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Atmospheric mercury concentrations at two sites in the Kyushu Islands, Japan, and evidence of long-range transport from East Asia

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HIGHLIGHTS

- We performed continuous monitoring of atmospheric mercury in Japan for one year.
- Monitoring was conducted at two sites, Fukuoka and Minamata, located 150 km apart.
- Discrete, synchronous events of high TGM levels were observed at the two sites.
- These events were generally associated with low atmospheric pressure conditions.
- Long-range transport from the Asian continent was evaluated using the TGM/CO ratio.

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ABSTRACT

Continuous monitoring of atmospheric gaseous mercury at Fukuoka and Minamata in the Kyushu Islands, western Japan, was carried out from June 2012 to May 2013 to investigate the influence of long-range transport of mercury in the Asian region. Speciation data at Fukuoka indicated that approximately 99% of the atmospheric mercury was in the gaseous elemental form. The average concentration of gaseous elemental mercury (GEM) at Fukuoka was slightly higher than that of total gaseous mercury (TGM) at Minamata. Synchronous pollution events of higher concentrations of both GEM at Fukuoka and TGM at Minamata were frequently observed from late fall to early spring. We infer that these events occurred due to long-range transport of mercury rather than local, domestic emission sources because the two sites are far apart (about 150 km), and local sources would be unlikely to synchronously influence concentrations at both sites over such a long distance. The results of backward trajectory analyses indicated that these events occurred when air masses came from the Asian continent. In addition, the pollution events were often the result of cold fronts or migratory anticyclones that passed over the Kyushu Islands, often accompanied by descending cool and heavy air currents. Thus, these results indicate that, under specific climate conditions, higher concentrations of atmospheric mercury are transported to the Kyushu Islands from the Asian continent, and are evident in ground-based observations there.

1. Introduction

Since the end of the 20th century, East Asia has been a major source of air pollution due to rapid economic growth and industrial development in the region. Air masses are transported eastward from the Asian continent to the Japanese islands, typically within several days by temperate westerly winds. These air masses often carry various air pollutants, including non-sea-salt sulfate (nss-SO_4^{2-}), sulfur oxides, oxidants (primarily O_3), heavy metals such as Pb, Se, and Te (Mukai and Suzuki, 1996; Kagawa et al., 2003; Sakata and Asakura, 2011; Kusunoki et al., 2012) and polycyclic aromatic hydrocarbons (PAHs) (Lang et al., 2008; Sato et al., 2008). The concentrations of these chemical components in air and wet deposition have increased during winter and spring at locations facing the Sea of Japan and in the Kyushu Islands, the regions closest to the Asian continent (Fujiwara et al., 2003; Hatakeyama

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et al., 2004; Naja and Akimoto, 2004; Tanimoto et al., 2005; Takami et al., 2005).

Total anthropogenic mercury (Hg) emissions from the Asian countries were estimated at about 900 tons for the 2010 global inventory, accounting for 40% of the global emissions (UNEP, 2013). Several studies reported that Hg emitted from the East Asian region was transported long-range to the North American continent due to a springtime Asian dust episode, a large-scale atmospheric transport event (Friedli et al., 2004; Jaffe et al., 2005; Obrist et al., 2008; Nguyen et al., 2010). It is well known that there are primarily three types of Hg in the atmosphere: gaseous elemental Hg (GEM), gaseous oxidized Hg (GOM), and particulate bound Hg (PBM) (Lindqvist, 1991; U.S. EPRI, 1996). More than 95% of the Hg in ambient air is GEM and GEM has a long residence time, estimated to be 0.6 years (Weiss-Penzias et al., 2003). During atmospheric transport, part of the GEM is converted to GOM and PBM, which have much shorter atmospheric residence times (ranging from several days to a few weeks), and they are more readily deposited onto surfaces compared to GEM (Fitzgerald et al., 1998; UNEP, 2013). This means that atmospheric mercury can be deposited in places far from the emission sources.

Atmospheric Hg monitoring in Japan began in 1997 due to a revision in the country's law on air pollution control. At present, total gaseous Hg (TGM) is measured using a gold amalgamation sampling method at more than 300 monitoring sites (Ikemoto et al., 2011). However, sampling is only carried out once a month, and the sampling day is different at each site. These monitoring data are suitable for obtaining the average concentration and spatial distribution across the Japanese Islands. However, they cannot be used to determine the influence of domestic emission sources and/or long-range transport from other regions, relationships with meteorological parameters, and variations in atmospheric concentrations. To obtain this type of information, continuous monitoring with a high time resolution is required. However, such continuous Hg monitoring data is currently not available in Japan (Osawa et al., 2007).

In this study, continuous monitoring of TGM at Minamata and speciated Hg at Fukuoka was carried out from June 2012 to May 2013. Fukuoka is the largest city in the northern Kyushu Islands (the part of Japan closest to the Asian continent), and it has many potential Hg emission sources. On the other hand, Minamata is a small city located in the southwestern part of the Kyushu Islands. There are few local Hg sources in Minamata, and thus it is clear that the air pollution there comes from other regions. We compared continuous monitoring data from these two sites in order to evaluate the impacts of Japanese domestic emission sources and long-range transport from the Asian Continent on atmospheric Hg concentrations in Japan.

2. Experimental

2.1. Site description

A map showing the locations of the sampling sites in the Kyushu Islands is shown in Fig. 1. The Fukuoka site (33°32′55″N, 130°21′52″E) is situated on the rooftop of a building (height above sea level: 20 m) on the campus of Fukuoka University, located in the southwestern part of the city. A highway exists to the south of the site. Fukuoka City has a population of 1.5 million. There are four large municipal solid waste (MSW) incinerators (disposal capacities: 600–900 ton day^{-1}) in the northwest, northeast, and southeast areas of the city. In addition, other potential anthropogenic Hg emission sources such as sewage sludge incinerators and exhaust fumes from marine vessels (Tsuzaki and Asakura, 2005) exist there. The Minamata site (32°12′13″N, 130°22′30″E) is located on the rooftop of the Minamata Disease Archive (height above sea level: 22 m) on a reclaimed area next to Minamata Bay. In the past, Minamata Bay was seriously contaminated by inorganic and methyl mercury discharged in the wastewater from a local chemical plant. Our monitoring site has a meteorological station where air temperature, relative humidity, air pressure, and solar radiation are measured continuously. In addition, there has been continuous monitoring of CO concentration there since 14 July 2012 using a continuous CO monitor containing an auto-calibration system (APMA370; Horiba Co Ltd.). Minamata City has about 25,000 inhabitants. In the center of the city, there is a small municipal solid waste incinerator (with a disposal capacity of 40 ton day^{-1}) and a large chemical plant that mainly manufactures chemical fertilizers and raw materials for liquid crystal production. An air pollutant (AP) monitoring station is also located in the center of the city (3.5 km northeast of the Minamata site), making continuous measurements of air pollutants such as SO_2, nitrogen oxides, oxidants (primarily O_3), and suspended particulate matter (SPM). The data obtained by the AP station were used in this study to supplement our own data.

2.2. Hg measurements

2.2.1. Mercury speciation at the Fukuoka site

Atmospheric concentrations of GEM, GOM, and PBM were continuously measured at the Fukuoka site using a Tekran system (Model 2537B, Model 1130 and Model 1135; Tekran Inc.) from June 2012 to May 2013. Ambient air containing GEM, GOM, and PBM was drawn at a flow rate of 10 L min^{-1} through an air inlet with an impactor to remove coarse particles larger than 2.5 μm. GOM was selectively adsorbed on the interior surface of a KCl-coated annular denuder, and PBM in particles smaller than 2.5 μm ($PBM_{2.5}$) was captured by a quartz fiber filter downstream of the denuder. During the sampling of GOM and $PBM_{2.5}$, GEM was measured every 5 min by two gold cartridges that alternately collected and thermally desorbed Hg, with subsequent measurement by cold-vapor atomic fluorescence spectrometry (CVAFS). The speciation system was operated on a 3 h cycle, with 2 h of GEM measurement and preconcentration of GOM and $PBM_{2.5}$ followed by 1 h of analysis. In addition, the system was automatically calibrated once a day using an internal permeation tube. Moreover, external manual injections using a saturated Hg standard gas (MB-1, Nippon Instruments Co., Ltd.) were performed every six months. The method detection limit (MDL) for GEM is less than 0.1 ng m^{-3} (Tekran Inc, 2002). The MDLs for GOM and $PBM_{2.5}$ were calculated based on blank values obtained from the third reading during the zero air flush, and they fluctuated depending on system stability (see Table 1). When the blanks exceeded monthly average plus twice the standard deviation, the associated Hg concentration data were excluded from further data analysis. However, the monthly average plus a standard deviation from December 2012 to February 2013 might be suitable as a reference value to consider whether the data are valid because the blanks fluctuated a great deal during this period.

2.2.2. TGM measurements at the Minamata site

TGM in air passing through a PTFE filter was determined using a continuous mercury monitor using gold amalgamation and CVAFS (AM-5; Nippon Instruments, Co., Ltd.). The monitor operated semi-continuously on a 15-min cycle, with 12 min of sampling at a flow rate of 0.5 L min^{-1} and 3 min of Hg measurement. The analyzer was calibrated manually once a week by manual injection of saturated Hg standard gas (MB-1, Nippon Instruments, Co., Ltd.) using a gas-tight syringe. The MDL was 0.26 ng m^{-3}, as calculated based on 42 blank measurements. The hourly mean concentrations of TGM were calculated from four measurement values to allow data alignment, with the hourly data for CO and other air pollutants obtained from the AP station.