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Eddy Correlation Measurements of NO, NO₂, and O₃ Fluxes*

by

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Eddy Correlation Measurements of NO, NO₂, and O₃ Fluxes

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ABSTRACT

The micrometeorological technique of eddy correlation was used to measure the vertical fluxes of nitric oxide (NO), nitrogen dioxide (NO₂), and ozone (O₃) in rural North Carolina during the spring of 1995 as part of a collaborative effort in the Natural emission of Oxidant precursors-Validation of techniques and Assessment (NOVA) field experiment. The net flux densities were measured at heights of 5 m and 10 m above an agricultural field with short corn plants and a large amount of exposed bare soil between the rows. Large upward eddy fluxes of NO₂ were seen, and strong NO emissions from the soil were measured by collaborators using environmental enclosures on the soil surface. The data indicate that approximately 50% of the nitrogen emitted from the soil as NO was converted into NO₂ flux at 5 m. The rest of the emitted nitrogen may remain as NO flux and be returned back to the vegetation and soil by deposition. Divergence of the NO₂ and O₃ fluxes was detected between 5 and 10 m. These results are consistent with the likely net NO₂ production and O₃ destruction rates. The data will be used to help develop parameterizations of the flux of nitrogen oxides (NO_x) into the lower troposphere.

INTRODUCTION

The emission of NO from the soil can contribute substantially to atmospheric NO_x (NO + NO₂), which play an important role in producing O₃ and changing the oxidizing capacity of the lower troposphere. Parameterization of soil NO emission has been difficult because of large variabilities in space and time. Moreover, NO emitted from the soil has a high reactivity and can be rapidly transformed to NO₂ through reaction with O₃, which is coupled with the photo-decomposition of NO₂ to produce O₃ during sunny conditions. Secondary products, NO₂ and O₃, can also be removed at the surface by dry deposition. The processes of biogenic emission, chemical transformation, and deposition are combined with turbulent mixing in the atmospheric surface layer to modulate the concentration and flux balances among these species. As a result, the actual rate of upward transport of NO_x into the atmosphere can differ from the rate of soil emission. Previous investigations using numerical modeling have shown that the fluxes of NO, NO₂, and O₃ change with height because of rapid chemical transformations in the atmospheric surface layer (Gao et al., 1991; Gao et al., 1993; Gao and Wesely, 1994), but field measurements are needed to confirm the results from numerical modeling.

The micrometeorological technique of eddy correlation was used to measure the vertical fluxes of NO, NO₂, and O₃ over a cornfield in rural North Carolina during the spring of 1995. The net mass flux densities measured at 5 m and 10 m were compared with the NO soil emission rates measured by collaborators using environmental enclosures, to investigate the influence of chemical reactions, deposition, and turbulent mixing on the NO_x budget.

EXPERIMENT AND MEASUREMENTS

The field measurements were taken over a cornfield near Plymouth ($35^{\circ} 52' 00''$ N and $76^{\circ} 44' 56''$ W) in eastern North Carolina from May 18 to May 25, 1995. An instrumented 15-m-tall tower was located at the northeast edge of the cornfield. The corn, which was approximately 40 cm tall at the beginning of the experiment and 70 cm tall at the end of the experiment, extended at least 1 km in the southwest, providing a sufficiently uniform fetch in southwesterly flow for measurements at 5 m and 10 m. The corn rows were oriented southeast-northwest and spaced about 3 ft. During the experiment, the surface was not fully covered by the canopy and had a fairly large amount of exposed soil. On May 20 (starting in the early morning), the farmer applied liquid nitrogen fertilizer (ammonia with 30% nitrogen) to the soil surface.

The fluxes of NO, NO₂, and O₃ were measured by an eddy correlation system, in which covariances between essentially instantaneous fluctuations of vertical velocity and the concentration of each gas were calculated to derive the eddy fluxes. Three components of turbulence velocity plus temperature were measured with a sonic anemometer (model SWS-211/3Sx from Applied Technology, Inc. [ATI]). To measure chemical concentrations, air was pulled through Teflon tubes with an internal diameter of 0.31 cm from the measurement heights to the chemical instruments housed at the bottom of the tower in an air-conditioned wooden box. The filtered inlets of the tubes were attached to krypton hygrometers about 50 cm downwind of the sonic anemometers. The tube lengths for the measurements at 5 m and 10 m were 9.8 m and 15 m, respectively. The sampling flow rates were 17.3 and 13.8 L min⁻¹ for the 5-m and 10-m levels, respectively. These flow rates and tube sizes yield Reynolds Numbers of 7209 and 5758 for the 5-m and 10-m levels, respectively, allowing a turbulent flow in the tubes. Given the Reynolds number, wind speed, and tube length, the attenuation of concentration for the air traveling through the tube can be calculated (Lenschow and Raupach, 1991; Massman, 1991). The calculated attenuation is less than 5% at 10 Hz. The time delays for air to travel through the tubes to the chemical sensors were about 1.1 s, 1.8 s, and 2.6 s for O₃, NO₂, and NO, respectively, at the lower level and were about 2.0 s and 2.4 s for O₃ and NO₂ at the upper level. These time delays were accounted for in the calculation of covariances between vertical velocity and chemical concentrations.

Nitric oxide concentration was measured with a modified NO_x analyzer (CSI Series 1600), under the NO mode of operation, by detecting the chemiluminescence resulting from the reaction of NO with O₃. The NO₂ measurements were made with two Scintrex LMA-3 Luminox systems, which detect the chemiluminescence produced when NO₂ encounters a surface wetted with a specially formulated luminol solution. Ozone concentration was detected with two Analytical Instrument Development, Inc. ozone analyzers, which detect the light produced from a vapor phase chemiluminescent reaction of ozone and ethylene. These chemical instruments generally have response times of 0.2 s for O₃, 0.7 s for NO₂, and 0.6 s for NO. Thus, a spectral correction was used in the calculation of the chemical fluxes (Wesely, 1983).

In addition, two KH₂O krypton hygrometers were mounted at 5 m and 10 m to measure turbulent fluctuations of water vapor density, and a CO₂ sensor (ATDD CO₂/H₂O IR analyzer) was mounted at 10 m to measure fluctuations of CO₂ concentration. The analog signals from the NO, NO₂, O₃, water-vapor, and CO₂ sensors were preamplified and then passed into the ATI electronic boxes, which have a built-in capability for analog-to-digital conversion. The digital signals were acquired by a computer system housed in a trailer approximately 100 m east of the tower. The system was able to monitor the data stream essentially in real time and to compute fluxes and various statistics for every half hour. The turbulence data were sampled 20 times per second. Deviations from a 200-s moving average were used to compute the covariances between vertical velocity and concentrations and other turbulent statistics. Webb effects for density variations were included in the flux calculations. Standard micrometeorological parameters were measured at the main tower and at a Bowen ratio

station located about 10 m southeast of the main tower. Total solar radiation and total ultraviolet (290-385 nm) radiation measured with Eppley radiometers (models 8-48 and TUVR, respectively) were used to estimate the photolysis rate for NO_2 .

RESULTS

SUBSTANTIAL UPWARD NO_2 FLUX

The net NO_2 fluxes measured at 5 m and 10 m were large and upward during the day but became small and downward during the night (Figure 1). The nighttime downward flux is indicative of surface removal by deposition. The flux increased rapidly in the early morning, reached a maximum at midday, and then gradually decreased in the afternoon. The small upward NO_2 flux continued in the late evening after sunset. The rate of increase in the morning appeared to be relatively larger than the rate of decrease in the afternoon. Smaller fluxes on May 19 were associated with reduced soil NO emission during cloudy conditions prior to fertilization. The NO_2 fluxes at 5 m and 10 m were smaller, in equivalent nitrogen, than emissions from the soil measured by the group from North Carolina State University with the environmental enclosure method. The midday NO_2 fluxes, averaged for measurements made from May 21 to May 26, were about 17 and 24 $\text{ng N m}^{-2} \text{s}^{-1}$ at 5 m and 10 m, respectively, compared with 37 $\text{ng N m}^{-2} \text{s}^{-1}$ emitted from the soil. Thus, approximately 46% and 65% of the nitrogen emitted from the soil in the form of NO was converted into NO_2 flux at 5 m and 10 m, respectively. The rest of the emitted nitrogen was either deposited or remained as NO or partially both. The NO flux at 5 m was measured, but the data were too noisy to analyze. Improved measurements of NO flux by the eddy correlation method would provide a more complete picture on the budget of NO_x in the lower atmosphere.

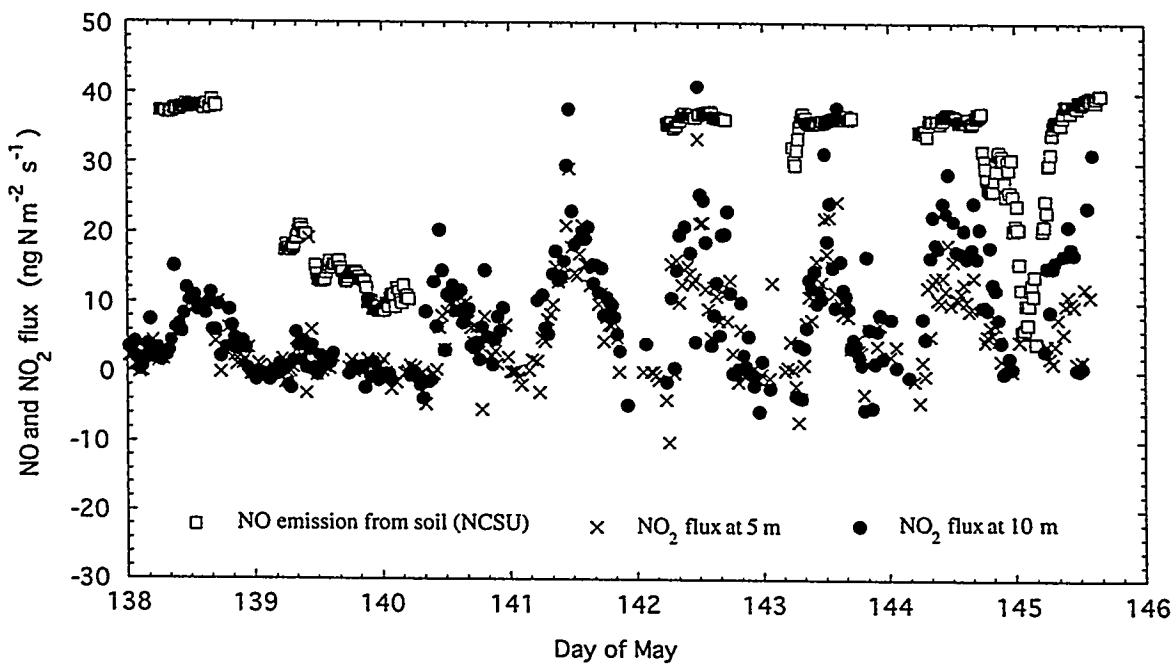


Figure 1. Diurnal changes of NO_2 fluxes measured by eddy correlation method at 5 m and 10 m above a cornfield in May of 1995, in comparison with soil NO emission measured by the group from North Carolina State University (NCSU).

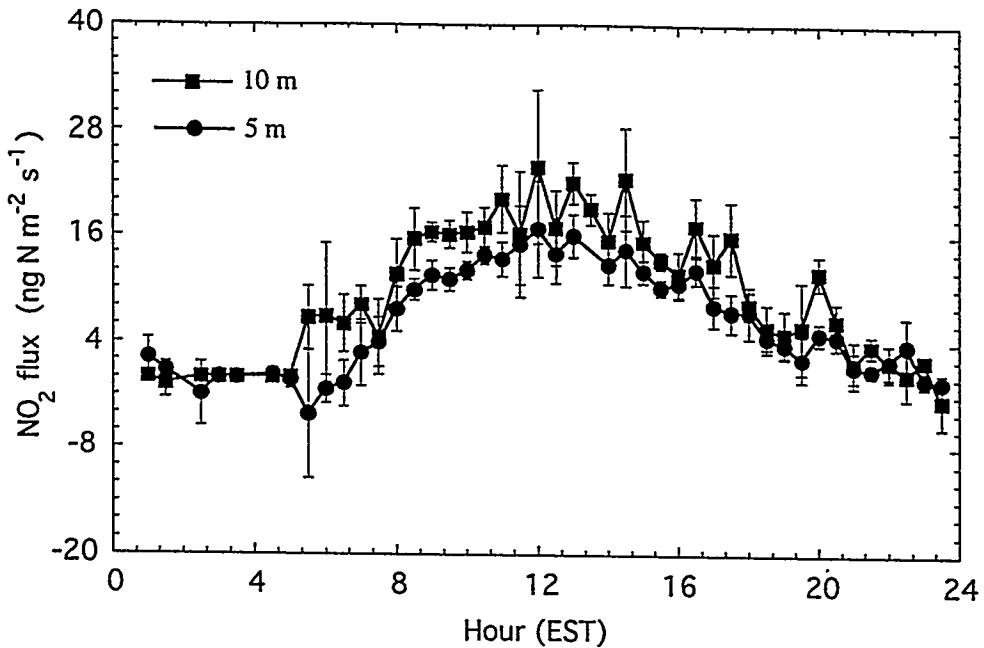


Figure 2. NO₂ fluxes measured at 5 m and 10 m averaged for four-to-five days during May 21-26, 1995. The error bars represent standard errors for averaged fluxes.

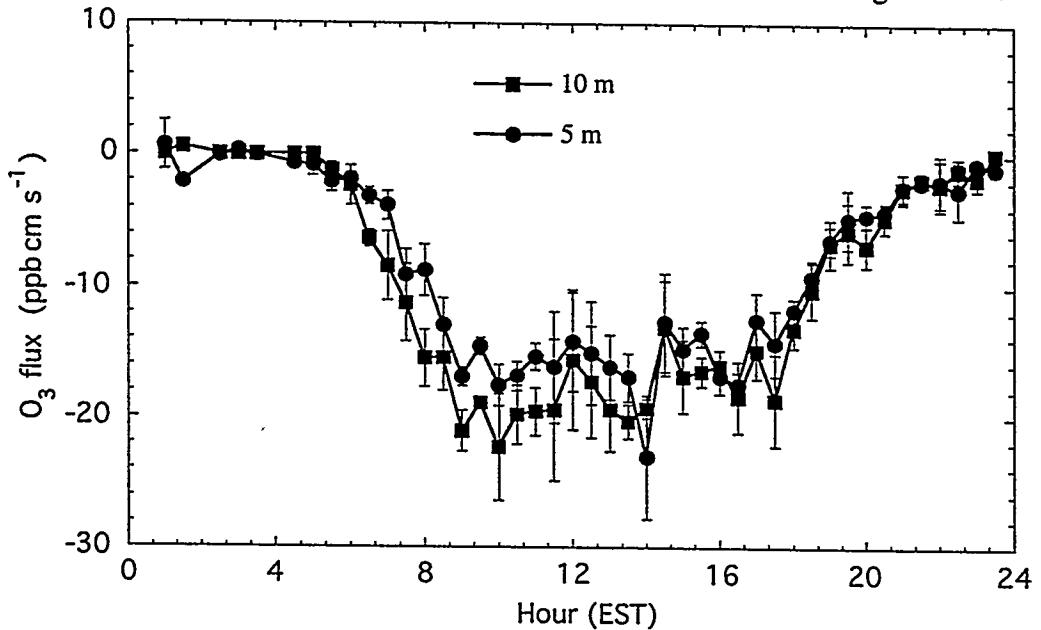


Figure 3. O₃ fluxes measured at 5 m and 10 m averaged for four-to-five days during May 21-26, 1995. The error bars represent standard errors for averaged fluxes.

FLUX DIVERGENCE

Magnitudes of daytime NO₂ flux at 10 m were 37% higher than those at 5 m (Figure 2). The difference likely results from NO₂ production within the layer from 5 to 10 m. The calculation of chemical transformations from measured concentrations indicates a strong NO₂ production at this site, probably because of the strong local NO emission from the soil after fertilization. Magnitudes of daytime downward O₃ flux at 10 m were approximately 30% higher than those measured at 5 m (Figure 3). During the

day, ozone aloft was transported downward by vertical turbulent mixing to compensate for the O₃ loss at the surface to dry deposition. Some portion of the ozone transported through the 10-m level may have been lost to chemical transformations in the layer between 10 m and 5 m to cause a smaller magnitude of O₃ flux to be observed at 5 m. Quantitative estimates of the balance between the flux divergence and chemical transformations will be made through numerical modeling with the use of these observations.

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