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Growing season total gaseous mercury (TGM) flux measurements over an *Acer rubrum* L. stand

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ABSTRACT

Relaxed eddy accumulation (REA) measurements of the total gaseous mercury (TGM) flux measurements were taken over a deciduous forest predominantly composed of Red Maple (*Acer rubrum* L.) during the growing season of 2004 and the second half of the growing season of 2005. The magnitudes of the flux estimates were in the range of published results from other micrometeorological mercury fluxes taken above a tall canopy and larger than estimates from flux chambers. The magnitude and direction of the flux were not static during the growing season. There was a significant trend ($p < 0.001$), from net deposition of TGM in early summer to net evasion in the late summer and early fall before complete senescence. A growing season atmosphere-canopy total mercury (TGM) compensation point during unstable daytime conditions was estimated at background ambient concentrations (1.41 ng m^{-3}). The trend in the seasonal net TGM flux indicates that long term dry deposition monitoring is needed to accurately estimate mercury loading over a forest ecosystem.

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1. Introduction

Deposition and cycling of mercury in the forest canopy has been identified as an important pathway for mercury accumulation in soils and watersheds (St. Louis et al., 2001; Fay and Gustin, 2007) and a source of natural mercury emissions to the atmosphere (Lindberg et al., 1998; Graydon et al., 2006). Since the first micrometeorological measurements of the mercury fluxes over a forest canopy (Lindberg et al., 1998), the direction and magnitude of the mercury biogeochemical cycle in the forested ecosystems has been an area of active debate (Lee et al., 2000; Demers et al., 2007; Graydon et al., 2006). Several natural mercury emission models have been developed to provide mercury emissions estimates from natural surfaces for the community multiscale air quality (CMAQ) (Byun and Schere, 2006) model (Bash et al., 2004; Gbor et al., 2006) and the SARMAP air quality model (SAQM) (Xu et al., 1999). These models estimate the terrestrial elemental mercury flux from forest canopies as a function of evapotranspiration where mercury is the soil water solution is assumed to be transported via the transpiration stream. The contribution of regional sources to local mercury deposition and concentrations indicate that the atmospheric lifetime of mercury over terrestrial systems may also be shorter than previously estimated (Keeler et al., 2006), or that alternative sources are needed to explain current levels of mercury concentrations (Sigler and Lee, 2006a). A shorter atmospheric lifetime of mercury over terrestrial systems suggests that there is likely an active atmosphere-terrestrial cycling of mercury.

Previous TGM flux measurements indicate that evasion from forest ecosystems may provide contribution to the atmospheric mercury pool equivalent to direct anthropogenic emissions (Lindberg et al., 2007; 1998). Previous micrometeorological TGM flux measurements over forest canopies have only spanned several weeks primarily during daytime hours (Lindberg et al., 1998) and used the modified Bowen ratio (Lindberg et al., 1998). The difficulties in successfully measuring a small scalar gradient over a forest canopy make micrometeorological gradient methods, i.e. modified Bowen ratio, uncertain for extended periods. In the experiment reported here, a relaxed eddy accumulation (REA) system was designed to quantify the total mercury flux over a hardwood forest (Bash and Miller, 2008). The REA technique measures mean concentrations in up- and downdraft air parcels rather than a fixed mean gradient and often results in larger concentration gradients (Bowling et al., 1998). This is beneficial in well mixed areas where a representative gradient must be measured over a vertical distance that is often larger than is feasible or when the precision of the chemical analyzer is limited (Bowling et al., 1998). State-of-the-science techniques were used to investigate the fetch and turbulent averaging periods for the

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use of micrometeorological fluxes at the study site (Bash and Miller, 2008).

The purpose of this study is to report on the dynamics and trends of the net total gaseous mercury (TGM) flux over a forest canopy taken during the growing season using the REA technique. Hourly TGM flux data from the automated REA system was collected from June to November 2004, and again from August to October 2005. The REA system was designed for automated collection of air–surface fluxes over tall vegetation for dry deposition monitoring, for details see Bash and Miller (2008).

2. Methods

2.1. Site description

Flux measurements were taken on a 40 m tall micrometeorology instrument tower in a Red Maple (*Acer rubrum L.*) forest on the University of Connecticut research farm in Coventry Connecticut (Lat. 41° 47′ 30″ N, Long. 72° 22′ 29″ W, 162 m in elevation). The single inlet REA system is comprised of a Tekran model 2537A mercury (Tekran Instrument Corporation, Knoxville, TN, USA) analyzer, a Campbell Scientific CR5000 data logger, a Campbell Scientific CSAT3 sonic anemometer (Campbell Scientific Inc., Logan, UT, USA), and a laptop computer. The REA system was mounted 25 m above the forest floor, 5 m above the forest canopy. In addition to the REA system, a suite of meteorological instruments were co-located measuring incoming solar radiation, temperature, humidity, rainfall, the soil heat flux, latent heat flux, and leaf wetness.

2.2. Sampling protocol

The REA system was partially assembled in the laboratory with new Teflon tubing and acid-cleaned Teflon valve bodies and fittings, double bagged and fully assembled on the tower following ultra clean techniques. The mercury analyzer was calibrated using a permeation source biweekly, and often more frequently due to interruption in the power supply from inclement weather. Particle filters were replaced on a weekly basis and analyzed for mercury content. Twice a week the REA system was pressure checked for leaks and a system blank was taken by drawing mercury free air through the up- and downdraft sampling trains. Sampling lines were insulated to prevent condensation but power limitations at the site prohibited the heating of the sampling lines to a constant temperature. The sampling lines and the orientation and level of the sonic anemometer were also inspected twice a week. During the growing season the REA system was taken down from the tower for maintenance approximately every six weeks. Maintenance primarily consisted of replacing the tubing, calibrating the mercury analyzer in the laboratory, and washing the Teflon valve bodies and unions in a 1.8% (V/V) nitric acid bath to avoid biases in the flux measurements that may be due to mercury build up in the system.

Precipitation samples were taken at the University of Connecticut experimental agricultural station in Storrs CT located approximately 3 miles East of the research tower. They were analyzed for mercury content following EPA method 1631 (U.S. Environmental Protection Agency, 1999) from June 2004 to September 2006. Samples and blanks were taken on weekly intervals until June 2005, after which samples and blanks were collected on an event bases. Event based precipitation samples were collected following EPA method 1669 (U.S. Environmental Protection Agency, 1996; Landis and Keeler, 1997).

Foliar concentrations of mercury were analyzed during the autumn leaf fall. A total of fifty litter fall samples were collected on a weekly basis during the fall senescence from October 8th through October 22nd, 2004. Samples of recently fallen leaves were collected in 16 collection baskets arranged along north–south and west–east transects centered on the tower. Leaves were not allowed to come into contact with the forest floor. All samples were collected following “clean hands dirty hands” protocols and double bagged (U.S. Environmental Protection Agency, 1996).

2.3. REA measurements

The design and operating characteristics of the single inlet, zero dead band REA system are reported in detail in Bash (2006) and Bash and Miller (2008). In general, REA is a conditional sampling technique combining fast response, 10 Hz sampling frequency, vertical anemometry to sense upward and downward air motions, with fast switching, 30 ms maximum response time, of intake air to isolate the air from the upward and downward motions. The mercury vapor carried in the isolated upward and downward moving air is then accumulated in separate sampling lines. Mercury free air is introduced to the up- and downdraft sampling trains when they are not sampling the ambient atmosphere to maintain a constant flow rate (Bash and Miller, 2008). The mercury concentrations in the sampling lines are measured with the available slow response, in this case the Tekran model 2537A, mercury vapor analyzer. The mercury analyzer was configured to sample mercury concentrations at a 5 min interval, although capable of faster rates, to improve the signal to noise ratio of the measurement. The flux is calculated following Businger and Oncley (1990).

$$F_{Hg} = \beta\sigma_w\left(\overline{C_{Hg}^{+}} - \overline{C_{Hg}^{-}}\right) \tag{1}$$

Where the mercury flux, F_{Hg} (ng m^{-2} h^{-1}), is the product of the mean mercury concentration difference in the up- and downdrafts, $\overline{C_{Hg}^{+}}$ (ng m^{-3}) and $\overline{C_{Hg}^{-}}$ (ng m^{-3}) respectively. σ_w (m h^{-1}) is the standard deviation of the vertical wind speed, and β (unitless) is the relaxation coefficient calculated following Bowling et al. (1998).

The ambient mercury concentration can be re-constructed from a single inlet, zero dead band REA system from the up- and downdraft concentrations and the fractions of sampling period in which up- and downdrafts were sampled as follows:

$$\overline{C}_{Hg} = \overline{C_{Hg}^{+}}\frac{\delta t}{\delta t^{+}} + \overline{C_{Hg}^{-}}\frac{\delta t}{\delta t^{-}} \tag{2}$$

where $\overline{C}_{Hg}$ is the ambient mercury concentration, δt is the duration of the sampling period, and δt^{+} and δt^{-} are the durations of the up- and downdraft sampling periods respectively.

$$\beta = \frac{\overline{w'T'}}{\sigma_w\left(\overline{T_u} - \overline{T_d}\right)} \tag{3}$$

where $\overline{w'T'}$ (K m s^{-1}) is the eddy covariance sensible heat flux. w' (m s^{-1}) is the vertical velocity perturbation; T' (K) is the temperature perturbation; and $\overline{T_u}$ and $\overline{T_d}$ (K) are the mean temperatures of the up- and downdrafts respectively. β was calculated using three months of sensible heat flux data and found to be 0.474 with an r^2 of 0.96 for the site.

The measured fluxes were corrected for density perturbations caused by vapor density fluctuations in the air flow through the thermal mass flow meters used in the system (Webb et al., 1980; Pattey et al., 1992; Lee et al., 2000).

As with all turbulent flux calculations the REA technique assumes that the wind vector and scalar concentrations are stationary over the flux averaging period. Also horizontal