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Evaluation of various methods to measure particulate bound mercury and associated artifacts

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Abstract

This study was performed to determine how sampling artifacts associated with various sampling methods including open faced filter (OFF) pack, micro orifice uniform deposit impactor (MOUDI), and Tekran speciation system (TekSpec) impact particulate bound mercury (PBM) measurements. PBM measured by the MOUDI for 48 h was statistically lower than that measured with the TekSpec every 2 h, indicating that negative artifacts were significant for long sampling durations. Negative artifacts were also identified in lab experiments as the Hg^0 and HgCl_2 concentrations associated with particulate matter on the filter significantly decreased when the filter was exposed to zero air. Positive artifacts were also investigated. The OFF sampling for 48 h, which is likely to be associated with both positive and negative artifacts, measured a significantly lower PBM concentration than the TekSpec while the OFF and MOUDI (48 h sampling – minimal positive artifacts) showed similar results, suggesting that positive artifacts were minor under the rural condition encountered (low atmospheric gaseous oxidized mercury and typical oxidants concentrations). The Hg speciation associated with particles varied with atmospheric temperature, with the contribution of less volatile species including HgO and HgS increasing and more volatile Hg^0 and HgCl_2 decreasing as atmospheric temperature increased. There was significant correlation for PBM larger than $2.5\ \mu\text{m}$ between TekSpec frit and MOUDI in this study, indicating that TekSpec frit is a good alternative sampler for measuring the concentration of coarse PBM.

1 Introduction

Mercury (Hg) is a globally distributed toxic pollutant (USEPA, 1997). It is emitted to the atmosphere by both natural and anthropogenic sources mainly in inorganic forms, which do not constitute a direct public health risk at the level of exposure typically found (Driscoll et al., 2007). Atmospheric Hg primarily exists in three forms; gaseous elemental Hg (Hg^0 or GEM), gaseous oxidized mercury (GOM), and particulate bound mercury

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(PBM) (Schroeder and Munthe, 1998). Most of Hg in ambient air exists as GEM while GOM and PBM generally contribute less than 10% of the total Hg measured (Lindberg and Stratton, 1998; Pirrone et al., 2010; Weiss-Penzias et al., 2009; Valente et al., 2007). However, GOM and PBM are extremely significant with respect to atmospheric deposition due to their large dry deposition velocities and scavenging coefficients although a few recent studies reported considerable GEM deposition in forested areas (Zhang et al., 2009; Huang et al., 2012). After Hg is deposited, it may be transformed into methyl mercury (MeHg), a toxic form, by sulfate reducing and other types of bacteria in aquatic ecosystem, followed by bioaccumulation in the food chain (Flemming et al., 2006; Mergler et al., 2007; US EPA, 2001). The major human exposure pathway to MeHg is, therefore, the consumption of contaminated fish. Hence, the quantification of atmospheric Hg deposition into the aquatic system is a critical step that is needed to track the fate of Hg in environmental media for risk analysis.

In order to estimate the amount of Hg deposited, it is necessary to identify the atmospheric concentration of speciated Hg including PBM. There are a few methods available to measure PBM concentrations, including the Tekran speciation unit (TekSpec) consisting of KCl-coated denuders and quartz filters, conventional open faced filter (OFF) packs, and multi-stage impactors such as the Micro Orifice Uniform Deposit Impactor (MOUDI) which can measure concentrations and also size distributions (Keeler et al., 1995; Sheu et al., 2001; Landis et al., 2002; Lynam and Keeler, 2005). Because physical and chemical processes consistently occur in ambient air, including adsorption, nucleation, and other gas-particle partitioning mechanisms, and ambient particle concentrations and meteorological conditions are highly variable, atmospheric concentrations and size distributions of PBM are not constant (Rutter and Schauer, 2007a, b; Xiu et al., 2009; Kim et al., 2012). In addition, PBM concentrations are typically found at ultra-low levels (pg m^{-3}); therefore, accurate quantification of PBM is one of the most difficult tasks in studies of atmospheric mercury speciation.

There have been a few studies that have attempted to identify artifacts associated with PBM measurements. Lynam and Keeler (2005) investigated the potential artifact

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caused by ozone using a KCl-coated denuder and quartz filter, and found that a significant portion of gaseous Hg was adsorbed on a denuded filter at elevated ozone concentrations possibly due to the oxidization of Hg during sampling. Malcolm and Keeler (2007) have also identified a sampling artifact for a conventional Hg sampling instrument, consisting of cyclone, gold trap, KCl-coated denuder, and filter. They found that a 12 h duration sample measured significantly lower PBM concentrations in PM_{10} (particles having diameter $< 10 \mu\text{m}$) than three successive 4 h samples, due to the loss of Hg from filters over the course of the longer sampling periods. Talbot et al. (2011) compared the PBM concentration measured with Teflon filter pack and the Tekran automated method, and found the consistently higher PBM on Teflon filter.

Although there are many studies reporting atmospheric PBM concentrations, studies identifying the size distribution of PBM are quite scarce. In addition, there have been few systematic studies identifying the artifacts associated with PBM measurements. This study was performed to determine how sampling artifacts associated with various sampling methods impact PBM measurements in a region far from large point sources. Concentrations and size distributions of PBM were measured using three difference methods including a TekSpec, MOUDI, and OFF, and compared with each other. Based on measurement data the importance of sampling artifacts was determined.

2 Experimental and methodologies

2.1 Site description

Particle samples were collected at two different sites including the Huntington Wildlife Forest (HF) in the Adirondack Park and Clarkson University (CU) in Potsdam, both in New York State (Fig. 1). At HF sampling was performed in a large open area surrounded by conifer forest and in Potsdam sampling was performed on the roof of the three-story building at CU which is situated about 0.5 km northwest of a very small airport and about 1 km from a main road. Both sites were not considered to be

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significantly impacted by local sources, although the HF site represents a more background site.

Atmospheric temperatures measured at Massena International Airport station (32 km north of the CU sampling site), obtained from the National Virtual Data System website operated by NOAA (www.ncdc.noaa.gov) were used in this study.

2.2 Sampling and analysis for PBM

A five-stage MOUDI (MSP corp.) was used to collect size segregated PBM (nominal cut points of 10 μm , 5.6 μm , 3.2 μm , 1.0 μm , and 0.18 μm) on quartz filters (47 mm with pore size of 0.2 μm) using a flow rate of 30 Lpm. The sampling durations for MOUDI were 2 days at CU and 7 days at HF. At CU 16 sets of samples were collected using the MOUDI from 15 March to 14 May 2012 while 8 sets of samples were collected at HF from 11 January to 28 February 2012. After sampling, the quartz filters were placed in the quartz container and flushed with zero air until the concentration reading of a Tekran 2537 dropped to $< 0.5 \text{ ng m}^{-3}$. The filters in the quartz container were then thermally desorbed using a furnace at 700 $^{\circ}\text{C}$ (the limit of the furnace used) to convert desorbed Hg to Hg^0 in a carrier gas of zero air, and introduced into a Tekran 2537B until the measured concentration dropped to $< 0.5 \text{ ng m}^{-3}$. Inside the quartz container quartz chips and glass wool were inserted to decrease the retention time and to convert the desorbed Hg to GEM. Detailed information about the analysis system can be found in Huang et al. (2011) and Lai et al. (2011).

A TekSpec consisting of Tekran 1130, 1135 and 2537 was used to measure GEM, GOM, and PBM concentrations during the same sampling period as the MOUDI at CU and HF. The system was operated in accordance with the EPA Mercury Monitoring network guidelines (Landis et al., 2002; NADP, 2008). Ambient air was drawn through an elutriator to remove particles $> 2.5 \mu\text{m}$, through a potassium chloride (KCl) coated annular denuder to remove GOM, and then through a regenerable particulate filter (RPF) to capture PBM at a flow rate of 10 Lpm. GOM and PBM were collected with a 2 h sampling interval followed by a 1 h thermal desorption period. Additional details for

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TekSpec are provided in other publications (Choi et al., 2008; Kim et al., 2009; Poissant et al., 2005).

An OFF method was also used to measure the total PBM. A quartz filter was placed in a Teflon filter holder which was connected to a pump operating at a flow rate of 15 Lpm. The height of OFF was same as the height of MOUDI inlet. The sampling durations were 2 days at CU and 7 days at HF during same sampling period as the MOUDI. Intotal 16 and 8 samples were collected at CU and at HF, respectively. After sampling, the filters were analyzed using the same method as MOUDI filters.

A novel Large Particle Inlet (LPI), filter holder, and vacuum pump were also used for artifact evaluation. The inlet was first developed to collect large particles by Lee et al. (2008). A pre-baked glass fiber filter (10.5 cm diameter, pore size of 1 μm) was placed in the filter holder connected to the LPI, and large particles were collected at a flow rate greater than 800 Lpm. Filters were weighed before and after sampling to measure the mass of collected particles. After sampling the filters were cut into eight equal size wedges, and two pieces were subjected to four different treatments including (1) immediate analysis, (2) exposure to GEM, (3) exposure to zero air, and (4) exposure to zero air followed by exposure to GEM. For exposure to GEM the filters were placed in a sealed 1 L bottle containing known GEM concentrations for four hours. For exposure to zero air, the filters were placed into a Teflon filter holder and zero air (UHP grade) was passed through them at a flow rate of 1 Lpm for four hours. After all treatments, the filters were thermally desorbed as described above. Another group of five LPI samples was also used only for evaluating positive artifacts. In these experiments each filter was divided into eight equal size wedges, and two pieces were exposed to different GEM concentrations.

Hg speciation in collected particles was also identified using a thermally induced desorption technique (Feng et al., 2004). In this study, Hg desorbed from the particles collected on an OFF were quantified at desorption temperature ranges of 30–120 $^{\circ}\text{C}$, 120–350 $^{\circ}\text{C}$, 350–500 $^{\circ}\text{C}$ and 500–700 $^{\circ}\text{C}$ corresponding to the initial release

3.2 Comparison of various sampling method

3.2.1 MOUDI vs. TekSpec for $\text{PBM}_{2.5}$

Many researchers have measured concentrations of PBM in $\text{PM}_{2.5}$ ($\text{PBM}_{2.5}$) using a TekSpec equipped with an impactor and elutriator in which particles $> 2.5 \mu\text{m}$ are removed (Lynam and Keeler, 2005; Weiss-Penzias et al., 2009). In order to compare PBM concentrations between the MOUDI and TekSpec, $\text{PBM}_{2.5}$ was estimated by summing the lowest MOUDI stages and adding 68 % of the particles collected in the stage of 1.0–3.2 μm (based on the ratio of (2.5–1.0 μm) to (3.2–1.0 μm)). While the TekSpec $\text{PBM}_{2.5}$ was approximately 26 % higher than with MOUDI on average (p value = 0.026), the correlation between the TekSpec and MOUDI was quite good ($r_s = 0.944$, $p < 0.001$) (Fig. 4). Lower concentrations in the MOUDI are expected since the particles might bounce, adhere, or Hg may blow-off when particles strike the impaction plate, resulting in a loss of some of the mass (Hinds, 1999). In addition, the sampling duration for the MOUDI was 48 h while the TekSpec measured $\text{PBM}_{2.5}$ every 2 h; therefore, there might be a greater negative sampling artifact due to the volatilization of $\text{PBM}_{2.5}$ after collection when the MOUDI is used. Although the TekSpec is expected to have minimal artifacts due to the short sampling time, previous research suggests that it may be associated with significant positive artifacts. Lyman et al. (2010) reported that KCl denuders used in TekSpec lost 29–55 % of the GOM collected in the presence of ozone, resulting in possible positive artifacts on downstream $\text{PBM}_{2.5}$ collection. Loss of GOM in the denuder could cause $\text{PBM}_{2.5}$ measured by the TekSpec to be higher than $\text{PBM}_{2.5}$ by MOUDI if the GOM not sorbed by the denuder is sorbed by the RPF. However, if the Hg from the denuder is liberated as GEM as suggested by Lyman et al. (2010) the consequent positive PBM artifact will be negligible. Possible positive artifacts during PBM measurement is further discussed below.

At HF where the MOUDI was operated for seven days for each sample, $\text{PBM}_{2.5}$ could not be compared between MOUDI and TekSpec because the last stage of the MOUDI was not used.

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3.2.2 MOUDI vs. TekSpec for $\text{PBM}_{>2.5}$

The TekSpec measures GOM and PBM on a short time-scale which may limit artifacts; however, the concentration of $\text{PBM} > 2.5 \mu\text{m}$ ($\text{PBM}_{>2.5}$) is not measured since it is removed in the impactor in order to prevent positive GOM artifacts resulting from particle loss in the denuder. In this study, $\text{PBM}_{>2.5}$ was measured by desorbing the removable impactor frit of the TekSpec after 48 h of sampling (same duration as the MOUDI samples). This concentration was compared with $\text{PBM}_{>2.5}$ collected with MOUDI. On average, $\text{PBM}_{>2.5}$ using the MOUDI was slightly higher than that using the TekSpec frit (Fig. 4), but the difference between the two groups was not high enough to exclude the possibility that the difference was derived by random sampling error (p value = 0.462). For $\text{PBM}_{>2.5}$ the TekSpec frit could also have negative artifacts due to GEM or GOM concentration decreases during the 48 h sampling duration similar to the MOUDI; therefore, this result cannot confirm that negative artifacts for the MOUDI were greater for $\text{PBM}_{2.5}$ than for $\text{PBM}_{>2.5}$. At HF where the MOUDI was operated for seven days for each sample, $\text{PBM}_{>2.5}$ measured using the TekSpec frit was approximately 27 % higher than that by MOUDI (but the difference was not significant; p value = 0.297). The correlation coefficient between two instruments did not decrease when compared with that obtained at CU, and was still statistically significant (Fig. 4). The significant correlation between TekSpec frit and MOUDI observed (Fig. 4) indicates that TekSpec frit is a good alternative sampler for measuring the concentration of coarse PBM.

3.2.3 Comparison with open faced filter pack (OFF)

\sum PBM concentrations measured using the MOUDI (all stages) and TekSpec (combining $\text{PBM}_{2.5}$ and $\text{PBM}_{>2.5}$ collected on frit) were compared with those measured by an OFF which is considered to be a conventional sampling technique for measuring PBM concentrations (Dvonch, 1995; Keeler et al., 1994, 1995). Statistically, there was a significant correlation between the MOUDI and OFF ($r_s = 0.926$, p value < 0.001), and the two datasets were not different (p value = 0.468) (Fig. 5) although \sum PBM measured

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by the MOUDI was approximately 1.2 times higher than Σ PBM measured by the OFF. The OFF is assumed to have both negative and positive artifacts while the MOUDI is thought to have only negative artifacts since the flow streamlines do not interact with the sampling surface (Copley, 2007). Therefore, the difference between Σ PBM measured by the OFF and MOUDI are due to positive artifacts (sorption of GOM), which these measurements suggest was not significant at this site.

Σ PBM concentrations measured by the OFF for various sampling durations (2 days, 7 days, and 13 days) were compared with Σ PBM measured by the TekSpec ($\text{PBM}_{>2.5} + \text{PBM}_{2.5}$) to determine the effect of long sampling duration on PBM measurements. Correlations of Σ PBM measured by both methods was strong and significant ($r_s = 0.789$, p value < 0.001); however Σ PBM concentrations measured by the OFF were consistently lower (approximately 42% lower, on average) than those measured by the TekSpec (p value < 0.001) (Fig. 5). In contrast Talbot et al. (2011) reported that PBM measured by a OFF (Teflon filter) was consistently higher than that measured by a TekSpec for both 3 h and 24 h sampling durations. They considered two possibilities with regards to this significant difference including first, that the OFF collected coarse PBM particles which were not collect by the TekSpec and second, that Hg from aerosols might be volatilized as they passed through the heated denuder (at 50 °C) as water was volatilized. The first possibility can be excluded in this study because both $\text{PBM}_{2.5}$ and $\text{PBM}_{>2.5}$ were measured. The second possibility examined by that Talbot et al. (2011) identified the influence of humidity on the difference between PBM measured by the OFF and TekSpec, and concluded it had minor importance; therefore, the two possibilities that Talbot et al. (2011) suggested do not explain the results seen in this study.

Lyman et al. (2010) found a possible positive artifact for PBM measured with the TekSpec from GOM lost from the KCl coated denuder and captured on the RPF. However, this positive artifact should be higher for the OFF than for TekSpec since no GOM is removed before the OFF. Therefore, the significant difference on PBM concentration between TekSpec and OFF seen in this study was likely due to a negative artifact from

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the OFF, caused by volatilization of Hg from particles on the OFF during the long sampling time. When considering only the samples obtained over long sampling durations (seven and 13 days) there was no statistical correlation ($r_s = 0.567$, p value = 0.112) between the methods suggesting that the loss of Hg from filters over the course of the longer sampling periods should be considered when reporting PBM concentration.

To further investigate positive artifacts caused by adsorption of GOM onto the filter and/or the particles collected on filter, PBM samples were divided by two groups of high GOM and low GOM concentrations depending on when they were collected (the criterion used was the average GOM concentration, 5.4 pg m^{-3}), and the relationships between OFF and TekSpec and between OFF and MOUDI were compared. The correlation equations were TekSpec = $5.24 + 1.34\text{OFF}$ ($r_s = 0.891$) and MOUDI = $1.13 + 1.11\text{OFF}$ ($r_s = 0.915$) for the samples having low GOM concentrations, and TekSpec = $0.03 + 1.71\text{OFF}$ ($r_s = 0.886$) and MOUDI = $0.66 + 1.03\text{OFF}$ ($r_s = 1.00$) for the samples having high GOM concentrations. For both groups, the correlations were good and statistically significant at the confidence level of 0.05, and the slope did not decrease for high GOM samples, showing that the positive artifact caused by adsorption of GOM is not significant under the conditions encountered in this study ($< 16.5 \text{ pg m}^{-3}$ and GOM and generally low levels of other pollutants). Talbot et al. (2011) also suggested that filter based PBM had minimal positive artifact from uptake of GOM even under the conditions encountered in the marine boundary layer where GOM concentrations are typically higher.

3.3 PBM speciation

In only a limited number of previous studies was Hg speciation in particles determined. Two different approaches have been used including sequential leaching procedures (Feng et al., 2000; Xiu et al., 2005, 2009) and a thermally induced desorption technique (Feng et al., 2004). In this study Hg desorbed from the particles collected on an OFF were quantified at different desorption temperature ranges of 30–120 °C, 120–350 °C, 350–500 °C and 500–700 °C (Feng et al., 2004). The amount of Hg released in the

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temperature range of 120–350 °C was highest, contributing 61.2% to 75.2% of the total, followed by the temperature range of 500–700 °C (12.5–20.2%) (Fig. 6). In the desorption temperature range of 120–350 °C both Hg⁰ and HgCl₂ can be released while Hg released for 350–500 °C and 500–700 °C temperature range mostly represent HgS and HgO, respectively (Feng et al., 2004), indicating that Hg⁰ and HgCl₂ were the dominant forms in particles collected in this study. In the study of Feng et al. (2004) the Hg⁰ and HgCl₂ together contributed approximately 51% of the total while HgS and HgO contributed 9% and 40% respectively, to the total Hg collected in Toronto. Their significantly higher contribution of HgO than in this study was possibly due to the fact that the sampling site in Toronto was impacted to a greater extent by local sources including combustion process than the site in this study.

Hg speciation in particles can vary with particle composition, source type, and atmospheric temperature. Since the particles in this study were collected at one remote sampling site (CU) and integrated over 48 h it is hypothesized that their composition were relatively consistent for all eight samples represented in Fig. 6, indicating that atmospheric temperature ranging from 2.2 °C to 16.7 °C was the important factor affecting Hg species in particles. Previous studies found that the activation energy which the system must absorb in order to initiate a Hg release from soils (Gustin et al., 2003) was the highest for HgO, followed by HgS, HgCl₂, and Hg⁰ (Feng et al., 2004; Kocman and Horvat, 2010). Therefore, it can be assumed that Hg⁰ and HgCl₂ can more easily volatilize from the particle surface as atmospheric temperatures increase while HgO is much less volatile because high activation energy is required. In this study the contribution of Hg⁰ and HgCl₂ (quantified as Hg desorbed at the temperature less than 350 °C) to total particle associated Hg decreased as atmospheric temperature increased, and a positive correlation was observed between HgO contribution and atmospheric temperature ($r_s = 0.759$, p value = 0.029). This result suggests that the type of Hg species associated with particles varies with atmospheric temperature as Hg species with high vaporization enthalpy increase as atmospheric temperature increases. However, it should be noted that the vaporization of Hg species from the

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aerosol is also dependent on their binding in the aerosol, which may vary with aerosol composition.

3.4 Artifact evaluation

To further explore PBM artifacts, five PBM samples were obtained using the LPI system for 36 h. Each filter was immediately cut into eight equal size wedges and each two pieces were subjected to four different treatments including (1) immediate analysis, (2) exposure to zero air, (3) exposure to GEM, and (4) exposure to zero air followed by exposure to GEM. The exposure time for zero air and elevated GEM was 4 h each. The final GEM concentrations in a sealed bottle and PBM concentration on the filter were measured after 4 h. After exposure to zero air the Hg mass on the filter decreased 11.4% (7.1–16.8%) (Fig. 7). This decrease was primarily due to the loss of Hg species desorbed in the temperature range of 120–350 °C (Fig. 7), indicating that either Hg⁰ or HgCl₂ or both were the main species involved in the negative artifact. After exposure to GEM, the Hg mass on the filter increased 11.8% (5.8–18.8%), at a final GEM concentration of approximately 30 ng m⁻³. The increase of PBM mass was mostly detected in the desorption temperature range between 120 and 350 °C as expected (Fig. 7). Since the GEM concentration used was much higher than ambient GEM concentrations typically found this may be the maximum positive artifact that can be caused by the sorption of GEM onto the filter and/or the particles collected on filter under the ambient conditions encountered. For the fourth group, the filters were exposed to zero air for 4 h followed by exposure to GEM in a sealed bottle for 4 h, and the result showed that PBM mass increased only 1.8 ± 3.3% above its original value (Fig. 7) even though the final GEM concentration in the bottle was approximately 30 ng m⁻³, significantly less than would be predicted from the isotherm experiments which were not exposed to zero air (see below). This difference between the Hg mass with and without exposure to zero air may have been due to loss of HgCl₂.

An additional five samples were collected using LPI system during 19 to 28 July 2012, and each filter was divided into eight equal size wedges, and two pieces were

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exposed to different GEM concentrations in order to develop adsorption isotherms. The empirically derived Freundlich isotherm equation indicated there is a linear relationship between logarithmic ω (equilibrium Hg sorbed/particle mass; ng-Hg/g-particle) and logarithmic C_a (equilibrium GEM concentration in air; ng m⁻³) (Fig. 8, p value < 0.01) as

$$\omega = 94.4 C_a^{0.037} \text{ where the units of } \omega \text{ and } C_a \text{ were ng g}^{-1} \text{ and ng m}^{-3}, \text{ respectively.}$$

Previous studies on the adsorption of Hg were carried out in order to identify the adsorption capacity of sorbents to remove Hg emitted during coal combustion (Li et al., 2002; Lin et al., 2006). There are also a few studies investigating Hg⁰ sorption by soil; however, no studies were found investigating adsorption of Hg⁰ by atmospheric particles. In the studies of Xin and Gustin (2007) and Fang (1978), it was found that the sorption of Hg⁰ vapor by soil increased linearly with increasing air Hg⁰ concentration. The ω calculated from the study of Fang (1978) ranged from 0.15 to 0.76 ng g⁻¹ for C_a of 10 ng m⁻³ for various types of soil, which is significantly less than our result (102.8 ng g⁻¹). The ω from Xin and Gustin (2007) (approximately 7×10^{-4} ng g⁻¹) was also much lower than what was found in this study. In another study, Xin et al. (2007) suggested that Hg⁰ adsorption by soil was not concentration dependent and did not follow the typical Langmuir isotherm although they used a higher Hg⁰ concentrations than was used in this study (up to 170 ng m⁻³).

The atmospheric temperature in the lab was relatively consistent (around 20 °C). Future experiments are required to determine the effect of temperature on adsorption capacity of atmospheric particles for different Hg species. The relatively large standard deviation of ω for similar C_a (Fig. 8) was probably due to different particle composition since the gas-particle partitioning is strongly affected by temperature, the particle surface area, and the particle surface chemistry (Liang et al., 1997; Pankow, 1991; Yamasaki et al, 1982, Rutter and Schauer, 2007a, b).

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4 Conclusion and implications

In this study the importance of sampling artifacts was determined by comparing PBM concentrations measured by three different techniques. The concentrations of PBM_{2.5} measured by the MOUDI for 48 h were statistically lower than with the TekSpec, indicating that negative artifacts when sampling with an impactor were significant for long sampling durations. PBM_{>2.5}, measured by desorbing the removable impactor frit of the TekSpec after 48 h of sampling had no statistical difference with the MOUDI PBM_{>2.5} suggesting that both the MOUDI and TekSpec were associated with similar negative artifacts and that TekSpec frit is a good alternative sampler for measuring the concentration of coarse PBM. Negative artifacts were also seen when an OFF was exposed to zero air for 4 h as Hg⁰ and HgCl₂ on the filter decreased 11.4 % on average. In addition, it was estimated that most of loss was attributed to HgCl₂ because the PBM mass after exposure to zero air followed by exposure to GEM was far less than PBM mass after GEM exposure. This result suggests the possibility that TekSpec which collects PBM for 2 h at a flow rate of 10 Lpm and is exposed to air with GOM removed, may also have negative artifacts.

OFFs, which are can potentially be associated with positive and negative artifacts, produced a statistically lower PBM concentration than the TekSpec while the OFF and MOUDI showed similar results, indicating that positive artifacts did not distort PBM measurements under the rural condition encountered in this study. It has been shown by others that gaseous Hg can cause positive artifacts when PBM is collected on denuded filter at elevated ozone concentrations possibly due to the oxidization of Hg during the sampling (Lynam and Keeler, 2005) or the decreasing collection efficiency of a denuder for GOM (Lyman et al., 2010). In the lab experiments, the filters exposed to high GEM concentration (~ 30 ng m⁻³) for 4 h increased measured PBM 11.8%, however, it cannot be concluded that positive artifacts are important under the normal atmospheric condition typically of 1–3 ng m⁻³ of GEM concentration.

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Exposure experiments for different GEM concentrations determined the empirical Freundlich adsorption isotherm equation for Hg^0 between air and the atmospheric particles as $\omega = 94.4 C_a^{0.037}$ where the units of ω and C_a were ng g^{-1} and ng m^{-3} , respectively. Using this isotherm PBM formed by sorption of GEM can be calculated. If atmospheric GEM and $\text{PM}_{2.5}$ concentrations are 1.5 ng m^{-3} (typical concentration in this study area; Choi et al., 2008) and $35 \mu\text{g m}^{-3}$ (24 h average National Ambient Air Quality Standard), respectively, the GEM amount sorbed onto the particles is approximately 95.8 ng g^{-1} and the equilibrium atmospheric concentration of PBM in $\text{PM}_{2.5}$ formed by sorption of GEM would be 3.4 pg m^{-3} . If the atmospheric concentration of GEM increases from 1.5 to 3.0 ng m^{-3} during PBM sampling a positive artifact can occur due to the sorption of GEM onto the particles collected on filter. Assuming the particles reach equilibrium the positive artifact would be 0.05 pg m^{-3} . However, the RPF of the TekSpec is typically exchanged biweekly (Choi et al., 2008), leading to a continuous accumulation of particles over that period. If these particles, which have undergone repeated heating, can also be characterized by a sorption isotherm similar to that shown above, the positive artifact could be significantly greater. It should be noted that the adsorption capacity and accompanying gas-particle partitioning mechanisms for Hg species can change with the various conditions including particle composition and temperature; therefore complete understanding of this phenomenon will require further investigation.

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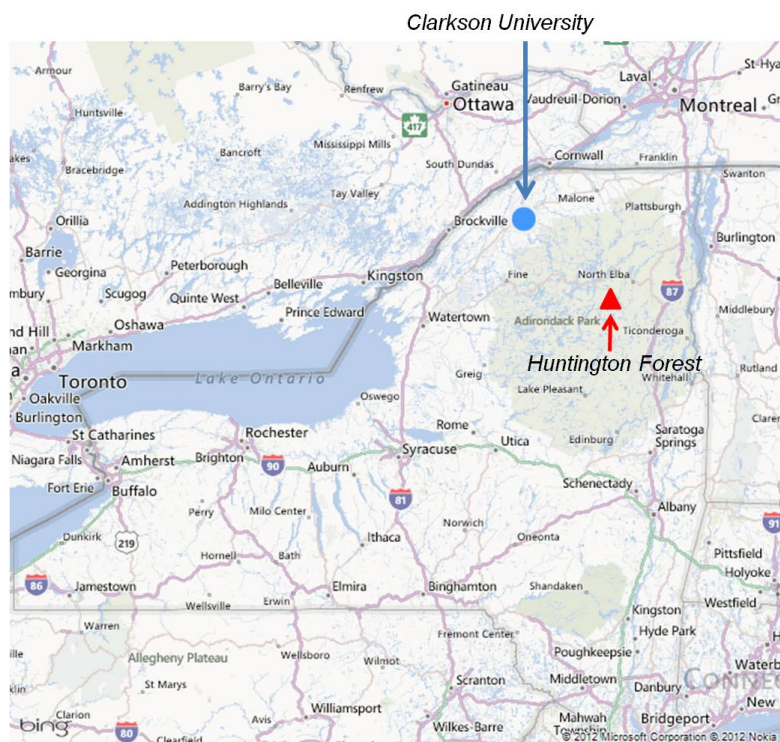


Fig. 1. Two sampling sites located at Clarkson University (CU) in Potsdam and Huntington Wildlife Forest in Adirondack Park (HF) in New York State.

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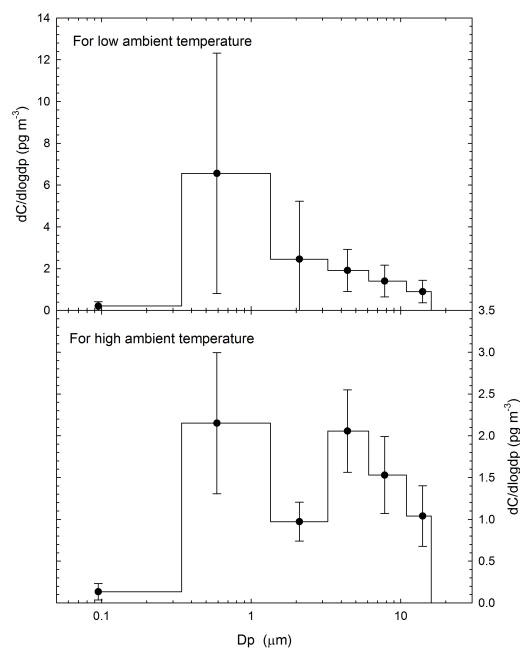


Fig. 2. Size distribution of PBM by MOUDI. PBM shifted toward to coarser mode when the atmospheric temperature was low. The error bar indicates one standard deviation.

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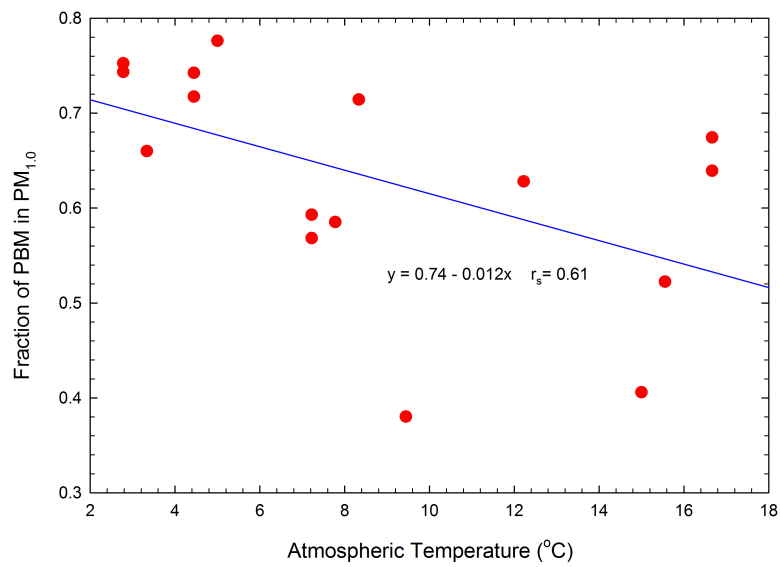


Fig. 3. The negative relationship between atmospheric temperature and fraction of PBM_{1,0} to total PBM.

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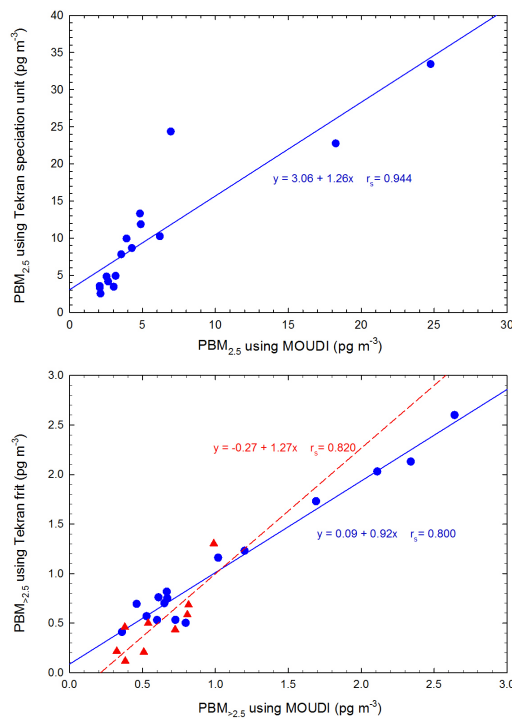


Fig. 4. Comparison between MOUDI and TekSpec for PBM_{2,5} (upper panel) and PBM_{>2,5} (lower panel). The blue circle and red triangle in lower panel indicate MOUDI results operated for 2 days at CU and for 7 days at HF, respectively.

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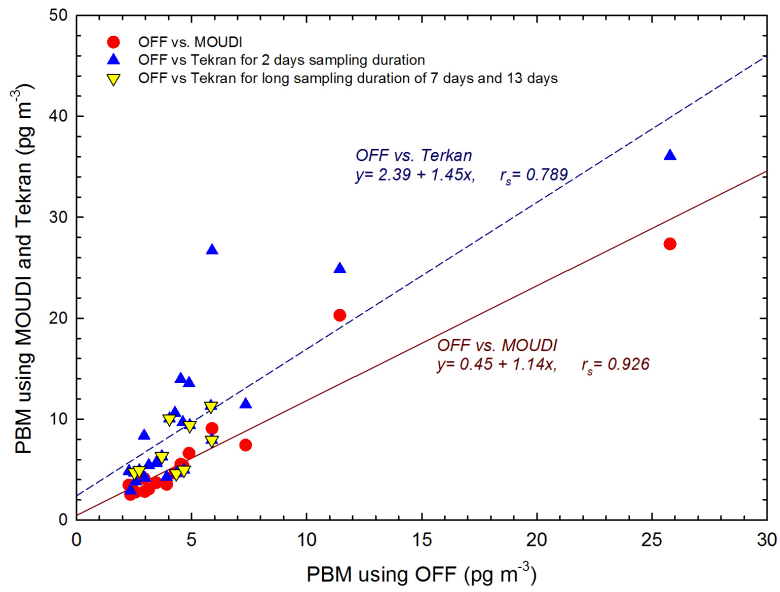


Fig. 5. Comparison of total PBM concentrations between OFF and MOUDI (red circle) and between OFF and TekSpec (blue triangle and yellow inverted triangle).

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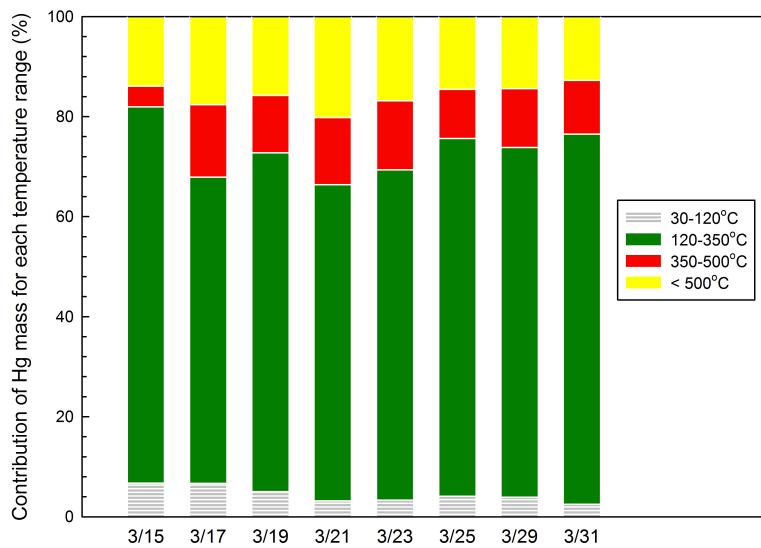


Fig. 6. Percentage of PBM mass released at different desorption temperature range.

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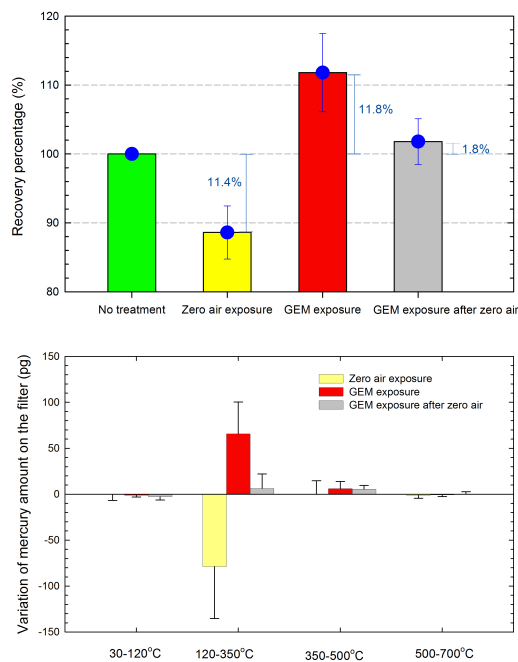


Fig. 7. Upper panel: percentage of the total Hg recovered after four different treatments: (1) immediate analysis, (2) exposure to GEM, (3) exposure to zero air and (4) exposure to zero air followed by exposure to GEM. Lower panel: variation of Hg amount at different desorption temperatures after four treatments.

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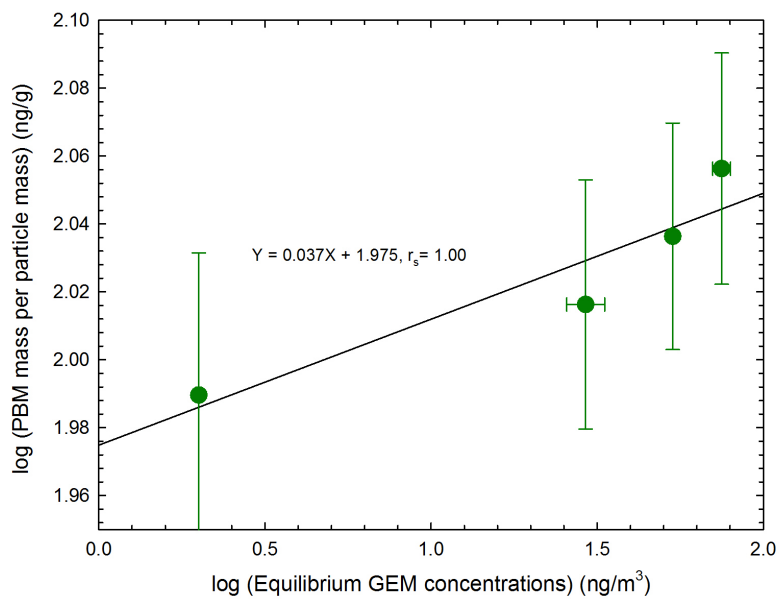


Fig. 8. Percentage increase in the PBM concentration after exposure to different GEM concentrations. The error bar indicates one standard deviation.

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