Deposition of HNO₃ to a Northeastern U.S. Forest and its Contribution to NOₓ Flux

I. Abstract

Nitric acid (HNO₃) and total reactive nitrogen (NOₓ) 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 HNO₃ was measured using a tunable diode laser 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 aerosol from the sample flow. The TDLAS specifically and quantitatively measured gas-phase HNO₃, eliminating interferences from other reactive nitrogen species such as PAN, hydroxy alkyl nitrates, NOₓ, and fine aerosols which are included in the NOₓ measurement. The hourly deposition velocity of HNO₃ was estimated using a dry deposition inferential method (DDIM) in which the deposition velocity, Vₛ, 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 HNO₃ concentration and inferred Vₛ. Diel correlations between HNO₃ concentration and Vₛ did not introduce substantial bias in the daily and weekly inferred flux when compared to the hourly values integrated over the same interval.

The measurements confirm that HNO₃ is often the primary NOₓ depositor and suggest conditions at Harvard Forest where other species are important. Under unfaulted, background flow conditions when winds are from the Northwest, HNO₃ deposition accounts for nearly all of NOₓ deposition. During southerly to westerly flow when the site is subject to warmer transport from polluted source regions, the deposition flux of HNO₃ accounts for half or less of measured NOₓ deposition, leaving as much as 5-10 µmol m⁻² s⁻¹ of the reactive nitrogen flux in the form of species not individually measured.

II. Methods (continued)

DRIY DEPOSITION INFERENTIAL METHOD (DDIM): The hourly deposition velocity Vₛ is modeled as a set of resistances in series depending on meteorological and site-specific conditions.

\[
\text{Flux} = [\text{HNO}_3] \cdot V_d = [\text{HNO}_3] \cdot (R_a + R_b + R_c)^{-1}
\]

**Aerodynamic Resistance:**

\[
R_a = \frac{u}{U^2} \cdot \frac{\nu}{kU} \cdot \psi
\]

where \( u \) = horizontal wind speed

\( U \) = friction velocity

\( k \) = von Karman’s constant

\( \psi \) = diabatic stability correction coefficient for heat transfer (function of measurement height z, zero plane displacement d, and Monin-Obukhov length scale L)

**Boundary Layer Resistance:**

\[
R_b = \frac{1}{U} \cdot \frac{\nu}{kU} \cdot \psi
\]

**Uptake Resistance:**

\[
R_c(\text{HNO}_3) = 0 \text{ (high solubility & surface reactivity)}
\]

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

III. Results

LONG-TERM DDIM BIAS

We found that diel correlations between HNO₃ concentration and Vₛ 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 \( \rho(\text{V}_s, [\text{HNO}_3])] \) was as large as 0.7, but over many weeks showed no trend toward positive or negative correlation. For HNO₃, 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.

\[
I = \frac{1}{N_{\text{hours}}} \sum_{\text{hour}} V_d \cdot [\text{HNO}_3]_b
\]

\[
A = \frac{1}{N_{\text{hours}}} \sum_{\text{hour}} \frac{V_d}{[\text{HNO}_3]_b}
\]

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

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.

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III. Results (continued)

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Figure 4. TOP: June, July, Aug. 2000; BOTTOM: Sep, Oct, Nov. 2000 median diel cycles of measured HNO₃ concentration (upper panels) and inferred deposition velocity (lower panels; negative values represent deposition). Dashed lines indicate 25th and 75th percentiles. Hours of data are shown above the HNO₃ concentrations.

Figure 5. PAN as a fraction of NO₃ during the summer of 2001. PAN accounted for 5-10% of NO₃ under northwesterly flows and 8-15% under southwesterly flows. The NO₃ budget deficit for southwesterly winds in figure 6 is not likely to be entirely due to PAN.

Figure 6. Median Concentrations (area plots, upper panels) and fluxes (line plots, lower panels) of NO and component species separated by season and wind direction. Vertical lines in the flux panels show 25th and 75th percentiles. Negative NO fluxes represent deposition. The NO₃ concentration and flux budgets are largely closed for northwesterly (unpolluted background) flows, whereas up to 50% of NO₃ and FNO₃ under southwesterly flows are in the form of PAN and other reactive nitrogen species not concurrently measured.

IV. Conclusions

1. The Dry Deposition Inferential Method for HNO₃ does not introduce a bias due to correlations between diel Vₜ and [HNO₃] when applied to daily or weekly average concentrations, assuming no other sampling biases in the data.

2. Unpolluted (NW flow), Summer-Fall 2000. NO₃=NO₂+HNO₃ and FNO₃=FNO₂+FHNO₃. [PAN] = 5-10% of NO₃ (2001).

3. Polluted (SW flow), Summer-Fall 2000: Observed NO concentration and flux budget shortfalls of 50%. [PAN] = 10-15% of NO₃ (2001). Additional NOₓ species are important.