



Observations of reactive gaseous mercury in the free troposphere at the Mount Bachelor Observatory

P. C. Swartzendruber,^{1,2} D. A. Jaffe,^{1,2} E. M. Prestbo,³ P. Weiss-Penzias,²
N. E. Selin,⁴ R. Park,⁴ D. J. Jacob,⁴ S. Strode,¹ and L. Jaeglé¹

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[1] We measured gaseous elemental mercury (GEM), particulate mercury (PHg), and reactive gaseous mercury (RGM), along with CO, ozone, and aerosol scatter at the Mount Bachelor Observatory (2.7 km above sea level), Oregon, from May to August 2005. The mean mercury concentrations (at standard conditions) were 1.54 ng/m³ (GEM), 5.2 pg/m³ (PHg), and 43 pg/m³ (RGM). RGM enhancements, up to 600 pg/m³, occurred at night and were linked to a diurnal pattern of upslope and downslope flows that mixed in boundary layer air during the day and free tropospheric air at night. During the night, RGM was inversely correlated ($P < 0.0001$) with CO ($r = -0.36$), GEM ($r = -0.73$), and H₂O ($r = -0.44$), was positively correlated with ozone ($r = 0.38$), and could not be linked to recent anthropogenic emissions from local sources or long-range transport. Principal component analysis and a composite of change in RGM versus change in GEM during RGM enhancements indicate that a nearly quantitative shift in speciation is associated with increases in ozone and decreases in water vapor and CO. This argues that high concentrations of RGM are present in the free troposphere because of in situ oxidation of GEM to RGM. A global chemical transport model reproduces the RGM mean and diurnal pattern but underestimates the magnitude of the largest observed enhancements. Since the only modeled, in situ RGM production mechanisms are oxidation of GEM by ozone and OH, this implies that there are faster reaction rates or additional RGM production mechanisms in the free troposphere.

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1. Introduction

[2] The extent to which oxidized forms of mercury are present in the atmosphere remains a key uncertainty in our understanding of the global cycling of mercury [Schroeder and Munthe, 1998; Stratton *et al.*, 2001]. Knowledge of the speciation of airborne mercury is important because of the radically different behaviors of each species and the resulting sensitivity on deposition fluxes [Shia *et al.*, 1999; Bergan and Rodhe, 2001]. Reactive gaseous mercury (RGM) is an operationally defined fraction of atmospheric mercury based on its collection by a KCl denuder [Landis *et al.*, 2002]. It is believed to be a divalent compound such as HgCl₂ or HgO, which, unlike gaseous elemental mercury (GEM), is rapidly deposited to particles and surfaces and is

efficiently sequestered by rain and cloud droplets. Consequently, the lifetime of RGM in the atmosphere is believed to be substantially shorter than the global mean residence time of GEM (6–24 months). Mercury which is bound to particles (PHg) is constrained to the lifetime of the carrier particle, typically less than 10 days, which is also considerably shorter than the lifetime of GEM.

[3] Atmospheric mercury is believed to be predominantly GEM. Natural emissions and reemissions are also believed to be almost entirely GEM [Mason and Sheu, 2002; Gustin *et al.*, 2000]. Anthropogenic emissions to the atmosphere are dominated by GEM (60–70%), with the balance being RGM and PHg [Carpi, 1997; Pacyna *et al.*, 2006; Streets *et al.*, 2005]. It has generally been assumed that there are negligible concentrations of reactive species distant from anthropogenic sources. The validity of this assumption has been challenged by recent studies in the polar regions [Lindberg *et al.*, 2002; Steffen *et al.*, 2002; Berg *et al.*, 2003; Ebinghaus *et al.*, 2002; Sprovieri *et al.*, 2002; Temme *et al.*, 2003] and over the open ocean [Laurier *et al.*, 2003; Sprovieri *et al.*, 2003] that have shown that RGM can be produced in remote regions from the oxidation of GEM.

[4] Low-altitude ground-based studies in the middle latitudes have supported the assumption that little RGM

¹Department of Atmospheric Sciences, University of Washington, Seattle, Washington, USA.

²Interdisciplinary Arts and Sciences, University of Washington-Bothell, Bothell, Washington, USA.

³Frontier Geosciences, Seattle, Washington, USA.

⁴Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts, USA.

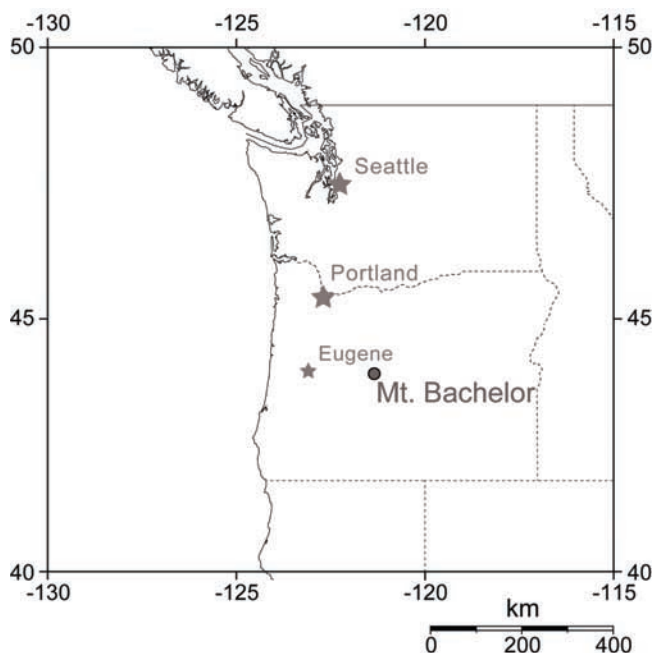


Figure 1. Location of the Mount Bachelor Observatory in the Pacific Northwest of the United States.

or PHg is present distant from sources. Most studies [e.g., Sheu and Mason, 2001; Landis *et al.*, 2002; Malcolm *et al.*, 2003; Weiss-Penzias *et al.*, 2003; Poissant *et al.*, 2005] report that the reactive and particulate fractions are less than 5% and often less than 2% of the total airborne mercury (THg = GEM + RGM + PHg).

[5] There have been few studies of mercury in the free troposphere. Several groups have conducted aircraft studies of mercury above the planetary boundary layer, but have generally measured only THg or have assumed that all of the mercury which was detected was present in the atmosphere as GEM. They found either little or no change in mercury mixing ratios with height [Ebinghaus and Slemr, 2000; Banic *et al.*, 2003] while several others report a slight decrease with height [Brosset, 1987; Kviatkus, 1995; Friedli *et al.*, 2004]. Recent mass spectrometer measurements near the tropopause have discovered mercury associated with particles and have suggested that large fraction of the mercury in the lower stratosphere may be in the particulate fraction [Murphy *et al.*, 2006]. Preliminary reports from measurements at the Mauna Loa Observatory and airborne measurements in Florida [Landis *et al.*, 2005] have suggested that there are elevated levels of RGM and PHg in the free troposphere.

[6] In the Pacific Northwest, Weiss-Penzias *et al.* [2003] studied mercury speciation at the Cheeka Peak Observatory near the coast of Washington State and reported very low levels of RGM and PHg (<3% of the total airborne mercury). More recently, Jaffe *et al.* [2005] report on observations of Asian outflow at Okinawa, Japan, and the detection of the long-range transport (LRT) of Asian THg to the Mount Bachelor Observatory (MBO) in Oregon. In the spring of 2004, they observed well correlated enhancements of THg and CO which were linked to Asian anthropogenic

emissions. Subsequently, Weiss-Penzias *et al.* [2006] describe observations from the site in greater detail and focus on the identification of free tropospheric air, LRT of pollution from Asia, and other air mass types.

[7] In this paper, we examine the speciation of Hg in the free troposphere at the Mount Bachelor Observatory and aim to improve our understanding of its chemistry by posing the following questions:

[8] 1. What are the concentrations and distributions of the three major mercury species (GEM, RGM, PHg) in the free troposphere?

[9] 2. If elevated concentrations of RGM or PHg are observed, can they be linked to anthropogenic emissions, from either local sources or long-range transport?

[10] 3. Is there any evidence for the in situ production of RGM and if so, what mechanisms are likely responsible?

[11] 4. How do observed concentrations and dominant reactions compare to our current understanding (i.e., as modeled)?

2. Methodology

2.1. Site Description

[12] All measurements in this study were made at the Mount Bachelor Observatory (hereafter MBO), Oregon (43.98N 121.69W, 2.7 km above sea level (asl)). The site location is shown in Figure 1. The site was established in 2004 and has been previously described by Jaffe *et al.* [2005] and Weiss-Penzias *et al.* [2006]. The summit sits approximately 1.4 km above the surrounding terrain and receives predominantly westerly winds. There are no emission points at the summit or in the surrounding area with the exception of the Mount Bachelor snow grooming equipment, but these can be easily identified from sharp enhancements in CO, NO_x, and aerosol scatter. The nearest source of anthropogenic pollution is the city of Bend which is approximately 30 km to the east but is only rarely upwind. MBO frequently samples free tropospheric air and has detected the long-range transport of anthropogenic pollutants such as CO, THg, and aerosols from eastern Asia [Jaffe *et al.*, 2005; Weiss-Penzias *et al.*, 2006]. The predominant free tropospheric influence at MBO was identified by a comparison to mean water vapor profiles from rawinsondes launched from Medford and Salem, Oregon [Weiss-Penzias *et al.*, 2006].

2.2. Atmospheric Chemical Measurements

[13] Measurements made in 2005 were real time or near real time and included Hg (GEM, RGM, PHg), CO, ozone, aerosol scatter (σ_{sp}), water vapor, CO₂, NO_x, condensation nuclei, and basic meteorology. Mercury measurements are described below and the remaining measurements are described in greater detail by Weiss-Penzias *et al.* [2006] and Jaffe *et al.* [2005]. Ozone was measured with a Dasibi 1008 RS which uses a standard UV absorption method. CO measurements were made with a Thermo Electron Corporation nondispersive infrared instrument (NDIR). Dry aerosol light scattering at 535 nm (σ_{sp}) was made with a Radiance Research nephelometer. Water vapor was calculated from temperature and relative humidity sensors (Campbell Scientific HMP 45C) and directly from a Licor 6262 (which also measures CO₂).

2.3. Mercury Measurement

[14] Gaseous elemental mercury (GEM) was measured with a Tekran 2537A on continuous, 5-minute cycles by preconcentration on alternating gold cartridges, thermal desorption, and quantification by cold vapor atomic fluorescence spectroscopy (CVAFS). The mercury speciation measurements were made with the Tekran 1130 and 1135 modules which are described by *Landis et al.* [2002]. RGM and PHg are operationally defined fractions of mercury based on their selective capture when passing through a KCl coated annular denuder and a quartz fiber filter, respectively. We assume that RGM is primarily gaseous Hg(II) compounds. After the completion of a speciation collection period (3 hours in this work), the RGM and PHg fractions are quantified by adding an excess flow of mercury-free air to the tip of the sampling train, and then sequentially heating the pyrolyzer, quartz fiber filter, and denuder. The adsorbed Hg fractions are either reduced to GEM immediately upon heating or are volatilized and passed to the downstream pyrolyzer where they are reduced to GEM and quantified by the 2537A as GEM.

2.4. Mercury Calibration and Quality Assurance

[15] An internal GEM permeation source in the 2537A was cross-referenced to manual injections before and after deployment to the field. A Tekran 2505 vapor source and precision microsyringe (Hamilton) were used to inject known amounts of gaseous mercury into a supply of zero air. Before deployment to the field, the measured permeation rate agreed with the rate certified by the manufacturer to better than 8%. After the end of the campaign, the permeation rate was again cross-referenced and was found to agree with the rate measured at the beginning of the campaign to better than 2%. While in the field, the Tekran 2537A was automatically calibrated to the internal permeation source every 40 hours. The relative standard deviation of these calibrations was less than 2%.

[16] The GEM measurements have an estimated method detection limit of 0.1 ng/m^3 (for a 5-minute collection time), a mean hourly precision of better than 2% ($1 - \sigma$), and an accuracy of 15%. This speciation method has shown good precision in field tests and has quantitatively measured an RGM proxy (HgCl_2) in the laboratory [*Landis et al.*, 2002]. To date, however, there have been no reports on the sensitivity of this method to other potential gaseous Hg(II) or Hg(I) species.

[17] The denuder and regenerable filter pack (RFP) were replaced approximately every 2–3 weeks with a freshly cleaned and recoated set. Both the denuder and RFP were cleaned by soaking in a 10% HNO_3 (trace metal grade) solution for 24 hours followed by rinsing with double deionized (DDI) water ($>17.6 \text{ M}\Omega\text{cm}$) followed by soaking for 24 hours in DDI. After cleaning, the denuder was recoated with a KCl solution and a new quartz fiber filter was installed in the RFP.

2.5. High-Volume Inlet

[18] Because of the extreme meteorological conditions often present at MBO (e.g., heavy riming, winds in excess of 20 m/s, and temperatures $< 0^\circ\text{C}$) the 1130–1135 unit was installed inside the building at the summit, and a high-volume tube was added to bring air to the 1130/5 sample

train. The high-volume system was designed to have a cut point of $2.5 \mu\text{m}$ in 20 m/s cross winds with a Reynolds number along its length of <1800 in order to allow laminar flow to subsequently develop. A $2.5 \mu\text{m}$ cyclone particle separator sampled from the center of the high-volume tube about 30 cm from the tip. The cyclone then connected to the zero-air manifold on the end of the sampling train. The high-volume tube and cyclone (URG Corporation) were Teflon coated and heated to 40°C . The flow through the high-volume system was about 120 lpm.

2.6. Principal Component Analysis

[19] The method of principal component analysis (PCA) is also commonly referred to as Factor Analysis or Empirical Orthogonal Function (EOF) analysis. PCA reduces a two-dimensional set of data to a series of functions along each of the dimensions. These functions (or principal components, PCs) are orthogonal structures which most efficiently reproduce the variance contained in the data set. The statistical uniqueness of each principal component relative to one another can be estimated on the basis of the autocorrelation and a hypothetical red noise spectrum [*North et al.*, 1982; *Bretherton et al.*, 1999]. For this work, we use the 95% confidence limits for the uniqueness of the PCs as described by *North et al.* [1982], which is based upon the number of degrees of freedom following *Leith* [1973]. A factor having statistical uniqueness, does not, by that fact alone, guarantee that it is physically meaningful. Real world factors, e.g., marine air versus continental air, may have properties which are not orthogonal to each other. Or, all components may be rotated in phase space simply for mathematical efficiency. Therefore assigning physical significance to the results of PCA should be done conservatively [*von Storch and Zwiers*, 1999].

2.7. Chemical Model

[20] This paper uses results from the first application of the GEOS-Chem model to global mercury which is described by *Selin et al.* [2006] and *S. Strode et al.* (Global simulation of air-sea exchange of mercury, submitted to *Global Biogeochemical Cycles*, 2006, hereinafter referred to as *Strode et al.*, submitted manuscript, 2006). The GEOS-Chem model has been extensively evaluated along the West Coast with respect to observations and transport of ozone, CO, and other chemicals [*Jaeglé et al.*, 2003; *Hudman et al.*, 2004; *Liang et al.*, 2004; *Goldstein et al.*, 2004; *Heald et al.*, 2006].

[21] GEOS-Chem is a global chemical transport (CTM) model driven by assimilated meteorological fields from the Goddard Earth Observing System (GEOS) Global Modeling and Assimilation Office [*Bey et al.*, 2001]. The chemical species are calculated at a resolution of 4° latitude by 5° longitude and at 30 vertical levels. Mercury emissions data were taken from the *Pacyna et al.* [2006] inventory of 2000 emissions. The modeled mercury reactions include oxidation of GEM to RGM by OH with the rate of *Sommar et al.* [2001] ($k = 7 \times 10^{-14} \text{ cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}$) and the oxidation of GEM to RGM by ozone with the rate of *Hall* [1995] ($k = 3 \times 10^{-20} \text{ cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}$). Note that the oxidation of GEM by halogens is not included at this time. Also included is the aqueous photochemical reduction of Hg(II) which is described by *Selin et al.* [2006] and an ocean

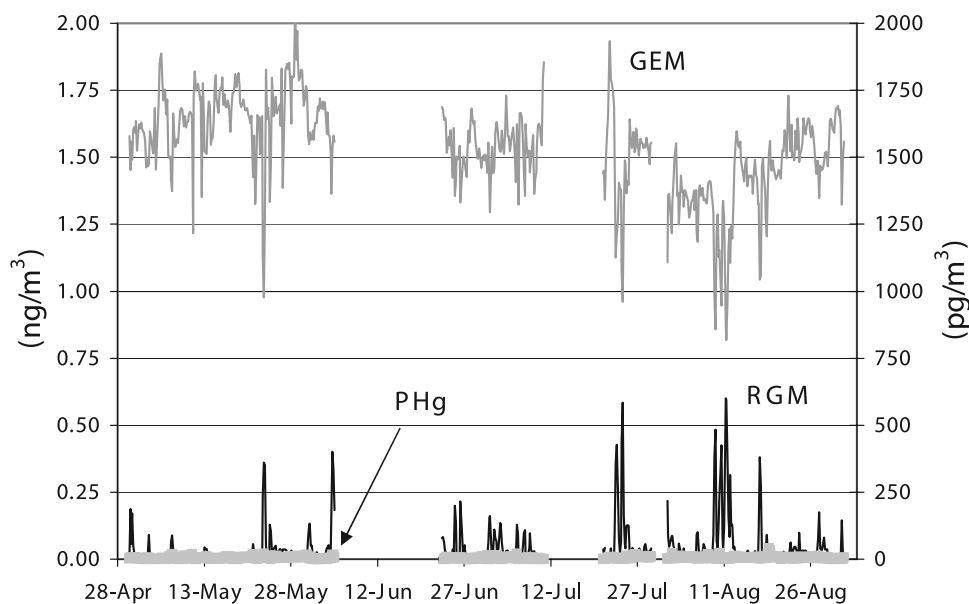


Figure 2. Time series of GEM, RGM, and PHg from 30 April to 30 August 2005. Note that there was very little PHg observed (approximately 4% relative to RGM during the highest quartile).

model which is described by Strode et al. (submitted manuscript, 2006).

3. Results and Discussion

3.1. Aggregate Data

[22] The data were collected from 30 April to 31 August 2005 and have been compiled into 3-hour means which correspond to the speciation collection period. The data recovery for this period of 124 days is 53% because the system is in speciation analysis mode every fourth hour and there were two extended periods with mechanical failures (30 days total). The mean concentrations for periods when all Hg values were available ($n = 527$) and their respective standard deviations ($1 - \sigma$) for GEM, PHg, and RGM are 1.54 (0.176) ng/m^3 , 5.2 (4.4) pg/m^3 , and 43 (82) pg/m^3 respectively. A complete time series of the three mercury species is plotted in Figure 2.

[23] Table 1 summarizes the concentrations during all available periods and the nighttime only. PHg and RGM ranged from below the estimated detection limit to 40 and 600 pg/m^3 , respectively. GEM concentrations ranged from 0.82 to 2.08 ng/m^3 and had a mean (1.54 ng/m^3) and median

(1.55 ng/m^3) which are in good agreement with low-elevation surface measurements [Ebinghaus et al., 1999; Weiss-Penzias et al., 2003; Poissant et al., 2005] and modeled values for remote regions in the middle latitudes [Seigneur et al., 2004]. This is consistent with the findings of Banic et al. [2003] that show little or no vertical gradient of GEM in the lower troposphere.

3.2. Diurnal Pattern

[24] We observed RGM enhancements of $>50 \text{ pg/m}^3$ during about one third of the nights. During these periods, PHg enhancements were also observed, but they averaged only 4.1% of the corresponding RGM enhancement. These enhancements were generally characterized by simultaneous shifts in water vapor, ozone, and GEM. Figure 3 shows an example of this pattern as observed on 23 May 2005 (day 143). Using 5-minute average data, during the beginning and end of these periods, the changes in water vapor, GEM, and ozone were generally well correlated. At the beginning of the event shown in Figure 3, water vapor and ozone were strongly anticorrelated ($r^2 = 0.93$). Unfortunately, GEM data were not available during the onset of this event

Table 1. Summary of Observed Data^a

	All							Night						
	GEM, ng/m^3	PHg, pg/m^3	RGM, pg/m^3	CO, ppb	O ₃ , ppb	H ₂ O, g/kg	σ_{sp} , (Mm) ⁻¹	GEM, ng/m^3	PHg, pg/m^3	RGM, pg/m^3	CO, ppb	O ₃ , ppb	H ₂ O, g/kg	σ_{sp} , (Mm) ⁻¹
n	530	527	527	530	530	530	439	203	203	203	203	203	203	86
Mean	1.54	4.4	39	126	46	4.6	2.9	1.51	4.3	60	123	48	4.1	5.8
5th percentile	1.36	^b	^b	91	28	1.9	^b	1.13	^b	^b	88	29	1.6	^b
25th percentile	1.51	^b	^b	112	41	3.5	0.63	1.41	^b	7.5	108	42	2.9	1.1
50th percentile	1.55	4.1	15	126	46	4.6	2.9	1.54	3.9	20	124	47	4.0	3.6
75th percentile	1.69	6.5	32	140	52	5.6	6.4	1.64	6.8	57	139	53	5.1	9.2
95th percentile	1.83	11	141	154	60	7.0	13	1.80	12	320	154	63	6.6	16
σ	0.176	4.4	75	22	10	1.5	6.1	0.196	4.5	100	25	10	1.6	7.0
RSD, %	11.4	100	193	17	22	34	133	12.9	105	167	20	21	39	120

^aHere, σ is the standard deviation, and RSD is the relative standard deviation; n is the number of 3-hour periods.

^bBelow estimated detection limit.

