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Pattern of atmospheric mercury speciation during episodes of elevated PM2.5 levels in a coastal city in the Yangtze River Delta, China☆

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ABSTRACT

Measurement of atmospheric mercury speciation was conducted in a coastal city of the Yangtze River Delta, China from July 2013 to January 2014, in conjunction with air pollutants and meteorological parameters. The mean concentrations of gaseous elemental mercury (GEM), particulate bound mercury (HgP) and reactive gaseous mercury (RGM) were 3.26 ± 1.63 ng m^{-3}, 659 ± 931 pg m^{-3}, and 197 ± 246 pg m^{-3}, respectively. High percentages of HgP during haze days were found, due to the increase in direct emissions and gas-particle partitioning of RGM. The average gas-particle partitioning coefficients (Kp) during moderate or severe haze days (PM2.5 > 150 μg m^{-3}) were obviously decreased. GEM and HgP were positively correlated with PM2.5, SO_2, NO_2 and CO, suggesting a significant contribution of anthropogenic sources. Elevated HgP concentrations in cold seasons and in the morning were observed while RGM exhibited different seasonal and diurnal pattern. The ratio of HgP/SO_2 and Pearson correlation analysis suggested that coal combustion was the main cause of increasing atmospheric Hg concentrations. The monitoring site was affected by local, regional and interregional sources. The back trajectory analysis suggested that air mass from northwest China and Huabei Plain contributed to elevated atmospheric Hg in winter and autumn, while southeast China with clean air masses were the major contributor in summer.

1. Introduction

Attention on atmospheric mercury has increased over the past decades due to its significant impact on the global mercury cycle and human and ecosystem health (Driscoll et al., 2013; Krabbenhoft and Sunderland, 2013). The US EPA has promulgated Mercury and Air Toxics Standard, while global mercury assessment report was launched periodically by the United Nations Environment Programme (USEPA, 2011; UNEP, 2013). However, there is very limited information on speciation pattern and fates of atmospheric Hg in developing countries of Asia, which contributed about 50% of the global total anthropogenic mercury emissions (Fu et al., 2011; Han et al., 2014).

Generally, atmospheric Hg exists as gaseous elemental (GEM, >90%) and reactive gaseous (RGM) as well as particulate bound (HgP) species (Poissant et al., 2004). They are emitted from various natural and anthropogenic sources, as the latter being considered as the major sources of atmospheric Hg (Fu et al., 2012). Owing to high volatility and long residence time, GEM can undergo long-range transport that can contribute to mercury pollution at regional and global scales (Lindqvist and Rodhe, 1985; Schroeder and Munthe, 1998). Due to high water solubility and adsorption on particles, HgP and RGM tend to affect the terrestrial ecosystem by wet and dry deposition (Xu et al., 2014). In North America and Europe, the average GEM concentrations were approximately

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2.5 ng m^{-3} at urban sites and 1.5 ng m^{-3} at rural sites, the latter being closer to background concentrations in the Northern Hemisphere (Choi et al., 2013; Kim et al., 2005). HgP and RGM concentrations in urban areas occur in the range of 10–50 pg m^{-3} and 5–80 pg m^{-3}, respectively (Kolker et al., 2013; Ren et al., 2014). However, in East Asia, atmospheric Hg is considerably higher, ranging between 2.0 and 18.4 ng m^{-3} for GEM, 4.8–368 pg m^{-3} for HgP and 2.8–61 pg m^{-3} for RGM (Fu et al., 2012; Han et al., 2014; Xu et al., 2015). Especially, percentage of HgP concentrations are usually very high in Asia/China: up to 10% HgP (Fu et al., 2012). Schleicher et al. (2015) reported that the averaged HgP concentrations for PM2.5 and TSP samples in Beijing were 270 pg m^{-3} and 570 pg m^{-3}, respectively.

According to field and modeling studies, key factors that impact the partitioning of atmospheric Hg include air temperature, relative humidity (RH), solar radiation (SR), and aerosol particle loadings (Amos et al., 2012; Mao et al., 2012; Rutter and Schauer, 2007a, 2007b; Rutter et al., 2012). Some studies found that differences in RGM production between upland and coastal sites might be affected by sea salt aerosols (Engle et al., 2008; Mao and Talbot, 2012). Ammonium sulfate, adipic acid and levoglucosan could cause RGM to partition to the gas phase, while sodium nitrate and the chlorides of potassium and sodium direct RGM to the particle phase (Rutter and Schauer, 2007b). Holmes et al. (2009) suggested that RGM is preferentially taken up by particles at low RH, increasing the chloride content of aerosols. Recently, due to the elevated PM2.5 levels induced by rapid industrialization and urbanization, effects of aerosol particle loadings on atmospheric Hg speciation in coastal areas of East Asia are continuously developed as a key scientific issue. Current researches suggested that anthropogenic activities have a strong impact on climate and air quality, not only by enhancing chemical concentrations (e.g., O_3, PM2.5, CO) but also by increasing deposition fluxes of atmospheric Hg (Glotfelty et al., 2014; Van Metre, 2012).

China is considered as a large and growing source region for atmospheric Hg emissions (Fu et al., 2012, 2015; Wang et al., 2014a,b). With about 500–800 t of anthropogenic mercury emissions, China contributes one-third of the global total (UNEP, 2013; Wang et al., 2014a,b). Coal combustion and non-ferrous metals smelting are the two biggest Hg emitter categories in China (Streets et al., 2005). In addition, battery and fluorescent lamp production, cement production, mercury mining, and biofuel burning are also major contributors of Hg emissions. Schleicher et al. (2016) reported that mitigation measures (including traffic reductions, industry closures and cleaner production techniques for industries, etc.) could largely reduce anthropogenic HgP pollution in Beijing, indicating the influence of human activities. In general, GEM concentrations in northern, southern, and eastern China were higher than those in northeastern, northwestern, and southwestern China (Fu et al., 2015). Especially, most coastal cities are densely populated and heavily industrialized. The high energy demand and the presence of other large point sources (e.g., coal-fired power plants, iron and steel production) contribute to the large GEM emissions. With the severe and persistent of poor air quality (e.g. extremely high concentrations of PM2.5) in recent years (Huang et al., 2014), an emerging challenge is to understand pollution characteristics of atmospheric Hg speciation in coastal areas (Chen et al., 2016; Yu et al., 2015). This region is under the influence of the seasonal monsoon and large emissions of air pollutants originated from intense human activities. Whereas our previous studies focused on the distribution and wet deposition of atmospheric Hg in a relatively clean coastal region (Xu et al., 2014, 2015), the Yangtze River Delta (YRD) offers an opportunity to study the speciation of atmospheric Hg in a highly populous and industrialized coastal region (Fu et al., 2013; Zhu et al., 2015). Ningbo, an important industrial city in the south wing of the YRD, is seriously polluted due to its proximity to many coal-fired power plants, steel plants and oil refineries. The objective of this study is to better understand speciation pattern and potential sources of atmospheric Hg during haze and non-haze days. Therefore, we set out to: (1) characterize seasonal and diurnal patterns of GEM, HgP and RGM concentrations; (2) apportion Hg species between low and high concentrations of PM2.5 by exploring relationships among Hg species, air pollutants (including O_3, SO_2, CO and NO_2) and meteorological data; (3) verify episodic Hg source input using modeled back-trajectories.

2. Materials and methods

2.1. Description of study site

The GEM, HgP, and RGM concentrations were measured on the Ningbo Polytechnic campus (Lat.: 29.89 N, Long.: 121.81 E), from July 2013 to January 2014 (Fig. 1). The Hg monitoring system was located ~5 m above the ground on the roof of a teaching building. Experiencing subtropical weather, subject to East Asian monsoons, Ningbo is an urbanized coastal city in the YRD. The prevailing wind in the Ningbo region is from the south in spring and summer, and the north in autumn and winter.

2.2. Atmospheric Hg sampling and analysis

Sample collection was described in our previous publication (Xu et al., 2015). Briefly, an automated Tekran 2537X, 1130 and 1135 (TekranInc.,Toronto, Canada) system was used to measure GEM, HgP, and RGM concentrations, respectively. The total air sampling rate was 10 L min^{-1}, where RGM and HgP were collected over 2-h intervals on a KCl-coated denuder and quartz filter, respectively. Hg^0 was collected using gold cartridges for 5-min intervals at a flow rate of 1 L min^{-1}. Sampling lines were initially flushed with zero gas, and the captured HgP and RGM were sequentially desorbed at 800 °C and 500 °C, respectively. Analysis was performed using a Cold Vapor Atomic Fluorescence Spectrometer (CVAFS).

The Tekran 2537X was calibrated automatically every 24-h using an internal permeation source. The inlet glassware, KCl-coated denuder, and quartz filter were replaced every two weeks according to our previous methods (Xu et al., 2015). The calibration curve for both gold cartridges showed good linearity ($R^2 > 0.995$). Calculated as 3 times the standard deviation (SD) of system blanks, the method detection limit (MDL) for RGM and HgP in this study was 1.25 pg m^{-3}. And the MDL for GEM is 0.06 ng m^{-3}. Based on air intake rate of 1 and 10 L min^{-1}, detection levels for GEM and RGM/Hgp were 0.0036 ng and 0.75 pg respectively for each 1 h sampling period.

2.3. Meteorological parameters and air pollutants

Meteorological parameters including wind speed (WS) and direction (WD), temperature (T), relative humidity (RH), and solar radiation (SR) were measured by portable automatic weather station (Xinpuhui CO., Wuhan, China) on the roof at the observation site. These data were averaged over 1 min intervals during the measurement period. Air pollutants (including O_3, SO_2, CO and NO_2) were simultaneously monitored using Air Quality Monitoring Systems (AQMS-9000, BMET CO., China). These data were averaged hourly during the measurement period, as described in Table 1. Mass concentrations of PM2.5 and PM10 were measured every 5 min on a heated (50 °C) air sample using a Tapered Element Oscillating Microbalance (TEOM) sampler (RP1400, Thermo Fisher Scientific, Waltham, MA, USA). The TEOM sampler was calibrated regularly by filters with measured masses.