Speciated Atmospheric Mercury during Haze and Non-haze Days in an Inland City in China

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Abstract. Long-term continuous measurements of speciated atmospheric mercury were conducted at Hefei, a mid-latitude inland city in east central China, from July 2013 to June 2014. The mean concentrations (± standard deviation) of gaseous elemental mercury (GEM), reactive gaseous mercury (RGM) and particle-bound mercury (PBM) were 3.95 ± 1.93 ng m\(^{-3}\), 2.49 ± 2.41 pg m\(^{-3}\) and 23.3 ± 90.8 pg m\(^{-3}\), respectively, during non-haze days, and 4.74 ± 1.62 ng m\(^{-3}\), 4.32 ± 8.36 pg m\(^{-3}\) and 60.2 ± 131.4 pg m\(^{-3}\), respectively, during haze days. Potential source contribution function (PSCF) analysis suggested that the atmospheric mercury pollution during haze days was caused primarily by local mercury emissions, instead of via long-range mercury transport. In addition, the disadvantageous diffusion during haze days will also enhance the level of atmospheric mercury. Compared to the GEM and RGM, change in PBM was more sensitive to the haze pollution. The mean PBM concentration during haze days was 2.5 times that during non-haze days due to elevated concentrations of particulate matter. A remarkable seasonal trend in PBM was observed with concentration decreasing in the following order in response to the frequency of haze days: autumn, winter, spring, summer. A distinct diurnal relationship was found between GEM and RGM during haze days, with the peak values of RGM coinciding with the decline in GEM. Using HgOH as an intermediate product during GEM oxidation, our results suggest that NO\(_2\) aggregation with HgOH could explain the enhanced production of RGM during the daytime in haze days. Increasing level of NOx will potentially accelerate the oxidation of GEM despite the decrease of solar radiation.
1. Introduction

Mercury (Hg) is an environmental pollutant that has received much global attention because of its toxicity and bioaccumulation via the aquatic food chain. The most important transport pathway of mercury is via the atmosphere (Schroeder and Munthe, 1998; Lindqvist and Rodhe, 1985). Operationally, atmospheric mercury is commonly differentiated into three forms: gaseous elemental mercury (GEM), reactive gaseous mercury (RGM) and particle-bound mercury (PBM). The sum of these three atmospheric speciated mercury is defined as total atmospheric mercury (TAM = GEM + RGM + PBM), and the sum of GEM and RGM is known as total gaseous mercury (TGM = GEM + RGM) (Gustin and Jaffe, 2010; Gustin et al., 2015). GEM is regarded as the predominant form of atmospheric mercury, accounting for over 95% of the total. GEM is stable in the atmosphere with a long residence time (0.5–2 yr) and can be transported at the regional to global scale (Schroeder and Munthe, 1998; Lindberg et al., 2007). GEM can be oxidized to RGM through photochemical processes, and further transformed to PBM on aerosol surfaces. Although GEM is the predominant form of mercury in the air, trace amounts of RGM and PBM control the mercury scavenged from the atmosphere (Lindberg and Stratton, 1998). RGM and PBM can be readily removed from the air by wet and dry deposition as a result of their high surface reactivity and water solubility (Lindqvist and Rodhe, 1985). Thus, the chemical transformations between GEM, RGM and PBM will directly influence the atmospheric lifetime of mercury.

As a result of the rapid industrial development and economic growth of recent decades, China has become one of the major contributors to anthropogenic mercury emissions to the environment (Wu et al., 2006; Pacyna et al., 2006; Streets et al., 2005).
Atmospheric mercury emissions from anthropogenic sources in China have been estimated to be in the range of 500-700 tons/yr, accounting for 25-30% of the total global anthropogenic mercury emissions (Streets et al., 2005; Wu et al., 2006). Research into atmospheric mercury in China is therefore critical to the understanding of mercury cycling at both regional and global scales. Long-term observation of atmospheric mercury has been conducted in different regions in China, including both urban and remote areas. TGM concentrations observed in urban and industrial regions of China were in the range of 2.7–35 ng m$^{-3}$, higher than the values reported for North America and Europe, and for the adjacent Asian countries such as Korea and Japan (Stamenkovic et al., 2007; Dommergue et al., 2002; Fang et al., 2009). TGM and PBM concentrations in remote areas of China were also found to be higher than those observed in North America and Europe (Fu et al., 2008a; Fu et al., 2008b; Fu et al., 2012; Liu et al., 2010).

In recent years, haze pollution has become a major concern in China due to its impacts on visibility, air quality, and climate. It is well known that haze formation is mainly dependent on the atmospheric relative humidity (RH) and the concentration of airborne particles (Chen et al., 2003; Sun et al., 2013). Most studies on haze have focused on the measurements of airborne particulate matter; few examined the influence of haze on the chemistry of atmospheric mercury, especially PBM. In this study, we conducted one year synchronous observations of speciated atmospheric mercury in Hefei, an inland city of China, which experiences frequent haze events. The comparison of atmospheric mercury under haze days and non-haze days during the study period allows us to examine the formation and deposition mechanisms of mercury, as well as their temporal variations.
2. Methods

2.1 Study site

Continuous measurements of speciated atmospheric mercury were undertaken in Hefei (31°52′ N, 117°17′ E) from July 2013 to June 2014. Hefei, the capital of Anhui Province, is located in east central China, between the Changjiang (Yangtze River) and the Huaihe (Huai River). Hefei has a humid subtropical climate with four distinct seasons: June-August is considered summer, September-November autumn, December-February winter and March-May spring. The prevailing wind is southeasterly in summer and northwesterly in winter. Like many Chinese cities, Hefei has experienced rapid growth in the past 20 years. The total permanent population is about 7.7 million.

The monitoring site was located on the Science Island, a small peninsula on the Dongpu Reservoir in the northwestern outskirts of Hefei (Fig. 1). The sampling and analytical instruments were installed 1.5 m above the rooftop (~ 20 m above the ground) of the main building of Anhui Institute of Optics and Fine Mechanics. Further information about the monitoring site can be found in a previous study (Hu et al., 2014). We chose this area as the monitoring site because it is one of the cleanest areas in Hefei, not adjacent to any direct pollution sources such as power plants, iron and steel works.

2.2 Measurements of speciated atmospheric mercury

From July 2013 to June 2014, simultaneous measurements of speciated atmospheric mercury concentrations were performed by an automated Tekran™ mercury speciation system. The system consisted of a Model 2537B mercury analyzer.
combined with a Model 1130 RGM unit and a Model 1135 PBM unit. The system was configured to measure GEM every 5 min., and RGM and PBM every 2 two hr.

The details about the Tekran-based mercury speciation system can be found in Landis et al. (2002). In general, the automated measurement process can be summarized as sample collection, thermal desorption and determination. During the collection period, ambient air was drawn to the system at a flow rate of 10 L/min. RGM and PBM in the air were captured by a KCl-coated quartz annular denuder in the 1130 unit and a quartz filter in the 1135 unit, respectively, whereas GEM would pass through the denuder and filter and be quantified on the Tekran 2537B by cold-vapor atomic fluorescence spectroscopy (CVAFS). After an hour of sampling, the 1135 quartz filter and the 1130 denuder would be switched to the thermal decomposition mode at 800°C and 500°C, respectively, with the resulting Hg⁰ quantified by the 2537B unit in the next hour, while the 1135 and 1130 components were flushed with zero-mercury gas for the next sampling.

The instrument maintenance followed typical protocols used in similar studies (Landis et al., 2002; Hu et al., 2014). The quartz annular denuder was recoated every two weeks, the quartz filter was replaced once a month, and the Teflon filter (pore size 0.2 µm) in the sample inlet was changed every two weeks. Automated recalibration of the Tekran 2537B was performed every 25 h using an internal mercury permeation source. No calibration standards were available for RGM and PBM, but the 1σ precision for RGM and PBM was about 15 % (Landis et al., 2002). The detection limit in ambient air is about 0.5 ng m⁻³ for GEM (or TGM) at a resolution of 5 min, and 1 pg m⁻³ for RGM and PBM at a resolution of 2 h (Gustin et al., 2015). Although the Tekran-based mercury speciation technique has been widely used around the
world, recent studies have shown that the technique does not efficiently collect all gaseous oxidized mercury and thus may substantially underestimate the concentration of reactive mercury (Huang et al., 2013; Gustin et al., 2013). Therefore, the RGM values reported in this study should be considered as the lower limits of gaseous oxidized mercury in the air (Wang et al., 2014).

2.3 Ancillary Data

Standard meteorological measurements including air temperature, air pressure, RH, wind direction and speed were observed with a 5-min resolution. CO was measured by an automated infrared carbon monoxide analyzer (Model EC9830T, Ecotech Inc., Australia), with a detection limit of 40 ppbv. O₃ was measured every 5 min by an ozone analyzer (Model EC9810B, Ecotech Inc., Australia); its detection limit and accuracy are 0.5 ppbv and 0.001 ppm, respectively. NO₂ was measured by a Multi axis differential optical absorption spectroscopy (MAX-DOAS) instrument. The collected spectra were analyzed using the QDOAS spectral fitting software suite developed at BIRA-IASB (http://uv-vis.aeronomie.be/software/QDOAS/). We used the geometric approximation for conversion between slant column densities (SCDs) and vertical column densities (VCDs) (Ma et al., 2013). PM₂.₅ (particulate matter less than 2.5 μm in diameter) data are collected from China air quality online analysis platform (http://www.aqistudy.cn/historydata/index.php). In addition, 24-hr PM₁₀ (particulate matter less than 10 μm in diameter) samples were collected on glass-fiber filters by a high-volume sampler during heavy pollution episodes (from 10 Nov to 9 Dec 2013, n=11). Water-soluble ions in the PM₁₀ samples were determined by ion chromatography (Model ICS-2100, Dionex). In order to identify the potential source
of mercury, NASA's satellite hotspots/fire locations information were obtained from the Fire Information for Resource Management System (FIRMS) (https://firms.modaps.eosdis.nasa.gov/firemap/).

2.4 Potential Sources Contribution Function (PSCF) analysis

To identify the possible influence of long-range transport on the distribution of atmospheric mercury in Hefei, we calculated backward trajectories of air masses using the HYSPLIT (Hybrid Single-particle Lagrangian Integrated Trajectory) model with the Global Data Assimilation System (GDAS 1°) developed by the National Oceanic and Atmospheric Administration (NOAA) (http://www.ready.noaa.gov (Draxler and Hess, 1998). Considering the atmospheric pollutants are mainly concentrated in the low altitude during heavy pollution days, the trajectory arrival heights were set at 500 m to represent the boundary layer where atmospheric pollutants were well mixed. In this study, 5-day back-trajectories were calculated in ensemble forms which calculate 27 trajectories from the selected starting point (31°52’N, 117°17’E) (Fain et al., 2009).

The contributions of other pollution source regions to the atmospheric mercury at Hefei was identified by the Potential Sources Contribution Function (PSCF) analysis with the TrajStat software (Wang et al., 2009). PSCF analysis has been shown to be useful in spatially identifying pollution sources for pollutants with a long lifetime such as elemental mercury and CO (Xu and Akhtar, 2010). The PSCF values for the grid cells in the study domain were calculated by counting the trajectory segment endpoints that terminate within each cell. The number of endpoints that fall in the $i$th cell is designated as $N_{ij}$. The number of endpoints for the same cell corresponding to
the atmospheric mercury concentration higher than an arbitrarily set criterion (4 ng m$^{-3}$ which was the mean GEM concentration during the whole study period) is defined to be $M_{ij}$. The PSCF value for the $ij$th cell is then defined as:

$$\text{PSCF}_{ij} = \frac{M_{ij}}{N_{ij} W_{ij}}$$  \hspace{1cm} (2)

$W_{ij}$ is an arbitrary weight function to reduce the effect of small values of $N_{ij}$. The PSCF values were multiplied by $W_{ij}$ to better reflect the uncertainty in the values for these cells (Polissar et al., 2001). The weight function reduces the PSCF values when the total number of endpoints in a particular cell is less than 3 times the average value of the end points per cell:

$$W_{ij} = \begin{cases} 
1.0 & N_{ij} \geq 3N_{\text{ave}} \\
0.70 & 3N_{\text{ave}} > N_{ij} \geq 1.5N_{\text{ave}} \\
0.40 & 1.5N_{\text{ave}} > N_{ij} \geq N_{\text{ave}} \\
0.20 & N_{\text{ave}} > N_{ij} 
\end{cases}$$  \hspace{1cm} (3)

3. Results

We intended to continuously monitor speciated atmospheric mercury concentration over the course of a year; however, interruptions were inevitable due to instrument maintenance, which resulted in loss of data for the following four periods: (1) 25 September to 9 October 2013; (2) 5-14 November 2013; (3) 9-25 February 2014; and (4) 1-14 April 2014. The rest of the data were grouped into haze days and non-haze days according to the China Meteorological Administration’s haze standard (QX/T 113-2010). Haze days refer to the days when the atmospheric visibility < 10 km and RH < 80% (Duan et al., 2016), and non-haze days refer to clear days with the atmospheric visibility > 10 km. The visibility and RH information were collected from the weather history data at the Luogang Airport of Hefei.
Through the study period of almost a year, a total of 56 days were identified to be haze days, and 253 days to be non-haze days. All the times reported herein are local time (UTC + 8 hr).

3.1 Overall characteristics of speciated atmospheric mercury

The time series of GEM, RGM and PBM concentrations at the study site throughout the study period are shown in Fig. 2, and their frequency distributions are shown in Fig. S1 (in the supporting information). The mean (± standard deviation) GEM, RGM and PBM concentrations during the whole study period were $4.07 \pm 1.91$ ng m$^{-3}$, $3.67 \pm 5.11$ pg m$^{-3}$, and $30.0 \pm 100.3$ pg m$^{-3}$, respectively (Table 1). The GEM concentrations in different seasons did not differ much. The highest GEM concentration occurred in autumn ($4.51 \pm 2.10$ ng m$^{-3}$), while the lowest in spring ($3.89 \pm 1.79$ ng m$^{-3}$). RGM concentrations varied greatly during the study period with much higher concentrations in autumn and the lowest in winter. A similar seasonal variation in the RGM concentration was observed at a remote site in Mt. Gongga of southwest China (Fu et al., 2008b). The seasonal trend in PBM was also observed in Hefei with its concentration decreasing in the following order: autumn > winter > spring > summer. The mean PBM concentration during the cold season was about 20 times that in summer, similar to the findings from many previous studies in China (Zhang et al., 2013; Fu et al., 2011; Fu et al., 2008b; Fang et al., 2001).

Comparisons of speciated atmospheric mercury concentrations with other urban and rural areas in China and a few other countries are shown in Table 2. The mean GEM concentration at Hefei is slightly higher than that in many remote areas in China (Fu et al., 2008a; Fu et al., 2008b; Fu et al., 2012; Wan et al., 2009a; Wan et al., 2010).
239 2009b; Zhang et al., 2015a), but is much lower than those in urban areas of industrial
240 cities such as Guiyang and Changchun where large point sources of mercury exist
241 (e.g., non-ferrous metal smelting, coal-fired power plants, and residential coal burning)
242 (Feng et al., 2004; Fu et al., 2011; Fang et al., 2004). Although Hefei is geographically
243 close to Shanghai, a mega urban centre in China, it is interesting to note that the TGM
244 concentration of Shanghai is much lower than that of Hefei. This may be due to the
245 fact that Shanghai is a coastal city that is influenced more by cleaner marine air
246 masses (Friedli et al., 2011). Table 2 also shows that the average concentration of
247 GEM in Hefei is typically more than two folds that in the urban and rural areas in
248 Europe and North America.

249 3.2 Speciated atmospheric mercury during non-haze days

250 The frequency distribution of GEM, RGM and PBM for the non-haze period are
251 shown in Fig. S1 (in blue). The mean concentration of GEM was 3.95 ± 1.93 ng m⁻³.
252 Its distribution was characterized by large fluctuations ranging from 0.2 to 23.8 ng
253 m⁻³, although more than half of the GEM values were in the narrow range 2-4 ng m⁻³.
254 The mean concentration of RGM was 2.49 ± 2.41 pg m⁻³ with a range of 0.5-33.5 pg
255 m⁻³, although most of the values were in the range of 1-4 pg m⁻³. High concentrations
256 of RGM (exceeding 10 pg m⁻³) only accounted for 1.4% of the total data. The mean
257 RGM concentration at the Hefei site is much smaller than that reported from other
258 study sites in China (Table 2), but is comparable to the values observed from many
259 European and North American sites (Brooks et al., 2010; Li et al., 2008; Liu et al.,
260 2010; Cheng et al., 2014). The mean PBM concentration at the Hefei site during the
261 non-haze days was 23.3 ± 90.8 pg m⁻³ with an exceptionally large range of 0.5-1827
The frequency distribution of PBM showed that high PBM concentrations (i.e., > 50 pg m\(^{-3}\)) accounted for 6.4% of the total data. The PBM concentration under the non-haze condition in Hefei is generally at a similar level to the remote areas, such as Mt. Gongga, Mt. Waliguan and Shangri-Li in western China.

Diurnal variations of GEM, PBM and RGM concentrations for non-haze days are shown in Fig. 3. Both GEM and PBM concentrations exhibited similar variations with elevated concentrations during night. The RGM concentration during the daytime was slightly higher than that in nighttime, typically peaking between 10:00 and 12:00.

### 3.3 Speciated atmospheric mercury during haze days

Haze pollution mainly occurred in December and January at our monitoring site. The four major haze pollution periods were identified in grey in Fig. 2. The mean concentrations of GEM, RGM and PBM during these haze days were 4.74 ± 1.62 ng m\(^{-3}\), 4.32 ± 8.36 pg m\(^{-3}\) and 60.2 ± 131.4 pg m\(^{-3}\), respectively (Table 1). The frequency distributions of GEM, RGM and PBM for the haze days are shown in Fig. S1 (in gray). Comparison of GEM, RGM and PBM concentrations during haze and non-haze days is shown in Fig. 4. GEM, RGM and PBM concentrations show significant differences between haze and non haze days (p<0.001, t-test). On average, the concentration of GEM in haze days was 1.2 times that in non-haze days. Similarly, the concentration of RGM in haze days was about 1-1.7 times those in non-haze days.

The largest impact of haze pollution is however on PBM, with the mean PBM concentration in haze days about 2.5 times that of non-haze days. High concentrations of RGM (exceeding 10 pg m\(^{-3}\)) and PBM concentrations (exceeding 50 pg m\(^{-3}\)) were
also more frequently observed than in non-haze days, accounting for 5.9% and 25%, respectively, of the total haze days.

Diurnal variations of GEM, PBM and RGM concentrations for haze days are shown in Fig. 3. GEM concentrations were higher during night, decreased during daytime. The opposite pattern was observed for RGM, which showed higher concentrations during daytime than during night; the duration of the RGM peak also lasted longer for haze days. On the contrary, the PBM typically peaked just before sunrise, with the lowest values occurred in the afternoon (14:00-16:00).

4. Discussion

4.1 Influence of atmospheric mercury emission source

The statistically significant difference in the GEM concentration between non-haze days and haze days suggests that haze pollution could directly affect the concentration of elemental mercury. In order to understand the mercury sources attribution during haze days, the PSCF model analysis was conducted by using the TrajStat software. As shown in Fig. 5, the area south to the monitoring site and the neighboring provinces were the main sources region during haze days. Thus, atmospheric mercury in haze days were mainly affected by local or regional emission sources.

The seasonal sources could also be inferred from the PSCF analysis with the year-round data. Fig. 6(A) showed the overall spatial contribution of mercury emission sources in China. As Hefei is located in east-central China, its atmospheric mercury concentration could be affected by both north and south emission sources, including those from the North China Plain (especially Shandong Province) and the
neighboring provinces of Henan, Jiangsu, Jiangxi and Hubei. Long-range transport could also impact the seasonal variations of atmospheric mercury in Hefei. As shown in Figure 6, in spring, the major contributors of atmospheric mercury to Hefei were from the southwestern region including the local area and the Jiangxi and Hunan provinces. In summer, the main contributors were from north of Anhui, as well as Henan and Jiangxi provinces, and even from the Pearl River Delta region in the far south. In autumn and winter, the prevalent seasons for haze pollution, the most important anthropogenic mercury sources to the monitoring site were the local emissions and those from the neighboring region of Shandong, Henan and the Yangtze River Delta region. The total mercury emissions from Henan and Shandong provinces were estimated to be over 50 and 45 tons in 2010, respectively, making them two largest Hg emitters in China (Zhang et al., 2015b).

GEM and CO normally share anthropogenic emission sources, such as industrial and domestic coal combustion (Wu et al., 2006). However, they also have their own sources, vehicles are another kind of dominant sources for CO, while power plants are another type of mainly sources for GEM. The correlation between the concentrations of GEM and CO during non-haze and haze days is shown in Fig. S2. The slope of the trend line represents the Hg/CO ratio. Emissions from power plants typically have a higher Hg/CO ratio (Wu et al., 2006), whereas biomass burning and residential coal combustion have a lower Hg/CO ratio due to incomplete combustion (Weiss-Penzias et al., 2007). The Hg/CO ratios from our study for both non-haze and haze days are in the range of 0.0003-0.0009 ng m^{-3} ppbv^{-1}, similar to the ratio reported for Alaska biomass burning (0.0014 ± 0.0006 ng m^{-3} ppbv^{-1}; Weiss-Penzias et al., 2007), indicating that biomass burning might have played an important role in mercury
emission in Hefei. This is further supported by the concentration of water-soluble potassium (K+) in PM\(_{10}\). K+ is a typical component of biomass burning aerosol and has been used as a tracer element for qualitative identification of biomass burning (Cachier et al., 1991). As shown in Fig. S3, K+ in PM\(_{10}\) shows a good correlation with air quality index (AQI) during the heavy pollution period of Nov-Dec, 2013. In addition, seven high-GEM events were identified during the whole monitoring period (Table S1). 5-day backward trajectories for each GEM heavy pollution event for the time of at maximum GEM concentration are shown in Fig. S4. Air masses with elevated GEM concentration were mainly from NW, SW and East directions. In combination with the NASA's satellite hotspots/fire locations information from the Fire Information for Resource Management System (FIRMS), there were potential biomass burning occurred in these regions when air masses passed over (Fig. S4, Events 1-7). Therefore, biomass burning can contribute to the observed higher mercury concentrations, which not only came from local sources (Events 1 and 4), but could also be affect by other regions through long-range transport processes (Events 2, 3, 6 and 7).

4.2 Impacts of meteorological factors for atmospheric mercury during haze days

Meteorological condition, especially wind direction and speed, could also impact the atmospheric mercury during haze days. The wind rose for the monitoring site during the study period is shown in Fig. 7. Easterly and southeasterly winds represented the prevailing wind directions at the study site. A wind rose diagram of GEM concentrations above the 90\(^{th}\) percentile value is shown in Fig. 7B. We found that 67\% of the high GEM concentrations occurred at low wind speed (below 1.5 m s\(^{-1}\)); however, wind speed below 1.5 m s\(^{-1}\) accounted for only 1.7\% of total study.
High RGM and PBM concentrations appear not to be related to high wind speed (wind speed: 3-5 m s\(^{-1}\)); only 1.4% and 2.6% of the high RGM and PBM concentrations were observed under high wind-speed conditions, respectively (Figs. 7C and 7D). In general, most of the high atmospheric mercury levels occurred in the low wind speed conditions. This slow wind speed condition is not conductive to the spread of mercury and thus favours the accumulation of atmospheric mercury, especially during haze days.

Both GEM and PBM concentrations exhibited great variations with elevated concentration during night or early morning, regardless of the presence of haze. Such a diurnal variation of GEM and PBM could be related to changes in the height of urban boundary layer, which is typically low in the morning and night, and high during the daytime (Yuan et al., 2005; Mao et al., 2006). The maximum PBM concentration (observed at 6:00) was more than 4 times higher than the minimum value (observed at 16:00) both under non-haze and haze days, and about 76% PBM were removed during this period (6:00-16:00). However, the reductions of PBM as a result of deposition during haze days was 62.7 pg m\(^{-3}\), which was about 2.4 times that in non-haze days, suggesting that haze pollution could increase the removal of PBM and thus reduce its atmospheric lifetime. Although PBM is not the major form of mercury emitted to the atmosphere, it is crucial in atmospheric mercury transport and removal processes due to its short atmospheric lifetime. As shown in Fig. 8, the PBM concentration co-varied with the PM\(_{2.5}\) concentration, especially in January when all the four PBM peak events were associated with increased PM\(_{2.5}\) concentrations. The co-variation in February is weaker, possibly due to the loss of PBM data because of instrument maintenance (see Section 2.3). Elevated PBM concentrations might be due to the poor diffusion.
conditions in cold months and high PM pollution. Although the concentrations of PM\(_{2.5}\) were similar from March to June, March showed higher PBM concentrations. This might be due to higher temperatures in the warmer months which do not favor mercury adsorption (Otani et al., 1986). These results indicate that both the PM\(_{2.5}\) concentration and temperature may play an important role in the formation of PBM.

### 4.3 Chemical process for RGM and the potential oxidation mechanism

In contrast with the diurnal variations of GEM and PBM, RGM shows different diurnal trend. The RGM concentration during daytime was slightly higher than at night. As discussed before in 4.2 section, the diurnal variation of GEM and PBM could be related to changes in the height of urban boundary layer. So the role of boundary layer for the enhancement of RGM during daytime would be limited. The weak correlation (r=0.164, p<0.01) between RGM and CO suggests that regional anthropogenic sources are not a major source of RGM in the air. As shown in Fig. 9 (haze days), the peak value of RGM coincided well with the lowest value of CO, suggesting that the production of RGM in haze days does not fully come from anthropogenic emission sources. Instead, RGM is more likely produced from the in situ oxidation of GEM; this is supported by the fact that the peak values of RGM coincided well with the decline of GEM. We found that the RGM concentration did not change much from 8:00 to 20:00 (local time) during haze days. This indicates that photochemical reaction between GEM and RGM still takes place during haze days, but the daytime change in the intensity of solar radiation has been greatly dampened due to the light-haze interaction.
Various atmospheric oxidants are capable of oxidizing GEM to RGM, including halogen radicals, ozone, hydroxyl radicals (OH), among others (Holmes et al., 2010; Wang et al., 2014). Halogen radicals, especially bromine atoms, are believed to be the primary oxidant for GEM in the global troposphere (Holmes et al., 2010). Unfortunately, we did not measure halogen radicals in this study. Ozone itself is not an efficient oxidant for GEM oxidation due to low reaction rate (Hall, 1995; Holmes et al., 2010). In the lower troposphere, ozone is produced from daytime photochemical reactions involving volatile organic compounds (VOC) and nitrogen oxides (NOx).

Due to fresh emissions of NO from vehicles can react with O3 to form NO2, so ozone could not fully represent photochemical oxidation processes in urban area (Herndon et al., 2008). Compared with ozone, odd oxygen (Ox = O3+NO2) is a more conserved tracer of the extent of photochemical processing in the urban atmosphere (Herndon et al., 2008; Wood et al., 2010). Because of such NO2 concentrations from MAX-DOAS are available only during the daytime, so we could only use Ox to be a indicator for GEM oxidation occurred in the daytime. Diurnal variations of GEM, RGM and Gas-Phase Data (Ox, O3, NO2 and CO) concentrations during non-haze and haze days are shown in Fig. 9. The increase of Ox is consistent with the increase of RGM during haze days, but seems to lag behind the increase of RGM during non-haze days, suggesting some oxidation processes might be at work during haze days. During haze days, both the RGM and Ox reached highest values around 16:00, along with the lowest value of GEM, indicating the chemical transformation between GEM and RGM occurred. However, this phenomenon is not found in non-haze days.

The OH radical is also an important oxidant for mercury in the atmosphere. Previous studies have shown that the major source of OH in the early morning is the
photolysis of HONO, which accumulates in the urban atmospheric boundary layer during night (Kleffmann et al., 2005). The formation of HgOH as an intermediate product of the Hg$^0$(g) + OH oxidation reactions has been proposed by (Sommar et al., 2001), although HgOH is highly unstable and could decompose back rapidly to Hg$^0$ and OH (Goodsite et al., 2004). It has been proposed that secondary reactants such as NO$_2$, HO$_2$, RO, RO$_2$, and NO could assist the formation of Hg(II) from the initial HgOH intermediate, which outcompetes with the decomposition of HgOH (Calvert and Lindberg, 2005). As an example, we calculated the transformation between GEM and RGM under the influence of NO$_2$, using the reactions and rate constants shown in Table S2. As shown in Fig. S5, the production rate of NO$_2$HgOH, $\text{d}[\text{NO}_2\text{HgOH}]/\text{d}t$, increased almost linearly with increasing NO$_2$ under low NO$_2$ concentrations, and eventually reached a steady state when the NO$_2$ concentration is high enough.

Based on the production rate of NO$_2$HgOH, we can estimate the production of NO$_2$HgOH during the 1 hr sampling period when RGM was captured by the KCl-coated denuder in the Tekran 1130 unit. As discussed earlier, a distinct diurnal relationship between GEM and RGM was observed both in non-haze and haze days (Fig. 9). The production of NO$_2$HgOH and $\text{d}[\text{NO}_2\text{HgOH}]/\text{d}t$ corresponding to different NO$_2$ concentrations is shown in Table 3. With the increase of the NO$_2$ concentration, the contribution of the NO$_2$HgOH production to RGM will increase. If the NO$_2$ concentration is within 100 ppbv (from 0 to 100 ppbv), the production of NO$_2$HgOH would be in range of 0.058-4.81 pg m$^{-3}$ during the 1h sampling period. The mean NO$_2$ concentration during haze days is 24.3 ppbv (unit conversion see the supporting information), which is higher than in non-haze days (17.4 ppbv). The increments of RGM from sunrise to peak (6:00-12:00) are about 2.14 pg m$^{-3}$ (growth
rate ≈ 0.36 pg m\(^{-3}\) h\(^{-1}\) ) and 0.41 pg m\(^{-3}\) (growth rate ≈ 0.068 pg m\(^{-3}\) h\(^{-1}\)) during haze days and non-haze days, respectively. As illustrated in Table 3, the level of NO\(_2\) in the urban atmosphere is enough for the production of RGM during the 1h sampling period. In addition, we found that the NO\(_2\) concentrations increased rapidly after sunrise to reach peak values around noon, consistent with the increases of RGM during haze days. We thus postulate that NO\(_2\) aggregation with HgOH may be a possible mechanism to explain the enhanced production of RGM during the daytime over the inland urban air. The NO\(_2\) level in urban air might have a more important influence on the chemical transformations between the GEM and RGM during haze days, rather than non-haze days. But unfortunately, we can not provide an adequate description about these oxidation processes. To solve this problem, new laboratory and mercury model studies on mercury oxidation mechanism are needed.

5. Summary

Continuous measurements of speciated atmospheric mercury were conducted at Hefei, a mid-latitude inland city in central China, from July 2013 to June 2014. Measurements of other trace gases (e.g. CO, O\(_3\), NO\(_2\)) and meteorological parameters were employed to better understand the sources and oxidation pathways of atmospheric mercury. The mean GEM, RGM and PBM concentrations during haze days were 4.74 ± 1.62 ng m\(^{-3}\), 4.32 ± 8.36 pg m\(^{-3}\) and 60.2 ± 131.4 pg m\(^{-3}\), respectively. Potential source contribution function (PSCF) analysis suggested that the local mercury emission rather than long-range transport is the most important contributor of atmospheric mercury pollution during haze days at our monitoring site. The Hg/CO ratio and NASA’s satellite fire locations information indicated that the biomass...
burning may play an important role in mercury emission. Haze pollution has considerable impact on PBM rather than on GEM and RGM. Both GEM and PBM concentrations exhibited greatly variations with elevated concentration during night. The diurnal variations of GEM and PBM might be related to the boundary layer depth; a lower boundary layer depth in the morning and night could elevate the mercury concentration. The slow wind speed condition is not conductive to the spread of mercury and thus favours the accumulation of atmospheric mercury, especially during haze days. We found that PBM concentrations co-varied with the PM$_{2.5}$ concentration especially in January when all the four PBM peak events were associated with increased PM$_{2.5}$ concentrations. In addition, PBM showed a remarkable seasonal pattern, with higher concentrations in cold seasons and lower in warm seasons. Elevated PBM concentrations might be due to both the high loadings of particle matter and disadvantageous diffusion conditions during haze days especially in cold months. The peaks of RGM were observed around noon, which is probably due to the higher intensity of solar radiation and photochemical oxidation processes at this time. Change in the odd oxygen (O$_X$ = O$_3$+NO$_2$) concentration is normally applied to be an indicator for photochemical reaction. The increase of O$_X$ is consistent with the increase of RGM during haze days, but seems to lag behind the increase of RGM during non-haze days, suggesting some oxidation processes might be at work during haze days. Based on HgOH as an intermediate product, we suggest that NO$_2$ aggregation with HgOH is a potential mechanism to explain the enhanced production of RGM during the daytime over the inland urban air. The NO$_2$ level in urban air might have a more important influence on the chemical transformations between the GEM and RGM during haze days, rather than non-haze days.
Acknowledgements

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Table 1. Summary of GEM, RGM and PBM concentrations measured in Hefei from July 2013 to June 2014.

<table>
<thead>
<tr>
<th>Season</th>
<th>GEM (ng m⁻³)</th>
<th>RGM (pg m⁻³)</th>
<th>PBM (pg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean ± σ</td>
<td>Range</td>
<td>N</td>
</tr>
<tr>
<td>Spring</td>
<td>3.89 ± 1.79</td>
<td>0.2-21.3</td>
<td>7890</td>
</tr>
<tr>
<td>Summer</td>
<td>4.08 ± 1.99</td>
<td>0.3-22.9</td>
<td>6050</td>
</tr>
<tr>
<td>Autumn</td>
<td>4.51 ± 2.10</td>
<td>0.4-23.8</td>
<td>3632</td>
</tr>
<tr>
<td>Winter</td>
<td>4.05 ± 1.81</td>
<td>0.9-12.2</td>
<td>6381</td>
</tr>
<tr>
<td>Total</td>
<td>4.07 ± 1.91</td>
<td>0.2-23.8</td>
<td>23953</td>
</tr>
<tr>
<td>Non-haze</td>
<td>3.95 ± 1.93</td>
<td>0.2-23.8</td>
<td>20345</td>
</tr>
<tr>
<td>Haze</td>
<td>4.74 ± 1.62</td>
<td>2.1-16.5</td>
<td>3608</td>
</tr>
</tbody>
</table>
Table 2. Speciated atmospheric mercury concentrations in Hefei and other urban and rural areas.

<table>
<thead>
<tr>
<th>Location</th>
<th>Classification</th>
<th>Time</th>
<th>TGM (ng m(^{-3}))</th>
<th>GEM (ng m(^{-3}))</th>
<th>RGM (pg m(^{-3}))</th>
<th>PBM (pg m(^{-3}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hefei</td>
<td>Suburb</td>
<td>Jul 2013-Jun 2014</td>
<td>4.1</td>
<td>4.07</td>
<td>3.67</td>
<td>30</td>
<td>This study</td>
</tr>
<tr>
<td>Hefei</td>
<td>Suburb</td>
<td>Feb-May 2009</td>
<td>2.53</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Hu et al. (2014)</td>
</tr>
<tr>
<td>Shanghai</td>
<td>Urban</td>
<td>Aug-Sep 2009</td>
<td>2.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Zhu et al. (2012)</td>
</tr>
<tr>
<td>Nanjing</td>
<td>Urban</td>
<td>Jan-Dec 2011</td>
<td>7.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Fang et al. (2004)</td>
</tr>
<tr>
<td>Guiyang</td>
<td>Urban</td>
<td>Nov 2001-Nov 2002</td>
<td>8.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Fu et al. (2011)</td>
</tr>
<tr>
<td>Changchun</td>
<td>Urban</td>
<td>Jul 1999-Jan 2000</td>
<td>18.4</td>
<td>-</td>
<td>-</td>
<td>276</td>
<td>Zhu et al. (2012)</td>
</tr>
<tr>
<td>Mt.Changbai</td>
<td>Remote</td>
<td>Aug 2005-Jul 2006</td>
<td>3.58</td>
<td>-</td>
<td>65</td>
<td>77</td>
<td>Fu et al. (2008a, b)</td>
</tr>
<tr>
<td>Mt.Gongga</td>
<td>Remote</td>
<td>May 2005-July 2006</td>
<td>3.98</td>
<td>-</td>
<td>6.2</td>
<td>30.7</td>
<td>Fu et al. (2008a, b)</td>
</tr>
<tr>
<td>Mt.Leigong</td>
<td>Remote</td>
<td>May 2008-May 2009</td>
<td>2.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Fu et al. (2010)</td>
</tr>
<tr>
<td>Detroit, USA</td>
<td>Urban</td>
<td>Jan-Dec 2004</td>
<td>-</td>
<td>2.5</td>
<td>15.5</td>
<td>18.1</td>
<td>Liu et al. (2010)</td>
</tr>
<tr>
<td>Dexter, USA</td>
<td>Rural</td>
<td>Jan-Dec 2004</td>
<td>-</td>
<td>1.6</td>
<td>3.8</td>
<td>6.1</td>
<td>Liu et al. (2010)</td>
</tr>
<tr>
<td>Houston, USA</td>
<td>Urban</td>
<td>Aug-Oct 2006</td>
<td>-</td>
<td>1.66</td>
<td>6.9</td>
<td>2.5</td>
<td>Brooks et al. (2010)</td>
</tr>
<tr>
<td>Göteborg, Sweden</td>
<td>Urban</td>
<td>Feb-Mar 2005</td>
<td>-</td>
<td>1.96</td>
<td>2.53</td>
<td>12.5</td>
<td>Li et al. (2008)</td>
</tr>
<tr>
<td>Nova Scotia, Canada</td>
<td>Urban</td>
<td>Jan 2010- Dec 2011</td>
<td>1.67</td>
<td>2.07</td>
<td>2.32</td>
<td>-</td>
<td>Cheng et al. (2014)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Northern Hemisphere background value</td>
</tr>
</tbody>
</table>
Table 3. The production of NO$_2$HgOH and d[NO$_2$HgOH]/dt at different NO$_2$ concentrations

<table>
<thead>
<tr>
<th>NO$_2$ (ppbv)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(NO$_2$HgOH)/dt (molecule cm$^{-3}$s$^{-1}$)</td>
<td>0.36</td>
<td>0.71</td>
<td>1.04</td>
<td>1.37</td>
<td>1.68</td>
<td>1.99</td>
<td>2.28</td>
<td>2.56</td>
<td>2.83</td>
<td>3.10</td>
</tr>
<tr>
<td>NO$_2$HgOH (pg m$^{-3}$, 1hr)</td>
<td>0.56</td>
<td>1.10</td>
<td>1.63</td>
<td>2.13</td>
<td>2.61</td>
<td>3.08</td>
<td>3.54</td>
<td>3.97</td>
<td>4.40</td>
<td>4.81</td>
</tr>
</tbody>
</table>
Fig. 1. Location of the monitoring site in Hefei, China.
Fig. 2. Time series of GEM, RGM and PBM concentrations, along with visibility, relatively humidity, at the monitoring site in Hefei from July 2013 to June 2014. The GEM data were at a 5-min resolution, and the RGM and PBM data were two-hour averages. The gray columns show the major haze pollution episodes occurred during the study period.
Fig. 3. Diurnal trends of GEM, RGM and PBM concentrations in Hefei during non-haze and haze days (Local time = UTC + 8 hr). The data were two-hour averages.
Fig. 4. GEM, RGM and PBM concentrations during non-haze and haze days. The GEM data were at a 5-min resolution, the RGM and PBM data were two-hour averages.
Fig. 5. Likely sources areas of GEM during haze days identified by PSCF analysis.
Fig. 6. Likely emission sources areas of GEM simulated by PSCF analysis. (A) overall (from July 2013 to June 2014), (B) spring, (C) summer, (D) autumn, (E) winter.
Fig. 7. Wind direction and speed at the Science Island Meteorological Station during the study period. (A) the wind rose for the whole study period; (B), (C) and (D) are the wind rose diagrams for GEM, RGM and PBM concentrations above the 90th percentile values, respectively.
Fig. 8. PBM and PM$_{2.5}$ concentrations from January to June, 2014.
Fig. 9. Diurnal variations of GEM, RGM and Gas-Phase Data (O_x, O_3, NO_2 and CO) concentrations during non-haze and haze days. Notes: bottom is the carbon monoxide mixing ratio. Middle are the averaged O_3, O_x (O_x = NO_2 + O_3) and NO_2 concentrations. Top are the hourly averaged GEM and RGM concentrations. The bars for NO_2 refer to the standard deviations.