Seasonal and Diurnal Variations of Hg° and its Dry Deposition in New England

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Atmospheric Mercury Basics

- Chemical forms: $\text{Hg}^\circ$, RGM ($\text{HgCl}_2 + \text{HgBr}_2 + \text{HgOBr} + \ldots$), and $\text{Hg}^\text{P}$
- Marine: 1.6 ng m$^{-3}$ over the North Atlantic [Laurier et al., 2007], 1.6 - 4.7 ng m$^{-3}$ over the North Pacific [Laurier et al., 2003], and 0.4 - 11.2 ng m$^{-3}$ over the Mediterranean Sea [Sprovieri et al., 2003]
- Land: 1.6 - 5.1 ng m$^{-3}$ [Sigler and Lee, 2006; Valente et al., 2007; Kim et al., 2005]
- Diurnal – annual variability is the key to understanding the regional budget of mercury.
- Dry depositional and chemical loss of $\text{Hg}^\circ$ are highly uncertain.
Measurements and Data

- Hg°, CO, O₃, NO, NOy, CO₂, SO₂, and CH₄ measured at Thompson Farm, Pac Monadnock and Appledore Island.
- Tekran model 2537A cold vapor atomic fluorescence spectrometer, 5-minute time resolution, LOD of 5-10 ppqv.
- An internal permeation tube calibration (±5% reproducibility) verified every six months using syringe injection from the headspace of a thermoelectrically cooled Hg° reservoir (Tekran model 2505).
- Standard additions of Hg° performed on ambient air during day and night to capture variations in temperature and specific humidity.
- Hg°: TF - starting on 01 November 2003; PM - 28 February 2005; AI - 08 July 8 - 06 September 2005. Data presented in UT.
Seasonal and Diurnal Variation is Pronounced

(1 ng m$^{-3}$ = 112 ppqv)
Thompson Farm
(24 m, 25 km from ocean)

Pac Monadnock
(700 m, 185 km from ocean)
Nighttime Depletion and Estimation of Dry Depositional Losses – Important Removal Pathways Poorly Characterized
ΔHg°/ΔNOy = 3.2 ppqv/ppbv

Investigation of nighttime removal.
Linear decreasing trends in Hg and NO$_y$ at night indicates a common loss mechanism.

– Dry deposition

\[ \Delta \text{NO}_y = 6 \text{ ppbv} \]
\[ \Delta \text{Hg}^0/\Delta \text{NO}_y = 3.2 \text{ ppqv/ppbv} \]
\[ \rightarrow \Delta \text{Hg}^0 \sim 20 \text{ ppqv} \]
\[ \leftarrow \text{net of anthrop., chem., dry dep.} \]
Total annual emission of mercury in the Strafford County, NH (1000 km²) was 6848.38 g [NESCAUM, 2005] \( \rightarrow \) \( \sim \) 9 ppqv Hg\(^0\) (assuming PBL=125 m)

- The dry deposition velocity of Hg\(^0\) was estimated to be 0.17 cm s\(^{-1}\) in 2004 and 0.20 cm s\(^{-1}\) in 2005.
  \( \rightarrow \) **Compare to** 0.01 cm s\(^{-1}\) in literature
Contrasting Interannual Variability

Steeper warm season decline rate in 2005 than in 2004

Processes on time scales >weekly might account for the more pronounced decreasing trend in 2005.

Hypothesis:
The dry conditions in summer 2005 may have contributed to the stronger decreasing trend.