Gaseous elemental mercury concentration in atmosphere at urban and remote sites in China

WANG Zhang-wei¹, CHEN Zuo-shuai¹, DUAN Ning², ZHANG Xiao-shan^{1,*}

1. Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China.

E-mail: wangzhw@rcees.ac.cn

2. Chinese Research Academy of Environmental Sciences, Beijing 100012, China

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Abstract

An investigation of gaseous elemental mercury concentration in atmosphere was conducted at Beijing and Guangzhou urban, Yangtze Delta regional sites and China Global Atmosphere Watch Baseline Observatory (CGAWBO) in Mt. Waliguan of remote continental area of China. High temporal resolved data were obtained using automated mercury analyzer RA-915⁺. Results showed that the overall hourly mean Hg⁰ concentrations in Mt. Waliguan were 1.7 ± 1.1 ng/m³ in summer and 0.6 ± 0.08 ng/m³ in winter. The concentration in Yangtze Delta regional site was 5.4 ± 4.1 ng/m³, which was much higher than those in Waliguan continental background area and also higher than that found in North America and Europe rural areas. In Beijing urban area the overall hourly mean Hg⁰ concentrations were 8.3 ± 3.6 ng/m³ in winter, 6.5 ± 5.2 ng/m³ in spring, 4.9 ± 3.3 ng/m³ in summer, and 6.7 ± 3.5 ng/m³ in autumn, respectively, and the concentration was 13.5 ± 7.1 ng/m³ in Guangzhou site. The mean concentration reached the lowest value at 14:00 and the highest at 02:00 or 20:00 in all monitoring campaigns in Beijing and Guangzhou urban areas, which contrasted with the results measured in Yangtze Delta regional site and Mt. Waliguan. The features of concentration and diurnal variation of Hg⁰ in Beijing and Guangzhou implied the importance of local anthropogenic sources in contributing to the high Hg⁰ concentration in urban areas of China. Contrary seasonal variation patterns of Hg⁰ concentration were found between urban and remote sites. In Beijing the highest Hg⁰ concentration was in winter and the lowest in summer, while in Mt. Waliguan the Hg⁰ concentration in summer was higher than that in winter. These indicated that different processes and factors controlled Hg⁰ concentration in urban, regional and remote areas.

Key words: gaseous elemental mercury; urban/remote sites; monitoring

Introduction

Mercury exists in the atmosphere predominant in its elemental gaseous form (Hg⁰), because it is not very water-soluble and is relatively unreactive (Hedgecock and Pirrone, 2001). Hg⁰ has approximately one year residence time, so it is possible for Hg⁰ to undergo a long distance transportation (Schroeder and Munthe, 1998; Lindqvist *et al.*, 1991). The global mercury concentrations increased to a peak in the 1980s, then decreased to a minimum around 1996, then the concentrations of Hg⁰ have been nearly constant (Slemr and Scheel, 1998). Global total atmospheric emission of mercury from anthropogenic sources in 1995 was 2143.1 t, approximately 56% of the total from Asia (Pacyna and Pacyna, 2002; Pacyna *et al.*, 2003). According to the results by Hylander (2001), anthropogenic emissions of mercury still increase in Asia because of coal-use increasing and industrialization. Preliminary estimates for the export of gas-phase mercury from China are approximately 150 t/a

from biomass/bio-fuel combustion, and approximately 600 t/a from industry, mostly from coal combustion (Friedli *et al.*, 2004).

Abundant data have been obtained after long-term monitoring for characterizing the temporal distribution of total gaseous mercury in the atmosphere in many regions of Europe and North America, while data of other regions are less available. Recent measurements of atmospheric gaseous mercury conducted in Seoul, Korea (Kim and Kim, 2000, 2001) and in Guiyang, China (Feng *et al.*, 2004) have shown that the mercury concentration in urban air is elevated comparing to that in the regions of Europe, North America and the global background area. China is believed to be a country of increasing atmospheric mercury emission (Hylander, 2001). However, only a few measurements of mercury in ambient air of China have been conducted. Great efforts are needed for more data to be able to describe and understand the temporal and spatial distribution characters of gaseous mercury in China. In particular, there is no literature related with atmospheric mercury in background area in China, whereas much information has been reported on background area in Europe and North America. In this paper, we presented the results

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*Corresponding author. E-mail: zhangxsh@rcees.ac.cn.

of gaseous elemental mercury concentration in atmosphere in the urban, suburban, regional and remote continental areas of China.

1 Experimental

1.1 Site description

Field measurements for gaseous elemental mercury were conducted in four locations in China: Beijing, Guangzhou urban, Yangtze Delta regional sites and China Global Atmosphere Watch Baseline Observatory (CGAW-BO) located in remote continental area of China. Beijing and Guangzhou represent northern and southern megacities, and both of them can be regarded as seriously anthropogenic polluted cities. Beijing site was located at Research Center for Eco-Environmental Sciences, between the fourth and fifth ring road in the northwest of Beijing urban area. Guangzhou site was set at the city meteorological observatory in Baiyun District, northern the city. Yangtze Delta regional site was located at Shuangqiao farm (30°50'N, 120°42'E) in Jiaxing County, which is in Zhejiang Province and tens kilometers away from cities. The dominant cropping system of the farm was the rotation of winter wheat-rice. CGAWBO is an official of World Meteorological Organization (WMO) Global Atmospheric Watch (GAW) station, a unique continental baseline observatory in Eurasia. It located on the top of Mt. Waliguan that lies in the northeast part of Qinghai-Tibet plateau in Gonghe County, Qinghai Province, with altitude of 3816 m. There is generally pristine area with arid and semi-arid grassland. The population density is less than 6 persons/km² and the station is relatively isolated from industrial and population centers.

1.2 Measurements

Measurements of gaseous elemental mercury were conducted with RA-915⁺ Mercury Analyzer (Lumex Ltd., St-Petersburg, Russia), which is based on the principle of Zeeman Atomic Absorption Spectrometry and High Frequency Modulated Light Polarization (ZAAS-HFM). RA-915⁺ Zeeman Analyzer provides continuous determination of Hg⁰ concentration. The detection limit (DL) is 1.5–2.0 ng/m³ with the response time being 1 s and 0.3 ng/m³ with the response time of 30 s during permanent air pumping through the multi-path analytical cell of the RA-915⁺ at a rate of 25 L/min. The RA-915⁺ mercury analyzer is equipped with a built-in mercury permeation source, and prior to monitoring the analyzer needs to calibrate in test mode for assurance the reliability and accuracy of measurement data. A more description of our monitoring method and its quality assurance and quality control (QA-QC) has been shown elsewhere (Sholupov and Ganeyev, 1995; Ganeyev *et al.*, 1995; Špiric and Mashyanov, 2000; Sholupov *et al.*, 2004).

In this study, real-time measurements of elemental gaseous mercury concentration were conducted in off-hand mode and the response time was set 1 min. One-hour continuous measurements were set to start at 02:00, 08:00,

14:00 and 20:00 in a monitoring day in all campaigns. Real time and hourly average Hg⁰ concentrations were then obtained and analyzed.

Four monitoring campaigns (including 10–20 monitoring days for each) in Beijing were performed in January, April, July and October in 2005, which represented winter, spring, summer and autumn respectively. Two monitoring campaigns were conducted at Mt. Waliguan in summer (two weeks in August) and winter (two weeks in December) and one campaign at Guangzhou in winter (two weeks in January) and Yangtze Delta regional site in autumn (two weeks in September) respectively in 2005.

2 Results and discussion

2.1 Real time Hg⁰ concentrations

The results of typical 1-h real time monitoring (1 min response time) of Hg⁰ concentration are shown in Fig. 1. It can be seen from Fig. 1a that very low Hg⁰ concentration was almost unchanged with time; this was only observed in Mt. Waliguan in winter. Usually most winter air flow come to Mt. Waliguan from the western plateau region with remote background features. Low concentration with a little fluctuation of Hg⁰ showed in Fig. 1c was monitored not only in Mt. Waliguan in summer cases but also in Beijing urban area in winter cases. In summer Mt. Waliguan air masses often come from eastern part of China. But in Beijing there usually gets clean air in winter for a period when strong cold wind passed. Fig. 1d shows high value and relatively large fluctuation of Hg⁰ concentration in 1-h monitoring period. It was the cases of serious air pollution observed in heating season of Beijing and in Guangzhou winter. Fig. 1b represents the others of the cases observed in Beijing and in Yangtze Delta site, in which local and regional emission of mercury disturbed more or less the Hg⁰ concentration in the air.

2.2 Remote continental background Hg⁰ concentrations

Fig. 2 shows the hourly mean Hg⁰ concentrations at 02:00, 08:00, 14:00 and 20:00 and the overall aver-

Fig. 1 Typical cases of real time Hg⁰ concentration during 1-h monitoring at Mt. Waliguan site in winter (a), Beijing urban site in spring, summer and autumn seasons and Yangtze Delta site (b), Mt. Waliguan site in summer and Beijing urban site in winter (c), and Beijing site in heating season and Guangzhou urban site in winter (d).

Fig. 2 Hourly mean Hg^0 concentrations at 02:00, 08:00, 14:00 and 20:00 during monitoring campaign in Mt. Waliguan Observatory. The asterisks represent maximum and minimum, the bar is $\pm SD$; the box plots are the 25th and 75th percentiles, respectively; the dot is mean; and the line is median. The same legend in the followings.

age concentration during each monitoring campaign in Mt. Waliguan Observatory. The overall mean Hg^0 concentrations were $1.7 \pm 1.1 \text{ ng/m}^3$ in summer monitoring campaign and $0.6 \pm 0.08 \text{ ng/m}^3$ in winter, which were comparable with the background levels of total gaseous mercury (TGM) in North hemisphere ($1.5\text{--}2.0 \text{ ng/m}^3$) and in South hemisphere ($1.1\text{--}1.4 \text{ ng/m}^3$) (Ebinghaus *et al.*, 2002; Schroeder, 2001; Lamborg *et al.*, 2002). The lower mean concentration of Hg^0 in winter than that in summer could due to the lower air temperature and lesser solar radiation in winter season. This seasonal variation was also consistent with those studies in North America and Europe finding that peak levels of Hg^0 were in spring or summer and reached the lowest values in winter (Slemer and Scheel, 1998). In summer Mt. Waliguan air masses often come from eastern part of China which suggested that long range transportation from eastern China influence the Hg^0 concentration. From Fig.2, a slightly diurnal variation of Hg^0 concentration can be found in Mt. Waliguan with the lowest Hg^0 concentration at 08:00 both in summer and winter. The diurnal variation amplitude in summer was larger than that in winter.

2.3 Regional background Hg^0 concentrations

Fig.3 shows the hourly mean Hg^0 concentrations at 02:00, 08:00, 14:00 and 20:00 and the overall average concentration during each monitoring campaign at Yangtze Delta regional site. The overall mean Hg^0 concentrations were $5.4 \pm 4.1 \text{ ng/m}^3$ in the monitoring campaign, which were higher the concentrations ($1.32\text{--}1.83 \text{ ng/m}^3$) in Canada rural sites (CAMNet) (Kellerhals *et al.*, 2003) and the concentrations ($1.63 \pm 0.35 \text{ ng/m}^3$) in summer season at Poland rural site (Zielonka *et al.*, 2005). Contrary to Mt. Waliguan, there was clearly diurnal variation of Hg^0 concentration in Yangtze Delta regional site, which exhibited a daytime dominant pattern of Hg^0 concentration during monitoring period. The Hg^0 concentration increased from midnight and reached the highest peak value at noon and then decreased. This was consistent with those measurements in CAMNet (Kellerhals *et al.*, 2003) and could be

explained to re-emission of mercury from surface soil of farmland for high temperature and solar radiation, or the transportation from the emission sources.

2.4 Hg^0 concentration in urban areas

Figs.4 and 5 show the hourly mean Hg^0 concentrations at 02:00, 08:00, 14:00 and 20:00 and the overall average concentration during each monitoring campaign at sites in Beijing and Guangzhou urban areas.

The overall mean Hg^0 concentration in Beijing reached the lowest $4.9 \pm 3.3 \text{ ng/m}^3$ in summer, the highest $8.3 \pm 3.6 \text{ ng/m}^3$ in winter, $6.5 \pm 5.2 \text{ ng/m}^3$ in spring, and $6.7 \pm 3.5 \text{ ng/m}^3$ in autumn (Fig.4). These concentrations were much higher than those measured in MT. Waliguan of remote continental background area, and slightly higher than that in Yangtze Delta regional background area. The highest Hg^0 concentration in winter was a little lower than the concentration (10.71 ng/m^3) reported by Liu *et al.* (2002) at the same monitoring site and the concentration (10.54 ng/m^3) in Guiyang (Feng *et al.*, 2004). The seasonal variation of Hg^0 concentrations in Beijing was consistent to that in Seoul of Korea (Kim and Kim 2001), but contrary to that in Mt. Waliguan. A high overall average Hg^0 concentration $13.5 \pm 7.1 \text{ ng/m}^3$ was also found in Guangzhou (Fig.5) indicating that strong local/regional anthropogenic sources

Fig. 3 Hourly mean Hg^0 concentrations at 02:00, 08:00, 14:00 and 20:00 during monitoring campaign in Yangtze Delta regional site.

Fig. 4 Hourly mean Hg^0 concentrations at 02:00, 08:00, 14:00 and 20:00 during monitoring campaign at Beijing urban site.

of mercury contributing to airborne Hg^0 not only in Beijing but also in Guangzhou.

Diurnal variation of Hg^0 concentration can be seen in Figs.4 and 5. It is obvious that the mean concentration reached the lowest value at 14:00 and the highest at 02:00 or 20:00 in all monitoring campaigns in Beijing and Guangzhou cities. These results contrasted with what's measured in Yangtze Delta regional site but were comparable to those reported of Lee *et al.* (1998) and Kim and Kim (2001). The features of diurnal variation in Beijing and Guangzhou could indicate the importance of local emission of Hg^0 in the urban areas. During nighttime local emission of Hg^0 accumulated in shallow boundary layer but during the daytime the concentrations of Hg^0 were

diluted by thermal mixing which results in the increases of the boundary-layer depth.

Summary of overall hourly average concentrations of Hg^0 at all sites during monitoring campaigns are given in Table 1.

3 Conclusions

The investigation of gaseous elemental mercury concentration in atmosphere conducted at Beijing and Guangzhou urban, Yangtze Delta regional sites and China Global Atmosphere Watch Baseline Observatory (CGAWBO) in Mt.Waliguan showed that the Hg^0 concentrations in continental background area, Mt.Waliguan, were comparable to that reported in global background area. However the concentrations in urban and regional sites were higher than what found in corresponding areas of Europe and North America. The Hg^0 concentrations in urban area were higher than those in regional background area and much higher than those in remote continental background in this study.

The features of concentration and diurnal variation of Hg^0 in urban areas indicated the importance of local anthropogenic sources in contributing to the high Hg^0 concentration in urban areas of China. Contrary seasonal variation patterns of Hg^0 concentration were found between remote continental and urban sites. These indicated

Fig. 5 Hourly mean Hg^0 concentrations at 02:00, 08:00, 14:00 and 20:00 during monitoring campaign at Guangzhou urban site.

Table 1 Summary of Hg^0 concentrations at all sites during monitoring campaigns

Site	Site type	Month	Mean (ng/m ³)	Minimum (ng/m ³)	Maximum (ng/m ³)
Waliguan	Remote continental	August	1.7±1.1	0.5	4.6
		December	0.6±0.08	0.5	0.8
Shuangqiao farm	Yangtze Delta regional	September	5.4±4.1	0.6	14.4
Guangzhou	Urban	January	13.5±7.1	6	31
		January	8.3±3.6	2.6	14.7
		April	6.5±5.2	2.3	29.1
		July	4.9±3.3	2	18.2
		October	6.7±3.5	3.4	13.2

that different processes and factors controlled Hg^0 concentration in urban, regional and remote areas.

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