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Characteristics and source appointment of atmospheric particulate mercury over East China Sea: Implication on the deposition of atmospheric particulate mercury in marine environment☆

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ABSTRACT

Total Suspended Particulate (TSP) samples were collected at Huaniao Island in northern East China Sea (ECS) from March 2012 to January 2013. Chemical analysis were conducted to measure the concentration of total particulate mercury (TPM) and speciated particulate mercury including HCl-soluble particulate mercury (HPM), elemental particulate mercury (EPM) and residual particulate mercury (RPM). The bromine (Br) and iodine (I) on particles were also detected. The mean concentration of TPM during the study period was 0.23 ± 0.15 ng m^{-3}, while the obviously seasonal variation was found that the concentrations of TPM in spring, summer, fall and winter were 0.34 ± 0.20 ng m^{-3}, 0.15 ± 0.03 ng m^{-3}, 0.15 ± 0.05 ng m^{-3} and 0.27 ± 0.26 ng m^{-3}, respectively. The statistically strong correlation of bromine and iodine to HPM was only found in spring with $r = 0.81$ and 0.77 ($p < 0.01$), respectively. While the strongest correlations between EPM and bromine and iodine were found in winter with $r = 0.92$ (Br) and 0.96 (I) ($p < 0.01$), respectively. The clustered 72-h backward trajectories of different seasons and the whole sampling period were categorized into 4 groups. In spring, the clusters passed a long distance across the East China Sea and brought about low concentration of mercury due to the deposition of mercury over the sea. The cluster of air mass across the sea had low concentration of HPM in winter, which suggested that the oxidation of mercury in winter might be related to other oxidants. During the whole sampling period, the air mass from the north of China contributed to the higher concentration of TPM in Huaniao Island.

1. Introduction

Mercury, with high toxicity and strong bioaccumulation, poses a great threat on human health and ecosystem (Lindberg and Stratton, 1998). Mercury is commonly emitted into the atmosphere from a variety of natural (e.g., surface waters, biomass burning and volcanoes) and anthropogenic sources (e.g. fossil-fuel combustion, metals manufacturing and incinerators) (Pirrone et al., 2010). Generally, mercury exists primarily in the atmosphere as three forms: gaseous elemental mercury (GEM, Hg^0), gaseous oxidized mercury (GOM, Hg^{2+}) and total particulate mercury (TPM) (Lindberg and Stratton, 1998). As the predominant form of mercury in the atmosphere, GEM has a relatively long atmospheric lifetime (0.5–2 years) due to its high volatility and stability and can be transported on the global scale (thousands of kilometers). While GOM and TPM, typically released from the combustion processes (i.e., coal-fired energy generating units), usually transport across much shorter distances (tens to hundreds of kilometers) due to their physical and chemical properties (Choi et al., 2013; Kim et al., 2009; Lindberg and Stratton, 1998; Schroeder and Munthe, 1998). Although atmospheric TPM accounts for less than 10% of the total atmospheric Hg (Xiu et al., 2005), it plays an important role in mercury deposition. Based on the previous studies (Duan et al., 2016; Xiu et al., 2005, 2009), the sequential extraction methods for mercury species in particles was adopted to define the three important forms including HPM (HCl-soluble particle-phase

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mercury), EPM (elemental particle-phase mercury) and RPM (residual particle-phase mercury), in order to reveal different deposition mechanisms during transportation of elemental mercury in the atmosphere. HPM is supposed to consist of such oxidized mercury as HgO, $HgSO_4$, $HgCl_2$, $HgBr_2$, HgI_2, while EPM were usually formed through condensation of elemental mercury on particles. RPM might contain HgS, HgSe, organic mercury, and some other species in the core of the particles.

It has been reported that halogen species play significant role in mercury deposition and were responsible for Atmospheric Mercury Depletion Events (AMDEs) (Lindberg et al., 2002; Schroeder et al., 1998). During AMDEs, the concentration of GEM rapidly decreased to a low enough level which is even below global background concentration, while the concentrations of GOM and TPM increased initially (Lindberg et al., 2002; Moore et al., 2013; Schroeder et al., 1998). AMDEs were originally thought to primarily occur at high-latitude regions or low temperature regions in the presence of reactive halogen species and sunlight. Recent studies (Duan et al., 2016; Gao et al., 2010; Xu et al., 2015) suggested that high level of halogens play the disproportionately large role in conversion from Hg^0 to Hg^{2+} in the marine boundary layer (MBL) in coastal cities, thereby leading to rapid deposition of gaseous elemental mercury to the ocean body.

Atmospheric mercury pollution must be one of the important problems in China because more than 50% of coal in the world was consumed there. Higher atmospheric mercury emission may result in elevated atmospheric Hg concentration and deposition flux in the neighbor regions of sources in China. In addition to the continental sources, the ocean was also recognized to be a special source of GEM and sink for oxidized mercury (i.e., gaseous oxidized mercury (GOM) and TPM) (Cheng et al., 2013, 2014). There are rich reactive bromine and iodine in ocean atmosphere which can potentially enhancing the oxidization of GEM to GOM, while the affinity of GOM with NaCl concentrated on sea salt aerosols over the ocean is also conductive to the partition of reactive mercury on particle surface (Rutter and Schauer, 2007). It therefore is important to study the potential impacts of marine atmosphere on the environmental behavior of atmospheric mercury. However, studies on the atmospheric TPM in the eastern coastal island remain limited. The objectives of this study were to investigate the levels, spatial distribution and seasonal variation of TPM in the atmosphere of East China Sea, and to ascertain the relationships between TPM and halogens (Br and I). Findings from this investigation are discussed in terms of better understanding the behavior and cycling of atmospheric TPM in the marine environment.

2. Materials and methods

2.1. Description of sampling site

Sampling was conducted on Huaniao Island (122.67 °E, 30.86 °N) which is located in the northern East China Sea (ECS). Fig. 1 shows the location of sampling site which is located approximately 100 km to continental area in the Yangtze River estuary. The sampling site was not influenced by the local emission since only about 200 fishermen households live there. This site was representative of the frontline of ECS influenced by the airflow transported from eastern China, the details are given by previous publication (Wang et al., 2016). In order to compare the different characteristics of mercury between oceanic aerosols and continental aerosols, previous data collected in Xuhui District of Shanghai (121.26 °E, 31.09 °N) by our group was also adopted (Duan et al., 2016).

2.2. Sample collection

Total Suspended Particles (TSP) samples were collected by a high volume sampler (Thermo Scientific) loaded with acid-cleaned Whatman Grade 41 cellulose filter (20.3 × 25.4 cm). The flow - rate was controlled at 1130 L min^{-1} and lasted for 24 h. All filters were conditioned under constant temperature (20 ± 1 °C) and a relative humidity (40± 1%) before and after sampling. The samples were packed and sealed in polyethylene plastic bags, and stored in a refrigerator at about −20 °C until analysis.

2.3. Analytical method and QA/QC

The total aerosol mass was determined gravimetrically through weighing the filters before and after sampling by an analytical balance (Sartotius, 2004, 0.01 mg, MP).

One thirty-second (1/32) of each TSP sample or operational blank was digested with 5 mL of ultrapure HNO_3 and 2 mL H_2O_2, 0.5 mL HF in CEM Mars Xpress microwave digestion system (PyNN Corporation,USA). The solutions were then transferred to a 50 mL flask and diluted to 50 mL with milli-Q water (18.2 MΩ cm^{-1}), 10 mL of the solutions were used for Hg detection. The rest were then added with 1 mL per-sulfate (20% $Na_2S_2O_8$) and 1 drop (about 0.05 mL) of silver nitrate (0.5% $AgNO_3$ solution). The samples were heated at 45 °C by a water bath for 10 min, and were cooled naturally down to ambient temperature, then stored for analysis of Br and I analysis.

One thirty-second (1/32) was cut and extracted by 10 mL of 1 mol/L HCl and 0.5 mL 1% $CuSO_4$, the solutions were identified as HCl-soluble particulate mercury (HPM); then 10 mL 2 mol/L HNO_3 was added, the solutions were identified as elemental particulate mercury (EPM); finally the filters were digested following the above way, the solutions were then transferred to 25 mL flask and diluted to 25 mL with milli-Q water (18.2 MΩ cm^{-1}), identified as residual particulate mercury (RPM).

All the Hg samples were detected by cold-vapor atomic fluorescence spectrometry (CVAFS) (AFS-9130, China). The Br and I were determined using an Inductively Coupled Plasma Mass Spectroscopy (ICP-MS PerkinElmer, USA). Detailed procedures for analysis of Hg, Br and I were given in previous studies (Duan et al., 2016; Gao et al., 2010).

2.4. Trajectories cluster analysis

72-h backward trajectories of air mass to Huaniao Island (our observation site) were calculated during sampling period by using HYSPLIT-4 model (Draxler and Hess, 1998). Data came from NCEP/NCAR Reanalysis meteorological database (http://arlftp.arlhq.noaa.gov/pub/archives/gdas1). The model was run four times per day at starting times of 00:00, 06:00, 12:00 and 18:00 UTC (08:00, 14:00, 20:00 and 02:00 LT-local time, respectively), and the starting height was set at 500 m. The method used in trajectory clustering was based on the GIS-based software TrajStat (http://www.meteothinker.com/TrajStatProduct.aspx) (Wang et al., 2009; Zhao et al., 2015).

2.5. Statistical analysis

The correlation analysis was carried out by SPSS 17.0. The one-way ANOVA test was used to determine the difference in TPM concentrations among different seasons.