

ON THE EFFECTS OF FAST CHEMICAL REACTIONS ON THE VERTICAL  
FLUXES OF NO AND NO<sub>2</sub> IN THE ATMOSPHERIC SURFACE LAYER

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## 11.3 ON THE EFFECTS OF FAST CHEMICAL REACTIONS ON THE VERTICAL FLUXES OF NO AND NO<sub>2</sub> IN THE ATMOSPHERIC SURFACE LAYER

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### 1. INTRODUCTION

Fast chemical reactions can cause the vertical mass flux densities of gases to change with height in the atmospheric surface layer. Theoretical and numerical studies have shown that either the reaction of NO with O<sub>3</sub> to produce NO<sub>2</sub> or the photodissociation of NO<sub>2</sub> can cause large changes with height in the vertical fluxes of NO and NO<sub>2</sub> (e.g., Lenschow, 1982; Fitzjarrald and Lenschow 1983; Kramm 1989; Gao et al. 1991, 1993; Vilà-Guerau de Arellano et al. 1995, Padro et al. 1998). The flux of NO is often affected most strongly, because its ambient concentration is typically smaller than those of the other primary reactants (NO<sub>2</sub> and O<sub>3</sub>). The flux of O<sub>3</sub> is usually the least affected. Much of the NO emitted from soils can be converted to NO<sub>2</sub>, which can then be removed by dry deposition processes (e.g., by uptake through plant leaf stomata). This conversion and deposition involving NO<sub>x</sub> (NO + NO<sub>2</sub>) might be particularly strong in plant canopies. As a result, applying parameterizations developed for NO emission from soils (e.g., Williams et al., 1992) in a manner independently of applying parameterizations for NO<sub>2</sub> dry deposition (e.g., Wesely 1989; Erisman et al. 1994) might lead to overestimates of NO<sub>x</sub> (NO + NO<sub>2</sub>) entering the lower atmosphere. A means of efficiently simulating the combination of emission, deposition, and fast chemical reactions is needed for numerical atmospheric chemistry models. Although past modeling studies have provided a theoretical understanding of the problem, field measurements are needed to evaluate the performance of the models.

### 2. OBSERVATIONS AND DISCUSSION

A collaborative field experiment during July and August 1996 for the National Emission of Oxidant Precursors-Validation of Techniques and Assessment (NOVA) was carried out to evaluate environmental-chamber methods of measuring NO emissions from soils (Aneja 1994). The study was conducted over a soybean field in rural eastern North Carolina (35° 44' 47" N and 76° 41' 14" W). Eddy correlation (covariance) measurements of NO flux made at a height of 5 m above the surface were compared with the average of several chamber measurements of emissions from the soil (Fig. 1). In addition, simultaneous eddy correlation measurements of ozone flux were made at heights of 5 and 10 m above the soybean field (Fig. 2). As described by Li et al. (1999)

and shown in Fig. 1, the NO eddy flux values were usually much smaller than those seen with the environmental chambers. The NO fluxes were small and sometimes difficult to measure by eddy correlation, so an attempt was made to increase soil emission by application of fertilizer on July 31 (day of year 213). Shortly thereafter, however, heavy rains prevented observations for a few days. The rains might have washed away some of the fertilizer, because the increase in NO emissions seen later was not as large as anticipated.

These measurements of NO flux suggest that 50-100% of the NO emitted can be converted to NO<sub>2</sub> below a height of 5 m, especially when the soil emission rates are large. Variations in the NO<sub>2</sub> deposition rate and the level of solar radiation are also important in determining the conversion of NO to NO<sub>2</sub>. The change of O<sub>3</sub> flux with height, however, does not appear to be significant. If all of a rather large amount of 10 ng N m<sup>-2</sup> s<sup>-1</sup> (1.8 ppbv cm s<sup>-1</sup>) of soil NO flux were entirely converted to NO<sub>2</sub>, the increase in downward O<sub>3</sub> flux would be only about 1.8 ppbv cm s<sup>-1</sup>, which would be difficult to detect relative to the magnitude and variability of the O<sub>3</sub> flux observations.

Models that describe fast chemical reactions and turbulent mixing within and above vegetative canopies need to be developed further and applied to improve understanding of the rapid conversion of NO to NO<sub>2</sub>. The interpretation of other NO flux measurement techniques, such as the gradient approach applied very close to the surface (Taylor et al. 1999), might need to take into account this rapid conversion process. Because the dry deposition of NO<sub>2</sub> to vegetative canopies can be fairly large during the daytime, the vertical flux of NO<sub>x</sub> might change rapidly with height very close to the surface. The measurements at NOVA include several quantities that will assist in evaluating model performance: concentrations of NO, NO<sub>2</sub>, O<sub>3</sub>, and hydrocarbons above the plant canopy; a few samples of NO, NO<sub>2</sub>, and O<sub>3</sub> concentrations inside the canopy; the fluxes of NO and O<sub>3</sub> above the canopy; and some hydrocarbon fluxes.

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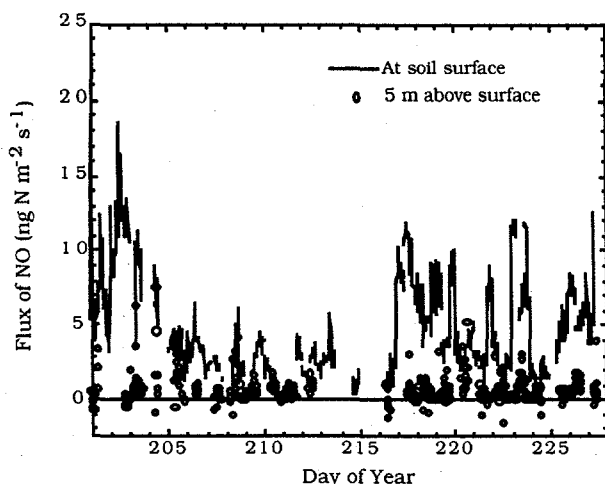


FIG. 1. NO emission rates measured with environmental chambers at the soil surface and eddy covariance results above the soybean canopy. The units of  $\text{ng N m}^{-2} \text{s}^{-1}$  can be converted to  $\text{ppbv cm s}^{-1}$  by multiplying the N flux by approximately 0.175.

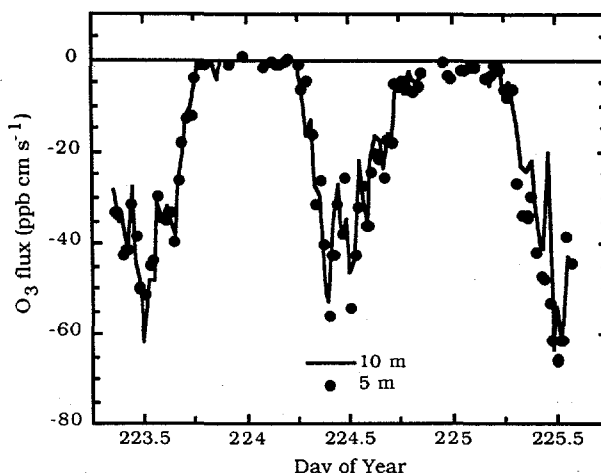


FIG. 2. Ozone fluxes measured at two heights above the soybean field.

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