



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

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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

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