



## CHARACTERIZATION OF NITROGEN OXIDE FLUXES FROM SOIL OF A FALLOW FIELD IN THE CENTRAL PIEDMONT OF NORTH CAROLINA

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**Abstract**-- NO<sub>x</sub> emissions from soils may contribute to the formation of O<sub>3</sub> in rural areas, especially when there is substantial emissions of natural hydrocarbons from surrounding vegetation, such as in the southeastern United States. Soil NO<sub>x</sub> flux measurements were made from 6 June 1992 to 7 July 1992 in the central Piedmont region of North Carolina (Southeast Oxidants and Nitrogen Intensive Analysis site, SONIA) in an effort to determine the role of natural emissions of NO<sub>x</sub> on rural atmospheric photochemistry. The overall average NO and NO<sub>2</sub> emission rates, using a dynamic chamber technique, were found to be  $1.79 \pm 1.37 \text{ ng-N m}^{-2} \text{ s}^{-1}$  (range: 0.13 to  $6.67 \text{ ng-N m}^{-2} \text{ s}^{-1}$ ) and  $-1.07 \pm 0.87 \text{ ng-N m}^{-2} \text{ s}^{-1}$  (range:  $-6.71$  to  $3.16 \text{ ng-N m}^{-2} \text{ s}^{-1}$ ), respectively. Over 85% of the NO<sub>2</sub> flux measurements were negative indicating net deposition to the soil surface. No negative NO flux rates were observed. NO flux was correlated with soil temperature. There was a positive correlation between NO concentration near the soil surface (~50 cm) and NO flux ( $r=0.35$ ). The NO compensation point (1.12 ppbv) was estimated from the relationship between NO emission rate and ambient NO concentrations measured at 10 m. Both positive and negative vertical gradients of NO concentration between 10 m and soil surface were detected. The positive vertical gradients are indicative of NO transport to the site from polluted air masses. A significant negative correlation between NO flux and ambient O<sub>3</sub> concentration ( $r=0.66$ ), however, supports the hypothesis that soil emissions of NO contribute to local production of O<sub>3</sub> in rural areas.

**Key word index:** Nitrogen oxides, NO<sub>x</sub> emission, dynamic chamber, NO compensation point, water-filled pore space, soil temperature.

### INTRODUCTION

Nitrogen oxide (NO<sub>x</sub>=NO+NO<sub>2</sub>) plays an important role in the ozone chemistry of the atmosphere. Moreover, the distribution of the hydroxyl radical (OH) has been shown to be sensitive to the level of NO<sub>x</sub> in the atmosphere (Liu *et al.*, 1987).

In urban areas, oxides of nitrogen are emitted into the atmosphere primarily by anthropogenic processes, such as combustion of fossil fuels at point sources (power plants), by mobile sources, and biomass burning (Logan, 1983). Since these anthropogenic sources are confined to small geographic areas, NO<sub>x</sub> budgets for urban areas can be reasonably well quantified. NO<sub>x</sub> budgets for rural areas are more difficult to assess. Natural sources of NO<sub>x</sub>, principally lightning and emission from soils, are more wide spread and less intense making quantitative estimation much more uncertain (Williams *et al.*, 1992a). In addition, the effect of soil parameters on NO<sub>x</sub> emissions is not well understood. NO<sub>x</sub> emission from soils exhibits high spatial and temporal variability because of variations in the soil physical, chemical and biological parameters that influence the rate of emissions. These parameters include soil water content, temper-

ature, nutrient content, organic carbon content and ambient NO concentration (Slemr and Seiler, 1984; Anderson and Levine, 1987; Williams *et al.*, 1987; Johansson *et al.*, 1988; Johansson and Sanhueza, 1988). Therefore, uncertainties in NO<sub>x</sub> budgets for rural areas could cause an incorrect assessment of the role of natural sources of NO<sub>x</sub> in atmospheric chemistry.

One use for NO<sub>x</sub> emissions data is as input data for photochemical models. For regional photochemical modelling studies it is important to accurately estimate the flux of NO<sub>x</sub> from soils, especially in rural areas, because emissions from natural sources may dominate those from anthropogenic sources transported to the site. Consequently, field measurements of NO<sub>x</sub> soil emissions from different locations are desirable to parameterize NO<sub>x</sub> emissions for a variety of environments.

Several techniques have been utilized to measure the emission fluxes from soils. These are the flow-through chamber, gradient, and eddy correlation methods. Thus far, most published measurements of NO<sub>x</sub> soil fluxes have relied on the flow-through chamber method (Galbally and Roy, 1978; Slemr and Seiler, 1984; Anderson and Levine, 1987; Williams *et al.*, 1987; Parrish *et al.*, 1987; Johansson *et al.*, 1988; Johansson and Sanhueza, 1988). Limited intercomparison analysis between the flow-through chamber method and gradient method indicates both tech-

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niques provide similar flux estimates (Parrish *et al.*, 1987; Kaplan *et al.*, 1988).

In this paper we present preliminary results of the measurement of  $\text{NO}_x$  flux from soil at a location characteristic of rural areas throughout much of the southeastern United States.  $\text{NO}_x$  flux measurements were made using a dynamic chamber technique (Aneja, 1975; Hill *et al.*, 1978; Aneja *et al.*, 1979) in an effort to gain insight into the role of natural emissions of  $\text{NO}_x$  on rural photochemistry. These flux measurements were complemented with observations of ambient ozone ( $\text{O}_3$ ). Observed relationships between  $\text{NO}_x$  flux, soil parameters, ambient  $\text{NO}_x$  concentration, and ambient  $\text{O}_3$  concentration are discussed.

## EXPERIMENTAL

### Sampling site

Flux measurements were made at the Southeast Oxidants and Nitrogen Intensive Analysis (SONIA) site (35.26° N, 79.84° W, ~170 m m.s.l.), which is operated by the Air Quality group at North Carolina State University, Raleigh, NC. The site is near Candor, NC on the eastern border of the Uwharrie National Forest which is in the central Piedmont region of North Carolina. The site is co-located with a National Dry Deposition Network (NDDN) site defined as rural. The sampling location was a fallow agricultural field (area ~1200 m<sup>2</sup>) which was previously used to grow soybeans (~10 years ago) and is surrounded by mixed deciduous and coniferous forest. The soil is a clayey, kaolinitic, thermic Typic Hapludult (Georgeville clay loam), which is a well drained, moderately permeable soil formed from weathered Carolina Slate or fine grained rock of the Piedmont uplands (Daniels *et al.*, 1984). The vegetative cover consisted of unmanaged pasture with areas of exposed soil.

### Flux measurements

$\text{NO}_x$  flux measurements were obtained from six sampling plots within a 20 m radius of the mobile instrumentation laboratory. The sampling plots were chosen at random and sampled during a period from 6 June 1992 to 7 July 1992.

Flux measurements at a given sampling plot were terminated if a rainfall event occurred during the planned measurement period. A new sampling plot was selected if measurements were to continue after the end of the rainfall

event. These flux measurements were usually resumed within two hours. No attempt was made to obtain flux measurements immediately following a rainfall event. Additional measurements included continuous monitoring of the concentrations of  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{O}_3$  at 10 m above ground level. Two 24 h experiments were conducted to examine the diurnal profile of  $\text{NO}_x$  flux. Meteorological data was continuously monitored throughout the sampling period.

Initial total soil water content at the start of each flux measurement was determined from soil samples collected using a bucket auger (0–15 cm depth), ~50 cm away from each sampling plot. Final total soil water content, pH, and elemental carbon and nitrogen content (Robarge and Fernandez, 1986) were obtained from soil samples taken after removal of the sampling chamber. Soil water content was converted to percent water-filled pore space using an average bulk density of 1.30 g cm<sup>-3</sup> and assuming a particle density of 2.65 g cm<sup>-3</sup>. Soil temperature measurements were obtained by inserting thermometers into the soil adjacent to the sampling chamber.

### Chamber design and operation

The dynamic chamber used in this study is a Teflon-lined cylinder (diameter ~27 cm, height ~42 cm, and volume ~25 l) held in place by a stainless steel frame driven into the ground to a depth of ~10 cm (Fig. 1). Ambient air is pumped through the chamber at a constant flow rate ( $Q=9$  l.p.m.), and the air in the chamber is well mixed by a motor driven Teflon stirrer (~20 cm diameter, 120 r.p.m.). Air samples were collected after reaching steady state conditions (~30 min of operation) at both ports of the chamber using Teflon bags (~10 l). The collection period was typically ~5 min. The air samples in these bags were then immediately analysed (<1 min) for their  $\text{NO}$  and  $\text{NO}_2$  concentrations.

### Instrumentation

Determination of the concentration of  $\text{NO}$  and  $\text{NO}_2$  in the air samples was carried out using a TECO 42S chemiluminescent high sensitivity  $\text{NO}$  analyser (Thermo Environmental Instruments Inc.), and a LMA-3 Luminol based  $\text{NO}_2$  analyser (Scintrex Ltd). The instruments were periodically calibrated according to protocol using multiple dilution with a mixture of 0.109 ppmv  $\text{NO}$  in  $\text{N}_2$  and a mixture of 0.116 ppmv of  $\text{NO}_2$  in  $\text{N}_2$  (Scott Specialty Gases, Inc., Plumsteadville, PA). Detection limits for these instruments are cited at 50 parts per trillion volume (pptv) for  $\text{NO}$  (Thermo Environmental Instrument, Inc., 1992) and ~5 pptv for  $\text{NO}_2$  (Scintrex, Ltd LMA-3 Operators Manual.

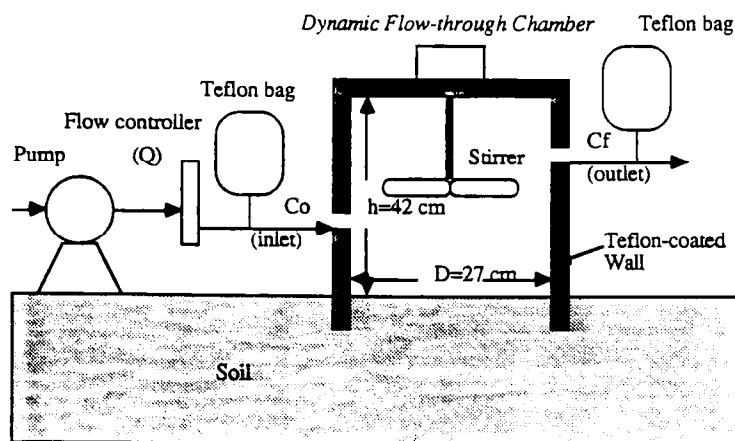


Fig. 1. The schematic figure of the dynamic flow-through chamber. The walls and all internal surfaces are fluorinated ethylene propylene (FEP) Teflon.

1987). Additional information concerning the instrumentation is described elsewhere (Kim *et al.*, 1993; Dickerson *et al.*, 1984; Scintrex Ltd, 1989).

Flux calculation

The mass balance for NO in the chamber is given by

$$\frac{dC}{dt} = \left( \frac{Q[C]_0}{V} + \frac{JA}{V} \right) - \left( \frac{LA[C]_f}{V} + \frac{Q[C]_f}{V} \right) + R \quad (1)$$

where

- A = soil surface area covered by the chamber;
- V = volume of the chamber;
- Q = flow rate through the chamber;
- J = emission flux per unit area;
- C = NO concentration in the chamber;
- [C]<sub>0</sub> = NO concentration at the inlet of chamber;
- [C]<sub>f</sub> = NO concentration at the outlet of chamber;
- L = loss term by chamber wall per unit area assumed first order in [C];
- R = chemical production, destruction rate in the chamber.

For a well-mixed chamber [C]<sub>f</sub> may be assumed to be equal to the NO concentration in the chamber.

The rapid oxidation of NO in the atmosphere requires that the calculated NO fluxes be corrected for possible chemical reactions within the chamber. NO is oxidized rapidly in the atmosphere. Generally, three oxidants have a major role in the oxidation of atmospheric NO. They are O<sub>3</sub>, HO<sub>2</sub> and RO<sub>2</sub> (Finlayson-Pitts and Pitts, 1986). NO<sub>2</sub> flux (even negative flux) is typically much lower than NO flux from soils (Slemr and Seiler, 1991; Johansson and Granat, 1984) and the low ambient concentrations of NO<sub>2</sub> at site SONIA are not expected to produce significant quantities of NO in the chamber. Thus, R in equation (1) can be written as

$$R = -(k_1[O_3] + k_2[HO_2] + k_3[RO_2])[NO] = -\left(\sum_{i=1}^3 k_i R_i\right)C \quad (2)$$

where R<sub>i</sub> is each reactant species and k<sub>1</sub>(=1.8 × 10<sup>-14</sup> cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>), k<sub>2</sub>(=8.3 × 10<sup>-12</sup> cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>) and k<sub>3</sub>(=7.6 × 10<sup>-12</sup> cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>) are reaction rates for O<sub>3</sub>, HO<sub>2</sub>, and RO<sub>2</sub> with NO, respectively. Equation (1) becomes

$$\frac{dC}{dt} = -\left(\frac{Q}{V} + \frac{L}{h} + \sum_{i=1}^3 k_i R_i\right)C + \left(\frac{J}{h} + \frac{Q[C]_0}{V}\right) \quad (3)$$

where h(= ~42 cm) is the height of the chamber. Solving equation (3) for the NO flux, J, under steady state condition, yields

$$J = h \left\{ \frac{Q}{V}(C_f - C_0) + \left( \frac{L}{h} + \sum_{i=1}^3 K_i R_i \right) C_f \right\} \quad (4)$$

Surface O<sub>3</sub>, RO<sub>2</sub> and HO<sub>2</sub> concentrations are necessary for the calculation of the chemical loss term. RO<sub>2</sub> concentrations have been calculated at Scotia, PA (Trainer *et al.*, 1991), and site SONIA (Hartsell, 1993); and measured at site ROSE, AL (Cantrell *et al.*, 1992). All are similar in magnitude. Maximum RO<sub>2</sub> concentrations for the three rural sites during strong photochemical conditions were on the order of 10<sup>9</sup> mol cm<sup>-3</sup>. For site SONIA, the average noontime RO<sub>2</sub> concentration was about 30 pptv (7.4 × 10<sup>8</sup> mol cm<sup>-3</sup>). HO<sub>2</sub> concentrations are expected to be ~30% of RO<sub>2</sub> and average daytime O<sub>3</sub> concentrations at site SONIA were about 50 ppbv. However, O<sub>3</sub>, HO<sub>2</sub> and RO<sub>2</sub> are rapidly deposited onto the interior surface of the chamber, and the enclosed vegetation and exposed soil. Near surface O<sub>3</sub> concentrations used for the flux calculation were assumed to be equal to the nighttime O<sub>3</sub> average (~5 ppbv) measured at the site. Estimates of the near surface concentrations of HO<sub>2</sub> and RO<sub>2</sub> (approximately 60% of ambient levels) were based on model projections (Trainer *et al.*, 1987a; Hartsell, 1993).

The loss of NO by reaction with the Teflon-coated wall of the chamber was estimated by taking the difference between

Table 1. Summary of NO flux for each plot, and soil characteristics of the emission locale

Plots	NO flux *(ng-N m <sup>-2</sup> s <sup>-1</sup> )		Soil measurements†				Ambient				
	All measurements	Sample number	Daytime 7 a.m.-7 p.m.	Nighttime 8 p.m.-4 a.m.	pH	Carbon (%)	Nitrogen (%)	WFPS‡ (%)	Soil temperature °C	[NO]* (ppbv)	[O <sub>3</sub> ]* (ppbv)
1	1.46 (0.36)	4	1.46 (0.36)		6.44	0.87	0.08	59	26.1 (2.1)	0.42 (0.13)	46.0 ( 6.7)
2	0.90 (0.65)	9	0.90 (0.65)		6.14	0.93	0.08	48	30.5 (1.2)	0.20 (0.14)	52.6 (11.4)
3	2.09 (0.88)	7	2.09 (0.88)		6.59	0.75	0.06	54	28.6 (1.9)	0.27 (0.11)	44.6 ( 5.8)
4	1.09 (0.99)	24	1.17 (1.01)	0.75 (0.41)	7.55	0.87	0.07	64	24.7 (2.8)	0.33 (0.10)	45.8 (14.1)
5	1.79 (0.35)	10	1.79 (0.35)		6.59	0.63	0.05	36	30.5 (2.1)	0.08 (0.12)	49.5 ( 5.7)
6	2.94 (1.72)	21	2.34 (1.27)	3.92 (1.97)	6.77	0.74	0.06	36	28.0 (2.6)	0.12 (0.09)	30.0 (15.8)
Average	1.79	75	1.63	2.34	6.68	0.80	0.07		27.6	0.24	44.8
S.D.	1.37		0.55	2.24	0.48	0.11	0.01		3.3	0.13	7.8

\* Average (1 standard deviation)

† Clayey, kaolinitic, thermic Typic Hapludult (Georgeville clay loam).

‡ Water-filled pore space.

the combined surface loss as proposed by Kaplan *et al.* (1988) and the chemical loss in the chamber as calculated by equation (2). This approach results in a wall loss,  $L$ , of  $0.02 \text{ cm s}^{-1}$ .

## RESULTS AND DISCUSSION

No difference was detected between the initial and final total soil water content for each sampling plot. The calculated water-filled pore space ranged from 36 to 64% (Table 1), which is approximately equal to the optimal range of moisture contents for nitrification and emission of NO (Davidson, 1991). Soil temperature averaged  $27.6 \pm 3.3^\circ\text{C}$ , and ranged from 16 to  $33^\circ\text{C}$  during the course of a single day. The average soil carbon (C) and nitrogen (N) contents were typical for this soil type and varied little among the sampling plots (Table 1). This is consistent with the influence of tillage operations on the soil surface, and the lack of a well developed root mass. The slightly acidic soil pH ( $6.68 \pm 0.48$ ) suggests the addition of lime at some point in the past. This is consistent with soybeans being the last row crop grown at this location.

NO emission data along with ambient concentrations of NO and  $\text{O}_3$  are also summarized in Table 1. The overall average NO emission rate was found to be  $1.79 \pm 1.37 \text{ ng-N m}^{-2} \text{ s}^{-1}$  with extremes of 0.13 and  $6.67 \text{ ng-N m}^{-2} \text{ s}^{-1}$ . This is comparable with NO flux in a temperate forest in central Pennsylvania ( $0.2\text{--}4.1 \text{ ng-N m}^{-2} \text{ s}^{-1}$ ) measured by Williams *et al.* (1988). There was a tendency for ambient NO concentrations at 10 m to decrease during the sampling period, while the ambient  $\text{O}_3$  concentration remained relatively constant.

Most field measurements have not detected  $\text{NO}_2$  emissions; however, Slemr and Seiler (1984) have reported that  $\text{NO}_2$  was emitted, ranging from negative to higher than  $250 \text{ ng-N m}^{-2} \text{ s}^{-1}$  on unfertilized soil. The overall average  $\text{NO}_2$  flux was found to be  $-1.07 \pm 0.87 \text{ ng-N m}^{-2} \text{ s}^{-1}$  with extremes of  $-6.71$  and  $3.16 \text{ ng-N m}^{-2} \text{ s}^{-1}$ . The majority (85%) of the  $\text{NO}_2$  flux measurements were negative in value indicating net deposition to the soil surface. Any remarkable conditions under which  $\text{NO}_2$  emission occurred were not detected.

### Diurnal variation of nitrogen oxides flux from soil

Figure 2 illustrates the diurnal variation in NO flux measured during the experimental period. Composite diurnal variations of NO and  $\text{NO}_2$  flux using only the data measured from 08:00 to 20:00 EST are shown in Fig. 3. The symbols indicate the average NO and  $\text{NO}_2$  fluxes for each hour while the error bars denote  $\pm$  one standard deviation. Maximum NO flux (approximately  $3.0 \text{ ng-N m}^{-2} \text{ s}^{-1}$ ) appears to occur around 10:00 EST, while a minimum is observed at 18:00 EST. The remainder of the time the average flux remains relatively constant ( $\sim 1.5 \text{ ng-N m}^{-2} \text{ s}^{-1}$ ). The increases in NO flux during the morning hours may be due to an increase in soil temperature. However, maximum daily soil temperature typically occurred at 14:00 EST. No trends were evident in the hourly variation of  $\text{NO}_2$  flux, indicating that deposition to the soil surface remained constant during daylight hours.

### Variation of NO emission rate with soil temperature

NO flux appeared to vary with soil temperature (Fig. 4), and visual inspection of the data suggests

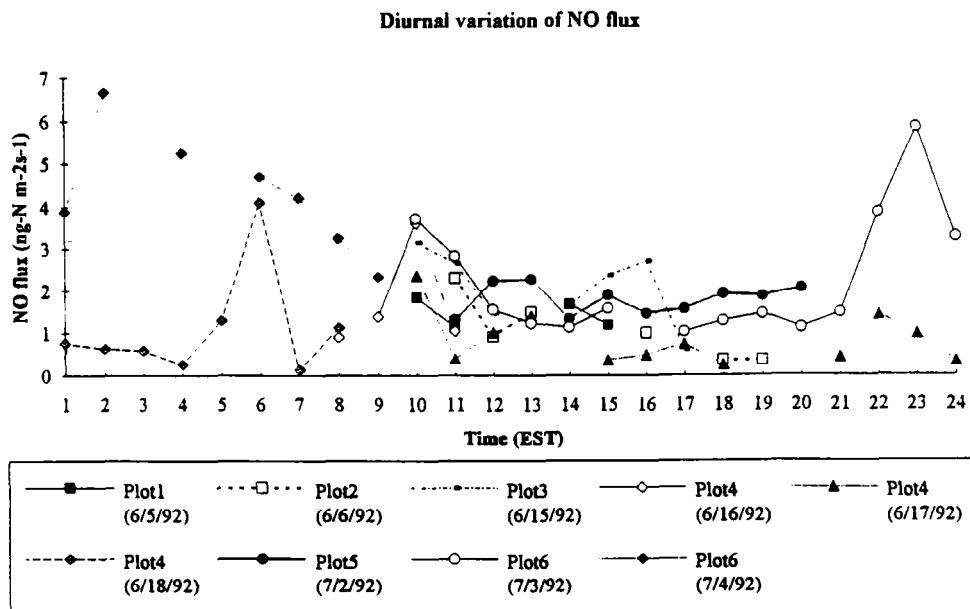
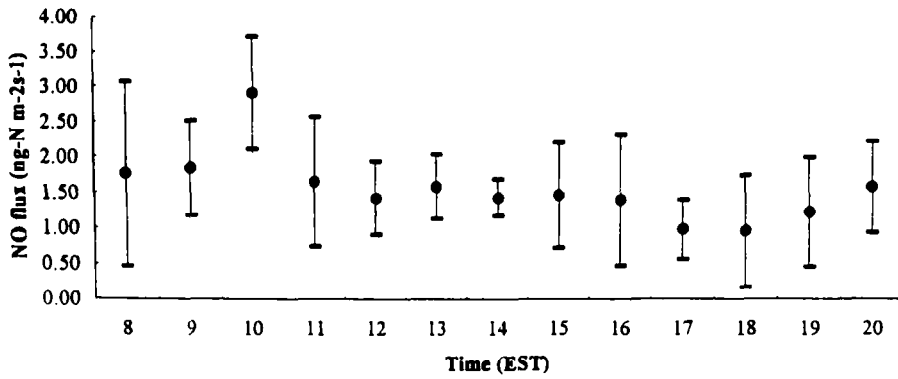


Fig. 2. Diurnal NO flux from six different plots on site SONIA.

Composite hourly variation of NO flux (08:00 - 20:00)



Composite hourly variation of NO<sub>2</sub> flux (08:00-20:00)

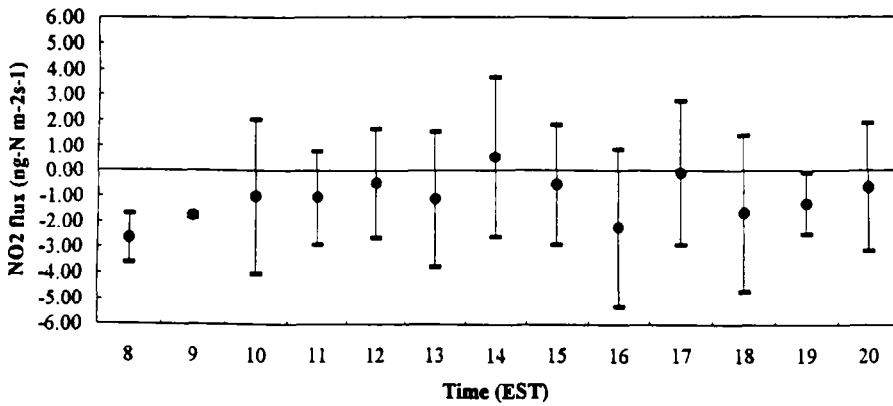


Fig. 3. Composite diurnal variations of NO and NO<sub>2</sub> emission rates during the daytime (0800-2000 EST).

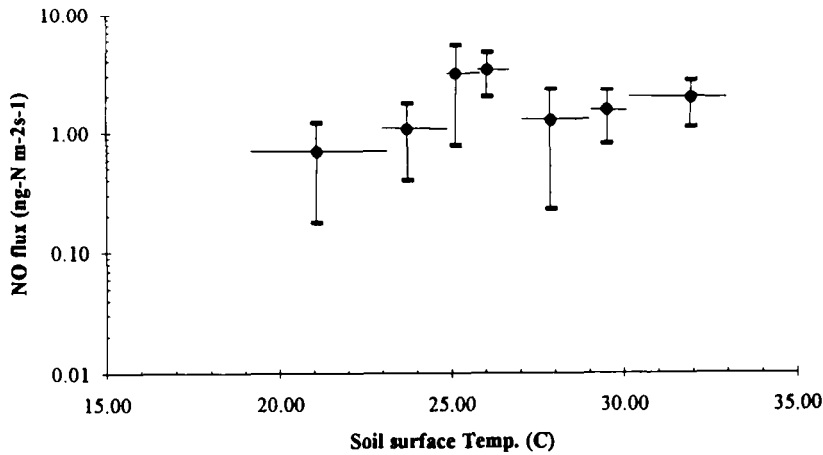


Fig. 4. Plot of NO flux vs soil temperature. Vertical lines indicate 1 standard deviation of the average NO flux, measured over the soil temperature range spanned by the horizontal bars.

a peak in NO emission rate at approximately 26°C. However, no statistically significant trend in the data was detected. The lack of a linear relationship between NO flux and soil temperature is consistent with

similar observations elsewhere in the southeastern United States (Williams and Feshenfeld, 1991). Emission of oxides of nitrogen from soils has been reported to have strong temporal and spatial variation because

of its dependence on controlling factors such as soil temperature, as well as soil pH, soil water content, porosity, plant cover, level of fertilization and ambient NO concentration above the soil (Williams *et al.*, 1992a, 1992b; Williams *et al.*, 1988; Anderson and Levine, 1987). Additional information will be required to determine why we were unable to detect a significant relationship between NO flux and soil temperature for the range of values observed in this study.

The range in NO emission rates and soil temperature at site SONIA is similar to that observed for other rural sites in the eastern United States. Average NO fluxes at site SONIA ranged from 0.9 to 2.9  $\text{ng-N m}^{-2} \text{s}^{-1}$  and are comparable with results from a wheat field in Rock Spring, PA (0.6–1.7  $\text{ng-N m}^{-2} \text{s}^{-1}$ ), and a forested rural site in Scotia, PA (0.2–2.1  $\text{ng-N m}^{-2} \text{s}^{-1}$ ) (Williams and Feshenfeld, 1991). All three sites experienced a similar span of soil temperatures (15–35°C).

#### NO compensation point

The NO compensation point is defined as NO mixing ratio in ambient air at which the net flux rate is zero, i.e. NO destruction equals NO formation (Slemr and Seiler, 1991). It is calculated from the negative correlation of all flux rates measured during the pertinent experiment with the corresponding ambient air mixing ratios. The existence of a NO compensation point has frequently been observed in the field, and knowledge of its value is important in the estimation of NO emission rates from soils. The compensation point represents values averaged over the length of the sampling period, and they will reflect the average soil conditions, such as fertilization, soil porosity, moisture, and temperature (Slemr and Seiler, 1991). The compensation point may also reflect various physiochemical processes at the experimental site because the levels of ambient NO concentration used in the calculation result from the coupled effects of physical processes (i.e. long-range transport and mixing processes), and chemical reactions in the atmosphere.

The compensation point was estimated from the relationship between NO emission rates and ambient NO concentrations. Figure 5 shows a scatter plot of NO flux measurements vs NO mixing ratio in ambient air at 10 m above ground level. There is a negative correlation ( $r=0.24$ ) between NO flux and ambient NO concentrations, but there is a considerable amount of scatter in the data. The NO compensation point estimated from the least-square fit of the data in Fig. 5 is 1.12 ppbv ( $n=75$ ), and the statistical confidence in the estimate of the compensation point is small because of the broad confidence interval ( $\pm 1.56$ ). Slemr and Seiler (1991) observed that correlation of NO flux rates with ambient NO concentrations were significant only on plant-covered plots. The value of the NO compensation points on these plots were sensitive to the soil fertilization. The NO compensation points estimated from the relationship between NO flux and ambient NO concentration ranged from 0.3 to 1.2 ppbv at a rural site in West Germany in their study.

The positive correlation between NO concentration near the soil surface ( $\sim 50$  cm) and NO flux from the soil ( $r=0.35$ ) is illustrated in Fig. 6. The positive correlation indicates that as NO flux increases, surface NO concentration increases as well.

Interaction of NO fluxes and NO concentration just above the surface, and 10 m are very complex. The mechanism which affects the NO concentration gradient between near surface level (0.5 m) and ambient level ( $\sim 10$  m) is complicated by several factors, including  $\text{O}_3$  levels, mixing conditions, soil factors, etc. However, in situations where ambient NO concentrations are low, i.e. in a rural environment, the dominant factors affecting NO concentration are probably soil factors.

If we assume that soil emission is the primary source of NO at SONIA, there may be a negative vertical gradient of NO concentration as one moves away from the soil surface. Measurements of ambient NO concentration at 10 m and in the near surface

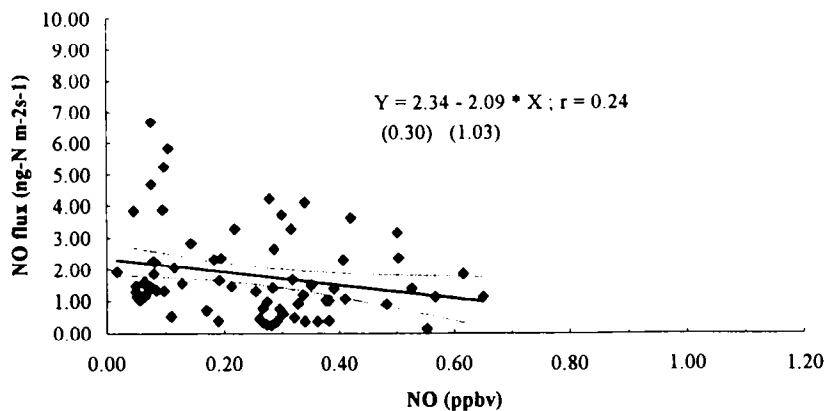


Fig. 5. NO flux vs ambient NO concentration. The solid line represents the regression equation and the dotted lines indicate 90% confidence intervals of NO flux.

layer (~50 cm) at site SONIA, however, showed both positive and negative vertical gradients of NO concentration. The number of positive and negative gradients was nearly equally distributed (48% positive, 52% negative,  $n=66$ ).

The positive and negative gradients observed appeared to be related to air mass type and origin. Over 60% of the negative vertical gradients were observed under conditions of an easterly wind. Easterly flow is expected to be mostly marine in origin and should have lower pollutant concentrations due to its oceanic origin and the lack of significant anthropogenic emission sources east of site SONIA. About 70% of the positive vertical gradients observed were associated with northerly and southwesterly winds. Northerly and southwesterly flow at site SONIA is continental in origin and is more heavily impacted by anthropogenic sources. Long-range transport of polluted air from anthropogenic source areas may provide NO aloft over site SONIA. This polluted air aloft is probably mixed down into the boundary layer and transported to the surface during the breakup of the

nocturnal boundary layer (Kim *et al.*, 1993; Trainer *et al.*, 1987b). This in turn would act to confound the relationship between NO concentration at the soil surface (~50 cm) and NO flux illustrated in Fig. 6.

*NO flux and ambient O<sub>3</sub> concentration*

In the atmosphere, NO is rapidly oxidized to NO<sub>2</sub> by reaction with O<sub>3</sub> especially during the night. Thus significant concentrations of NO and O<sub>3</sub> are usually not found in the same air mass. Additionally, O<sub>3</sub> does not accumulate during a photochemical air pollution episode until the NO concentration has fallen to low values (Finlayson-Pitts and Pitts, 1986). A significant negative correlation was observed between NO flux and ambient O<sub>3</sub> concentrations (Fig. 7;  $R=0.66$ ) at site SONIA. NO flux at low levels of O<sub>3</sub> concentration (<30 ppbv) varied widely (from 0.1 to 7 ng-N m<sup>-2</sup> s<sup>-1</sup>), while the range in NO flux at high levels of O<sub>3</sub> concentration (>60 ppbv) was limited from 0.5 to 2.5 ng-N m<sup>-2</sup> s<sup>-1</sup>. These results may suggest that NO emission from the soils increases ambient NO concentrations and that the locally produced

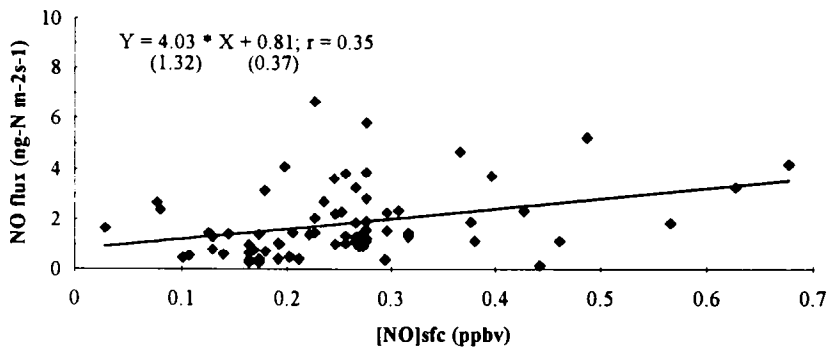


Fig. 6. NO flux vs ambient NO concentration near the surface (~0.5m).

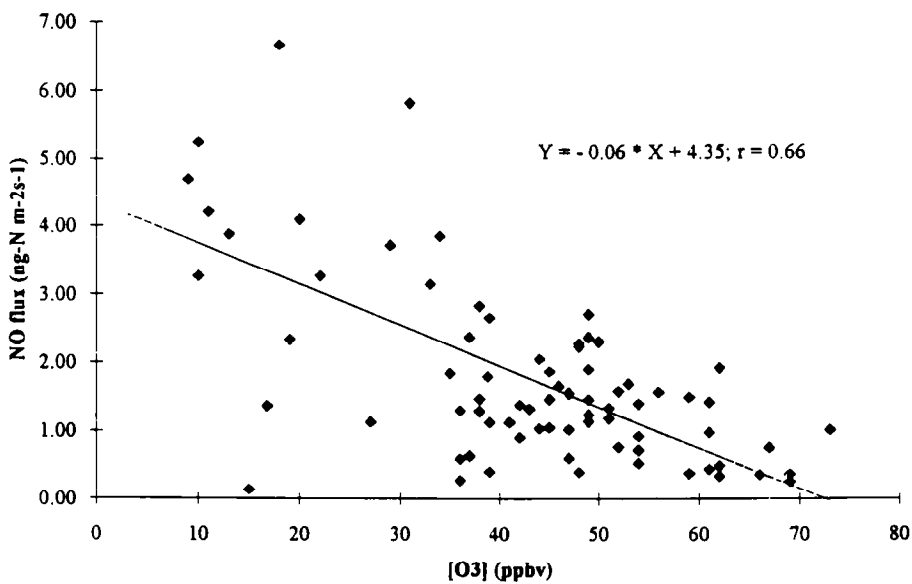


Fig. 7. NO flux vs ambient O<sub>3</sub> concentration at site SONIA.

NO may form O<sub>3</sub> after reaction with peroxy radicals to form NO<sub>2</sub>. The large natural hydrocarbon emissions in the rural southeast United States due to dense vegetation and high temperature (Chameides *et al.*, 1992; Khalil and Rasmussen, 1992; Cantrell *et al.*, 1992) may provide the necessary RO<sub>2</sub> to fuel O<sub>3</sub> accumulation. Thus consumption of available NO from soil emission in the presence of natural hydrocarbon emissions may contribute to local production of O<sub>3</sub> at site SONIA.

#### SUMMARY

The range in NO emission rates from the soil we observed at site SONIA (0.13–6.67 ng-N m<sup>-2</sup> s<sup>-1</sup>) is similar to those reported for other locations in the eastern United States (Williams and Fehsenfeld, 1991). The negative correlation between NO soil flux and O<sub>3</sub> concentrations suggests that local production of NO from soil emission at this location does contribute to the production of O<sub>3</sub>. However, the presence of positive vertical gradients of NO (48% of the total observations) points to a significant contribution of NO from aloft during breakup of the nocturnal boundary layer. The source of this NO is probably long-range transport of polluted air from anthropogenic sources to site SONIA.

These results from site SONIA demonstrate that the emission of NO from soils might be an important source of atmospheric NO concentration in the rural southeastern United States. Smith *et al.* (1990) have observed that, under well-aerated conditions in non-fertilized systems, NO production followed the order of coniferous forest > native shortgrass prairie > follow agricultural fields. The majority of landmass in the southeastern United States is covered by coniferous forests (Buol, 1973). It is clear that more comprehensive research into the role of naturally produced nitrogen species from soils and their emission rates are needed to enhance our understanding of the chemical climatology of the southeast region. The understanding gained from many widespread field measurements for naturally produced nitrogen species are of great importance to a well-developed photo-chemical model of the southeastern United States.

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