Deposition of HNO_3 to a Northeastern U.S. Forest and its Contribution to NO_y Flux

I. Abstract

Nitric acid (HNO_3) and total reactive nitrogen (NO_y) were measured at the Harvard Forest Environmental Measurement Site in central Massachusetts along with micrometeorological and supporting data during the summer and fall of 2000. The concentration of HNO_3 was measured using a tunable diode laser absorption spectrometer (TDLAS) installed on a tower above the forest canopy. The inlet was designed to keep the residence time short, to minimize wall effects, and to exclude aerosols from the sample flow. The TDLAS specifically and quantitatively measured gas-phase HNO_3, eliminating interferences from other reactive nitrogen species such as PAN, hydroxy alkyl nitrates, NO_x, and fine aerosols which are included in the NO_y measurement. The hourly deposition velocity of HNO_3 was estimated using a dry deposition inferential method (DDIM) in which the deposition velocity, V_d, is modeled as a set of resistances in series depending on meteorological and site-specific conditions. The flux was computed as the product of measured HNO_3 concentration and inferred V_d. Diel correlations between HNO_3 concentration and V_d did not introduce a substantial bias in the daily and weekly inferred flux when compared to the hourly values integrated over the same interval.

The measurements confirm that HNO_3 is often the primary NO_y depositor and suggest conditions at Harvard Forest where other species are important. Under unpolluted, background flow conditions when winds are from the Northwest, HNO_3 deposition accounts for nearly all of NO_y deposition . During southwesterly flow when the site is subject to warmer transport from polluted source regions, the deposition flux of HNO_3 accounts for half or less of measured NO_y deposition, leaving as much as 5-10 µmol m^{-2} hr^{-1} of the reactive nitrogen flux in the form of species not individually measured.

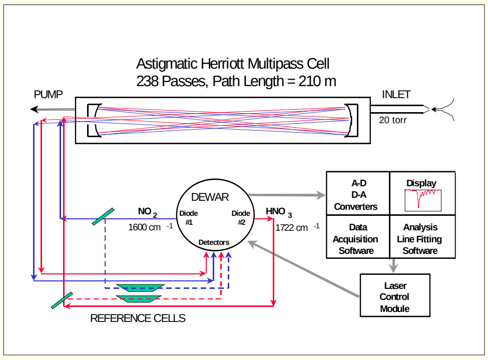

Figure 1. Tunable Diode Laser Absorption Spectrometer (TDLAS) instrument schematic.

II. Methods

TDLAS

The TDLAS instrument employs two infrared diodes tuned to absorption lines of HNO_3 and NO_2. Light from the diodes is multiply-reflected through an enclosed astigmatic Herriott flow cell at 20 torr for a total light path of 210 m. The diodes are turned on, tuned across multiple absorption features ($\Delta\nu \sim 0.2$ cm^{-1}), and shut off to obtain complete spectra at a rate of 2KHz. Spectra are integrated for 1s in eddy covariance mode (NO_2) or 30 minutes (HNO_3 concentration mode) and analyzed with a non-linear least squares fit to obtain the concentration. Fit parameters come from the HITRAN spectroscopic database, the independently-calibrated light path length, the measured pressure and temperature, and the frequency tuning rate of the diode. The sample flow is modulated with scrubbed ambient air every 10 minutes to obtain a signal-free background spectrum (Horii et al., 1999).

OTHER MEASUREMENTS

Instrumentation at the Harvard Forest Environmental Monitoring Station tower, approximately 200 hundred meters from the TDLAS tower, includes an ATI Sonic Anemometer, an NO_y chemi-luminescence system (catalytic conversion to NO at the inlet), an O_3 UV spectrometer, a NO_x photolysis/O_3 chemiluminescence instrument, PAR sensors, and a 1-channel PAN gas chromatograph (Munger et al. 1996, 1998).

HARVARD FOREST

The Harvard Forest site in central Massachusetts (42.54N, 72.18W; elevation, 340 m) is a 50- to 70-year old mixed deciduous forest consisting primarily of red oak and red maple, with scattered hemlock, red pine, and white pine stands. The terrain is roughly 95% forested and moderately hilly; closest paved roads are more than 1 km away, small towns greater than 10 km distant. Dominant winds are from the northwest and southwest. The TDLAS system was installed at a height of 19 m on the top of a scaffolding tower. A coated quartz and pyrex inlet extended an additional 3 m to sample above the canopy.

Figure 2. Left: Harvard Forest, central Massachusetts. Right: TDLAS instrument being hoisted to the top of the tower, August 1999.

II. Methods (continued)

DRY DEPOSITION INFERENTIAL METHOD (DDIM):

The hourly deposition velocity V_d, is modeled as a set of resistances in series depending on meteorological and site-specific conditions:

$$\text{Flux} = [HNO_3]\, Vd = [HNO_3]\,(Ra + Rb + Rc)^{-1}$$

Aerodynamic Resistance:

$$R_a = \frac{u}{u*^2} - \frac{\psi_H}{ku*}$$

Boundary Layer Resistance:

$$R_b \approx \frac{7.1}{u*}$$

where u=horizontal wind speed
u^* = friction velocity
k = von Karman's constant
Ψ_h = diabatic stability correction coefficient for heat transfer (function of measurement height z, zero plane displacement d, and Monin-Obukhov length scale L)

Uptake Resistance:

$R_c(HNO_3) \approx 0$ (high solubility & surface reactivity)

(Wesley and Hicks, 1977; Meyers et al., 1989 and others)

III. Results

LONG-TERM DDIM BIAS

We found that diel correlations between HNO_3 concentration and V_d did not introduce a substantial bias in daily and weekly inferred fluxes when daily or weekly averages (A) were compared to the hourly values integrated over the same interval (I) (Matt and Meyers, 1993). For any given week, the correlation coefficient r(V_d, $[HNO_3]$) was as large as ±0.5, but over many weeks showed no trend toward positive or negative correlation. For HNO_3, it appears that DDIM can safely be applied to weekly averaged data only over timescales of months or seasons and provided that the data itself does not contain a preexisting bias.

$$I = \frac{1}{N_{hours}} \sum_{hour} Vd_h [HNO_3]_h \qquad A = \frac{1}{N_{hours}} \sum_{hour} Vd_h \overline{[HNO_3]}_T$$

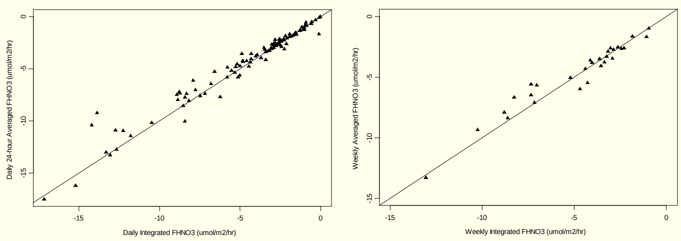

Figure 3. Comparison between daily (left) and weekly (right) averaged inferred fluxes vs. integrated inferred fluxes. The 1:1 line is shown in each case.

[1]**Harvard University: Department of Earth and Planetary Sciences, 617-495-5361, cvh@io.harvard.edu,** http://www-as.harvard.edu/chemistry

[2]**Aerodyne Research, Inc.: Center for Atmos. and Environ. Chem., 781-663-9500, mz@aerodyne.com,** http://www.aerodyne.com/caec.html

Cassandra Volpe Horii[1], J. William Munger[1], Steven C. Wofsy[1], and Mark S. Zahniser[2]

III. Results (continued)

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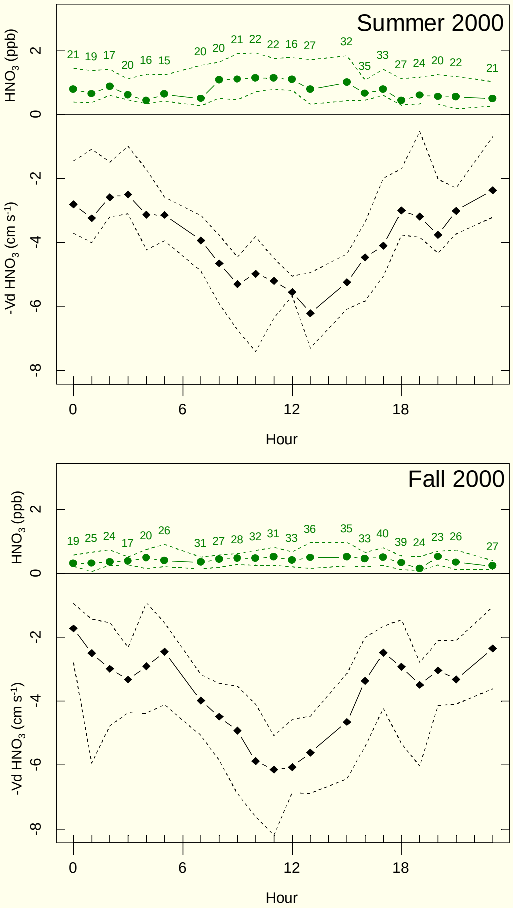

Figure 4. TOP: June, July, Aug. 2000; BOTTOM: Sep, Oct, Nov. 2000 median diel cycles of measured HNO_3 concentration (upper panels) and inferred deposition velocity (lower panels; negative values represent deposition). Dashed lines indicate 25th and 75th quartiles. Hours of data are shown above the HNO_3 concentrations.

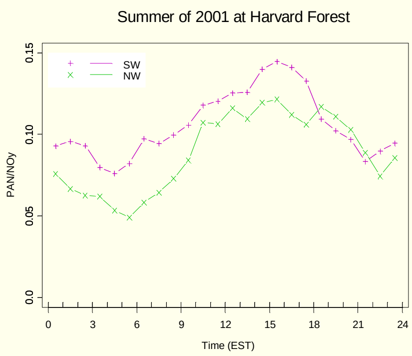

Figure 5. PAN as a fraction of NO_y during the summer of 2001. PAN accounted for 5-10% of NO_y under northwesterly flows and 8-15% under southwesterly flows. The NO_y budget deficit for southwestly winds in figure 6 is not likely to be entirely due to PAN.

References & Acknowledgements

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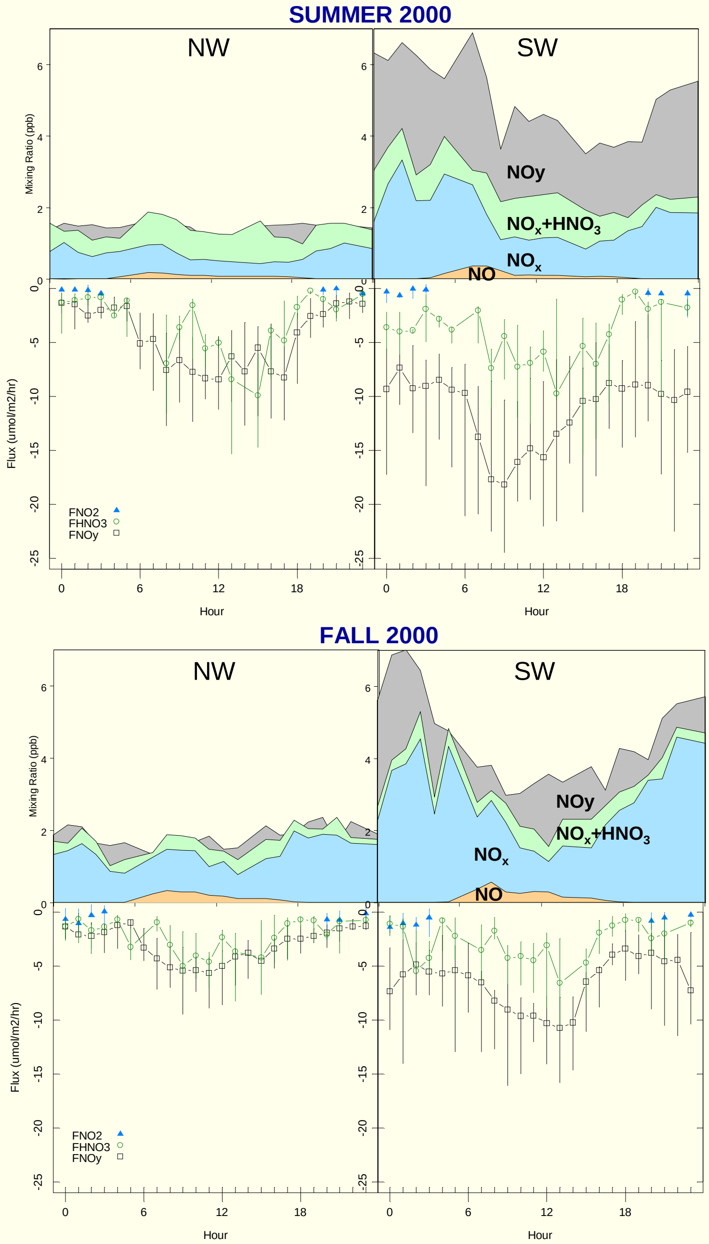

Figure 6. Median Concentrations (area plots, upper panels) and fluxes (line plots, lower panels) of NO_y and component species separated by season and wind direction. Vertical lines in the flux panels show 25th and 75th quartiles. Negative fluxes represent deposition. The NO_y concentration and flux budgets are largely closed for northwesterly (unpolluted background) flows, whereas up to 50% of NO_y and FNO_y under southwesterly flows are in the form of PAN and other reactive nitrogen species not concurrently measured.

IV. Conclusions

1. **The Dry Deposition Inferrential Method for HNO_3** does not introduce a bias due to correlations between diel V_d and $[HNO_3]$ when applied to daily or weekly average concentrations, assuming no other sampling biases in the data.
2. **Unpolluted (NW flow), Summer-Fall 2000.** $NO_y \approx NO_x + HNO_3$ and $FNO_y \approx FNO_x + FHNO_3$. [PAN] ≈ 5-10% of NO_y (2001).
3. **Polluted (SW flow), Summer-Fall 2000:** Observed NO_y concentration and flux budget shortfalls of 50%. [PAN] ≈ 10-15% of NO_y (2001). Additional NO_y species are important.