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Change characteristic of atmospheric particulate mercury during dust weather of spring in Qingdao, China

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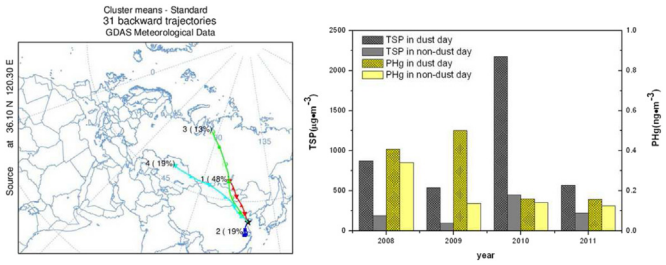
HIGHLIGHTS

- Atmospheric particulate Hg was measured in dust day of spring from 2008 to 2011.
- Atmospheric particulate Hg in dust was higher.
- Mean mercury deposition flux in a dust day accounts for almost 1% annual flux.
- Slow transport speed and passing polluted area caused Hg to accumulate in the dust.

GRAPHICAL ABSTRACT



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ABSTRACT

Atmospheric aerosol samples were collected during dust weather of spring from 2008 to 2011 in Qingdao, in which the concentrations of atmospheric particulate mercury (PHg) were measured to analyze its distribution characteristics and source. PHg concentration during the study ranged from 0.050 ng m^{-3} to 0.788 ng m^{-3} with the average 0.292 ng m^{-3} in dust day, while 0.085 ng m^{-3} to 0.444 ng m^{-3} with the average 0.188 ng m^{-3} in non-dust day. PHg concentration in dust day is far higher than that in some cities of South Korea and Japan and comparable to some cities in China. There was a statistically power function between PHg/TSP and TSP concentrations, which meant that intense dust (high TSP) brought particles with low mercury content. The estimated dry deposition flux of PHg is 0.9 −14.2 ng m^{-2} h^{-1} with the mean 5.26 ng m^{-2} h^{-1} in dust day. The mercury deposition flux in a dust day accounts for almost 1% annual flux, which should be paid attention in the regional and global cycle of mercury. The trajectories are categorized into 4 sectors. Cluster 1 and cluster 4 were the main routes of dust to Qingdao, coming from Kazakhstan and north of Mongolia individually. There is higher TSP, and lower PHg/TSP in dust of cluster 4 compared with cluster 1, because of longer transport distance and faster movement speed. There is highest PHg/TSP in cluster 2 because of passing polluted East China. The slow transport speed, long stay at polluted developed region caused pollutants to accumulate in the aerosols. Differences of transport route, movement speed affects the mercury content significantly.

1. Introduction

Mercury (Hg) is a highly toxic metal that can cause great harm to the environment and human health. Due to its volatility, Hg can be transported over a long distance via the atmosphere to remote areas once emitted from sources. Generally, atmospheric Hg

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consists of three operationally defined forms including gaseous elemental mercury (Hg^0, GEM), gaseous oxidized mercury (Hg^{II}), and particulate mercury (PHg) (Lindberg and Stratton, 1998). These different forms of mercury have different characteristics in terms of transport, deposition and influence on ecosystems (Schroeder and Munthe, 1998; Lin and Pehkonen, 1999; Boening, 2000). The transport and fate of atmospheric mercury is a subject of much interest because it is a neurotoxin and methyl mercury has a high rate of bioaccumulation in aquatic ecosystem. Long-term research (Hammerschmidt and Fitzgerald, 2006) showed that Hg concentration in fish is related to the atmospheric Hg deposition. PHg accounts for less than 10% of total Hg in the air (Lu and Schroeder, 2004), it's not the major form emitted directly to the atmosphere (Pacyna et al., 2003). However, very fast transfer from Hg^{II} to PHg and oxidation of Hg^0 during transport of air masses would contribute an increased concentration of PHg (Poissant et al., 2005; Lynam and Keeler, 2005). Therefore, PHg played an important role in global Hg cycle. The residence time of PHg in the atmosphere ranged from several days to a few weeks (Lindqvist and Rodhe, 1985; Slemr et al., 1985). Aerosol particle dry deposition is driven by meteorological conditions, particle size, and deposition surface. Usually, it is likely to be deposited at intermediate distances from the source, but when combined with fine particulates, PHg can transported for a long distance.

Dust storms are frequent in the arid and semi-arid areas of Asian continent during spring due to strong winds and little rainfall. The dust affects the mid-latitudes (25°–40°N) and can be transported to the tropical North Pacific (Duce et al., 1980; Merrill et al., 1989; Gao et al., 1992). Many scientific studies have been focused on dust storm, including its main sources, developing process, mechanisms of transport and its influence on the environment (Gao et al., 2000, 2002; Lu and Pu, 2002; Guo et al., 2004). Some studies also reported the chemical composition of dust aerosol and its harm to human health (Zhuang et al., 2001; Onishi et al., 2012; Chen et al., 2004; Wang et al., 2007), however, there have been few studies investigating the variation of PHg in dust-day. The emitted mercury by China is the largest in the world (Wu et al., 2006; Pirrone et al., 2010). The removal of Hg in dust day might be important to the cycle of mercury. The sources of PHg was complicated in dust-day, including both local sources (coal combustion, vehicle exhaust, resuspension of previously deposited PHg, etc.) and long-transportation sources (the dust aerosols and aerosols mixed with local aerosols on the pathway). PHg can be efficiently removed via dry-deposition in dust-day, resulting atmospheric removal in east part of China with higher Hg content.

Qingdao is in the transport path of the Asia dust storms when they move to the Yellow Sea and is also an important exit point of the dust storms to the North Pacific. The main purpose is to provide mercury pollution characteristics of Asian dust particles just before they leave the continent. In this study, total suspended particulates (TSP) were sampled in dust day and non-dust day in the spring from 2008 to 2011, with subsequent analysis of mercury content. The dry deposition flux of PHg was estimated. The influence of different dust sources and transport routes on characteristics of PHg in Qingdao was discussed.

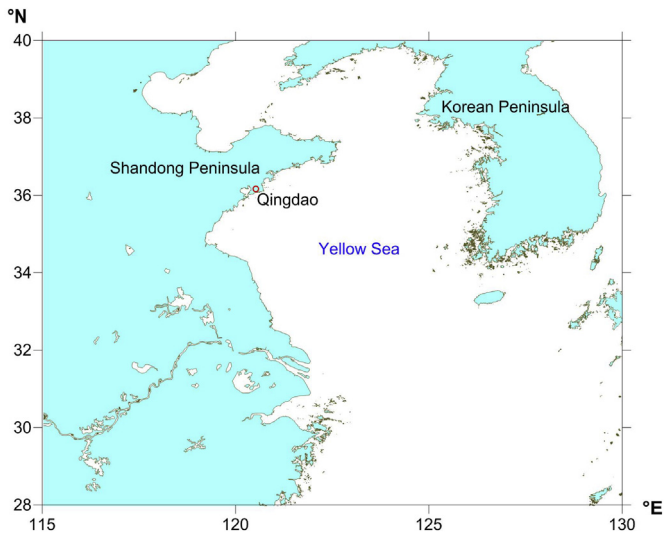

Fig. 1. Location of the sampling site in Qingdao, China.

2. Materials and methods

2.1. Sampling site

Qingdao (36°16′N, 120°50′E) is a coastal city, located at the south of the Shandong Peninsula of Northern China, near the Yellow Sea (Fig. 1). Qingdao is located downwind of the origin of the Asian dust storms in spring when northwest winds prevail. In recent years, Qingdao suffers a lot from dust storms in spring. Therefore, Qingdao is an important exit point of the dust storms from China mainland to the Pacific. TSP samples were collected on the rooftop of a three-storey meteorological station on top of Baguan Hill on the campus of the Ocean University of China. The elevation of Baguan Hill is about 70 m. The main city of the Qingdao is in the north of the sampling site.

TSP samples were collected for 4 h using High flow TSP Sampler (Type KC-1000, Qingdao Laoshan Electronic Instrument Factory Co., Ltd) when the dust storm events appeared in spring. The sampling flux was 1 m^3 min^{-1}. The quartz filter (Whatman QM-A) was used to analyze PHg content. All filters were sealed in a clean bag during transportation to the sampling site and back to the laboratory to prevent contamination. Seventeen sets of dust samples and fourteen sets of non-dust samples were collected from 2008 to 2011. The sampling information of each sample is listed in Table 1.

Meteorological data from Weather Underground (http://www.wunderground.com/) was used. The dust day was judged finally by meteorological mapping data of MICAPS (Meteorological Information Combine Analysis and Process System) coming from the China Meteorological Administration.

2.2. Sample analysis

The TSP samples were balanced until the weights were constant. The sample films were cut into several portions for the analysis of different compound concentrations. The samples were digested using a microwave digestion system to extract PHg according to the EPA method IO-5.0 (U.S. EPA, 1999). They were soaked in Teflon digestion bottles containing 20 mL of HNO_3 solution (10% HNO_3, 1.6 M). The samples were heated at 160 °C and 70 psi for 20 min in microwave digestion system (CEM, U.S.). The extracted samples were analyzed following EPA method 1631E (U.S. EPA, 2002). In briefly, after the extracted sample was cooled at room temperature for 60 min, 5 mL of the sample was added into the 50 mL tube and then diluted with 20 mL of distilled water. BrCl (0.5% of the sample volume) was then added to oxidize all mercury forms to Hg^{II}. 0.5 mL of $NH_2OH{\cdot}HCl$ was added into the bubbler with BrCl-oxidized sample and 30 mL of distilled water. 0.5 mL of $SnCl_2$ solution was added to reduce all Hg^{II} to Hg^0, and the sample was purged onto a gold trap with N_2 for 20 min. Then the concentrations of mercury in gold trap were measured by the method of cold vapor atomic fluorescence spectrometry (CVAFS) using Brooks Rand Model III.