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Atmospheric mercury speciation in Shanghai, China

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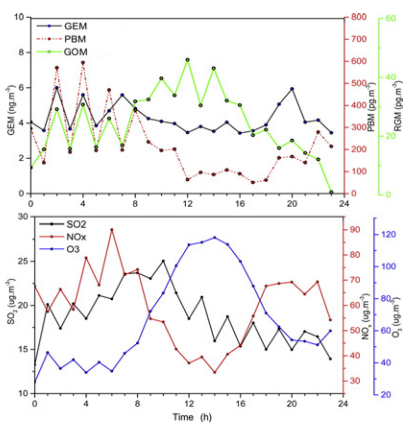
HIGHLIGHTS

- Hg species at a suburban site in Shanghai were lower than that in most urban areas of China.
- Three kinds of atmospheric speciated mercury exhibited totally different diurnal pattern.
- No significant correlations between Hg species and air pollutants were found.
- PSCF result showed that Shanghai was mainly impacted by local emission.

GRAPHICAL ABSTRACT



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ABSTRACT

GEM (Gaseous elemental mercury), fine fraction (<2.5 μm) PBM (Particle-bound mercury) and GOM (Gaseous oxidized mercury) were continuously monitored from Jun 1 to Dec 31 2014 at a suburban site in Shanghai. The average concentrations of GEM, PBM and GOM were 4.19 ± 9.13 ng·m^{-3}, 197 ± 877 pg·m^{-3}, 21 ± 100 pg·m^{-3}, respectively, which were all much higher than those at urban sites in Europe and North America and rural areas of China, but lower than those at urban sites of China. The concentrations of the three mercury species were all found with the highest concentration in December than those in summer. Overall, GEM varied little and PBM exhibited higher level during the night, while GOM typically peaked in the noon and afternoon which is consistent with that of ozone, indicating that GOM may depend on the stronger photochemical reactions during the daytime. Despite of the weak correlations of GEM with SO_2 ($r = 0.14$, $p < 0.0001$) and NO_X ($r = 0.17$, $p < 0.0001$), GEM, PBM, SO_2 and NO_x exhibited similar diurnal trend, suggesting that coal combustion might be the important sources of mercury in Shanghai because there is no mercury mining companies and few mercuric manufacturers in Shanghai. The strong correlation of PBM with GEM and GOM showed that directly anthropogenic emission was an important source of GEM and PBM, but the gas-particle partitioning of GOM and GEM might be also another source of PBM. The lower GEM/CO ratio of 3.9 (ng·m^{-3}·ppmv^{-1}) in Shanghai than that for mainland China and non-ferrous smelting factories were related to the few non-ferrous smelting factories

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around Shanghai. The results from the potential source contribution function (PSCF) model furtherly illustrated that in Shanghai the concentration of GEM in summer and autumn might be highly impacted by the local and regional source but wasn't heavily affected by long-range transport.

1. Introduction

Mercury (Hg) is a global toxic pollutant with bioaccumulation along food chain and poses a great threat to human health and environment effects (Schroeder and Munthe, 1998). It has both natural and anthropogenic sources. Natural sources mainly include volcanoes, forest fires and evaporation from soil and water surface, while anthropogenic emissions mainly consist of coal combustion, metal production, municipal and biomedical solid waste incineration (Kim et al., 2009; Xu et al., 2015). Generally, atmospheric mercury is operationally defined as three forms including gaseous elemental mercury (GEM or Hg^0), gaseous oxidized mercury (GOM or Hg^{2+}), and particulate bound mercury (PBM). Due to different physicochemical characteristics and associated reactivity in various environmental media, the different forms of mercury play discrepant roles in wet and dry deposition, evasion from soil, and sedimentation in aquatic and terrestrial ecosystems (Kim et al., 2005; Mason et al., 2005). It is of great significance to understand the temporal and spatial distribution of speciated mercury. Many studies have shown that GEM is the dominant existing form of mercury in the atmosphere and comprises the majority of mercury (~95%). Because of its higher volatility and water insolubility, GEM has a long residence time (around 0.5–2 years) in the atmosphere and can transport over long distance. In theory, mercury can be converted from one to another form via various photochemical oxidation or reduction reactions during long-range transportation. For example, Hg^0 can be oxidized to Hg^{2+} by reactions with O_3, OH, and other oxidants through various photo-chemical reactions; on the contrary, Hg^{2+} may be transformed to Hg^0 by reduction with SO_2 (g) or SO_3^{2-} (aq) (Pal and Ariya, 2004; Schmidt et al., 2015; Zhao et al., 2006). The major reduction pathways of Hg^{2+} are in the aqueous phase, which include reductions with sulfite (SO_3^{2-}) and iron, and photo-reduction (Lyman and Jaffe, 2012; Zhang and Lindberg, 2001). The deposition of GEM and GOM through bounding with the particles resulting in the higher fraction of PBM in the atmosphere. PBM and GOM are supposed to deposit quickly through wet and dry deposition, therefore, PBM and GOM are more significant in the regional cycle than global transportation. Long term measurement of atmospheric mercury (Fu et al., 2012a; Fu et al., 2012b; Zhang et al., 2013) is essential to reveal the behaviors of regional atmospheric mercury and identify the contribution of local or regional emission sources.

Currently, China has been undergoing a fast economic growth and the rapid urbanization and industrialization resulted in enormous consumption of energy and raw material. Mercury is surely one important byproduct of energy consumption, so plenty of studies have been conducted in both rural and urban areas on the source, sink and exchange rules of long- or short-range transportation (Cheng et al., 2014; Choi et al., 2013; Kim et al., 2009; Liu et al., 2010; Nair et al., 2012). Some field measurements have also been reported on urban and mining/industrial regions in China (Friedli et al., 2011; Fu et al., 2011; Xu et al., 2015). But Shanghai must have different stories because it is not only a metropolis with a population of 24.2 million and massive traffic volume of nearly three millions, but also an industrialized city crowed with such heavy industries as petrochemical and united iron & steel companies. The higher coal consumption for electricity and industrial boilers must lead to higher atmospheric mercury. Another interesting point is that Shanghai located in special weather belt impacted by interaction between marine and inland airflows. However, few studies of GEM, GOM and PBM in Shanghai have been published (Friedli et al., 2011). Particularly, haze pollution has become a disturbing problem for Shanghai people in recent time. Several studies began to be concerned the change of atmospheric behavior of mercury during the haze days (Duan et al., 2016; Zhu et al., 2015).

In this study, atmospheric GEM, PBM, GOM as well as CO, O_3, SO_2, NO, NO_2, NO_x and $PM_{2.5}$ were measured simultaneous in the Dianshan Lake in Qingpu, Shanghai, by Tekran speciation systems from June to December in 2014. This monitoring site is representative of suburban areas in Shanghai, without major industrial sources of mercury nearby. A main goal of this paper is to study temporal distributions of atmospheric Hg species and its dependence on other air pollutants at typical suburban site in Shanghai. The factors affecting its behaviors and the potential sources of mercury were screened and identified by utilizing the basis of Potential Sources Contribution Function (PSCF) model.

2. Methods

2.1. Site description

Atmospheric speciated mercury were observed on the top roof (latitude: N31°05′53.25″ longitude: E120°59′52.90″, height: 17 m) of a four story building, an environment monitoring station of Shanghai located in Qingpu, Shanghai. As shown in Fig. 1, the observation site is adjacent to a highway intersection with moderate traffic volume and located 0.5 km away from Dianshan Lake in Qingpu District. Qingpu District is famous for the Dianshan Lake which is the largest freshwater lake in Shanghai. The surrounding areas within 20 km of the site are largely suburban, without large point sources in any direction.

2.2. Measurement of atmospheric mercury species

The mercury measurement campaign was conducted from 1st June to 31st December 2014. A Tekran analyzer (Tekran® Corporation, Inc., 2537B/1135/1130, Toronto, Ontario, Canada) was employed in this study for measurements of GEM, PBM, and GOM. During the 1 h of sampling period, the ambient was drawn into the sampling train with the flow rate of 10 $L\cdot min^{-1}$, where GOM and PBM were collected onto the KCl-coated quartz annular denuder followed by the quartz filter (47 mm). The air with 1 $L\cdot min^{-1}$ then entered the unit 2537B of Tekran for GEM measurement with a time resolution of 5 min. In the following 1 h for desorbing, the sampling lines were firstly flushed with zero gas, and the captured PBM and GOM were sequentially desorbed at 800 °C and 500 °C, respectively, and then quantified as GEM by the Tekran 2537B.

2.3. Other pollutant data and meteorological data

The air pollutants including O_3, SO_2, CO, NO_x and $PM_{2.5}$ were simultaneously monitored at the observation site by Thermo Fisher 49i, 43i, 48Itle, 43i and 1405F, respectively. The detection limits of O_3, SO_2, CO, NO_x and $PM_{2.5}$ were 1.0, 0.5, 25, 0.4 and 0.1 $\mu g/m^{-3}$, respectively. All the data were hourly averaged. The instruments were tested and calibrated periodically.

2.4. Quality assurance and quality control (QA/QC)

The Tekran 2537B instrument routinely undergoes automated daily calibrations using an internal GEM permeation source and external manual calibration when necessary. Two-point calibrations including (zero calibration and span calibration) were performed separately for each pure gold cartridge. Manual injections were used to evaluate