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Emissions of NO From Soil at a Rural Site in Central Tennessee

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Field measurements of soil emissions of NO from a Mountview silt loam soil with three land uses (forest, fertilized pasture, and fertilized corn) were made on a commercial farm during a summer and autumn sampling period. A new automated closed-chamber sampling system was developed to allow simultaneous measurements on five chambers per 100 m^2 plot. Individual chambers with hinged tops, covering 0.3 m^2 of soil area were pneumatically operated via data logger control to sample soil NO flux every third hour. Spatial variability in emission rates was high. For each land use type the range from the lowest to the highest emitting chamber was approximately threefold. Land use type significantly affected soil NO emissions. The fertilized pasture had the highest mean emission rate (44.1 ng N m^{-2} s^{-1}), followed by the fertilized corn (27.0 ng N m^{-2} s^{-1}), and the forest (8.4 ng N m^{-2} s^{-1}). NO emission rates and soil nitrate levels at the forest plot were considerably higher than at other forest sites in the region, possibly due to runoff from an adjacent fertilized hayfield. The results of this study, when extrapolated to a regional estimate, suggest that emissions of NO from soils could play a significant role in summertime tropospheric ozone photochemistry in the southeastern United States.

INTRODUCTION

Fossil fuel combustion is the major source of NO_x (NO + NO_2) in the atmosphere [*Logan*, 1983], but recent studies indicate that biogenic emissions of soil NO_x (primarily emitted as NO) may represent a significant source [*Williams and Fehsenfeld*, 1991]. Measurements of soil flux of NO_x indicate that in some instances, comparable emission rates exist between anthropogenic emissions in urban areas and agricultural areas [*Williams et al.*, 1988; *Williams et al.*, 1992]. Understanding and quantifying soil emissions of NO_x is of importance in understanding the formation of tropospheric ozone. This is particularly true in rural areas where man-made sources of NO_x are minimal since ozone production will be dependent upon biogenic sources of NO_x.

Prediction of the distribution of tropospheric NO_x and ozone have been made using general circulation models [*Penner et al.*, 1991], but correctness of the source areas is uncertain due to large spatial and temporal variation in soil NO_x efflux [*Davidson et al.*, 1991*a*]. Even in locations which are characterized as homogeneous, the coefficient of variation in measured NO_x emissions is typically 100% or greater. *Johansson and Sanhueza* [1988] reported that emission rates within a 50 m^2 plot varied by a factor of 2–3, depending on the plot replicate. Attempts to correlate soil NO_x emissions with NO_x soil parameters and thereby improve the predictions of soil efflux of NO_x, have met with mixed results. In the studies of *Johansson and Granat* [1984] and *Williams et al.* [1987, 1988], strong correlations were found between NO_x emissions and soil temperature. But similar correlation analysis of soil temperature, soil chemistry, and soil NO_x efflux by other researchers have not indicated a relationship [*Anderson and Levine*, 1987; *Slemr and Seiler*, 1991; *Johansson et al.*, 1988]. Several studies have shown that N gas loss is not always tightly coupled with synthesis [*Parsons et al.*, 1991; *Jury et al.*, 1982]. *Jury et al.* [1982] demonstrated that a substantial lag time (12 or more hours) may elapse before a steady state is reached for N_2O produced during denitrification to equal the rate at which it is released at the soil surface. Their analysis indicated that several factors determine the length of time before a steady state is reached, including, (1) the soil diffusion coefficient (which is strongly influenced by soil moisture), (2) the location of the gas production zone within the soil, and (3) the soil gas storage capacity which is related to soil texture, structure, and water content. Given the influences of such factors, it is not surprising that simple correlation analysis between NO emissions and soil temperature, moisture, and chemical properties do not always reveal significant relationships.

To date, few measurements of soil NO_x emissions have been made in the southeastern United States, except for the measurements of *Williams and Fehsenfeld* [1991] in Tennessee. However, clearly, a better understanding of the importance of biogenic NO_x emissions in the formation of ozone in this region is needed since (1) approximately 40% of the ozone nonattainment areas in the United States are found in the southeast [*Lindsay et al.*, 1989] and (2) rural summertime ozone concentrations are among the highest recorded in the United States [*Pinkerton and Lefohn*, 1988].

At present we are involved in a multiyear project to develop a soil NO_x inventory for the Tennessee Valley region, which encompasses almost 24 million ha (2.4×10^{11} m^2). Our plans include estimating soil NO_x emissions from representative soil types from the major land use areas and cover types in this region. These data will be used to develop an inventory of biogenic NO_x emission for modeling ozone formation and transport in the region.

In the present study we report on soil NO_x measurements made in central Tennessee. This study had three major objectives, (1) to develop and test an automated closed-chamber technique for the measurement of soil NO_x flux, (2) to assess the impact of land use on soil NO_x emissions by making measurements on a single soil type covered in forest, corn, and a grass-legume pasture, and (3) begin the collection of data needed to produce an inventory of biogenic NO_x to be used in modeling ozone formation in the region.

MEASUREMENT TECHNIQUE

Chamber design. Soil NO_x measurements were performed using an automated closed-chamber system shown

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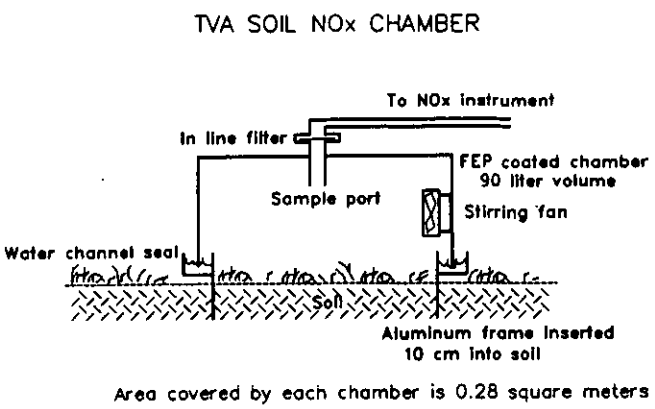

Fig. 1. Schematic illustration of soil NO_x emission measurement chamber.

schematically in Figure 1. The 90-L aluminum chambers are coated on the interior with flourinated ethylene propylene (FEP) Teflon, and each chamber covers 0.28 m^2 of soil area. The hinged chambers are fitted externally with small air cylinders (Bimba Manufacturing Company, Monee, Illinois) powered with air pressure at 650 kPa so that the tops can be automatically raised and lowered onto the frame for a measurement. The aluminum base frames are inserted into the soil to a depth of 10 cm and include a rectangular U-shaped channel filled with water that forms a seal when the chamber tops swing down into position for a measurement. A small, brushless 12 volt dc plastic fan (Sprint model, Rotron Inc., Saugerties, New York) is mounted inside the chamber and keeps the air stirred (about five exchanges per minute occur) so that samples withdrawn at any time will be representative of the NO in the chamber. A Teflon filter holder is mounted at the top center of each chamber and fitted with a 47-mm diameter, 2-um pore size Zeflour Teflon filter (Gelman Sciences, Inc., Ann Arbor, Michigan) to keep particles (and insects) out of the FEP Teflon sampling lines.

During the measurement sequence, an ambient sample is taken just before the chamber top is lowered, and measurements of NO in each of the five chambers are performed at 10-minute intervals during 1 hour. The measurements for this study were performed every third hour, that is, the chambers would be lowered for 1 out of every three hours. The lowering of the five chambers is staggered at 2-min intervals so that all the measurements may be performed with one NO_x instrument. Each time a sample is taken, 1.4 L of air (1.5% of the chamber volume) are withdrawn from the 90-L chamber over 2 min. The withdrawal volume and duration is dictated by the flow rate of the NO_x instrument (Thermo-Environmental, Inc., Franklin, Massachusetts), the length of the sample tubing, and the time required for the reading to stabilize. The sample lines are 0.63 cm O. D. FEP Teflon, 30 m in length, and the line loss tests have been performed in the field, indicating that less than 5% line losses of NO occur with this arrangement even when droplets of moisture are present in the tubing.

Chamber tests. In operating a closed chamber above the soil, consideration must be given to the effect on the measurement of withdrawing air from the chamber for sampling. Several different techniques have been reported in the literature for operating chambers. We have experimented by operating our chambers in two different ways; first by replacing withdrawn air with an identical metered flow rate of zero air (NO mixing ratio less than 1 ppb) via a port in the side of the chamber and second, with no replacement of air withdrawn for analysis. Our concern was that even though only a small percentage of the chamber air volume (1.5%) was allowed to well up from the soil during a sample, it was still possible that if the NO concentrations in the soil pores near the surface were high compared to the air in the chamber, an overestimate of the emission flux could result. To test the importance of this effect, we compared the two modes of operation during this study in a chamber at the Giles County field site by performing two separate hourlong measurement runs. In the first run we pumped zero air into the chamber whenever chamber air was being sampled and in the second run we capped off the replenishment port and allowed soil air to replenish sampled air. Figure 2 shows the results of this comparison. The two methods yielded very similar NO increases in the chamber leading us to conclude that operating without the zero-air replacement flow does not cause an appreciable bias in the emission flux measurement with our chambers, at least for this site.

We have also subsequently performed this same test at another field site (on a sandy loam soil) with similar results. It is interesting to note that even after five samples have been withdrawn from the chamber (50 min in Figure 2), corresponding to a 7.5% air change, there is still no appreciable difference in the chamber concentrations whether sampled air is replaced with zero air or air from the soil pores near the surface. The absence of any significant difference seems to suggest that the soil macropores nearest the surface tend not to have extremely high NO concentrations, at least at the sites we have tested. We do suspect that a bias would develop, however, if we were to reduce the volume of the

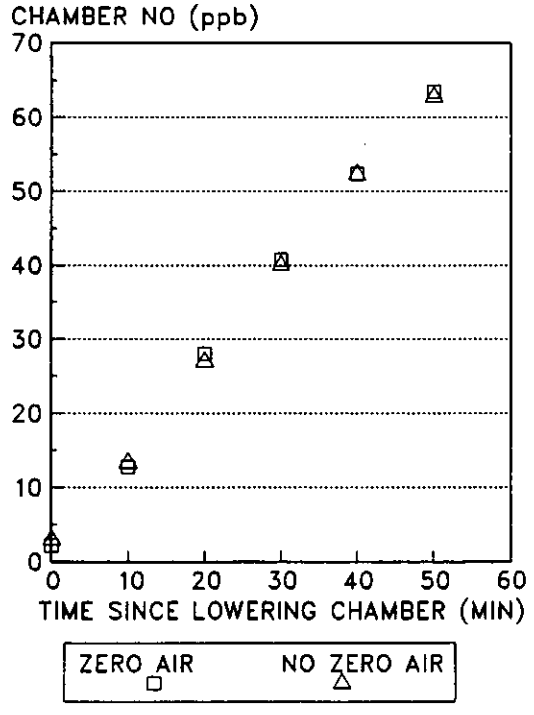

Fig. 2. Comparison of two techniques for treating withdrawn sample air. Squares indicate a measurement run during which sampled air was replaced with zero air, and triangles indicate a run during which sampled air was replenished with soil air.

chamber or increase the sampling flow rate. Other investigators should also be wary for these effects and perform similar tests with their own chambers and use vents or zero-air replacement if needed.

In an additional test of the overall operation of our chamber system (chamber design, sampling lines, analytical instrumentation, and data reduction technique) we have also recently performed a blind field comparison (R. J. Valente et al., Field comparison of static flow-through chamber techniques for measurement of soil NO emission, submitted to the *Journal of Geophysical Research*, 1993) between our closed chamber technique and the zero-air flow-through chamber system developed by *Williams et al.* [1987] of the Aeronomy Laboratory of the National Oceanic and Atmospheric Administration. These tests were performed at a fertilized cotton field in Alabama during the summer of 1992. These comparison results (Figure 3) show a correlation coefficient of 0.98 and a regression slope of 0.96 for 25 collocated measurements (two NOAA frames were installed within each of the Tennessee Valley Authority (TVA) frames) with emission rates ranging from less than 1 to over 100 ng N m^{-2} s^{-1}.

Data analysis technique. When a chamber is lowered onto a frame inserted in the soil, the concentration builds up most rapidly immediately after the chamber is lowered, then as the concentration builds up in the chamber, the rate of increase slows and approaches a steady state asymptotic value when the emission rate is evidently balanced by the loss rate to the soil. Figure 4 shows the results of a typical measurement run. This pattern of observed NO in the chamber with time is quite ubiquitous and can be described well for nearly all the measurements that we have performed with a model (equation (1)) incorporating a constant gross emission rate term (k_1) and a loss term (k_2) proportional to the concentration building up in the chamber:

$$\frac{d[\mathrm{NO}]}{dt} = k_1 - k_2[\mathrm{NO}] \tag{1}$$

This first-order differential equation can be solved by rearranging terms and multiplying both sides by exp ($k_2 t$):

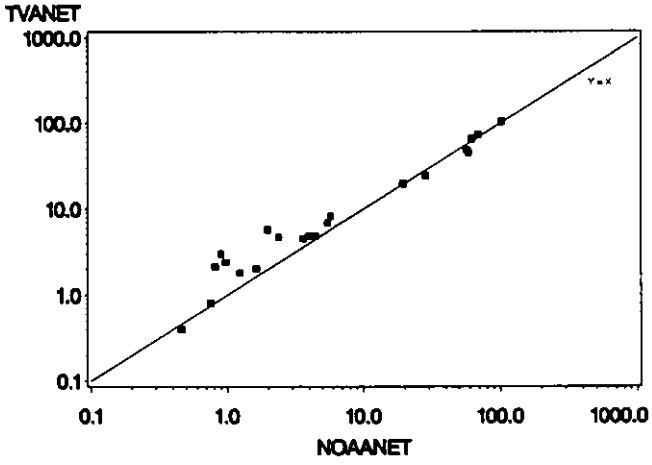

Fig. 3. Field comparison between a TVA closed chamber and NOAA zero-air flush chamber techniques for soil NO emission measurements. These tests were performed at a fertilized cotton field in Alabama.

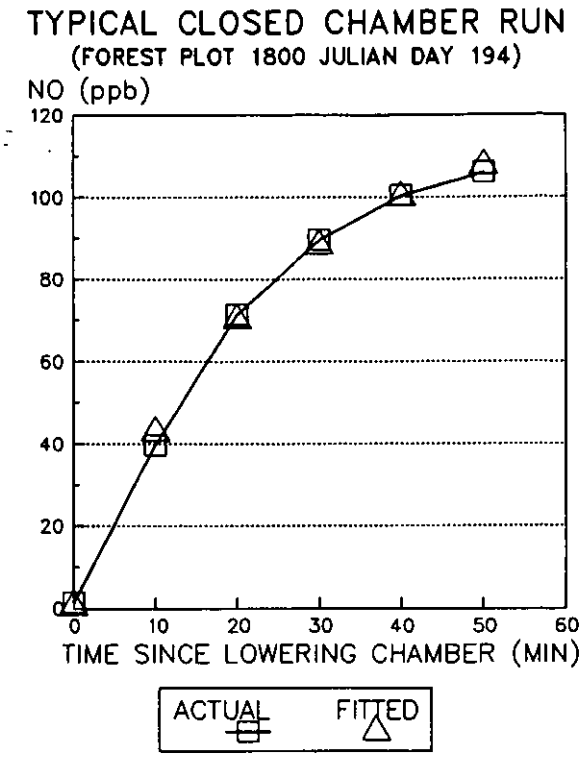

Fig. 4. NO concentration in the chamber during a typical measurement run. Fitted values were derived using (2).

$$e^{k_2 t}\frac{d[\mathrm{NO}]}{dt} + k_2 e^{k_2 t}[\mathrm{NO}] = k_1 e^{k_2 t} \tag{2}$$

then applying the chain rule and integrating

$$\int \frac{d}{dt}[\mathrm{NO}]e^{k_2 t}\,dt = \int k_1 e^{k_2 t}\,dt \tag{3}$$

to give an expression for the NO concentration in the chamber as a function of time:

$$[\mathrm{NO}](t) = \frac{k_1}{k_2} + Ce^{-k_2 t} \tag{4}$$

where C is a constant of integration. Just after the chamber is lowered ($t = 0$), the NO concentration is equal to the ambient level at chamber height ($\mathrm{NO_{amb}}$). Given this initial condition, C is determined and the solution to (1) becomes

$$[\mathrm{NO}](t) = \frac{k_1}{k_2} + \left([\mathrm{NO}]_{\mathrm{amb}} - \frac{k_1}{k_2}\right) e^{-k_2 t} \tag{5}$$

By fitting the NO curve for each measurement run with a nonlinear regression based on (5), the gross emission rate and the loss rate in the chamber are calculated.

Field Measurement Site Description

The field plots used in determining soil NO_x flux were located on a farm located approximately midway between Pulaski and Lawrenceburg, Tennessee. Determinations of NO_x emissions were made from three land use types: an oak-hickory forest, corn, and pasture. All three sites were located on Mountview silt-loam soil (fine-silty, sileous, ther-

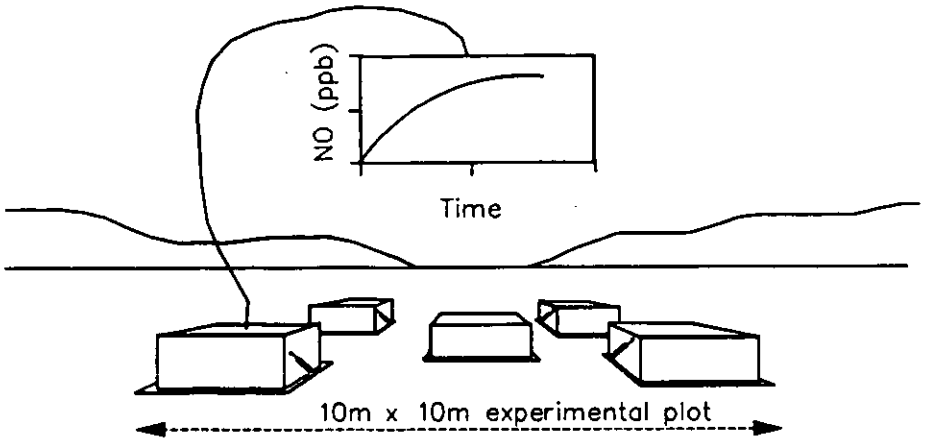

Fig. 5. Layout of chambers on an experimental plot.

mic, Typic Paleudult). This is a common soil of the Highland Rim physiographic province, found on broad, rolling ridge tops. These soils are formed in loess and typically are underlain by cherty clay. Native fertility of these soils is low but response to agricultural management practices such as liming and fertilization makes this soil very productive. The corn and pasture plots sampled were within 100 m of one another and the forest plot was about 500 m from the corn and pasture areas. Measurement plots for each land use were established on a 10 × 10 m area. The five measurement chambers were located at the four corners and one in the center of the square plot in order to assess small-scale spatial variability. Figure 5 shows a schematical layout of the chambers on a plot. In an attempt to better characterize temporal variability, two measurement campaigns were conducted on each of the land use types. The first site visit was from July 6 to August 12, 1991, and the second set of measurements were from November 15 to December 6, 1991.

No-till corn was planted in mid-April 1991 into unimproved pasture which was killed prior to planting by applying Gramaxone (paraquat) at a rate of 0.5 kg/ha (10,000 m^2) active ingredient. A broadcast application of bulk fertilizer delivered 111 kg of N, 66 kg of P, and 111 kg of K per hectare to the site prior to planting. The field was periodically limed to maintain soil acidity between pH 5.7 and 6.0. The pasture site had received no lime or fertilizer for several years and was one of several fields on the farm that was used in rotating cattle for grazing throughout the year.

For each measurement location and date, soil samples taken from the surface 15 cm of the soil profile were collected approximately 50 cm from two randomly chosen corners of each chamber. These samples were combined for each chamber location and analyzed by the University of Georgia soil test laboratory. Total soil N was determined by Kjeldahl digestion with H_2SO_4-salicylic acid and NO_3^--N and NH_4^+-N were extracted with 2N KCl and titrated. Soil cation determinations were made using Melich III procedures [*Melich*, 1984] followed by inductively coupled plasma (ICP) determination. Table 1 lists the results of the chemical analysis of the soil collected at the three measurement locations.

TABLE 1. Soil Chemical Properties of the Land Use Types for the Two Measurement Periods of the Soil NO Study in Giles County, Tennessee

Land Use	NO_3^-*	NH_4^+*	Ca*	Mg*	Organic† Matter	pH
			Spring 1991			
Corn	18.0	9.5	597.0	30.0	2.1	5.7
Forest	19.7	15.9	182.0	15.6	3.3	4.5
Pasture	26.7	14.4	685.0	57.0	2.2	5.5
			Autumn 1991			
Corn	13.0	16.0	784.0	38.0	2.5	6.1
Forest	13.7	25.9	265.0	23.7	3.9	5.2
Pasture	10.6	25.4	997.0	91.0	4.3	5.8

*Measurements given in milligrams per kilogram.
†Measurements given in grams per kilogram.

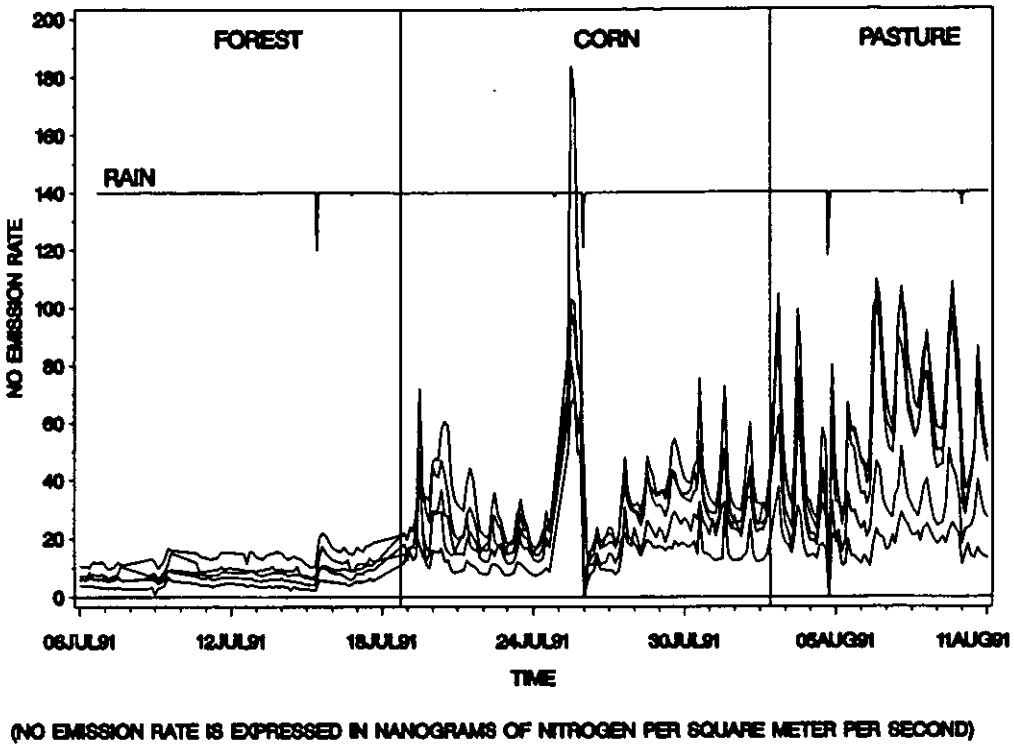

Fig. 6. Time series of soil NO_x emissions at Giles County, Tennessee, during summer measurements of 1991 at three land use plots. Rainfall is indicated by downward spikes on a horizontal line labeled "RAIN."

RESULTS AND DISCUSSION

Figure 6 shows the time series of NO emissions at the Giles County site during the summer 1991 measurements, and Table 2 summarizes the results for summer and fall. At this site, spatial variability is typically a factor of 3 from the lowest to the highest emitting chamber on a plot. (The spatial variability value in Table 2 is the difference between the highest and lowest emitting chambers on a plot expressed as a percentage of the mean emission rate for the five chambers on the plot.) Diurnal cycles in emission during the summer are strong for the corn and pasture (exhibiting swings of 100% or so from 0300 to 1500 LT) but very weak in the forest. Rainfall appears to have an effect that depends on both rainfall intensity and soil porosity. On the highly porous forest floor, even heavy rains of about 20 mm appear to enhance the emission rates; however, on the more compacted corn and pasture plots, rainfall events of 20 mm appear to seal off the soil pores and eliminate nearly all emissions. Interestingly, following a week with no rain, a very light rainfall event (2 mm) on the morning of July 25 produced a tenfold enhancement of the emission rate from the corn plot.

To investigate the influence of soil temperature on emissions at these locations, thermocouple probes were inserted,

TABLE 2. Statistical Summary of Soil NO Emission Measurements

	Forest	Corn	Pasture	Total
Summer 1991 Measurements				
Number of observations	375	550	365	1290
Mean soil temperature, C	22.6	26.2	27.3	25.4
Mean emission rate	8.4	27.0	44.1	26.4
Median emission rate	8.0	24.0	41.9	23.3
Standard deviation of emission rate	1.6	15.2	16.0	18.8
Coefficient of variation	19.7%	56.4%	36.4%	71.3%
Spatial variability	118%	85%	98%	98.4%
Fall 1991 Measurements				
Number of observations	188	168	219	575
Mean soil temperature, C	14.4	7.99	11.5	11.0
Mean emission rate	4.38	2.85	2.75	3.30
Median emission rate	4.27	2.45	1.13	3.44
Standard deviation of emission rate	0.637	1.18	3.47	2.42
Coefficient of variation	14.5%	41.4%	126.5%	73.1%
Spatial variability	85.3%	150.5%	148.1%	128.4%

NO emission rate statistics are expressed in ng N m^{-2} s^{-1}. Spatial variability is the range expressed as a percentage of the mean for five chambers.

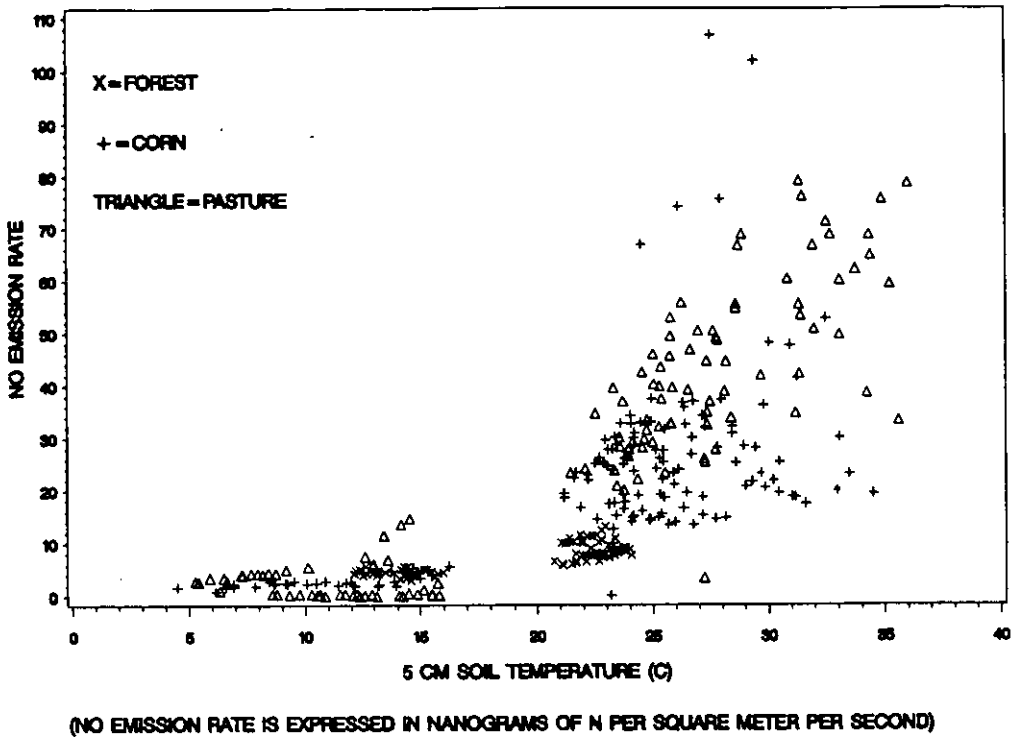

Fig. 7. Relationship between soil temperature at 5 cm and soil NO emission rate at the Giles County location. Data on the right-hand side of the plot are from summer 1991 and data on the left-hand side of the plot are from fall 1991.

and data were logged continuously for depths of 5 and 15 cm inside two of the chambers and at one location outside the chambers. The presence of the opaque chambers was found not to influence the soil temperatures at these depths (data not shown). The relationship between emission rate and soil temperature is shown in Figure 7. The relationship is exponential with temperature, in concurrence with observations of other investigators [*Williams et al.*, 1992*b*]. Table 3 shows the results of a regression analysis of the logarithm of the emission rate against the soil temperature (in degrees Celsius) of the form

$$\text{NO emission rate} = Ae^{BT} \qquad (6)$$

where the emission rate is expressed in ng N m^2 s^{-1}, T is the 5-cm soil temperature (in degrees Celsius), and A and B are the fitted parameters shown in (6).

Figure 8 compares the diurnal cycles of NO_x emission with the diurnal soil temperature cycles for the summer data from Giles County. The shade provided by the forest canopy greatly reduces the amplitude of the soil temperature cycle compared to the more open corn and pasture plots, with a similar pattern evident in the NO emission cycles. The large increases in emission rate that occur as soil temperatures rise to summertime values, suggests that the soil NO_x contribution to regional NO_x levels is likely to be most significant during the summer months, the period of interest for ozone episodes.

TABLE 3. Results of Linear Regression Analysis of the Logarithm of NO Emission Rate Versus 5-cm Soil Temperature

Land Use	Number of Observations	R^2	A	B
Forest	98	0.759	1.53	0.0758
Corn	144	0.679	0.753	0.130
Pasture	122	0.564	0.165	0.189
Overall	364	0.571	0.353	0.158

Land-use influenced soil NO_x emissions. The pasture had the highest mean emission rate (44.1 ng N m^{-2} s^{-1}), followed by corn (27.0 ng N m^{-2} s^{-1}), with the forest having the lowest rate (8.4 ng N m^{-2} s^{-1}). These findings are consistent with reports in the literature which report lower-emission rates for forest ecosystems than for managed agricultural systems such as row crops and pasture [*Anderson and Levine*, 1987]. The mean rate for the forest site is higher than previously reported measurements for temperate deciduous forests. Previous studies by *Williams and Fehsenfeld* [1991] and *Williams et al.* [1988] have reported mean emission rates of 0.28 and 1.2 ng N m^{-2} s^{-1} for forests in Tennessee and Pennsylvania, respectively. During the spring and early summer of 1992 we also evaluated soil NO emissions in an oak-hickory forest in Mississippi that averaged 0.05 ng N m^{-2} s^{-1} and an oak-hickory forest in the Appalachian Mountains of North Carolina that averaged 0.13 ng N m^{-2} s^{-1} [*Thornton and Valente*, 1992]. We are not certain why this particular forest site had higher emissions compared to these values cited in the literature. A possible explanation for greater NO emissions at this forest site are high-NO_3^- values for soil (19.7 and 13.7 mg NO_3-N kg^{-1} for the spring and autumn periods, respectively; see Table 1). These soil values are much greater than those typically reported for mixed oak forests of the southeastern United States (<0.01 to 1.0 mg NO_3^--N kg^{-1} [*Johnson and Todd*, 1987; *Van Miegroet et al.*, 1990] and may reflect export of N fertilizer via overland or subsurface flow from a fertilized hayfield immediately adjacent to and uphill from the forest measurement site. (The forest measurements were per-

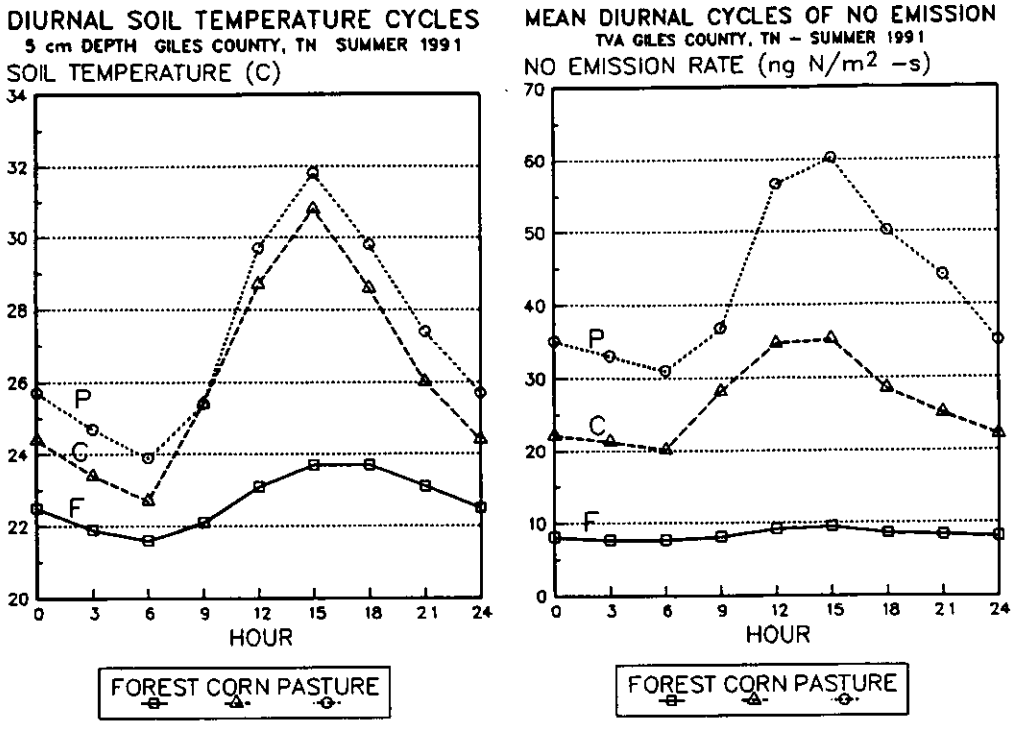

Fig. 8. Comparison of diurnal NO emission cycles with diurnal soil temperature cycles for three land uses at Giles County, Tennessee.

formed just inside the forested plot, about 40 m from the hayfield.) Another possible avenue for enhanced nutrient availability at this site results from the fact that cattle are occasionally permitted to traverse this forested plot enroute to watering areas and other pasture lands. These findings suggest that forested areas on the rim of agricultural lands may exhibit NO emission values different than and possibly higher than values found in more remote, undisturbed forested regions.

Emission rates similar to these have been reported in tropical forests. Mean emission rates of 7.8 and 10.2 ng N m^{-2} s^{-1} have been measured in Brazilian tropical forests [*Bakin et al.*, 1990; *Kaplan et al.*, 1988]. However, it is apparent that compared to crop or pasture land, forests do not appear to be a significant source of NO; a conclusion of *Williams et al.* [1992*b*] also made from their analysis of various sources in developing a national inventory of soil NO_x. They estimate that forest soils only contributed about 6% of the total NO_x flux for the United States, although forested land occupied 40% of total land area.

Soil NO_x values for the pasture and corn sites, when compared to previous measurements in the literature, also illustrate the wide divergence in emission rates that can be found at different sites. The mean emission rate for our pasture site was of an order of magnitude larger than those typically reported in the literature. *Galbally and Roy* [1978] found emission rates on an ungrazed pasture in Australia to vary between 0.6 and 2.6 ng N m^{-2} s^{-1} with a mean value of 1.6 ng N m^{-2} s^{-1}. However, in the same study, grazed pastures had twice the emissions of ungrazed areas; emission rates ranged from 1.5 to 7.3 ng N m^{-2} s^{-1} with a mean of 3.5 ng N m^{-2} s^{-1}. Recent studies by *Davidson et al.* [1991*b*] have also shown a significant increase ($p = 0.01$) in NO_x emissions from a grassland in California that was grazed compared to nongrazed sites (2.77 versus 0.77 ng N m^{-2} s^{-1} for the grazed and ungrazed sites, respectively). The higher-emission rates in the grazed systems are most likely due to the input of animal wastes that create areas of more favorable *C* and *N* regimes for soil microbes, resulting in NO_x emissions from both nitrifying and denitrifying activity. Previous estimates of NO_x emissions from temperate grasslands in the midwestern United States have also indicated lower emission rates, on average, than we report here [*Williams and Fehsenfeld*, 1991].

The mean value for the corn emissions at our site of 27 ng N m^{-2} s^{-1} is approximately one-third the average value of 94 ng N m^{-2} s^{-1} reported by *Williams et al.* [1988] from corn in Pennsylvania, and 4 times that of corn measured in Virginia by *Anderson and Levine* [1987]. The corn site exhibited the greatest variance in emissions rates of the three sites, ranging from a low of 0.5 to 185 ng N m^{-2} s^{-1}. *Williams et al.* [1992*b*] also reported large spatial variation (a factor of 50 or more) at several measurement locations they have studied. The greater emissions rates of *Williams et al.* [1988] may, in part, be explained by the higher soil nitrogen level at their site. Average NO_3^--N and NH_4^+-N soil levels in the study of *Williams et al.* [1988] were 82 and 22 ppm respectively; in the current study the average soil values were 18 and 9.5 ppm, respectively. Simple correlation coefficients were obtained to represent the relationship between soil NO_3^--N and NH_4^+-N and soil NO_x efflux. These results indicated a weak positive relationship for nitrate ($R^2 = 0.33$, $p = 0.007$) and ammonium ($R^2 = 0.20$, $p = 0.01$). When the data were segregated to represent the fall and summer sampling periods, in an attempt to partition the temperature effect, no significant correlations ($p > 0.05$) were found. These results are very similar to the findings of *Anderson and Levine* [1987], who reported cor-

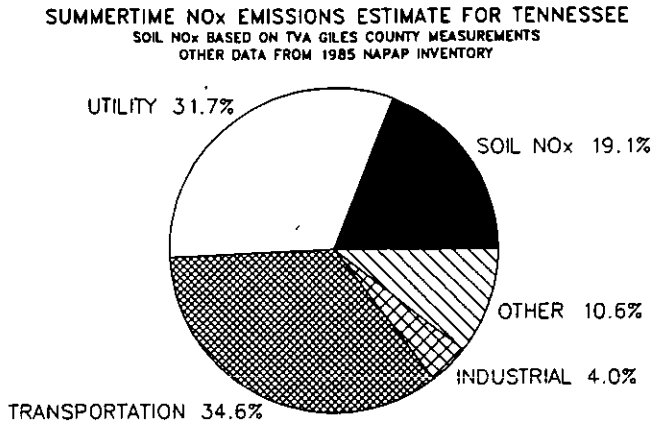

Fig. 9. Comparison of summertime NO_x emissions for Tennessee, assuming that soil NO measurements at Giles County represent the entire state.

relation coefficients of 0.25 to 0.33 for soil NO_x emissions with various soil parameters for a soybean field in Virginia.

Finally, in order to make a preliminary estimate of the relative importance of summertime soil NO_x emissions in this region as compared with other sources, we have extrapolated the measurements at Giles County to the entire state of Tennessee, making the admittedly tenuous assumptions that these three plots represent all the crop, pasture, and forest plots in the state and calculating a weighted average emission rate based on the distribution of these three broad land use categories in the state. Then the National Acid Precipitation Assessment Program (NAPAP) 1985 [*Placet et al.*, 1990] emission inventory was employed for an estimate of utility, transportation and other sources in the state. We also used a more conservative value for the forest emissions term than the Giles data would suggest because we believe that the data from Giles County are probably at the upper end of the range expected in forests in the state. Our forest value of 8.1 ng N m^{-2} s^{-1} was significantly higher than those cited in the literature [*Williams and Fehsenfeld*, 1991; *Williams et al.*, 1988; *Thornton and Valente*, 1992]. Using a more conservative value of 1 ng N m^{-2} s^{-1} for forests, the overall contribution to the biogenic component dropped from 22.2 to 19.1%. As Figure 9 shows, these measurements suggest that summertime soil emissions are a significant term in the total tropospheric NO_x budget. For example, this estimate suggests that soils may be emitting about 60% as much NO_x as all utilities in the state during the summer. Also, in an effort to characterize the variance of these biogenic estimates, we calculated the estimated emission rates at one standard deviation above and below the means for each land use category. These results indicated that the biogenic component could range from 25.9% (+1 s.d.) to 12.3% (−1 s.d.) of the total inventory. This upper estimate has significance in that on hot summer days when soil temperatures are high, one would expect biogenic NO to be particularly important. We stress that the purpose of all these estimates is to assess the potential importance of soil NO emissions and emphasize that considerable additional work is needed to lessen the uncertainty implicit in scaling up a small spatial sample to an entire region.

Clearly, soil emissions need to be considered when developing improved models of summertime ozone photochemistry. The preliminary estimates we have presented obviously include considerable uncertainty; nevertheless they point out the importance of improving these estimates by sampling more soil types and land use plots in the region. Future work should also include micrometeorological measurements to compare NO_x flux from the soil with flux at the top of the crop or tree canopy so that chemical conversion of NO to NO_2 and possible redeposition to plant surfaces may be considered to improve the estimates of soil emissions to the atmospheric boundary layer. Current plans at TVA call for chamber measurements from at least six sites in the region during the next 3 years.

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