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Reactive and particulate mercury in the Asian marine boundary layer

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ABSTRACT

The variability of atmospheric mercury in elemental, reactive, and particulate forms has been studied at a remote site (Cape Hedo Observatory, CHO) at Okinawa Island (Japan) March 23 to May 2, 2004, downwind of the major Asian source regions. Under prevailing meteorological conditions, episodes of higher levels of atmospheric mercury and other atmospheric species are observed at CHO. The mean ($\pm 1\sigma$) concentrations of gaseous elemental mercury (GEM), reactive gaseous mercury (RGM) and particulate-bound mercury (PHg) are 2.04 ± 0.38 ng m^{-3}, 4.5 ± 5.4 pg m^{-3} and 3.0 ± 2.5 pg m^{-3}, respectively. In Asian outflow the combined contribution of RGM and PHg constitutes less than 1% of the GEM in the boundary layer, which indicates that most mercury export in the marine boundary layer is due to the GEM form, and direct outflow of RGM and PHg is very low. While the data from Okinawa suggest minimal export of RGM and PHg, this does not preclude greater export of these species at higher elevations. Based on the correlations of PHg and submicron aerosol mass (SAM), we found a ΔPHg/ΔSAM ratio of 0.20 μg g^{-1} ($R = 0.58$, $p < 0.01$), which we believe to be characteristic of East Asian industrial aerosols during outflow. A diurnal variation is observed in RGM with a peak near noon. Using a rate constant of 9×10^{-14} cm^3 molecule^{-1} s^{-1} for the OH oxidation rate (Sommar, J., Gardfeldt, K., Stromberg, D., Feng, X., 2001. A kinetic study of the gas phase reaction between the hydroxyl radical and atomic mercury. Atmospheric Environment 35, 3049–3054; Pal, B., Ariya, P.A., 2004a. Gas-phase HO center dot-initiated reactions of elemental mercury: kinetics, product studies, and atmospheric implications. Environmental Science and Technology 38 (21), 5555–5566.) and a typical OH concentration of $1–5 \times 10^6$ cm^{-3} would result in RGM production rates of 0.6–3.0 pg m^{-3} h^{-1}. Although OH may not be the sole oxidant, this is consistent with the observed change in concentration during daytime of 1.4 ± 1.5 pg m^{-3} h^{-1}. A significant correlation is found between GEM and CO; GEM and SAM; and PHg and SAM. Lower ΔSAM/ΔCO and ΔGEM/ΔCO are observed for transport events with rainfall and for air parcels remaining in the mixed layer. Back trajectory analysis along with the correlation study suggests that the air from China has a higher GEM concentration compared to the air coming from southern Japan.

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1. Introduction

Mercury is an atmospheric pollutant with a complex biogeochemical cycle (Schroeder and Munthe, 1998). Atmospheric mercury exists in three operationally defined forms: gaseous elemental mercury (GEM), divalent reactive gaseous mercury (RGM) and particulate mercury (PHg). The transport and fate of atmospheric mercury are a subject of much interest primarily for reasons of human health. Mercury is a neurotoxin and some mercury compounds such as methyl mercury have a high rate of bio-accumulation through the food chain (Lipfert et al., 2005 and references therein). Because of its long lifetime, long-range transport of GEM at the inter-continental scale has been observed (Carpi, 1997; Jaffe et al., 2005; Weiss-Penzias et al., 2006). The atmospheric lifetime of gas phase elemental mercury (GEM) has been estimated to be 0.5–2 years (Schroeder and Munthe, 1998; Bergan et al., 1999; Bergan and Rodhe, 2001). More recent studies have indicated a shorter lifetime of 0.5–6 months in certain marine boundary layer environments (Weiss-Penzias et al., 2003; Hedgecock et al., 2005). It is also generally assumed that gas phase RGM should have very low concentrations in clean, background air because of rapid deposition (Landis et al., 2002) and scrubbing by clouds and raindrops.

The major oxidation pathways of atmospheric GEM are believed to be the gas phase reactions with ozone and OH, and the gas + aqueous oxidation by ozone, which takes place in fog and cloud droplets (Lin and Pehkonen, 1999; Selin et al., 2007) and to some extent in deliquesced aerosol particles (Pirrone et al., 2000). There is considerable uncertainty over the reaction rates and mechanisms for RGM production (e.g. Pal and Ariya, 2004a; Calvert and Lindberg, 2005; Holmes et al., 2006). However, global scale models suggest the prevalence of the OH oxidation over O_3, in RGM formation (Selin et al., 2007). Less is known about halogen containing compound concentrations and their variation in space and time, which makes it difficult to estimate the importance of these reactions on a global scale (Holmes et al., 2006).

Current estimates suggest that over half of the global anthropogenic atmospheric mercury emissions are from Asia, with the large majority (50% of Asian emission) coming from China (Pacyna et al., 2003; Pan et al., 2006). Out of the total Hg emissions in China, the reported breakdown by species is 56% as GEM, 32% as RGM and 12% as PHg (Streets et al., 2005). Fang et al. (2004) have shown that only 12% of the mercury emitted from coal combustion is deposited locally; the rest participated in the regional or global Hg cycle, although no details on Hg speciation were provided.

To date, few atmospheric measurements have been made to verify the large Asian emissions reported in the inventories of Wang et al. (2000); Pacyna et al. (2003) and Streets et al. (2005). In order to better interpret the nature of source regions, source types and characterization of mercury outflow from East Asia, an intensive field campaign was conducted at Cape Hedo Observatory (CHO) on the island of Okinawa, Japan. These data have been analyzed with respect to the outflow of GEM from Asia, with particular focus on comparing the GEM/CO ratio to the emission inventory (Jaffe et al., 2005). In that work we found that the total GEM export (including natural + re-emissions) exceeded the emission inventory by ~100%. This result was confirmed by the modeling studies of Pan et al. (2006) and Selin et al. (2007).

The research presented here is a further analysis of the data collected at Cape Hedo on the island of Okinawa, with an emphasis on the sources, variability and regional transport of RGM and PHg. In particular, we will focus on answering the following questions: (1) What is the magnitude of RGM and PHg during outflow from East Asia? (2) What controls the concentration of RGM and PHg? (3) What are the relationships between RGM, PHg and other compounds? (4) What characteristics of the Asian outflow events explain the observed concentration of mercury species on an event basis?

2. Instrumentation and methods

The Cape Hedo Observatory (CHO; 26.8°N, 128.2°E, 60 m amsl) is located on the north end of the island of Okinawa, away from the island's major population centers (Fig. 1). Being situated in the Pacific marine environment, downwind of the major Asian emission region, this site has unique importance for the study of atmospheric pollution. In winter (January–March), winds carry Asian (mostly Chinese) pollution and spread it over the Pacific Ocean. At Okinawa, April/May is the meteorological transition period and winds from either the east or west can be encountered. During summer and autumn seasons, winds at Okinawa are from west to east, with cleaner air from the Pacific Ocean. Thus spring (March–May) is an optimum period to study the transport of pollution from Asia to the Pacific Ocean. Due to meteorological and geographical importance, this site has been used for a number of years to study the outflow of pollution from East Asia and China (Kanaya et al., 2001; Kato et al., 2004; Takami et al., 2005).

Measurement of a variety of aerosols and trace gases was made during the spring of 2004 at CHO (Table 1). Gaseous elemental mercury (GEM), reactive gaseous mercury (RGM) and fine (<2.5 μm) particulate-bound mercury (PHg) were measured from March 23 to May 2, 2004. The slopes from the correlation of GEM, RGM and PHg with CO are used to calculate the export of RGM and PHg. Details of the CO, O_3, and GEM measurements are given in Jaffe et al. (2005), so only a brief description is given here.

An automated mercury speciation system (Tekran 2537-1130-1135) was used to determine the concentrations of GEM, RGM and PHg. The mercury fractions are collected by sequential capture, RGM is sequestered by a KCl-coated annular-denuder, and all remaining fine particulate matters are then captured on a quartz-fiber filter. GEM passes through all steps quantitatively and is pre-concentrated on alternating gold cartridges, thermally desorbed, and detected by cold vapor atomic fluorescence spectroscopy (CVAFS). The RGM and PHg fractions are quantified by thermal desorption and reduction to GEM in a mercury-free carrier gas, and then quantified as GEM. GEM analysis occurs every 5 min, whereas RGM and PHg are accumulated on the denuder/filter combination for 3 h prior to