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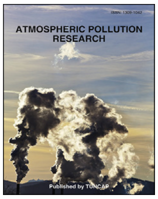

Original article

Mercury concentration in fine atmospheric particles during haze and non-haze days in Shanghai, China

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ABSTRACT

Concentrations of fine particulate mercury (PHg), particulate matter $\le 2.5\ \mu m$ ($PM_{2.5}$), and particulate matter $\le 10\ \mu m$ (PM_{10}) were monitored for the whole year of 2013 in Shanghai, China. The average concentrations of PHg were 1270 ± 716 pg/m^3 and 341 ± 187 pg/m^3 during haze and non-haze days respectively. The average PHg concentration throughout the whole year 2013 was 642 ± 616 pg/m^3. It was observed that PHg concentrations on haze days were 3 times higher than on non-haze days. The concentration of PHg on non-haze days in 2013 varied from 0.25 to 0.48 ng/m^3. The mean monthly PHg concentration was highest in December (1.92 ng/m^3), while the minimum mean concentration was observed in February and August (0.80 ng/m^3), and there was a clear seasonal variation: winter (1.67 ng/m^3), autumn (1.08 ng/m^3), spring (1.02 ng/m^3), and summer (1.00 ng/m^3) during haze days. The correlation between PHg and $PM_{2.5}$ was strong ($r = 0.96$ on haze days; $r = 0.90$ on non-haze days), while the correlation between PHg and PM_{10} was weaker ($r = 0.85$ on haze days; $r = 0.57$ on non-haze days). The PHg concentration on haze days was always higher than on non-haze days, indicating that haze conditions were accelerating the formation of PHg. The result also indicated that PHg was inclined to combine with fine particles. The existence of strong correlations between the concentrations of $PM_{2.5}$, PM_{10}, and PHg indicated the commonality of the contributing sources, such as traffic, industrial emissions, and the combustion of coal.

1. Introduction

Mercury (Hg) is a persistent, toxic, and bio-accumulative heavy metal. Its particular chemical and physical properties enable its long-range transport, and it is considered a global-scale pollutant. Atmospheric mercury exists primarily in three forms: gaseous elemental mercury (GEM), including elemental mercury (Hg^0) and divalent mercury (Hg^{2+}); particulate mercury (PHg); and reactive gaseous mercury (RGM) (Lindberg and Stratton, 1998). These three types of Hg have different physical and chemical properties. Mercury species occurring in airborne particulate matter could include both volatile mercury adsorbed on the particle surface, and oxidized inorganic mercury species, such as HgO, and HgS, bound with the particles (Brosset, 1987). Although atmospheric PHg comprises less than 10% of the total atmospheric Hg (Lu and Schroeder, 2004), it plays a crucial role in the atmospheric deposition of this metal. Studies (Dabrowski et al., 2008; Ito et al., 2006; Glodek and Pacyna, 2009) have indicated that one third or more of the anthropogenic Hg in the atmosphere is emitted by the combustion of coal worldwide. When Hg is released into the atmosphere, it can be transported over long distances (Boening, 2000). RGM is highly reactive and is rapidly scavenged by moist particles and surfaces, with the particulate and oxidized forms of mercury persisting for as long as one week. Therefore, these species are largely deposited locally, close to the source (Lindberg and Stratton, 1998). RGM concentrations are likely to be highly variable and related to point sources, meteorological conditions, and oxidant levels in the air. In contrast, PHg, whose residence time in the atmosphere is shorter than gaseous mercury, is associated with

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airborne particles, such as dust, soot, sea-salt aerosols, and ice crystals, or can be produced by the adsorption of RGM species on to atmospheric particles (Lu and Schroeder, 2004). Gaseous elemental mercury can be transported long distances, whereas PHg and gaseous oxidized mercury reflect more local sources.

Due to the chemical speciation of PHg it is vital to understand the cycling, transport, transformation, and deposition of Hg in the environment (Lu et al., 2001). Atmospheric particles are important surfaces for gaseous mercury to undergo adsorption and chemical transformation, which is critical in the biogeochemical cycle of mercury. First, PHg could enter the soil and water environment by dry and wet deposition, which is an important pathway for gaseous mercury (especially Hg^0) to settle and cause ecological damage (Schroeder and Munthe, 1998). Therefore, the PHg pollution problem has attracted increasing attention in recent years, and the characteristic of PHg under different weather conditions is becoming an important research topic. Zhang et al. (2013) quantified the total mercury and major ion concentrations in snow samples to understand the importance of this pathway and the sources of Hg deposited in Shanghai. Wang et al. (2004), found the mass concentration of PHg in fine particles was more than twice that in coarse particles, regardless of the season, the mercury in particulate matter $\leq$2.5 μm ($PM_{2.5}$) accounted for more than 70% of the mercury in particulate matter $\leq$10 μm (PM_{10}) in Shanghai. This indicates that mercury pollution in atmospheric particulate matter is liable to associate with fine particles, and also suggests that fine particles have a stronger ability to bind with mercury than coarse particles, which is consistent with other studies (Ferrari et al., 2002). Total PHg concentrations were measured in Changchun (Fang et al., 2001), a city in northeastern China, while Schleicher et al. (2015) measured PHg concentrations in total suspended particulate (TSP) and $PM_{2.5}$ samples in Beijing and found a strong seasonality as well as spatial differences within the city. Day—-night-differences were also investigated.

In recent decades, haze pollution has become a significant air pollution issue across China. High concentration of $PM_{2.5}$ is the main characteristic of haze pollution and is the primary factor causing the reduction of visibility, but they also have the potential to adversely impact human health and ecological systems, and lead to climate change. When a haze day occurs, the concentration of particles increases substantially, which provides a large surface for complicated oxidation and reduction reactions with species such as ozone (O_3), hydroxyl radical (OH), sulfur dioxide (SO_2), and the chloride ion (Cl^-). This could impact on the transformation of different mercury species, and the wet deposition of PHg which is one of the most important processes leading to the removal of mercury in the atmosphere.

The studies mentioned above have provided an understanding of the bioavailability of Hg and the toxicity of Hg present in atmospheric particulate matter. To determine the characteristics of mercury during hazy weather, this study examined extensive data sets for a full year of continuous measurements of PHg together with SO_2, nitrogen dioxide (NO_2), PM_{10}, O_3, $PM_{2.5}$, and carbon monoxide (CO) concentrations, and discusses PHg formation mechanisms, its relationships with other pollutants, and the relationship between PHg, and $PM_{2.5}$ and PM_{10}.

2. Methods

2.1. Sampling sites and ambient monitoring program

Sampling was undertaken at the three locations of Xu Jiahui Park, Cao hejing Development Zone Park, and Guilin Park (near Shanghai Normal University). Fig. 1 shows the site locations and confirms that they were not influenced by local pollution sources and also avoided buildings and residential emission sources such as coal or oil burning boilers, furnaces, and incinerators. These sites were representative of the urban district of Shanghai due to the mixture of residential areas, streets, hospitals, schools, public green spaces, office buildings, commercial buildings, squares, parks, and other public facilities. The sampling locations were on the roof of ten-story buildings (about 35 m above ground). There were no obstacles in the vicinity. During rain a large awning was used to protect the monitors from rain water damage. The PHg in fine particles, together with SO_2, NO_2, PM_{10}, $PM_{2.5}$, O_3, and CO were collected from the 1st January 2013 to 31st December 2013, throughout the whole year of 2013 and represented one year of continuous sampling, with nearly 366 data points for each indicator.

2.2. Experiments and methods

In this study, O_3 was measured with an EC9811 ozone photometer (Ecotech, Victoria Australia), CO was measured by instruments EC9830B (Ecotech, Victoria Australia), NO_2 was measured by Analyzer 42i-DNMSDAA (Thermo Scientific, Massachusetts USA), SO_2 was measured by 43i-DNSAA analyzer (Thermo Scientific, Massachusetts USA). Their detection limits were 0.5, 5, 0.5, and 0.5 ppb respectively, and the time resolution was 5 min for all instruments. The $PM_{2.5}$ and PM_{10} samples were collected using a TH-150C III sampler (Wuhan rainbow company, Wuhan China) (flow rate was 100 L/min, sampling time was 24 h), and the sample membrane was a quartz fiber filter membrane (diameter, 9.0 cm) (Whatman, Maidstone UK). Before sampling, all the membranes were calcinated in a muffle furnace at a temperature of 450 °C for 5 h, and then placed in a sealed bag after cooling. Before and after sampling, the membrane was balanced for 24 h, then the concentrations of each membrane were determined by analytical balance. After measuring the $PM_{2.5}$ concentration, the quartz fiber filters were cut into five circle parts, with four parts from around the edge and one part from the center, five parts were placed into Direct Mercury Analyzer (DMA-80, Milestone, Sorisole Italy) to analyze mercury concentrations. The certified Chinese reference material GBW11159 (coal, Chinese National Reference Materials Center, Beijing) was used to check the accuracy of the DMA method, with recoveries of 95–110%. Standards varied little over time and were within the calibrated ranges. The accuracy and precision of the methods were evaluated by addition and recovery tests. The accuracies ranged from 97.6 to 103.5% while the precision ranged from 3.3 to 5.8% for the DMA method under repeatable conditions. In addition, one blank sample was added to every batch of 10 samples, and no appreciable Hg contamination of blank sample was detected. The operation conditions for DMA-80 used throughout this work were based on the EPA Method 7473 protocol.

3. Results and discussion

3.1. Fine PHg concentrations

A comparison of PHg concentrations between Shanghai and other cities is given in Table 1. The average concentrations of PHg were 1270 ± 716 pg/m^3 and 341 ± 187 pg/m^3 during haze and non-haze days in Shanghai, respectively, and the total mean concentration of PHg throughout the whole year of 2013 was 642 ± 616 pg/m^3. The PHg concentrations on haze days were 3 times higher than on non-haze days, suggesting that PHg pollution on haze days was more severe than on non-haze days. The PHg concentration in Shanghai was higher than reported in other citiesm, but due to their different geographical locations, energy consumption, and environmental circumstances, different cities have different PHg

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