Atmospheric Pollution Research xxx (2016) 1–8

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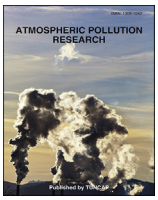
Contents lists available at ScienceDirect

Atmospheric Pollution Research

journal homepage: http://www.journals.elsevier.com/locate/apr



Original article

Seasonal variation of atmospheric particulate mercury over the East China Sea, an outflow region of anthropogenic pollutants to the open Pacific Ocean

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ARTICLE INFO

Article history:
Received 24 February 2016
Received in revised form
29 April 2016
Accepted 4 May 2016
Available online xxx

Keywords:
Particulate mercury (PHg)
Seasonal variation
East China Sea (ECS)
Outflow
Source implication

ABSTRACT

In this study, PM2.5 and total suspended particulate (TSP) aerosol samples were collected to investigate atmospheric mercury pollution on a pristine island in the East China Sea (ECS) from October 2011 to August 2012. The sampling site is located in the downwind path of the outflow of anthropogenic pollutants from East Asia to the Pacific Ocean, driven by the East Asian monsoon. Average concentrations of particulate mercury (PHg, in pg/m^3) were 16.6 for PM2.5 and 24.2 for TSP. Particulate mercury was mainly present in the fine mode, with 68.5% of the total PHg being present in PM2.5. Obvious seasonal variations were observed for both PM2.5 and TSP. The dry deposition flux of PHg over the ECS was estimated to be 1.69 μg m^{-2} yr^{-1}. Three episodes of high PHg concentrations were observed during the sampling period. An episode in fall (84.1 pg/m^3 in TSP) was induced by biomass burning in East China, and PHg was more concentrated in the fine mode (PM2.5/TSP = 0.91). An episode in winter was triggered by serious anthropogenic emissions in northern China, with PHg levels reaching 132.7 pg/m^3 in TSP. An episode in spring was attributed to the long-range transport of Asian dust mixed with anthropogenic aerosols, with increased levels of PHg in the coarse mode (PM2.5/TSP = 0.61). Principal component analysis (PCA) indicated that fossil fuel combustion and biomass burning from the Asian mainland were the two major sources of atmospheric PHg over the ECS.

1. Introduction

Mercury (Hg) is a global toxic pollutant and has generated significant concerns due to its serious harm to human health via the consumption of food from aquatic systems (Lindqvist et al., 1991). Ambient air is critical to the transport and transformation of mercury from sources to receptors (Mason et al., 1994). Atmospheric mercury exists in three forms: gaseous elemental mercury (GEM), reactive gaseous mercury (RGM), and particulate mercury (PHg) (Lindberg et al., 2007). Unlike other heavy metals, mercury in the atmosphere exists mainly as GEM (>90%), with a very small fraction present as PHg (Poissant et al., 2005). Because of its physicochemical properties, the residence time of GEM at the hemispheric scale is about 0.5–2 years, while it is only several days or weeks for PHg and RGM, which are readily removed by wet and dry deposition due to their large dry deposition velocities and scavenging coefficients (Schroeder and Munthe, 1998). As a result, PHg and RGM are more important with respect to migrating to terrestrial and aquatic environments from ambient air, which has a significant effect on the ecological cycle and environmental health.

Natural sources (such as soil and rock erosion, and volcanic eruptions) and anthropogenic activities both contribute to mercury levels in the atmosphere. Most PHg originates from direct anthropogenic emissions, particularly from heating and power production, while the transformation of RGM is another important source (Fang et al., 2001). Mercury pollution has become increasingly serious due to human activities. Globally, approximately 2000 tons of mercury per year are released through anthropogenic activities

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Peer review under responsibility of Turkish National Committee for Air Pollution Research and Control.

http://dx.doi.org/10.1016/j.apr.2016.05.004

(Pacyna et al., 2006), with about half of this attributed to Asia, due to the rapid expansion of the continent's economies (Wu et al., 2006). China is considered a huge and growing source region because of its rapid economic and industrial development along with a coal-dominated energy structure (Wu et al., 2006). The Yangtze River Delta (YRD) is one of the most highly developed regions in China, and is considered one of the major anthropogenic sources of mercury pollution (Street et al., 2005).

Deposition from the atmosphere is an important source of mercury in most terrestrial and aquatic environments, especially for the open-ocean and remote islands. Some studies on mercury in the coastal and marine atmosphere have been conducted. Beldowska et al. (2012) showed that a major source of PHg in the coastal Baltic Sea was the combustion of fossil fuels, especially the burning of coal for home heating, while in Pompano Beach, Florida, a potential source of PHg was suggested to be the transfer from GEM or RGM (Malcolm et al., 2003). With regard to the ocean atmosphere, Sprovieri and Pirrone (2008) reported that high PHg concentrations over the Adriatic Sea were associated with high GEM levels when air masses originated from the European mainland, and the higher elevations of PHg in the Asian marine boundary layer might be due to emissions from the East Asian continent (Chand et al., 2008).

The East China Sea (ECS) is one of the largest marginal seas in the western Pacific. The YRD region, adjacent to the ECS, is situated in central-eastern China, which incorporates Zhejiang and Jiangsu provinces and Shanghai municipality, the most industrialized and urbanized regions in China. Due to the rapid economic development and high population density, environmental pollution (particularly air pollution) in the YRD region has become an increasing concern in recent years (Zhu et al., 2012). The atmosphere over the ECS is particularly subjected to the East Asian monsoon and receives a large outflow of pollutants from mainland China. There have been several studies on the pollutant outflow from mainland China to the ECS. For example, Zhu et al. (2013) reported the dry deposition fluxes of NO_3^-, NO_4^+, and soluble P over the ECS, and Wang et al. (2014) apportioned the sources of polycyclic aromatic hydrocarbons in PM2.5. However, there have been few studies of atmospheric mercury over the ECS, and the extent of mercury contamination in the region is still unknown. Because air pollution in China is an increasingly serious problem, it is imperative to quantify mercury levels and determine the sources and deposition of mercury over the ECS. Huaniao Isle is located in the main transport path of pollutants from the Asian continent to the Pacific Ocean, making it an ideal place to assess the influence of pollutants from the Asian continent to the marine environment. In this study, seasonal mass concentrations of PHg in PM2.5 and TSP were observed on Huaniao Isle from October 23rd, 2011 to August 20th, 2012. The aims of this study were to: (1) evaluate the outflow of PHg through long-range transport from the Asian mainland to the ECS; (2) characterize the sources of PHg, especially during episodes of high PHg concentrations over the ECS; and (3) estimate the dry deposition flux of aerosol-bound mercury over the ECS.

2. Materials and method

2.1. Sampling

2.1.1. Sampling site

The sampling site, being 66 km away from the east coast of Shanghai, is located on the Huaniao Isle (30.86°N, 122.67°E) in the ECS (Fig. 1). The Isle has a land area of 3.28 km^2 and a population of less than 1000, most of which is concentrated on the southeast of the island where a wharf is situated. The local residents live mainly on fishing, and no industrial emissions are present around. In order to minimize the possible influence from local anthropogenic activities, the sampling apparatus were placed on the top of a three-storey building on the northwest side of the Isle, and the elevation of the sampling site is about 50 m above the sea level.

2.1.2. Sample collection

PM2.5 samples were collected on quartz filters (20 × 25 cm^2, 2600QAT, PALL, USA) by a sampler (Guangzhou Mingye Huanbao Technology Company) at a flow rate of 18 m^3/h, while TSP samples were collected on quartz filters (9 cm in diameter, QM-A, Whatman, UK) by a sampler (Beijing Geological Institute) at a flow rate of 4.1 m^3/h. 187 of PM2.5 and TSP samples were obtained from October 23, 2011 to August 20, 2012. Sampling for PM2.5 and TSP was both carried out approximately in 24 h intervals. Filter was also put in the same sampler for 24 h (without pumping) at the sampling site using as the blank, and at least two blanks were obtained in every season. The empty quartz filters were first wrapped in aluminum and baked at 450 °C for 4 h to remove residual mercury, and then, all filters were weighed before and after sampling with an analytical balance (Sartorius BT 25 s, reading precision 10 μg) after stabilizing under constant temperature (20 ± 1 °C) and humidity (45 ± 5%) for at least 24 h. The filters were sealed in polyethylene plastic bags right after sampling and preserved in a refrigerator (−20 °C). All the procedures were strictly quality-controlled to avoid any possible contamination of the samples.

2.2. Chemical analysis

2.2.1. PHg

The PHg was directly analyzed by a Direct Mercury Analyzer (DMA-80 TRICELL, Milestone, Italy), which equipped with an automatic sampler, a quartz furnace, a cobalt-manganese oxide catalyst, a gold-coated sand amalgamator and an atomic absorption detection cell with three different path lengths (Melendez-Perez and Fostier, 2013). The analysis methodology was based on thermal decomposition of the sample and collection of Hg vapor on a gold amalgamator. The aerosol sample was introduced into the quartz furnace with a nickel boat (sample holder), and then was heated up to 200 °C for 60 s and then 650 °C for 105 s, which allowed all chemical species of mercury in the sample to be reduced and evaporated as gaseous mercury under an oxygen atmosphere. The gaseous mercury trapped in the amalgamator was then released at 850 °C for 3 s and measured at 253.7 nm. The catalyst was remained at 650 °C throughout the whole analysis process and air was used as carrier gas.

2.2.2. Other chemical species

Elements (Al, Fe, Mn, Mg, Ca) in the aerosol samples were analyzed by ICP-OES (SPECTRO ARCOS), while cations (K^+, Mg^{2+}, Na^+) and anions (SO_4^{2+}, NO_3^-, Cl^-) were analyzed by Ion chromatography (IC, Dionex ICS 3000, USA). The detailed analysis procedures were described in (Deng et al., 2011).

OC and EC (organic carbon and elemental carbon) in the aerosol samples were determined by using IMPROVE thermal/optical reflectance (TOR) method with Thermal/Optical Carbon Analyzer (Model, 2001) from Desert Research Institute (DRI). The detailed analytical procedures were shown in (Wang et al., 2015b).

Principle component analyses (PCA) of these chemical species above were performed with SPSS (Version 19.0, Polar Engineering and Consulting, AK, USA) in this study.

2.3. Quality assurance/quality control (QA/QC)

In order to ensure the analytical accuracy and precision, standard reference materials (SRMs) were analyzed for every 20 aerosol

Please cite this article in press as: Qin, X., et al., Seasonal variation of atmospheric particulate mercury over the East China Sea, an outflow region of anthropogenic pollutants to the open Pacific Ocean, Atmospheric Pollution Research (2016), http://dx.doi.org/10.1016/j.apr.2016.05.004