



Comparison of atmospheric PM_{2.5}-bounded mercury species and their correlation with bromine and iodine at coastal urban and island sites in the eastern China



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ABSTRACT

A year-long observation of PM_{2.5}-bounded mercury (PBM) and its species was conducted at a urban site (Shanghai, Xuhui; XH) and an island site (Shengsi, SS) in eastern China from September 2014 to August 2015. The seasonal variation of mercury species including hydrochloric soluble particle-phase mercury (HPM), element soluble particle-phase mercury (EPM) and residual soluble particle-phase mercury (RPM), as well as particulate halogen (Br, I) were determined. Annual average concentration of PBM at urban was $0.32 \pm 0.13 \text{ ng} \cdot \text{m}^{-3}$, and was $0.22 \pm 0.18 \text{ ng} \cdot \text{m}^{-3}$ at island, which might be attributed to anthropogenic sources. Include more results here, such as EPM, RPM, and with comparison like “The speciated mercury in PM_{2.5} was found to be HPM > RPM > EPM at the urban site, while RPM > HPM > EPM at island site, respectively.” The speciated mercury in PM_{2.5} showed distinct different concentrations between the two sites. HPM concentration is the highest at urban, but RPM showed the largest fraction at island. Higher mass contents of all PM_{2.5}-bounded mercury species were found at island site than those at urban site, which indicated atmospheric mercury is more easily scavenged by particles at ocean atmosphere. Additionally, the correlation between bromine and mercury was stronger at urban site than that at island site, while iodine had the stronger correlation with mercury at island site than that urban site. These results showed marine aerosols played an important role to the transport of mercury.

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1. Introduction

Mercury (Hg) is a volatile heavy metal, which is causing global concerns for its impact on environment, and the atmosphere is the dominant medium for its transport in global scale via different physical, chemical, and photochemical processes and interactions (Lin and Pehkonen, 1999). Therefore, it is important to characterize Hg emission, to better understand its chemical transports in the atmosphere. The sources of atmospheric mercury were classified into anthropogenic sources: coal combustion, metal production, waste incineration and artisanal gold mining and natural sources: soils, vegetation, agriculture and the oceans (Rasmussen, 1995; Pirrone et al., 2001; Pyle and Mather, 2003; Selin, 2009; Pirrone et al., 2010). Even though the contribution of oceanic emission has not been taken into account in global atmospheric mercury budget, several data have shown that oceanic emission of mercury possibly count for as much as 39% of global emissions (Mason and Sheu, 2002). Therefore, it is necessary to study the forms, behaviors of mercury in the marine environment to investigate its contributions to the global mercury pollution.

There are three mercury forms in the atmosphere: gaseous elemental mercury (GEM), reactive gaseous mercury (RGM) and particle-bounded mercury (PBM). RGM and PBM have a residence time of a few days or weeks so that they both have higher deposition rates. PBM was around 0.3–0.5% of GEM, except in the industrialized regions (possibly up to 20% of TGM) (Schroeder and Munthe, 1998; Lin and Pehkonen, 1999). In general, PBM only constitutes as a small part of total airborne Hg, but the fast transfer from Hg^{II} to PBM and oxidation of Hg⁰ in certain conditions during air masses transport could lead to a higher concentration of PBM (Lynam and Keeler, 2005; Poissant et al., 2005). Overall, PBM plays an important role in global mercury cycle. In our previous study (Xiu et al., 2009), the mercury in particles was extracted and defined operationally into four species: exchangeable particulate mercury (EXPM), HCl-soluble particulate mercury (HPM, mainly Hg²⁺), elemental particulate mercury (EPM, Hg⁰) and residual particulate mercury (RPM). Actually, emission sources, particle components, regional atmospheric chemistry, and near-ground micro-meteorological conditions may influence the temporal variation and spatial distribution of atmospheric mercury species, concentration, and deposition flux (Poissant and Hoenninger, 2004; Poissant et al., 2005; Jen et al., 2014; Zhao et al., 2015). The relationships among speciated mercury and other compositions in particles might reflect three pathways for gaseous mercury

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formation: the direct nucleation of gaseous mercury after atmospheric reaction with oxidants such as ozone, halogen; the heterogeneous interaction of gaseous mercury with aerosol particles; the recombination of gaseous mercury with particle through condensation. However, the detailed gas-particle transformation mechanism of the mercury is still unclear. The available experimental and observation data in surface air suggested that the oxidation of mercury must be photochemical reaction (Auzmendi-Murua et al., 2014). Therefore, it is necessary to study the relationship between the speciated mercury and oxidants in particles to provide some evidences of gas-particle partition mechanism.

It has been speculated that gaseous elemental Hg (Hg^0) can be oxidized by abundant halogen species, such as bromine (Br), BrO and BrCl, to reactive gaseous Hg compounds in marine environments, which might bring higher deposition rate during cross-ocean transport (Sprovieri et al., 2003; Hedgecock et al., 2005; Steffen et al., 2015). Moreover, bromine and iodine are important trace components in atmosphere, which participate in chemical reactions and lead to effective O_3 -losses and new particle production in coastal regions, oxidation of DMS (Dimethyl sulfide), as well as removal of nitrogen oxides. Some studies noticed the halogenation chemistry of mercury under ambient or near ambient conditions (Leblanc et al., 2006; Enami et al., 2007). Thus, halogen, which is mostly originated from ocean and acts as significant scavenger for air pollutants, is important to the global mercury cycle (Prados-Roman et al., 2015). Normally, if halogen can accelerate the conversion of mercury species, the relationship of the mercury species and halogen in particles might be different in coastal and island atmosphere. However, there are few reports about the role of halogen in atmospheric mercury deposition during the middle-scale transport.

Continuous measurements of atmospheric particulate mercury concentration and speciation play a key role in identifying characteristics and sources of particulate mercury. The aim of this study is to compare the levels of mercury species and halogens at two sites to investigate the interaction of atmospheric mercury in ocean and continental aerosol.

2. Experiment and methods

2.1. Sampling

One site (XH), representing coastal-urban site, was set up at the top of a four-floor building in East China University of Science and Technology (ECUST) (N31°8'43", E121°25'31"), about 15 m above ground, which is surrounded by a residential area and has no major anthropogenic industrial sources. At this site, the weather data was collected from weather history for Shanghai Hongqiao airport, China, weather underground (<http://www.wunderground.com/>), meanwhile, the normal atmospheric pollutants data were collected from Shanghai Municipal Environmental Protection Bureau (<http://www.sepb.gov.cn/fa/cms/shhj/index.htm>).

Another site (SS) is located in the southernwest part of Shanghai, representing coastal-island site. The instrument is set up at the top of a four-floor building in CAIYUAN middle school (N30°43'52", E122°27'27"), about 16 m above ground. The island site is located at the east of Hangzhou Bay, in Shengsi Island, Zhejiang province. There are no major anthropogenic industrial sources. At this site, the weather and normal atmospheric pollutants data were collected from Shengsi environmental monitoring station.

All daily $\text{PM}_{2.5}$ samples were collected at two sites (110 samples for XH and 75 samples for SS, respectively) from the 15th of September 2014 to the 20th of August 2015, representing fall (September, October, November), winter (December, January, February), spring (March, April, May), and summer (June, July, August), respectively. A medium-volume-sampler (TH-150C, China) loaded with 90 mm quartz filter (Whatman, USA) was used to collect $\text{PM}_{2.5}$ samples from 9:00 am to next 8:00 am operated at flow rate of $100 \text{ L} \cdot \text{min}^{-1}$. Each filter sample was wrapped in individual aluminum foil and was then sealed in Teflon bags. All samples were stored at $-18 \text{ }^\circ\text{C}$ prior to analysis. The quality

assurance (QA)/quality control (QC) for the analysis were conducted the same as described previously (Xiu et al., 2005, 2009), and field blanks (one blank per ten sampling filters) were collected.

2.2. Analytical procedure

2.2.1. Concentrations of $\text{PM}_{2.5}$

All filters were conditioned at a temperature of $(25 \pm 1) \text{ }^\circ\text{C}$ and at a relative humidity of $(40 \pm 5) \%$ for 24 h and weighed by using an electronic Balance (Sartorius, Germany) with a detection limit of 0.01 mg. The $\text{PM}_{2.5}$ mass trapped on each filter was measured by weighing the filter before and after sampling, and the corresponding $\text{PM}_{2.5}$ concentration was calculated by mass/sampled air volume. Before analysis, each filter was cut into four pieces to be pretreated for different analysis.

2.2.2. PBM

For the analysis of PBM in $\text{PM}_{2.5}$, a quarter of $\text{PM}_{2.5}$ filter was digested in a high pressure microwave digester, in which 20 mL of HNO_3 solution (10% HNO_3 , 1.6 M) was added according to the EPA method IO-5.0 (U.S. EPA, 1999). The samples were heated at $160 \text{ }^\circ\text{C}$ and 70 psi over 20 min in CEM Mars Xpress (PyNN Corporation, USA). Once the heating program was finished, the digesters were cooled down to ambient temperature, leaving a residual pressure in the vessels. According to EPA method 1631E (U.S. EPA, 2002), 5 mL of the digested solutions were added into the 50 mL tubes and diluted to 20 mL with distilled water. After the elemental and mono-divalent mercury forms were oxidized to Hg^{2+} by the addition of BrCl (0.5% of the sample volume), 0.5 mL of $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution, 30 mL of distilled water and 0.5 mL of SnCl_2 solution were then added to reduce all Hg^{2+} to Hg^0 . Finally, the sample was purged onto a gold trap with N_2 for 20 min and then determined by Atomic Fluorescence Spectrometry (AFS-9130, China).

2.2.3. HPM, EPM and RPM

A three-step extraction method was applied to measure the particle phase mercury with a quarter of $\text{PM}_{2.5}$ filter. HPM (mainly Hg^{2+} including HgCl_2 , HgO_2 , and HgBr_2), EPM (Hg^0) and RPM had been analyzed based on the experimental protocols described in previous studies (Xiu et al., 2005, 2009). All of mercury species were determined by Atomic Fluorescence Spectrometry (AFS-9130, China). In this study, the detection limit was $0.05 \mu\text{g} \cdot \text{L}^{-1}$ and the recovery of mercury was 95%. The RSD of replicate measurements was 4.1% for mercury. Detailed quality assurance for measurement had been shown in previous study (Xiu et al., 2005).

2.2.4. Bromine and iodine

Total bromine and iodine in a quarter of $\text{PM}_{2.5}$ filter were digested in CEM Mars Xpress (PyNN Corporation, USA), in which 5 mL HNO_3 , 2 mL H_2O_2 and 2 drops of HF (about 0.1 mL) were added. The samples were heated to $120 \text{ }^\circ\text{C}$ in 5 min firstly and then kept at $200 \text{ }^\circ\text{C}$ for 15 min. Once the heating program was finished the digester was cooled down to ambient temperature, leaving a residual pressure in the vessels. The solution was then transferred to a 50 mL flask and diluted to 20 mL with ultra-pure water. After 1 mL per-sulfate (20% $\text{Na}_2\text{S}_2\text{O}_8$) and 1 drop (about 0.05 mL) of silver nitrate (0.5% AgNO_3 solution) were added, the samples were then heated in a $45 \text{ }^\circ\text{C}$ water bath for 10 min, cooled down to ambient temperature and then diluted to 50 mL with distilled water. Finally, inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer, USA) was used to measure the total Br and I. The main method was reported by previous study (Gao et al., 2010).

In this study, the detection limits of bromine and iodine were $3.2 \mu\text{g} \cdot \text{L}^{-1}$ and $1.1 \mu\text{g} \cdot \text{L}^{-1}$, respectively. The relative standard deviations at the $30 \mu\text{g} \cdot \text{L}^{-1}$ level for bromine and iodine were 2.5% and 9.5% ($n = 4$), respectively. The recoveries of bromine and iodine (spiked samples with $10 \mu\text{g} \cdot \text{L}^{-1}$) were 98% and 109% respectively. The bromine and

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