Eddy Covariance Fluxes of NO and NO_2 above a Northeastern U.S. Forest

I. Abstract

Although tropospheric NO, NO_2, and O_3 rapidly interconvert in a fast photochemical cycle, the processes governing their removal rates, interactions with ecosystems, and human interest in their mitigation are distinctly different. Thus a detailed understanding of their behavior at the atmosphere-biosphere interface is crucial. The reactivity of this family of gases has often confounded measurements in the past, and the question of biospheric emission and uptake of NO_x remains open (Lerdau et al., 2000).

In order to address these issues, we present concurrent eddy covariance fluxes of NO, NO_2, and O_3 at the rural, deciduous, mixed hardwood Harvard Forest in central Massachusetts during the summer and fall of 2000. The independent measurements were conducted above the forest canopy, at similar heights, on two towers within several hundred meters of one another. NO was measured using an existing photolysis-chemiluminescence detector in the eddy covariance mode, and NO_2 using a new tunable diode laser absorption spectrometer (TDLAS). O_3 concentrations, profiles, and fluxes were also measured at the site. At night, NO fluxes were effectively zero while small but persistent downward NO_2 fluxes were observed. Fluxes of NO_2 during the day were generally upward and coupled with downward NO fluxes of similar magnitude. The opposing NO and NO_2 fluxes confirm the predictions of some canopy exchange models that include the effect of the light gradient within the canopy on photo-reactive species (e.g. Gau et al. 1993).

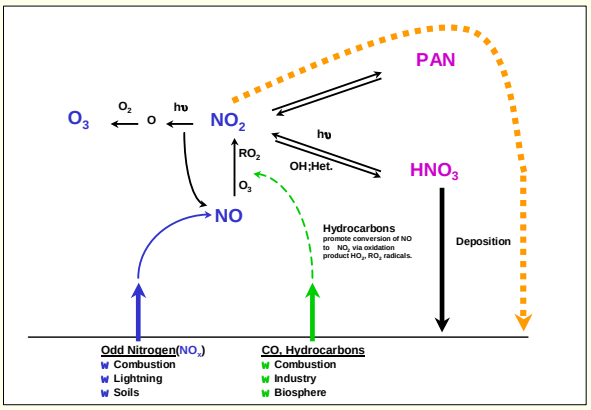

Figure 1. Simplified schematic of tropospheric NO-NO_2-O_3 and reactive nitrogen chemistry.

II. Methods

INSTRUMENTATION:

From late August to mid-October, an existing chemiluminescence detector (29 m sampling height) was configured to measure NO concentrations at 8 Hz. At other times, the chemiluminescence detector measured slow profiles and concentrations of NO and NO_2, converted to NO in a photolysis cell prior to detection. We installed a new tunable diode laser absorption spectrometer (TDLAS) on a nearby tower to measure NO_2 (22 m sampling height) at 8 Hz. The TDLAS concentration measurements were verifiably species-specific, spectroscopically calibrated, and compared very well to ongoing photolysis-chemiluminescence NO_2 measurements at the site (figure 3). For further TDLAS details, refer to accompanying poster A51F-0132 and references (Horii et al. 1999). Continuing O_3 concentration and flux measurements employ C_2H_4-chemiluminescence (29 m sampling height) and UV absorbance instruments, respectively. Three-axis sonic anemometers facing into the prevailing wind direction (west) at the sampling heights on both towers provided the vertical and horizontal wind velocities and virtual temperatures needed to compute eddy covariance fluxes of heat, momentum, NO, NO_2, and O_3 (Munger et al. 1996, 1998).

EDDY COVARIANCE FLUXES:

We compute 30-minute fluxes from the covariance of detrended vertical wind velocity (w') with fluctuations of detrended temperature (T') or detrended trace gas concentration (C'). Compared to those of temperature and vertical wind speed (w), lagged correlations and copsectra for NO_2 exhibit expected offset and smearing due to instrument lag time and response function (figure 4). Small corrections of order 20% are routinely applied to the NO_2 eddy covariance fluxes to account for these instrumental properties.

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. Carbon exchange, meteorology, trace gas concentrations, and eddy covariance fluxes have been measured at the site for over a decade.

Figure 2. Left: Inlet and sonic anemometer at a height of 22m. The canopy height averages 20 m. Right: View of Harvard Forest with sampling tower location marked.

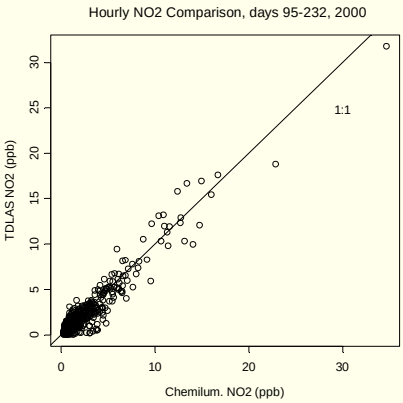

Figure 3. Hourly TDLAS and photolysis-chemiluminescence NO_2 concentrations at Harvard Forest. The two instruments operated from separate towers roughly 200 m apart at 22m (TDLAS) and 29m (chemilum.) sampling heights. Orthogonal distance fit y=a+bx (errors at 95th confidence interval): a = -0.2 ± 1.0, b = 1.1 ± 0.2, R^2 = 0.91.

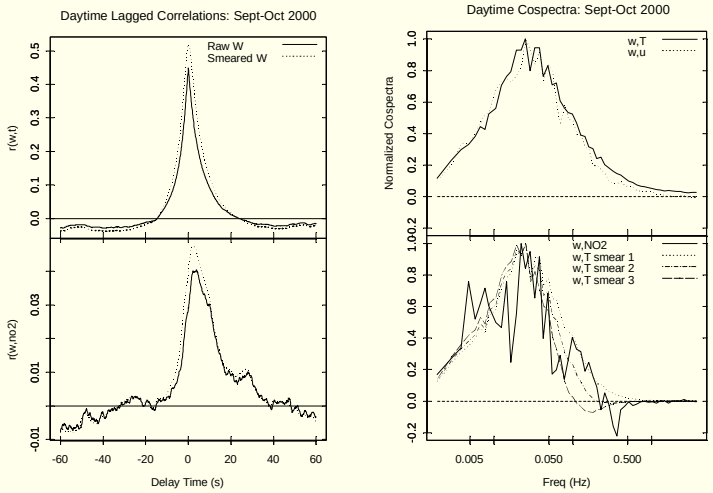

Figure 4. Average daytime lagged correlations and cospectra for (w,T) and (w,NO_2). R(w,NO_2) is lagged compared to r(w,T) due to transit time in the inlet, and the peak is rounded due to an exponential instrument response function with time constant 1 second. The cospectrum of w with NO_2 confirms that the response function is as expected when compared with cospectra of w with T smeared by 1s, 2s, and 3s exponentials.

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III. Results

TIME SERIES

A typical Harvard Forest NO_x and O_3 time series shows photochemical production of NO during the day and conversion to NO_2 at night. Daytime coupled fluxes of NO_2 (upward) and NO (downward) arise from photochemical cycling and turbulent transport in the presence of a forest canopy-influenced light gradient. Higher light above the canopy favors production of NO (NO_2+hνà NO+O); lower light below favors conversion back to NO_2 (NO+O_3à NO_2+O_2). Although the daytime fluxes appear imbalanced, the difference in measurement height of NO (29 m) and NO_2 (22 m) implies a flux ratio close to that observed. O_3 concentrations and fluxes at the site are typically an order of magnitude greater than those of NO_x.

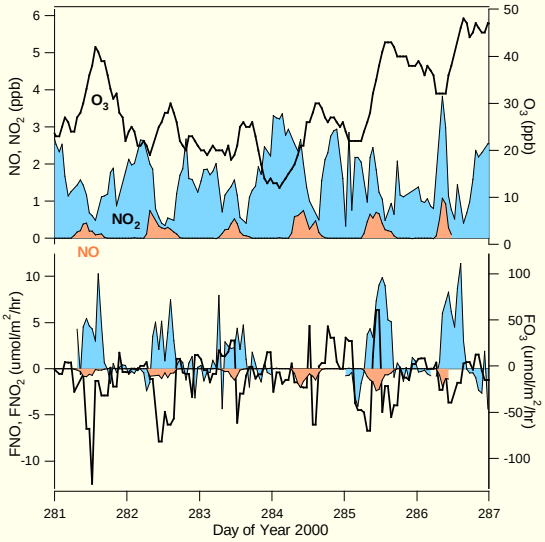

Figure 5. Time series of hourly NO, NO_2, and O_3 concentrations (upper panel) and fluxes (lower panel), Oct 7-12, 2000. NO_2 measurements were taken at a sampling height of 22 m, NO and O_3 at 29 m on a nearby tower.

NIGHT

At night, NO concentration and flux fall to zero and the NO_2 flux captures total NO_x deposition. The observed nighttime NO_2 flux was generally small and tended to be downward. An apparent quadratic dependence of NO_2 flux on NO_2 concentration could imply deposition via formation of the NO_2 dimer on surfaces, and is also similar to the dependence of observed nighttime HONO emissions on NO_2 concentration (Harrison et al., 1996). If the NO_2 flux represents net deposition of NO_x at night, the process would depart from standard model parameterizations, especially for higher NO_2 concentrations.

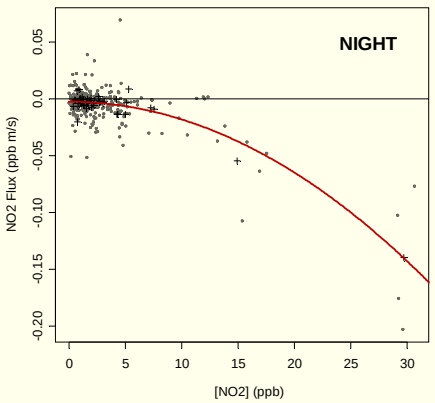

Figure 6. Nighttime mean hourly (dots) and nightly (pluses) NO_2 flux vs. concentration. A negative slope represents deposition velocity of NO_2. Quadratic fit to hourly data: Flux ~ -0.00247 + -1.6e-04 * $[NO_2]^2$ (R^2 = 0.6). $V_d(NO_2)$ appears to increase from ~0.02 cm/s at 1 ppb to ~ 0.4 cm/s at 25 ppb.

References & Acknowledgements

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DAY

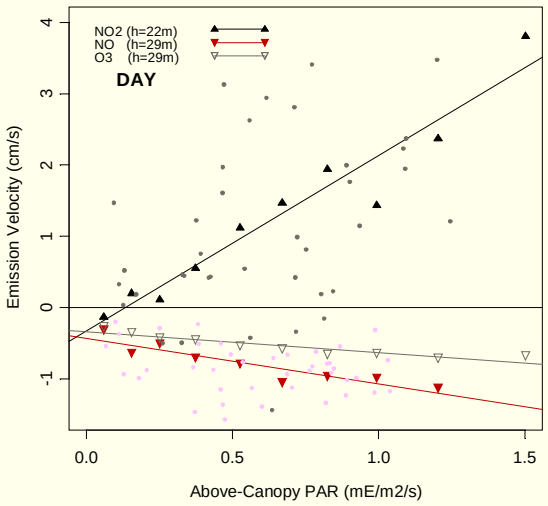

Figure 7. Daytime emission velocities (V=Flux/Concentration) for NO_2, NO, and O_3 plotted as medians of hourly data within quantiles of measured above-canopy photosynthetically- active radiation (PAR). Daily median values of NO and NO_2 velocities are plotted as small dots. V(NO_2) data span spring through fall 2000, while V(NO) data were collected late August to early October 2000 only. Linear fits to block median points: V(NO_2) = -0.33 + 2.5 * PAR, R^2 = 0.93.
V(NO) = -0.43 - 0.64 * PAR, R^2 = 0.84. V(O_3) = -0.34 - 0.29 * PAR, R^2 = 0.85

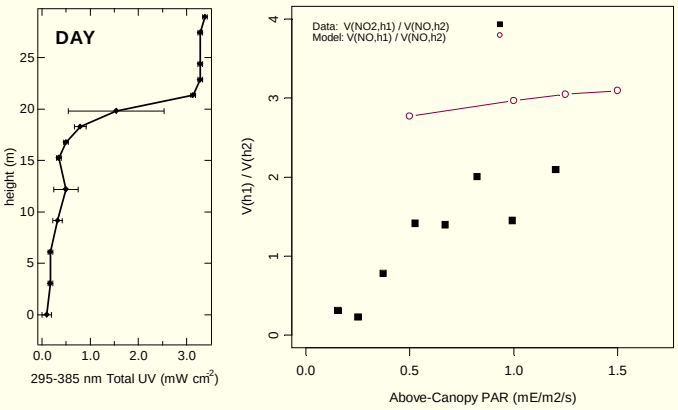

Figure 8. Left: UV profile (Oct 4, 2001, local noon, clear sky); error bars are observed variability at the measurement height. **Right:** Ratio of block median daytime NO_2 emission velocities (measured at h1=22m) to NO deposition velocities (measured at h2=29m) as a function of above-canopy PAR. Also shown are outputs from a simple model of NO_x photochemical cycling using typical NO and NO_2 lifetimes, and UV light and eddy diffusivity profiles. The model solves the continuity equation for NO at each of 100 levels below and above the canopy height, assuming no net emission or deposition of NO_x, $d/dz(-K_c(dNO/dz)=P_{NO}-L_{NO}$, where K_c is eddy diffusivity, P_{NO} is photochemical production (NO_2+hνà NO+O), and L_{NO} is chemical loss (NO+O_3à NO_2+O_2). The over-prediction of the velocity ratio in the model is consistent with net deposition of NO_x to the forest in the observed data.

IV. Conclusions

1. **DAY: Coupled NO and NO_2 fluxes** in opposite directions are consistent with canopy light gradient-driven photo-chemical cycling of NO_x with some net deposition.
2. **NIGHT: NO_x deposition depends quadratically on $[NO_2]$** and is on average non-zero. Deposition via non-stomatal pathways or to non-foliar surfaces may be more important than previously thought. Heterogenous production of NO_2 dimer and/or HONO may also play a role in deposition.