Spatial and temporal distribution of gaseous elemental mercury in Chongqing, China

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Abstract In order to investigate the spatial and temporal variability of atmospheric mercury (Hg) in Chongqing, China, gaseous elemental mercury (GEM) was measured from August 2006 to September 2007, using Lumex® multifunctional mercury analyzer RA-915+ (Lumex Ltd., Russia). The mean GEM concentration was 6.74 ± 0.37 ng m⁻³ in Chongqing, much higher than the accepted global background values (1.5–2 ng m⁻³). The GEM concentrations were different in different function areas. GEM in transport, industrial and commercial areas were 7.07 ± 1.04, 7.05 ± 0.96 and 6.71 ± 1.10 ng m⁻³, respectively, while GEM was 6.14 ± 1.30 and 4.32 ± 1.04 in the educational/recreational and nature conservation areas, suggesting that Hg emissions from mobile vehicles and industrial sources (specially coal combustion) were the most important contributors to atmospheric Hg in Chongqing. Mean Hg concentrations also had monthly variations with highest in November (8.24 ± 0.50 ng m⁻³) and lowest values in August (5.36 ± 0.70 ng m⁻³). Additionally, the diurnal variation of GEM concentrations was dependent on the local/regional atmospheric conditions. At Jinyun Mountain site (natural conservation area), hourly GEM concentrations had much higher values in daytime than at night. At Power Plant site, however, the hourly GEM concentrations were lower in daytime than at night. GEM concentrations in the air were correlated significantly with meteorological parameters except for barometric pressure.

Keywords Gaseous elemental mercury (GEM) · Atmospheric mercury · Variation · Distribution

Introduction

Atmospheric mercury (Hg) can adversely impact human health due to its deposition to, and biomethylation and bioaccumulation in terrestrial and aquatic systems. Mercury in the atmosphere exists mainly in three forms: gaseous elemental mercury (Hg⁰), gaseous divalent compounds [Hg(II)] and associated with particulate matter [Hg(p); Wångberg et al. 2003]. Elemental mercury is predominant in the atmosphere (more than 98%; Poissant et al. 2005; Cobbett and Heyst 2007; Valente et al. 2007). Due to its low solubility and high stability, Hg⁰ has a residence time of 0.5–2 year and thus can undergo long range transport.
Atmospheric Hg(II) and Hg(p), which are operationally defined forms and identified by applying different sampling techniques (Zielonka et al. 2005; Valente et al. 2007), are very reactive forms. They can enter the terrestrial/aquatic systems via wet and dry deposition processes in local/regional areas (Poissant 2000; Weiss-Penzias et al. 2003).

As an air pollutant, Hg has complex biogeochemical cycles including oxidation/reduction and deposition/emission from the anthropogenic (primarily coal combustion, waste incineration, metal refining and manufacturing) and natural sources (emission from soils, water bodies, and vegetation surfaces, wild forest fires, volcanoes activities and geothermal systems; Schroeder and Munthe 1998; Pirrone et al. 2001; Gustin 2003; Hylander and Meili 2003; Wang et al. 2006b). Since the industrial revolution, amount of mercury emitted into the atmosphere has increased two to five times (Hudson et al. 1995). During the past 10–15 years, atmospheric mercury has been widely measured in Europe and America and an average concentration of approximately 1.5 ng m$^{-3}$ has been obtained for total gaseous mercury (TGM) in background air (Nadim et al. 2001; Baker et al. 2002; Lynam and Keeler 2005; Sprovieri et al. 2005; Hall et al. 2006; Kuo et al. 2006). Slemr et al. (2003) found that in Europe atmospheric mercury concentrations increased from the late 1970s until the 1980s, then decreased to a minimum in 1996, and have remained nearly unchanged since then. Controlling Hg emissions from anthropogenic sources might contribute to such decrease in atmospheric Hg (Hylander 2001; Pacyna et al. 2001).

However, atmospheric Hg is still a major concern in many other regions, especially in Asia. In this region, anthropogenic Hg emissions would increase continuously due to rapidly expanding economy and increasing amount of coal combustion (Kim and Kim 2000). Asia has now become the largest contributor of anthropogenic atmospheric Hg, accounting for 56% of the global anthropogenic budget, followed by Europe, North America, Africa, Central and South America and Oceania, contributing to about 28.8%, 15%, 5.2%, 3.4% and 1.6% to the total emissions, respectively (Pirrone et al. 1998; Pacyna and Pacyna 2001).

**Fig. 1** The grey part in Chongqing map (b) is where all the 13 sampling sites were located and the map (a) was schematic diagram.
Using Hg⁰/CO ratio and a recent inventory for CO emissions, Jaffe et al. (2005) estimated 1460 metric tons year⁻¹ of Hg⁰ emissions from Asia. It was estimated that Hg emissions in China were 556 t in 1999 and approximately 45% of emitted Hg came from non-ferrous metals smelting, 38% from coal combustion and 17% from miscellaneous activities (Streets et al. 2005). Results from Wang et al. (2006b) showed that anthropogenic mercury emission in Chongqing, China, was approximately 8.85 t in 2001, with more than 50% from coal combustion and 23.7% from other industrial processes (including cement production, metal smelting and chemical industry).

In addition, acid rain deposition is another environmental concern in Chongqing. It was enriched with SO₄²⁻, Ca²⁺ and NH₄⁺ (Larssen and Carmichael 2000; Wang et al. 2000; Han et al. 2006). Its reduced pH and elevated SO₄²⁻ may have impacts on biogeochemical behaviors of Hg, resulting in a high washout ratio and formation of MeHg (Branfireun et al. 1999; Wong et al. 2006).

The objectives of this study were: (1) to measure atmospheric mercury concentrations in Chongqing, China; (2) to determine the temporal and spatial variation of mercury concentrations and (3) to identify the correlationship between mercury concentrations and various meteorological parameters.

### Materials and methods

#### Site description

Chongqing is situated in the upper reaches of the Yangtze River in China, as shown in Fig. 1a. It

<table>
<thead>
<tr>
<th>Number</th>
<th>Site</th>
<th>Latitude (N)–longitude (E)</th>
<th>Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Jiefangbei Square</td>
<td>29°33′52″–106°36′25″</td>
<td>Com</td>
<td>A quite crowded commercial place surrounded by many buildings; commercial center of Chongqing region</td>
</tr>
<tr>
<td>2</td>
<td>Sanxia Square</td>
<td>29°33′25″–106°27′26″</td>
<td>Com</td>
<td>A crowded place with lots of markets</td>
</tr>
<tr>
<td>3</td>
<td>Nanping Street</td>
<td>29°32′52″–106°35′22″</td>
<td>Com</td>
<td>A busy place with lots of markets with many people</td>
</tr>
<tr>
<td>4</td>
<td>Power Plant</td>
<td>29°29′12″–106°32′03″</td>
<td>Ind</td>
<td>A site located at about 5 km west from coal-fired power plant of Chongqing, which was built in 1952 and is the most coal-consumer in Chongqing</td>
</tr>
<tr>
<td>5</td>
<td>Steel Plant</td>
<td>29°30′04″–106°29′11″</td>
<td>Ind</td>
<td>A place situated at approximately 7 km north from the steel-iron plant of Chongqing</td>
</tr>
<tr>
<td>6</td>
<td>High-tech Park</td>
<td>29°31′13″–106°29′28″</td>
<td>Ind</td>
<td>A site inside the high-tech park of Chongqing, accommodating lots of enterprises</td>
</tr>
<tr>
<td>7</td>
<td>CQ University</td>
<td>29°34′03″–106°27′57″</td>
<td>Edu</td>
<td>A site on the Chongqing University campus with population of 52,000</td>
</tr>
<tr>
<td>8</td>
<td>Shaping Park</td>
<td>29°33′13″–106°27′08″</td>
<td>Edu</td>
<td>A main recreation place in Shaping district of Chongqing, with a certain entertainment facility and relatively clean environment</td>
</tr>
<tr>
<td>9</td>
<td>Nanfang Residence</td>
<td>29°34′58″–106°33′52″</td>
<td>Edu</td>
<td>A residential area with good vegetation cover and strict waste managements</td>
</tr>
<tr>
<td>10</td>
<td>Yanggong Crossroad</td>
<td>29°33′54″–106°27′02″</td>
<td>Tra</td>
<td>A crossroad with heavy traffic flows in Shaping district of Chongqing</td>
</tr>
<tr>
<td>11</td>
<td>Hongqi Crossroad</td>
<td>29°35′02″–106°31′28″</td>
<td>Tra</td>
<td>A busy crossroad highway connecting three districts of Chongqing</td>
</tr>
<tr>
<td>12</td>
<td>Railway Station</td>
<td>29°33′11″–106°32′40″</td>
<td>Tra</td>
<td>A traffic hub of Chongqing running trains and buses</td>
</tr>
<tr>
<td>13</td>
<td>Jinyun Mountain</td>
<td>29°52′14″–106°23′10″</td>
<td>Nat</td>
<td>A forest site in the Jinyun Mountain nature conservation area of China, with little anthropogenic impacts</td>
</tr>
</tbody>
</table>

Com, Ind, Edu, Tra and Nat represent the commercial, industrial, 25 educational/recreational, transport and nature conservation areas, respectively
covers an area of 82,400 km$^2$ with population of $\sim$31,000,000. The climate is subtropical humid monsoon with annual average temperature of 18°C, and annual average precipitation of 1,200 mm with most occurring in the summer. Chongqing is an important industrial region in southwest China, and consumes large amount of energy, more than 70% of which is coal. Consequently, Hg pollution and acid rain are regarded as major environmental burdens in Chongqing.

Thirteen sampling sites were chosen in the main municipal area of Chongqing for the current study (Fig. 1b). Table 1 describes the general characteristics of each of the sampling sites. All sampling sites can be classified into five types, i.e. commercial, industrial, educational/recreational, transport and natural conservation areas according to land-use or the atmospheric conditions.

Measurements of GEM and meteorological parameters

Field measurements of GEM were performed in the chosen sites from August 2006 to September

### Table 2 GEM concentration (ng m$^{-3}$) in Chongqing and other cities

<table>
<thead>
<tr>
<th>Sampling site and time</th>
<th>GEM/TGM</th>
<th>Method</th>
<th>Site description</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chongqing, China, 2006–2007</td>
<td>6.7</td>
<td>Automatic$^b$</td>
<td>A main economical activity area of Chongqing including the residential, industrial, commercial area, etc.</td>
<td>This study</td>
</tr>
<tr>
<td>Beijing, China, 2005</td>
<td>4.9–8.3</td>
<td>Automatic$^a$</td>
<td>An urban site located at Research Center for Eco-Environmental Sciences between the fourth and fifth ring roads in Beijing, China</td>
<td>Wang et al. (2007)</td>
</tr>
<tr>
<td>Guiyang, China, 2000–2001</td>
<td>7.4</td>
<td>Automatic$^b$</td>
<td>A dense residential area surrounded by a lot of industries such as Guiyang coal fired power plant and Guizhou cement production plant</td>
<td>Feng et al. (2003)</td>
</tr>
<tr>
<td>Seoul, Korea, 2003</td>
<td>5.0</td>
<td>Automatic$^a$</td>
<td>A complex urban area surrounded by a large-scale public park, a residential area and a commercial area</td>
<td>Kim et al. (2006)</td>
</tr>
<tr>
<td>Tokyo, Japan, 2000–2001</td>
<td>2.8</td>
<td>Automatic$^e$</td>
<td>A study site located in metropolitan area surrounded by nine municipal solid waste incinerators</td>
<td>Sakata and Marumoto (2002)</td>
</tr>
<tr>
<td>Reno, USA, 2002–2005</td>
<td>2.3</td>
<td>Automatic$^d$</td>
<td>An urban area (population $\sim$200,000) in a semi-arid valley with a gas-diesel fired power plant located 27 km away</td>
<td>Stamenkovic et al. (2007)</td>
</tr>
<tr>
<td>Detroit, USA, 2003</td>
<td>2.2</td>
<td>Automatic$^d$</td>
<td>A site in the metropolitan area including iron-steel manufacturing, refineries, sewage sludge incineration, etc.</td>
<td>Liu et al. (2007)</td>
</tr>
<tr>
<td>Tuscaloosa, USA, 2003</td>
<td>4.1</td>
<td>Automatic$^d$</td>
<td>A medium-sized US city containing numerous small mercury sources (i.e. foundry operations, waste incineration)</td>
<td>Gabriel et al. (2005)</td>
</tr>
<tr>
<td>New York, USA, 2000–2003</td>
<td>1.8–3.0</td>
<td>Automatic$^e$</td>
<td>Three sites located near small airport, main road and nature preserve, respectively</td>
<td>Han et al. (2004)</td>
</tr>
<tr>
<td>Toronto, Canada, 2001–2002</td>
<td>2.4</td>
<td>Automatic$^b$</td>
<td>An area sited by commercial, public and private buildings in downtown Toronto</td>
<td>Denis et al. (2006)</td>
</tr>
<tr>
<td>Mexico, Mexico, 2002</td>
<td>9.8</td>
<td>Automatic$^d$</td>
<td>A place with residential and industrial areas close to each other, as well as a high traffic zone mainly with heavy trucks</td>
<td>Rosa et al. (2004)</td>
</tr>
</tbody>
</table>

$^a$Lumex RA-915
$^b$Tekran 2537A and Gardis 1A
$^c$Nippon AM-2
$^d$Tekran 2537A
$^e$Manual method: pre-concentration, thermal desorption and then detected by atomic fluorescence spectroscopic (AFC) analyzer
2007. The whole measurements were completed in two phases: (1) From August 2006 to February 2007, monthly measurements were conducted at the sites 1–12; (2) Between January 2007 and September 2007, an intensive measurement was carried out only at site 4 and site 13. The GEM concentrations were determined using the Lumex® multifunctional mercury analyzer RA-915+ (Lumex Ltd., Russia). This instrument can real-time detect extremely low Hg concentration in ambient air (detection limit was 0.3 ng m$^{-3}$ at response time of 30 s and flow rate of 20 l min$^{-1}$), and can also be automatically recalibrated by internal mechanical devices (5 min interval; Sholupov et al. 2004; Oyarzun et al. 2007). The data can be output to a PC through a RS-232 cable. Additional information about use of RA-915+ can be found in the paper of Higueras et al. (2006).

For monthly measurements of sampling sites 1–12, determinations were conducted in 2 or 3 h after 12:00 at about 1.5 m above the ground in connective 3 days (four sites per day), and then repeated once in the following 3 days. A total sampling time of 30 min was employed each time at every site and the Hg concentrations obtained from 30-s intervals were averaged to obtain the mean GEM concentration. For intensive measurements of sites 4 and 13, determinations was continuously carried out in connective 3 days for the diurnal variation.

A set of environmental parameters that may affect GEM concentrations in the air was also collected concurrently with the atmospheric Hg measurement. The temperature, relative humidity and barometric pressure were all simultaneously monitored with Kestrel 4000 Pocket Weather tracker (Nielsen–Kellerman, USA). The solar radiation was determined with a TES-1332A Digital Lux meter (TES, Taiwan, China).

**Results and discussion**

**Atmospheric Hg status in Chongqing and its comparison with other cities**

Average GEM concentrations (± standard deviation) during the study period ranged from 1.55 to 10.08 ng m$^{-3}$ with a mean value of 6.74 ± 0.37 ng m$^{-3}$ in Chongqing, China. It was approximately four times of the accepted global background concentrations (1.5–2 ng m$^{-3}$; Kock et al. 2005; Temme et al. 2007; Valente et al. 2007). Previous studies from various city areas in the world showed that GEM concentrations ranged from 1.8–9.8 ng m$^{-3}$ with much higher GEM concentration in Asia than in North America, exception for Mexico (Table 2). This may be due to increased anthropogenic emissions of Hg from increasing coal combustion during the industrialization in Asia (Pacyna and Pacyna 2002).

**Spatial variability**

The GEM concentrations in the air of Chongqing were greatly influenced by the land-use and/or the ambient environment, as seen from Fig. 2. The mean values of GEM decreased in order of Tra > Ind > Com > Edu > Nat. The GEM had no differences among the transport, industrial and commercial areas, but were obviously higher than in the educational/recreational and natural conservation areas, suggesting that mobile emission sources (cars, trucks, buses, etc.) may contribute to atmospheric Hg in urban regions (Stamenkovic et al. 2007). Lynam and Keeler (2006) reported that motor vehicle emission was significant contributor of ambient mercury concentrations in Detroit, USA. While Hg emission from coal combustion has been well known to be a major part of anthropologic Hg sources (Schroeder and Munthe}
Fig. 3 Mean monthly concentrations of GEM in Chongqing. Whiskers indicated standard deviation.

1998; Liu et al. 2002; Pacyna and Pacyna 2002; Wang et al. 2006b), the highest GEM concentrations were not detected near the coal-fired power plant and iron-steel plant in the present study. This might be attributed to the control of Hg emission by installing flue gas desulfurization equipments (Mukherjee et al. 2000; Pavlish et al. 2003). Our results showed that there was serious atmospheric Hg pollution in the commercial areas, where the GEM concentration was very close to that in the transport and industrial areas. Relatively low GEM concentrations were expected in the educational/recreational and natural conservation areas with the lowest at the natural conservation area where no local anthropogenic sources existed.

Monthly variation

The GEM showed temporal variation during the study period (Fig. 3). The highest concentration (8.24 ng m$^{-3}$) was observed in November, whereas the lowest (5.36 ng m$^{-3}$) was observed in August. The similar trends were already observed in other studies (Fu et al. 2008; Kellerhals...
et al. 2003). This variation may be related to the emission sources, meteorology and atmospheric oxidant levels (Poissant and Hoenninger 2004). In the present study, lower GEM concentrations were found during the winter (December to February), which was obviously different from the previous study (Zielonka et al. 2005). The peculiar meteorological conditions in the winter of Chongqing may contribute to lower GEM. Long and frequent raining may efficiently remove Hg from the air through wet deposition (Wängberg et al. 2001). Also, warmer weather (6–8°C in

Table 3  Correlations between GEM concentration and meteorological parameters

<table>
<thead>
<tr>
<th></th>
<th>Jinyun mountain</th>
<th>Power plant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>September</td>
<td>January</td>
</tr>
<tr>
<td>Temperature</td>
<td>0.571&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.004</td>
</tr>
<tr>
<td>Solar radiation</td>
<td>0.824&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.000</td>
</tr>
<tr>
<td>Relative humidity</td>
<td>0.865&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.037</td>
</tr>
<tr>
<td>Barometric pressure</td>
<td>0.815&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.000</td>
</tr>
</tbody>
</table>

The data for correlation analysis were from the diurnal variation measurements. Due to the meteorological system used by other study, the data were not performed during the measurement in January, at Power Plant site

<sup>a</sup>Correlation is significant at the 0.01 level

<sup>b</sup>Correlation is significant at the 0.05 level
winter) greatly reduces coal burning for domestic heating, thus diminishing Hg emission to the air.

Numerous studies showed seasonal variations of atmospheric Hg concentrations with higher Hg occurring mostly in winter and lower in summer (Ebinghaus et al. 2002; Munthe et al. 2003; Kock et al. 2005; Zielonka et al. 2005; Temme et al. 2007). In summer, both higher contents of oxidants such as O\(_3\) and HO, which may result in quick oxidation of Hg\(^0\) to Hg\(^{2+}\), and larger amount of rainfall, which may remove Hg via wet deposition from the air, contribute to lower GEM (Schroeder et al. 1991; Slemr and Scheel 1998; Ariya et al. 2004). Other potential oxidants including HO\(_2\), NO\(_2\), Cl\(_2\) and Br\(_2\) might be also involved in transformation of GEM into reactive mercury forms (Ariya et al. 2002). In winter, however, higher GEM might be caused by increased coal combustion for domestic heating, which was supported by good relationship between TGM and daily sulfur dioxide (SO\(_2\)) at Egbert (Blanchard et al. 2002).

Diurnal variation

At Jinyun Mountain site, GEM concentrations were distinctly higher during the day than at night for winter and summer months (Fig. 4). The GEM peak occurred approximately at 12:00–14:00 P.M. in January and 9:00–11:00 A.M. in September. Our results were generally in agreement with those from CAMNet (Kellerhals et al. 2003). The enhanced Hg concentrations during daytime might be ascribed to temperature-driven emission (Denis et al. 2006). In a study on emission of elemental mercury from soils amended with municipal sewage sludge, Carpi and Lindberg (1997) also found a strongly positive correlation between soil temperature and Hg\(^0\) emissions. Solar radiation may enhance photochemical reduction of Hg\(^{2+}\) species and photo-induced biological processes (Ariya et al. 2004; Wang et al. 2006a). In addition, lower midday peaks in September were probably because of Hg removal by high concentrations of air oxidants in summer (Poissant et al. 2005).

On the contrary, the GEM was found to be higher at night at the site of Power Plant. The same phenomenon was observed by Feng et al. (2003). The formation of inversion layer was proposed to help maintain high Hg levels during night time (Lee et al. 1998). Whereas, at Jinyun Mountain site, the air temperature mildly descended from the midday to night and then there was no sharp diurnal variation of surface heating, which might strongly restrain the forming of inversion layer. Also, several small peaks during the measurements indicated the effect of anthropogenic sources at the sampling site (the Iron-steel Plant of Chongqing was located 20 km away). The phenomenon was previously observed in other studies (Kim and Kim 2001; Denis et al. 2006).

The concentrations of GEM in the air were correlated significantly with the meteorological parameters with exception of barometric pressure (Table 3 and Fig. 4). However, such relationship obviously varied with areas. At Jinyun Mountain site, GEM concentrations were strongly positively correlated with temperature and solar radiation, while GEM had negative correlation with both parameters at Power Plant. There was positively significant relationship between relative humidity and GEM concentrations at both sites. Poissant et al. (2005) found that GEM concentrations were significantly correlated with air temperature and solar radiation, but anti-correlated with relative humidity. Rosa et al. (2004) observed positive correlation between TGM and temperature in a beach resort surrounded by tropical forest without industrial activities nearby \((r = 0.7089)\), but weak negative correlation at the site of a semi-urban city surrounded by rustic brick manufactures \((r = -0.3342)\).

Conclusions

The mean GEM concentration \((6.74 \pm 0.37 \text{ ng m}^{-3})\) was significantly elevated in Chongqing, much greater than the global background values \((1.5–2 \text{ ng m}^{-3})\). The GEM concentrations had no obvious spatial variations among the transport, industrial and commercial areas, but higher than those in the educational/recreational and natural conservation areas. The monthly mean Hg contents showed great variations with the highest concentrations in November and the lowest in August. The concentrations of GEM in the air...
were correlated significantly with meteorological parameters except for barometric pressure. The results suggested that there was still serious Hg pollution in the atmosphere in Chongqing and that the Hg emissions from mobile vehicles and industrial sources were the most important contributors to atmospheric Hg in Chongqing.

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References


