



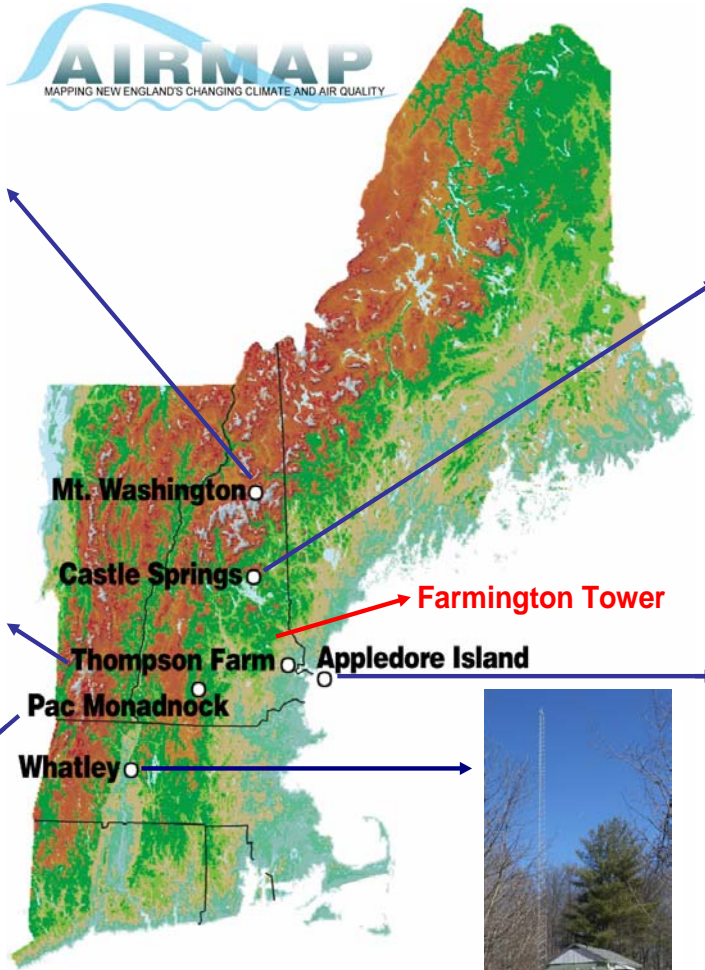
Seasonal and Diurnal Variations of Hg^0 and its Dry Deposition in New England

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and Jennifer Hegarty

Mao et al., Atmospheric Chemistry and Physics, 8, 1403-1421, 2008.

Atmospheric Mercury Basics

- Chemical forms: Hg^0 , RGM ($\text{HgCl}_2 + \text{HgBr}_2 + \text{HgOBr} + \dots$), and Hg^{P}
- Marine: 1.6 ng m^{-3} over the North Atlantic [*Laurier et al.*, 2007], $1.6 - 4.7 \text{ ng m}^{-3}$ over the North Pacific [*Laurier et al.*, 2003], and $0.4 - 11.2 \text{ ng m}^{-3}$ over the Mediterranean Sea [*Sprovieri et al.*, 2003]
- Land: $1.6 - 5.1 \text{ ng m}^{-3}$ [*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 Hg^0 are highly uncertain.

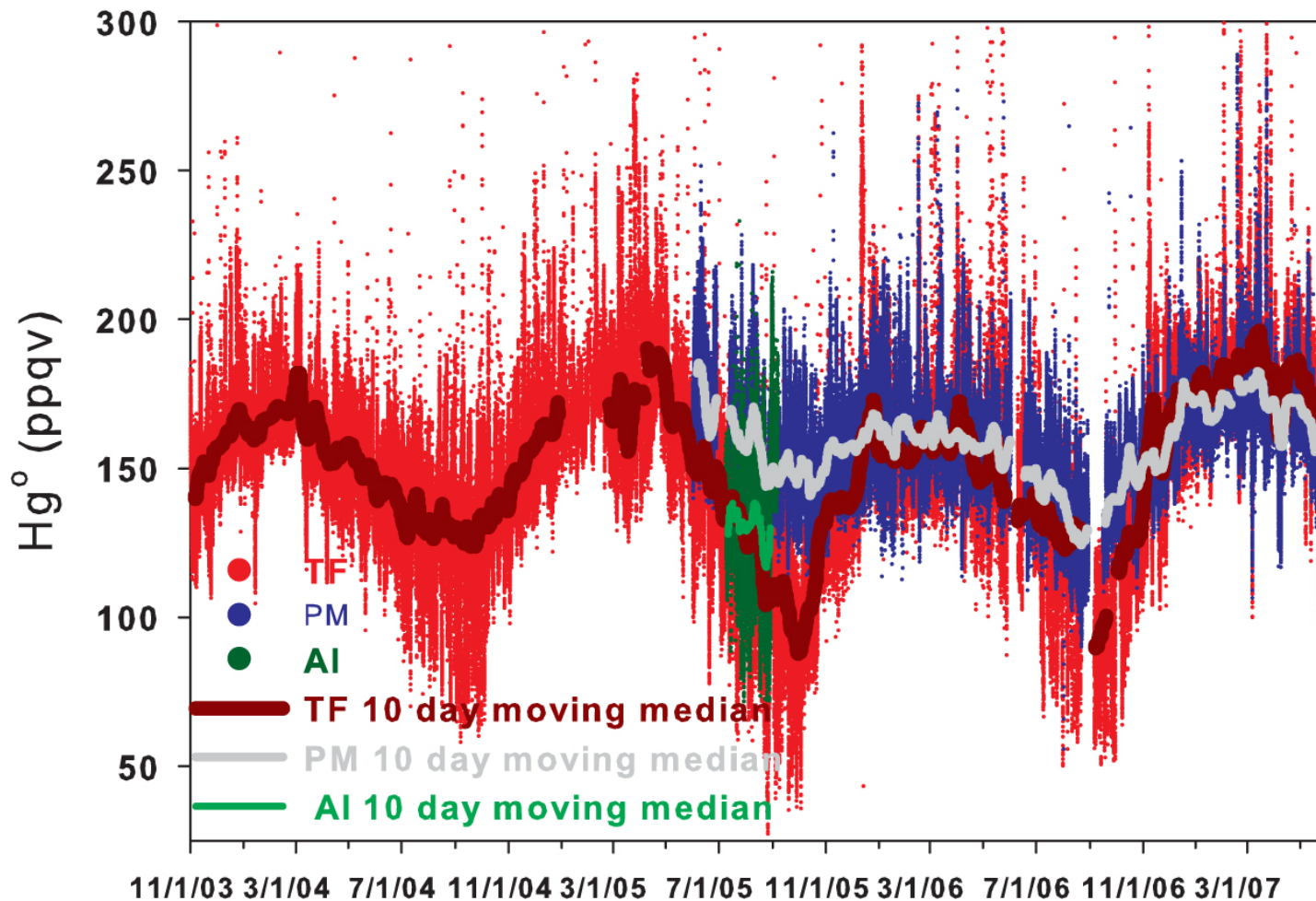


Measurements and Data

- Hg^0 , CO , O_3 , NO , NO_y , CO_2 , SO_2 , and CH_4 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 ($\pm 5\%$ reproducibility) verified every six months using syringe injection from the headspace of a thermoelectrically cooled Hg^0 reservoir (Tekran model 2505).
- Standard additions of Hg^0 performed on ambient air during day and night to capture variations in temperature and specific humidity.
- Hg^0 : TF - starting on 01 November 2003; PM - 28 February 2005; AI - 08 July 8 - 06 September 2005. Data presented in UT.
- Daily VOCs measurements at TF during Jan. 2004 – present.
- Hourly VOCs measurements at TF and AI in summers 2004 and 2005.

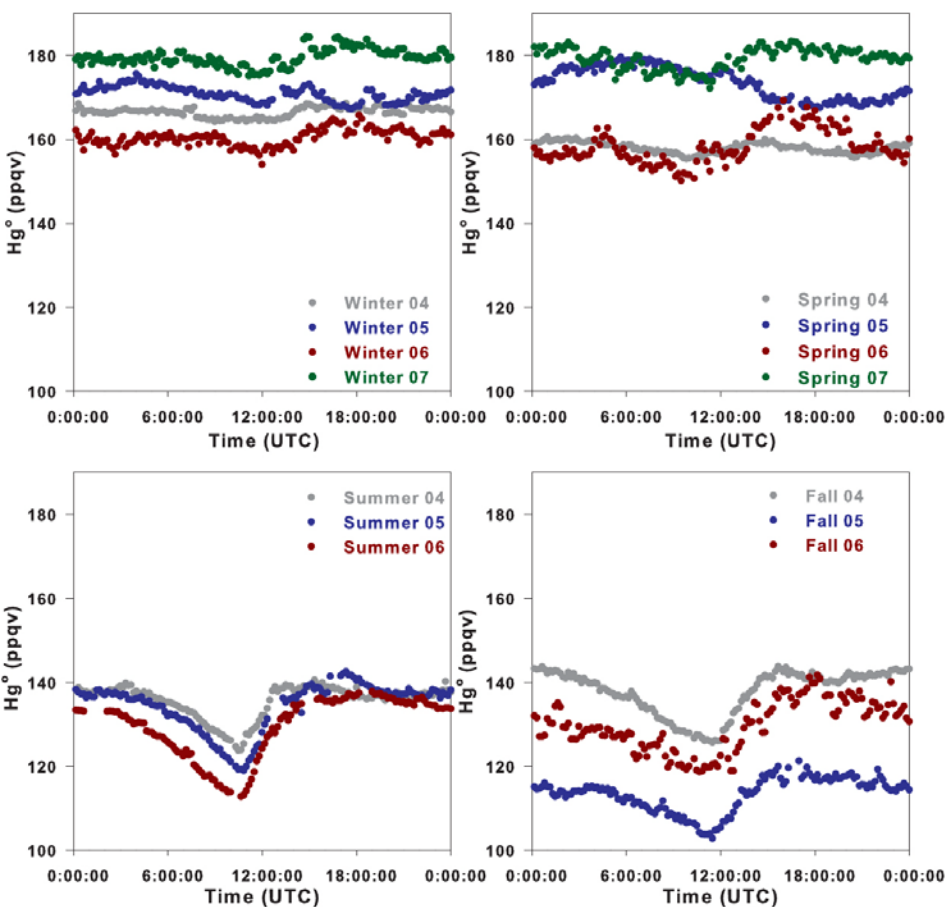
Seasonal and Diurnal Variation is Pronounced

(1 ng m⁻³ = 112 ppqv)



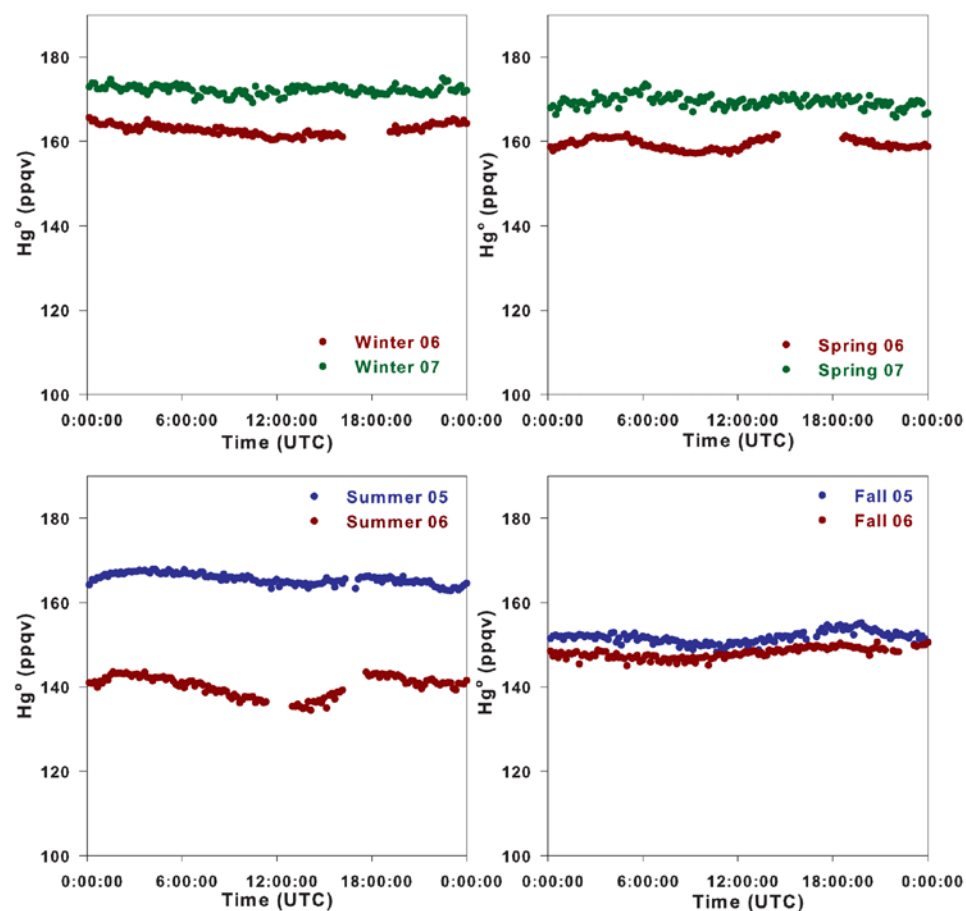
Thompson Farm

(24 m, 25 km from ocean)

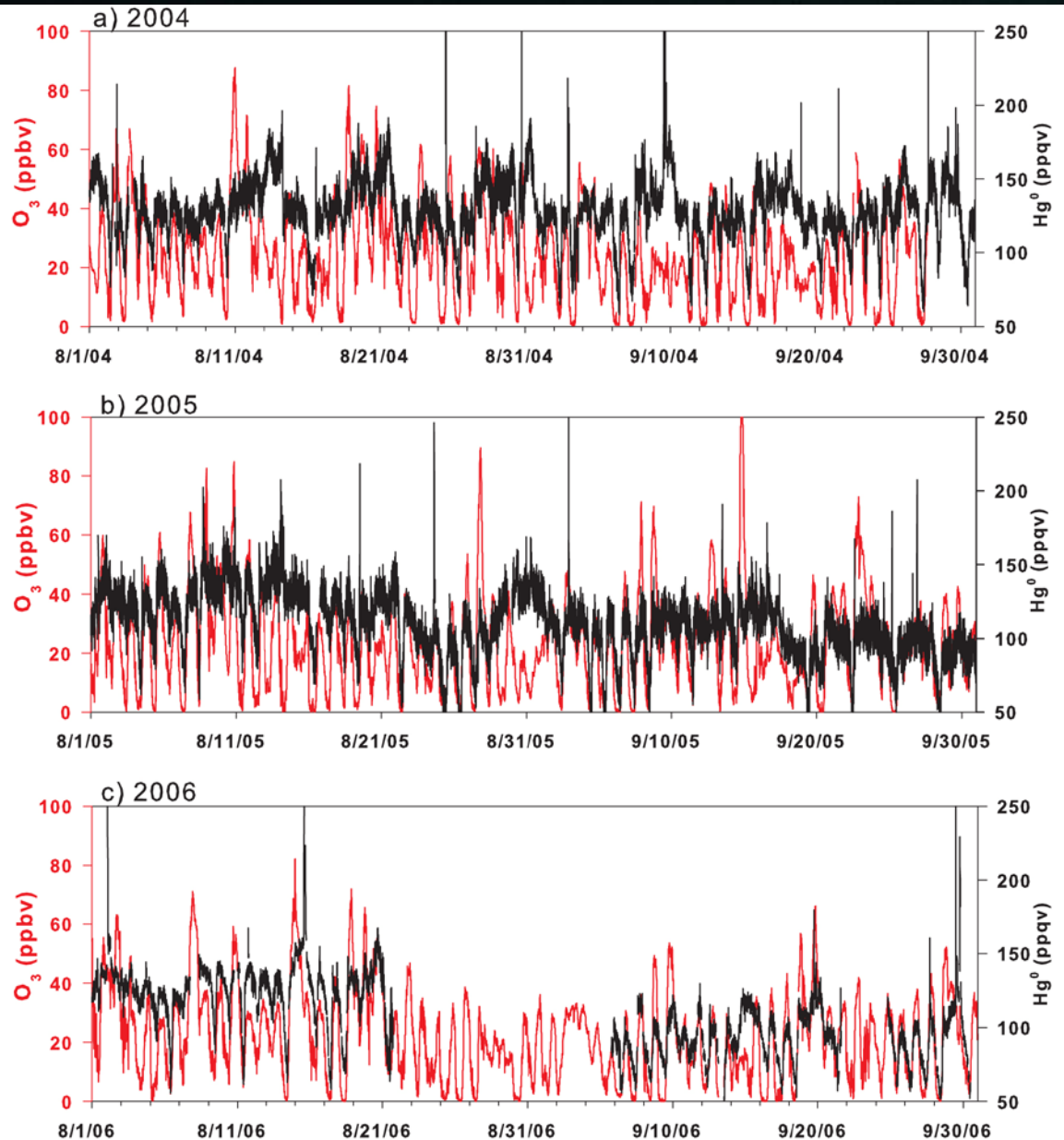


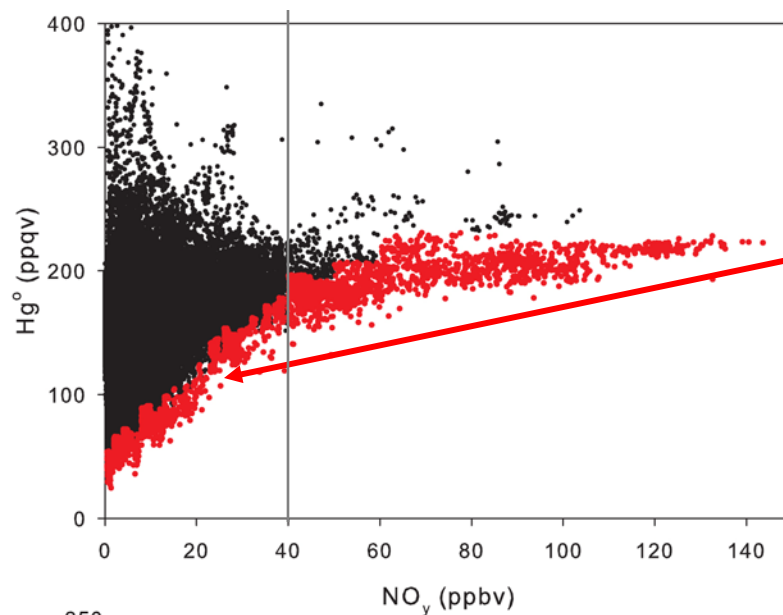
Pac Monadnock

(700 m, 185 km from ocean)



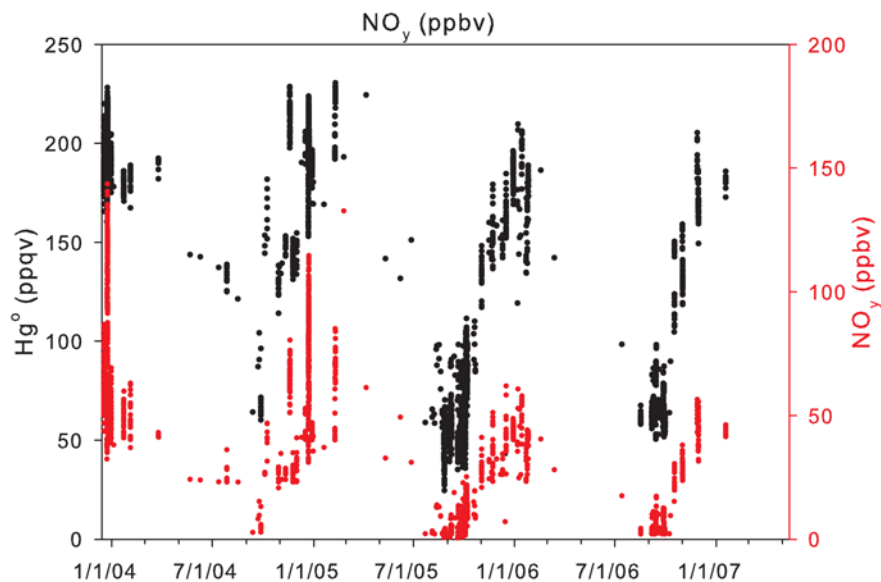
**Nighttime
Depletion and
Estimation of Dry
Depositional
Losses –
Important Removal
Pathways Poorly
Characterized**



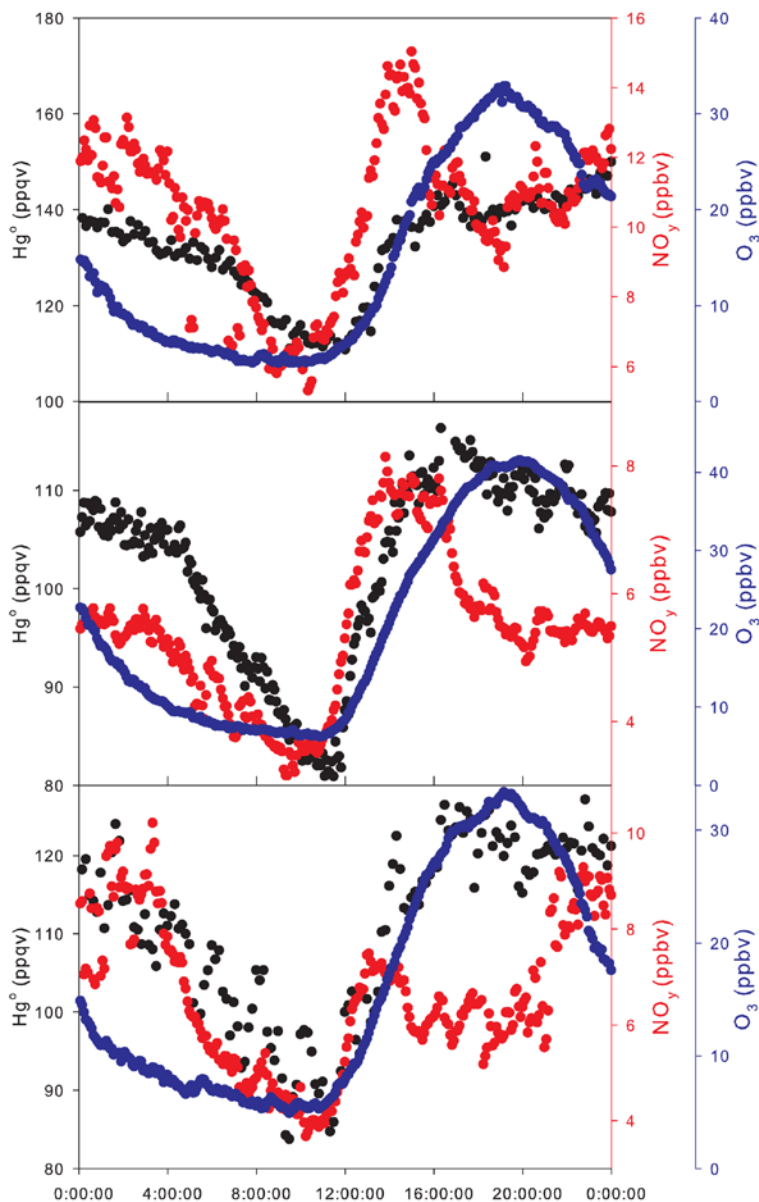


$$\Delta\text{Hg}^\circ/\Delta\text{NO}_y = 3.2 \text{ ppqv/ppbv}$$

Investigation of nighttime
removal.



2004



2005

2006

Linear decreasing trends in Hg° and NO_y at night indicates a common loss mechanism.

– Dry deposition

$$\Delta \text{NO}_y = 6 \text{ ppbv}$$

$$\Delta \text{Hg}^\circ / \Delta \text{NO}_y = 3.2 \text{ ppqv/ppbv}$$

$$\rightarrow \Delta \text{Hg}^\circ \sim 20 \text{ ppqv}$$

← net of anthrop., chem., dry dep.

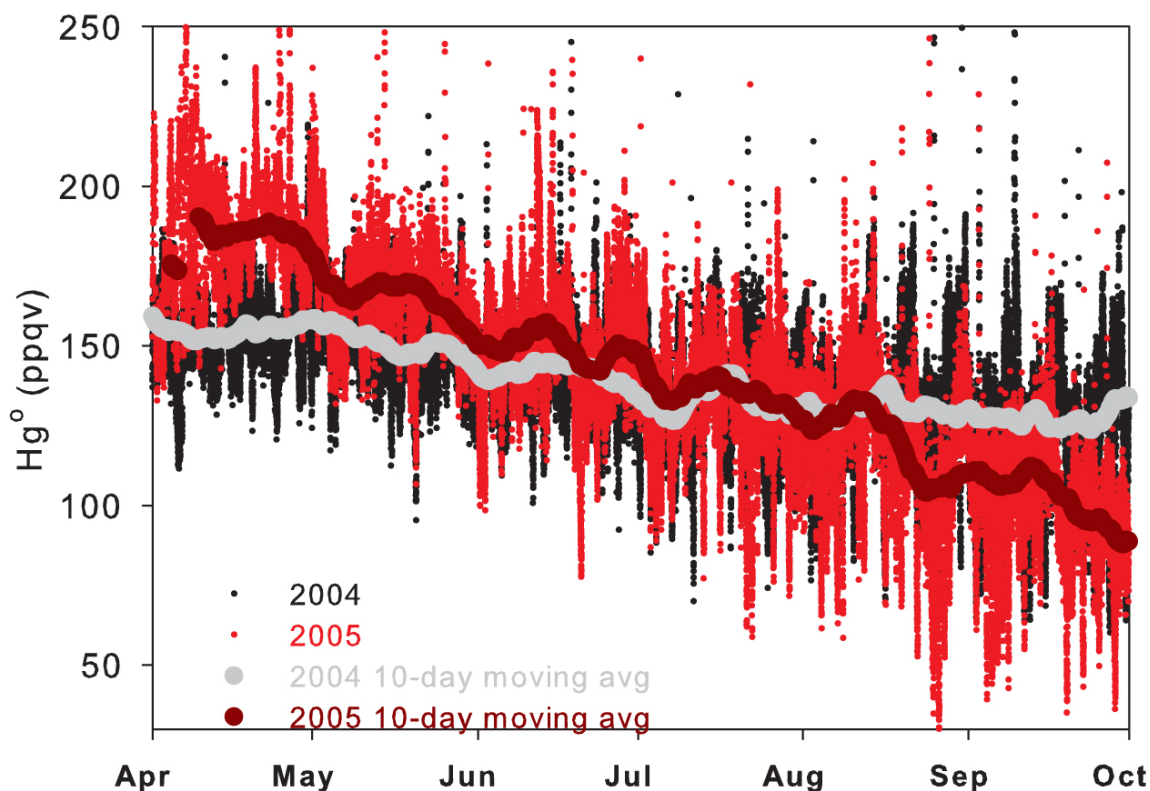
	Daytime	Night	Daily
$7.5 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ — O_3^1	4.16	2.66	7.82
$3.2 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ — O_3^2	0.17	0.11	0.28
OH	0.50	-	0.50
NO_3	-	3.5	3.5

8.32
0.78

- Total annual emission of mercury in the Strafford County, NH (1000 km²) was 6848.38 g [*NESCAUM*, 2005] → ~ 9 ppqv Hg⁰ (assuming PBL=125 m)
- The dry deposition velocity of Hg⁰ was estimated to be 0.17 cm s⁻¹ in 2004 and 0.20 cm s⁻¹ in 2005.
→ 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 .