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Evidence for a sampling artifact for particulate-phase mercury in the marine atmosphere

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Abstract

During a coastal environment study an artifact associated with a widely used particulate mercury (Hg) sampling method was discovered that produces inconsistent results for Hg in PM_{10} samples of different duration (12 versus 4-h). The artifact is attributed to loss of Hg from filters over the course of the longer sampling periods, perhaps due to chemical reaction, enhanced by high humidities common to the marine boundary layer. On the seven days on which three successive 4- and 12-h duration samples were obtained, the mean Hg concentration of PM_{10} was significantly higher for the 4-h samples (22.5 $\mathrm{pg\,m^{-3}}$) than for the 12-h samples (8.4 $\mathrm{pg\,m^{-3}}$) ($p = 0.012$). The day-to-day differences between 4- and 12-h samples ranged from -1 to 29 $\mathrm{pg\,m^{-3}}$. No consistent difference was observed in the Hg concentration of $PM_{2.5}$ of different durations. Adsorption of reactive gaseous mercury (RGM) onto $PM_{2.5}$ was also evaluated by collection of samples with and without an upstream KCl denuder for RGM removal. Concentrations were not significantly different, indicating that RGM adsorption was not evident in this low aerosol, low RGM environment. The discovery of an artifact related to sample duration demonstrates the need for continued evaluation and validation of the currently accepted methods for atmospheric Hg measurements.

Keywords: Mercury; Sea salt; Aerosol; Annular denuder; Florida

1. Introduction

The metal mercury (Hg) differs from other heavy metals in ways that give it a unique environmental behavior. First, it has a high vapor pressure (Budavari et al., 1989), which results in gaseous Hg species in addition to particle bound Hg existing in the ambient atmosphere. Second, Hg can be methylated, and subsequently bioaccumulated in aquatic environments in its most toxic form. The predominance of a gaseous Hg form affects atmospheric transport and deposition, and makes accurate sampling for Hg much more difficult than for other metals. Potential sampling artifacts for particulate Hg could be positive, causing measured concentrations to be higher than actual, or negative, causing measured values to be lower than actual concentrations. This study evaluated the potential for artifacts affecting one of the most common methods of particulate Hg sampling.

Atmospheric Hg is classified in three forms by chemical and physical properties, and sampling and

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analysis capabilities (Lin and Pehkonen, 1999). The most abundant form (>90%) is the elemental gas, $Hg^0(g)$. Gaseous Hg(II) also exists, and is often referred to as reactive gaseous mercury (RGM), due to its faster removal from the atmosphere. RGM is believed to include several compounds, primarily $HgCl_2$, HgO and $Hg(OH)_2$, although these have not been individually identified in the atmosphere. Hg is also found associated with particles, presumably due to adsorption on existing aerosols, dissolution in wetted aerosols, inclusion of Hg containing minerals in crustal aerosols (Forlano et al., 2000), and as the result of direct emissions.

2. Methods

The three types of Hg are typically sampled in three different ways: elemental gaseous Hg by amalgamation onto gold-coated beads in a "gold trap" (Fitzgerald and Gill, 1979), RGM by collection on a potassium chloride (KCl)-coated quartz denuder (Xiao et al., 1997; Feng et al., 2000; Landis et al., 2002), and particulate mercury onto filters (Keeler et al., 1995). Hg is then liberated for analysis by either thermal desorption (for gold traps, denuders, or filters) or extracted into solution (denuders or filters). Hg is subsequently analyzed by cold vapor atomic fluorescence. For this study, $Hg^0(g)$ and RGM were sampled and analyzed using Tekran 1130 and 2537 instruments, which use thermal desorption. Particulate mercury ($Hg_{(p)}$) was sampled, extracted and analyzed following the method described by Keeler et al. (1995), with the exception that quartz filters (Gelman Pallflex) instead of glass-fiber filters were employed. Prior to sampling, filters were heated at 550 °C for 2 h under Hg-free N_2 to remove contaminants (including Hg). Teflon-coated cyclones (University Research Glassware) were used for size segregation ($PM_{2.5}$ and PM_{10}), downstream of acid-cleaned filter packs. Filters were stored in acid-cleaned Petri dishes, sealed with Teflon tape, and frozen at −40 °C until analysis. Mercury was extracted from the filters by microwave digestion in 10% Suprapur nitric acid. Sample preparation and analysis was performed in a class 100 clean room at the University of Michigan Air Quality Laboratory utilizing clean techniques. Standards for daily calibration curves were prepared by digesting an unused filter spiked with Hg(II) in nitric acid, followed by microwave digestion. Sixteen field blanks for Hg were collected. Uncertainty in the particulate mercury measurements was calculated by evaluating the uncertainty in the measurement of air volume sampled, the variation in the Hg field blank, and the Hg analysis method. The standard error calculated from the calibration of the dry test meters was less than 0.001 m^3, which is less than 0.01% of the volume for a 4-h sample, is much less than the uncertainty of blanks and analytical replication, and was therefore neglected. The total uncertainty was estimated as

$$\text{Uncertainty} = ((\sigma-\text{blanks})^2 + (\sigma-\text{replication})^2)^{0.5}/\text{air volume},$$

where σ-blanks is the standard deviation of the blanks in pg per filter and σ-replication is the standard deviation of the absolute difference between two replicate analyses in pg per filter. The estimate was done separately for each type of $Hg_{(p)}$ sample collected and ranged from 0.6 to 1.9 $pg\,m^{-3}$.

Five distinct samples were collected for $Hg_{(p)}$ and are summarized in Table 1. These included particulate samples in two different size fractions, $PM_{2.5}$ (particles smaller than 2.5 μm in diameter) and PM_{10} (particles smaller than 10 μm in diameter). For the duration of the study, three different 12-h long $Hg_{(p)}$ samples were collected from 8:00 to 20:00 and 20:00 to 8:00 (local time): (1) a $PM_{2.5}$ sample preceded by a KCl-coated annular denuder; (2) a $PM_{2.5}$ sample without an upstream denuder; and (3) a PM_{10} sample without an upstream denuder, all at a flow rate of 16.7 LPM. Additionally, several samples of 4-h duration were collected from 8:00 to 12:00, 12:00–16:00 or 16:00–20:00 to improve daytime temporal resolution. The 4-h $PM_{2.5}$ and PM_{10} samples were collected without an upstream KCl denuder. All PM_{10} samples were collected at 16.7 LPM. To increase the mercury mass per filter for the 4-h $PM_{2.5}$ samples, two cyclones were attached to one filter pack with a Y-connector with a sampling rate of 33.4 LPM. The denuder–no denuder comparison for the $PM_{2.5}$, 12-h samples

Table 1
Summary of particulate Hg samples collected at Pompano beach

Size range	Duration (h)	KCl denuder upstream?
$PM_{2.5}$	12	Yes
$PM_{2.5}$	12	No
PM_{10}	12	No
$PM_{2.5}$	4	No
PM_{10}	4	No