previous studies (Feng et al. 2003, 2004; Shang et al. 2003; Fu et al. 2011; Liu et al. 2011). The combined effect of location, concentration, prevailing winds, and the other factors mentioned, resulted in the contribution order of different sources being GPP, GWCP, GFP, and GAP from highest to lowest. Some measures are urgently needed to curb atmospheric Hg pollution from typical emission sources in the area.

4 Conclusions

This study presents data on atmospheric Hg speciation emitted from four typical anthropogenic sources at GPP, GWCP, GFP, and GAP in Guiyang, southwestern China. For GEM, the contribution order is GPP>GWCP> GFP>GAP. The levels of PHg and RGM follow similar orders: GPP>GFP>GWCP>GAP, and GPP>GWCP> GFP>GAP, respectively. In this study, two factors may

ascribe to the elevated results in these four typical areas: (1) the backward dust removal equipment, which had a low particle-removal efficiency during processing and (2) the cold weather during the campaigns, which can decrease the conversion rate of GEM to RGM. From the distribution of GEM, we can speculate as to its affected areas, and check the contribution rate. Long-term measurements of these typical sites can be conducted in the future to identify regional mercury sources, and to develop a specific Hg-emission inventory in Guiyang. Other parameters are needed to establish and perfect the pre-warning mechanism for pollution in future.

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