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ENVIRONMENTAL VARIABLES CONTROLLING NITRIC OXIDE EMISSIONS FROM AGRICULTURAL SOILS IN THE SOUTHEAST UNITED STATES

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Abstract—Fluxes of nitric oxide (NO) were measured during the summer of 1994 (12 July to 11 August) in the Upper Coastal Plain of North Carolina in a continuing effort to characterize NO emissions from intensively managed agricultural soils in the southeastern United States. Previous work during a similar time of year on the same soil type was characterized by severe moisture stress conditions. The summer of 1994 provided a more diverse weather pattern and as a result represented a set of measurements more typical of soil temperature and soil moisture relationships for the southeastern United States. In order to ascertain NO flux response to fertilization and crop type, measurements were made on fields with three distinct fertilizer practices and crop types, namely corn, cotton, and soybean. Average NO fluxes were 21.9 ± 18.6, 4.3 ± 3.7, and 2.1 ± 0.9 ng N m^{-2} s^{-1}, respectively, for corn, cotton, and soybean. NO flux increased exponentially with soil temperature when soil water content was not limiting [> 30% Water Filled Pore Space (%WFPS)]. During conditions when soil water content was limiting, NO flux was inhibited and had no relationship with soil temperature. Above a value of 30% WFPS, increasing soil water content had no effect on NO emissions (the upper limit of %WFPS could not be estimated due to a lack of data in this regime). Below 30% WFPS, increasing soil moisture increased NO production and lower soil moistures led to decreased NO flux. Increased nitrogen fertilization rates led to higher NO fluxes. However, differences in physiological growth stages between crops confound extractable nitrogen values as decomposing root biomass in the mature corn crop added an undetermined amount of available nitrogen to the soil. Interactions between soil water content, fertilizer application, and soil temperature make it very difficult to predict day-to-day variations of NO flux from our data. There appears to be no simple relation between NO flux and the environmental variables measured in Clayton, NC during the summer of 1994. Copyright © 1996 Elsevier Science Ltd

Key word index: Natural emissions, nitric oxide, environmental variables.

INTRODUCTION

The role of reactive nitrogen species in atmospheric chemistry and their relation to ozone formation are now well understood (Aneja *et al.*, 1996). However, despite regulation of ozone (O_3) precursors for the past 30 years, there has not been the reduction of ozone episodes that was once hoped for (National Research Council, 1991). Part of the problem in quantifying and modeling ozone is the uncertainty of the NO_x(=$NO + NO_2$) budget (National Research Council, 1991). Global estimates of NO_x sources are equally distributed between natural and anthropogenic emissions (Watson *et al.*, 1992). Of particular attention is that portion of the NO_x budget which is attributed to emission of nitric oxide (NO) from soils. Logan (1983) quantified emissions of NO from soil to be 50% of all natural emissions of NO_x, while Ehalt and Drummond (1982) estimated soil emissions to be 25% of all NO_x natural emissions. It is this uncertainty in the NO budget, and its relation to O_3, that motivates a need for measurements and modeling of NO flux from soils. The southeastern United States (U.S.) is NO_x limited, which means an increase of NO emissions into the atmosphere will lead to increased O_3 production (SOS, 1993). A careful inventory of the flux of NO from soils in the southeastern U.S. may help to explain the high values of O_3 seen in semi-rural areas.

There have been numerous measurements of NO flux from various ecosystems with fertilized plots (Galbally and Roy, 1978; Johansson and Granat,

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1984; Anderson and Levine, 1987; Parrish *et al.*, 1987; Kaplan *et al.*, 1988; Williams *et al.*, 1988; Bawkin *et al.*, 1990; Davidson *et al.*, 1991; Shepherd *et al.*, 1991; Slemr and Seiler, 1991; Williams and Fehsenfeld, 1991; Williams *et al.*, 1992a, b; Skiba *et al.*, 1992; Cardenas *et al.*, 1993; Valente and Thorton, 1993; Jambert *et al.*, 1994; Sanhueza *et al.*, 1994; Serca *et al.*, 1994; Kim *et al.*, 1994) but relatively few have addressed the emissions from agriculturally managed fields. The researchers who have studied NO flux from fertilized row crops (Anderson and Levine, 1987; Williams *et al.*, 1988; Valente and Thorton, 1993; Jambert *et al.*, 1994; Aneja *et al.*, 1995) have noted several factors that control the emissions of NO from these fields. The three most reported environmental variables that control NO flux from soils are soil temperature, soil water content, and application of N (nitrogen based) fertilizer. The objective of this study was to measure the flux of NO from agriculturally managed soil typical of the Upper Coastal Plain of North Carolina during the summer season and to relate this flux with certain soil characteristics (soil temperature, soil water content, and applied N fertilizer).

METHODS AND MATERIALS

Sampling site

Flux measurements were made at the Central Crops Research Station (~105 m MSL) which is owned by the North Carolina Agricultural Research Service and operated by North Carolina State University. This facility is located approximately 14 miles east–southeast of Raleigh, NC, on the border of Wake and Johnston counties, in the Upper Coastal Plain of NC. The research station is accessible by U.S. Route 70 which bisects the farm in a general northwest–southeast pattern. The dominant soil type in each of the fields sampled is Norfolk sandy loam (Fine-Loamy, Siliceous, Thermic Typic Paledult; Daniels *et al.*, 1984). One type of each field was sampled containing a different row crop (corn, cotton, and soybean) grown using fertilizer rates and management techniques representative of those commonly used by farmers throughout the Coastal Plains region of the southeastern United States. During the extent of this measurement period the Clayton research station did not irrigate any of the fields in which NO flux was measured. The three crops were not at the same vegetative growth stage during the measurement period. The cotton crop was measured from 12 July to 26 July 1994 just as the plants were beginning to flower. The soybean crop, measured from 31 July to 4 August 1994, was in a vegetative stage and did not flower for another month. The last crop studied, corn, was measured from 7 August to 11 August 1994 and was ready to be harvested as corn grain.

Planting and fertilizer management

The amount of fertilizer applied during the 1994 growing season is based upon records maintained by the supervisor of the Central Crops Research Station. Prior to planting in the spring of 1994 the cotton and corn fields received a broadcast fertilizer application of 27 kg N ha^{-1}, with corn being fertilized on 15 March 1994 and cotton on 26 April 1994. The fertilizer was applied to the top of the soil in the form of granules in a blended, ammonia-based fertilizer (formulation: 6-6-36, 6% nitrogen in the form of ammonia, 6% phosphorous, and 36% potassium, source: Southern States Inc.). After application, the fertilizer was disked into the soil prior to preparation of the planting beds. Because of a tillage pan which occurs at a depth of 20–30 cm, a ripper-bedder was used to allow root penetration into the subsoil and increase rooting volume. Seeds were planted in the center of each bed, with approximately 1 m spacing between beds and 30 cm spacing between plants. The planting dates for corn and cotton were, in order, 18 April 1994 and 28 April 1994. The corn crop received two side dressings of fertilizer consisting of two bands of fertilizer on either side of the planting mound. This first side dressing was applied on 3 May 1994 at a rate of 114 kg N ha^{-1} (formulation 34-0-0; ammonium nitrate based). The second side dressing was applied on 25 May 1994 at a rate of 34 kg N ha^{-1} (formulation 34-0-0; ammonium nitrate based). The cotton crop also received two side dressings of fertilizer at a rate of 27 kg N ha^{-1} (formulation 12-6-24; ammonia based). The fertilizer dates were 9 June 1994 and 17 June 1994, respectively. The soybean crop received no fertilizer during the 1994 growing season, but the plot had been fertilized the previous year. The planting date for the soybean crop was 24 May 1994.

Soil analysis

Bulk soil chemical properties from each of the three fields were obtained from composite soil samples submitted to the Agronomic Division of the North Carolina Department of Agriculture (Table 1). These included humic matter content based on a 0.2 M NaOH extraction, extractable base cations using a solution composed of 0.2 M CH_3COOH, 0.25 M NH_4NO_3, 0.015 M NH_4F, 0.013 M HNO_3, and 0.001 M EDTA, and exchangeable acidity using a buffer solution. Effective cation exchange capacity (ECEC; expressed on a volume basis) was obtained by summing extractable cations and exchangeable acidity. Base saturation of the ECEC was determined by (ECEC-exchangeable acidity)/ECEC. Soil bulk density for the 0 to 15 cm depth ($n = 10$) was determined using the core method (345 cm^3) near each chamber sampling point in each field (Blake and Hartge, 1986). Total soil water content and extractable ammonium (NH_4^+) and nitrate (NO_3^-) (2 M KCl; expressed on a weight basis) were determined on composite soil samples collected from the inside of the chamber using a bucket auger (0–20 cm depth) at the end of each measuring period. Total soil water content was calculated as (initial weight − oven dry (105°C) weight)/oven dry weight. NO_3^- and NH_4^+ in the 2 M KCl extract (Keeney and Nelson, 1982) were determined using standard auto analyzer techniques (Lachat Instruments, 1990). Total soil water content at 15 and 0.1 bar was determined from soil moisture release curves using a pressure plate (Klute, 1986) and used as estimates of "permanent wilting point" and "field capacity", respectively (Cassel and Nielsen, 1986). The average values listed in Table 1 are based on numerous soil samples collected over the past ten years at the Central Crops Field Laboratory (D. Cassel, Department of Soil Science, North Carolina State University, personal communication).

Flux measurements

Utilizing an open bottom, flow through, dynamic chamber technique (Aneja *et al.*, 1995), NO flux measurements were made from 12 July to 18 August 1994. Four experiments were run in each of the three crops, lasting 12 h each (6:00 AM–6:00 PM). These measurements were conducted on four randomly selected plots (2 m × 2 m) within the range of a mobile laboratory (≈154 m^2 sampling area). The night before each experiment, the chamber was inserted into the soil within the row after removing the minimum amount of plants necessary by cutting the stalks at the soil surface. This process was done in such a way as not to alter the canopy above the chamber, leaving the flux chamber within leaf coverage. Ambient air was passed through the chamber

Table 1. Physical and chemical soil parameters determined for each research field. Soil type: Norfolk sandy loam (Fine-loamy, Siliceous, Thermic, Typic Paledult)

Parameter	Unit	Soybean	Cotton	Corn
pH		5.7	6.2	6
ECEC[a]	meq 100 cm^{-3}	2.5	3.2	2.7
Base saturation[b]	% (by volume)	84	87	85
Acidity	meq 100 cm^{-3}	0.4	0.4	0.4
Humic matter[c]	% (by volume)	0.5	0.5	0.5
Bulk density[d]	g cm^{-3}	1.73 (0.08)	1.67 (0.14)	
Water content[e]				
"wilting point"	% (by weight)	2.8	2.8	2.8
"field capacity"	% (by weight)	10.8	10.8	10.8
N application	kg N ha^{-1}	0	81	168

[a] Sum of extractable base cations.

[b] Sum of extractable base cations as % ECEC.

[c] 0.2 M NaOH extractable humic matter.

[d] Standard deviation in parentheses.

[e] D. Cassel, Department of Soil Science, North Carolina State University, personal communication.

during the 12 h before the experiment to eliminate NO accumulation in the chamber that might have effected NO production in the soil. One and a half hours before startup, zero air was started through the chamber at 4 liters per minute (l min^{-1}) and the sample line was hooked up to the NO analyzer in order to let the chamber equilibrate before readings were taken in the experimental run. Zero air was used as the flush gas for this experiment to eliminate reactions in the flux chamber and to lessen the effect of humidity on the detection of NO concentration (Parrish *et al.*, 1987; Kaplan *et al.*, 1988; Williams *et al.*, 1992b).

The soil temperature was measured via a Fisher digital meter attached to a probe buried (5 cm depth) adjacent to the chamber. Air temperature was evaluated utilizing the same digital meter and an air temperature probe hanging off of the chamber surface. The air temperature probe was shielded from direct sunlight by the plant canopy and was at chamber height (42 cm). At the conclusion of each experiment the chamber was removed and a soil sample was taken from the center of the chamber footprint.

Instrumentation

Analysis of the chamber NO concentration was carried out by using a Thermal Environmental Instruments Incorporated (TECO) Model 42S chemiluminescent high sensitivity NO analyzer (Thermal Environmental Instruments, Inc., 1992). Calibration of this instrument was carried out following written protocols using a TECO 146 gas dilution/titration instrument, a mixture of 589 pptv NO in N_2 (Scott Specialty Gases, Inc., Plumsteadville, PA), and compressed zero air (National Welders, Raleigh, NC). A multipoint calibration was performed before the summer intensive and the instrument was zeroed and then spanned to 15 ppbv before each experiment. The TECO 42S NO analyzer was housed in a mobile laboratory (modified Ford Aerostar van). Temperature inside the mobile laboratory was controlled by a 13,500 Btu air conditioning unit and maintained at 30°C ± 2°C. A laptop computer using Labview software acted as a chart recorder and data collection system. This system yielded 60 s rolling average NO measurements and 15 min binned averages of chamber NO readings. Fifteen min binned averaged values of all data were used in the data analysis.

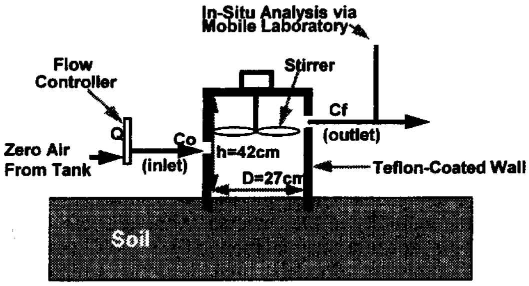

Fig. 1. A schematic of the dynamic flow-through chamber used for measuring the flux of NO from soils. The walls and all internal surfaces are fluorinated ethylene propylene (FEP) Teflon.

Chamber design and operation

A cylindrical dynamic flow through chamber (diameter = 27 cm, height = 42 cm, and volume = 25 l) constructed from a polycarbonate material was used for flux measurements (Fig. 1). Five mil (0.005 in) thick fluorinated ethylene propylene (FEP) Teflon was used inside the chamber to reduce the loss of NO to the walls of the chamber. The chamber was held in place by a stainless steel ring driven into the ground to a depth of approximately 10 cm. Zero air (0% hydrocarbons, 0% humidity, 0% NO) was flushed through the chamber at a flow rate of 4 l min^{-1} and the internal air volume was well mixed by a motorized Teflon stirrer (≈20 cm diameter at 100 rpm). The outlet port of the chamber was connected to a TECO Model 42S NO analyzer through a PFA Teflon sample line (1/4" O.D., 1/8" I.D.). The sample line was approximately 15 m long resulting in a maximum residence time of 70 s.

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 is the soil surface area covered by the chamber, V the volume of the chamber, Q the flow rate of carrier gas through the chamber, J the emission flux, C is the NO concentration in the chamber, $[C]_0$ is the NO concentration at the inlet of the chamber, $[C]_f$ is the NO concentration at the outlet of the chamber, L is the loss term by chamber wall per unit area assumed first order in $[C]$ and R the chemical production/destruction rate in the chamber.

Because of the use of zero air there is no inlet concentration of NO and no chemical reactions in the chamber to produce/destroy NO. For a well-mixed chamber $[C]_f$ may be assumed to be equal to the NO concentration everywhere in the chamber. Finally, at steady state the change of concentration with regards to change in time goes to zero and the above equation reduces to

$$J = [C]_f \left[\frac{Q}{A} + L\right]. \qquad (2)$$

The wall loss term used in this calculation was set equal to 0.02 cm s^{-1}. This value was obtained by using the combined surface loss as proposed by Kaplan *et al.* (1988).

Chamber effects

Due to the nature of the flux chamber used in this experiment there were two unavoidable consequences, a raising of the temperature in the chamber ("greenhouse effect"), and increased humidity in the chamber and sample lines. Experiments were done to compare air and soil temperatures on the inside and outside of the chamber. On average the difference in air temperature inside and outside the chamber was 3.77 ± 2.52°C. Flux values calculated with these temperatures were only 1.6% smaller than those calculated without temperature correction. On average the difference in soil temperature on the inside and outside of the chamber was 0.23 ± 1.0°C.

The flux chamber also created increased humidity (100%) in both the sample lines and the chamber itself. To help alleviate this problem, zero air was used in an attempt to lessen the humidity in the chamber. Although zero air decreased the moisture accumulation in the sample lines, there was still moisture (droplets) present in the sample lines throughout each experimental run. To study the effect of moisture on the measurement of NO concentrations, the TECO analyzer in this experiment was spanned to a known concentration of NO with a short (< 1 m), dry sample line and then spanned to the same concentration utilizing a long (20 m), wet (water droplets present) sample line. These measurements showed no loss of sensitivity to NO measurement using long sample lines that contain heightened humidity. These results corroborate findings of other researchers on the effect of moisture on NO sampling. Kaplan *et al.* (1988) and Williams *et al.* (1988) observed moisture (100% humidity) either does not affect the measurement of NO or may lead to a slight decrease in NO measurement and thus produce a conservative estimate of NO emissions.

RESULTS AND DISCUSSION

Site characterization

At the start of the measurement period, a high-pressure system existed over central North Carolina producing consistently high daily mean temperatures and very little rainfall. A cold front moved through Clayton, NC on 29 July 1994. As a result, average soil temperature decreased during the measurement period (12 July–11 August 1994) (Fig. 2). However, when sampling within a given crop, average soil temperature increased daily, differing by as much as 4°C between the first and last measurements. Although each crop's mean soil temperature is in the 15–35°C range proposed by Williams and Fehsenfeld (1991) for maximum NO flux, the non-uniform conditions between crops may contribute to differences in the response of NO flux to soil temperature.

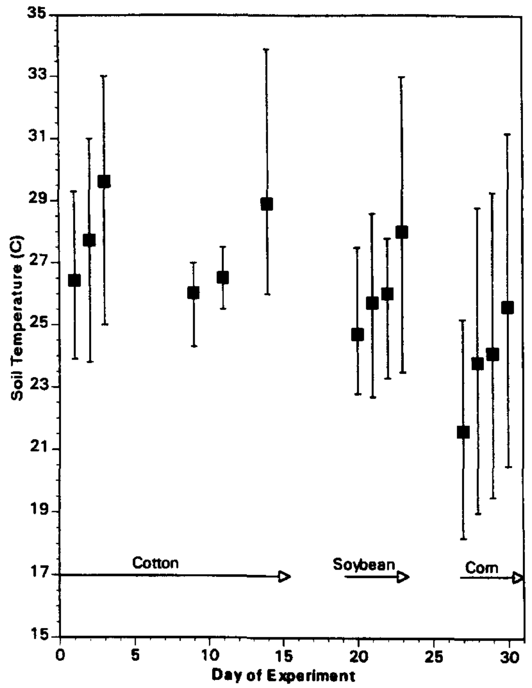

Fig. 2. Graph of average soil temperature vs day of experiment. Experiments were run from 12 July–13 August 1994. Error bars are indicative of minimum and maximum temperature for each day measured.

The change in soil water content during the measurement period is shown in Fig. 3. No measurable amounts of precipitation had fallen at the study site for approximately one month before the start of the measurement period. As a result the first 10 days of the experiment were characterized by a low soil water content (< 3%). A thunderstorm on day 10 of the experiment (21 July 1994) and a rain event on 29–30 July 1994 were the only significant sources of moisture added to the soil during the extent of the measurement period. The effect of these rain events was to increase the amount of moisture in the soil, particularly for flux experiments in the soybean crop.

Several researchers have commented on the role of soil moisture on NO flux (Anderson and Levine, 1987; Davidson, 1991; Slemr and Seiler, 1991; Cardenas *et al.*, 1993; Valente and Thorton, 1993). These researchers generally agree that there is a range of soil moisture for optimum NO flux. A paucity of soil moisture leads to moisture stress for soil microbes and a decrease in NO flux. Too much soil moisture and the physical transport of NO gas to the surface of the soil is hindered as water fills all available pore space. Cardenas *et al.* (1993) put the range of optimum soil water content for NO flux at 9–18% for sandy loam soils (bulk density 1.59 g cm^{-3}). For the Clayton, NC

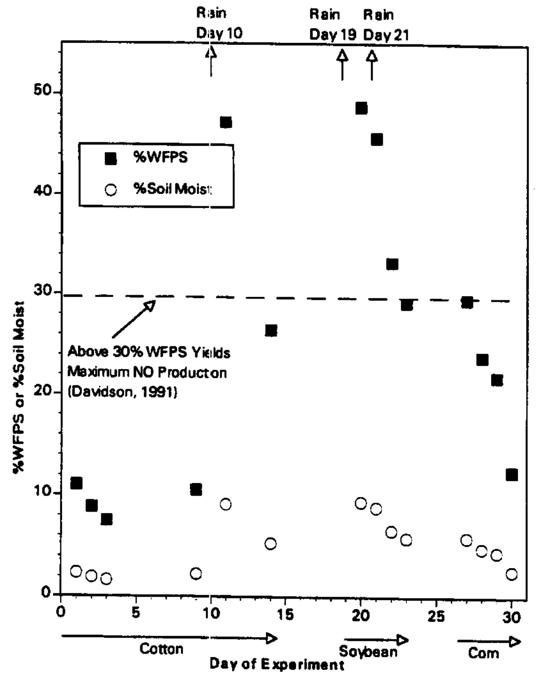

Fig. 3. Change in percent water filled pore space (%WFPS) or soil water content over the length of the experiment and its relation to rain events and percent soil moisture content (Day 1 = 12 July 1994; Day 31 = 13 August 1994).

soils, soil water content at field capacity is approximately 12%, which is typical for the sandy surface horizons for soils of the southeastern U.S. The fact that this value is near the lower limit cited by Cardenas *et al.* (1993) illustrates the difficulty in predicting NO flux across soils of differing texture using soil water content expressed as a percentage. A more suitable expression of soil water content is percent water filled pore space (%WFPS) (Davidson, 1991). The calculation of %WFPS utilizes the soil water content measurement but standardizes the amount of space water occupies in the soil by accounting for each soil's differing bulk density. By using %WFPS, confounding factors between soils (particle density, pore space, and bulk density) are reduced and the effect of water content on NO flux from differing soil types can be compared more readily.

Davidson (1991) has proposed a model of NO production from soils in which optimum %WFPS for NO flux is 50%, although no significant change of NO flux is to be expected between 30 and 70% WFPS. During the summer measurement period in Clayton, NC, the flux measurements in the soybean crop were in the optimum zone for NO production, while flux measurements for corn and cotton were made when the soil water content were below Davidson's optimum range of %WFPS. Because of the difference of %WFPS between crops, the effect of %WFPS on NO flux from cotton and corn will be more pronounced than its effect on NO flux from the soybean crop.

Several other differences besides soil temperature and soil moisture existed between the three crops. The NO flux from the corn crop was measured approximately two and a half months after the last application of fertilizer while the cotton crop was measured one and a half months after the final side dressing of fertilizer was applied. This difference in time since fertilizer application should be considered when examining the effect of fertilizer on NO flux from the different crops. The three different crops also represented three distinct physiological growth stages. The soybean crop was in a vegetative growth stage; cotton was in flower; and the corn crop was ready for harvest as corn grain. Because the corn crop had completed its growth, the root biomass was beginning to decompose and release available nitrogen back into the soil. As a result, the exact source of nitrate and ammonium in soil collected from the corn crop is in doubt. A portion of the available nitrogen is from root mineralization while a portion is from residual fertilizer.

Daily flux measurements

NO flux increased with increasing amounts of applied fertilizer. The average fluxes from the corn, cotton, and soybean fields were 21.9 ng N m^{-2} s^{-1} (range 7.1–106.2 ng N m^{-2} s^{-1}), 4.3 ng N m^{-2} s^{-1} (range 0.0–15.3 ng N m^{-2} s^{-1}), and 2.1 ng N m^{-2} s^{-1} (range 0.4 to 5.9 ng N m^{-2} s^{-1}), respectively. The corresponding total fertilizer application rates for the fields were 168 kg N ha^{-1} (corn), 81 kg N ha^{-1} (cotton), and 0 kg N ha^{-1} (soybean). Although there was a definite increase of NO emissions with increasing fertilizer, the nature of that increase does not appear to be linear. A doubling of fertilizer from cotton to corn led to a five fold increase of NO flux. This result shows that the relation between fertilizer and NO flux could possibly be exponential. However, there are several confounding factors that may have effected the role of fertilizer on NO flux. The two most important among these are the drought conditions that existed in cotton during the first half of the measuring period (Fig. 2) and the interaction between NO flux and crop type. Differing amounts of root biomass, age of root biomass, and differing growth stages of the crops sampled, probably have a significant effect upon the apparent influence of nitrogen fertilization on NO flux.

Figures 4a–c show the daily variation of NO flux through the summer period of 1994 for each crop. The effects of soil water content and soil temperature can be seen in each figure. For the corn and soybean crops the emission of NO from the soil closely follows an increase in soil temperature. Typically, NO flux exhibits a profile that tracks soil temperature with a maximum NO flux occurring in the mid-afternoon corresponding to the highest soil temperature. The response of NO flux to an increase in soil temperature has been observed by several other researchers (Williams *et al.*, 1988; Shepherd *et al.*, 1991; Slemr and Seiler, 1991; Valente and Thorton, 1993; Kim *et al.*, 1994). The daily average NO flux between soybean measurements were very close, while the daily average NO flux in the corn crop was more varied. The probable reason for this response was the water content in the soil. According to Davidson (1991) (Fig. 3) the soybean crop was in a %WFPS regime in which the maximum NO production from soils would be expected. The %WFPS data for the corn crop fall below the predicted optimum moisture regime and this may have resulted in more variation in mean daily NO flux. Contrary to the other two crops, the NO flux from the cotton crop did not correlate well with soil temperature. The reason for this difference was probably the low soil water content for the majority of NO flux measurements from the cotton crop. At the beginning of the cotton measurement period (Figs 2 and 3) the %WFPS in the cotton crop was very low due to lack of rainfall conditions. The measurements of NO flux done during this period show no relationship to temperature and only after soil moisture content increased did the fluxes from the cotton crop seem to respond to changes in soil temperature. As with the corn crop, the %WFPS of the cotton crop is below the optimum %WFPS regime predicted by Davidson's model (1991). As a result,

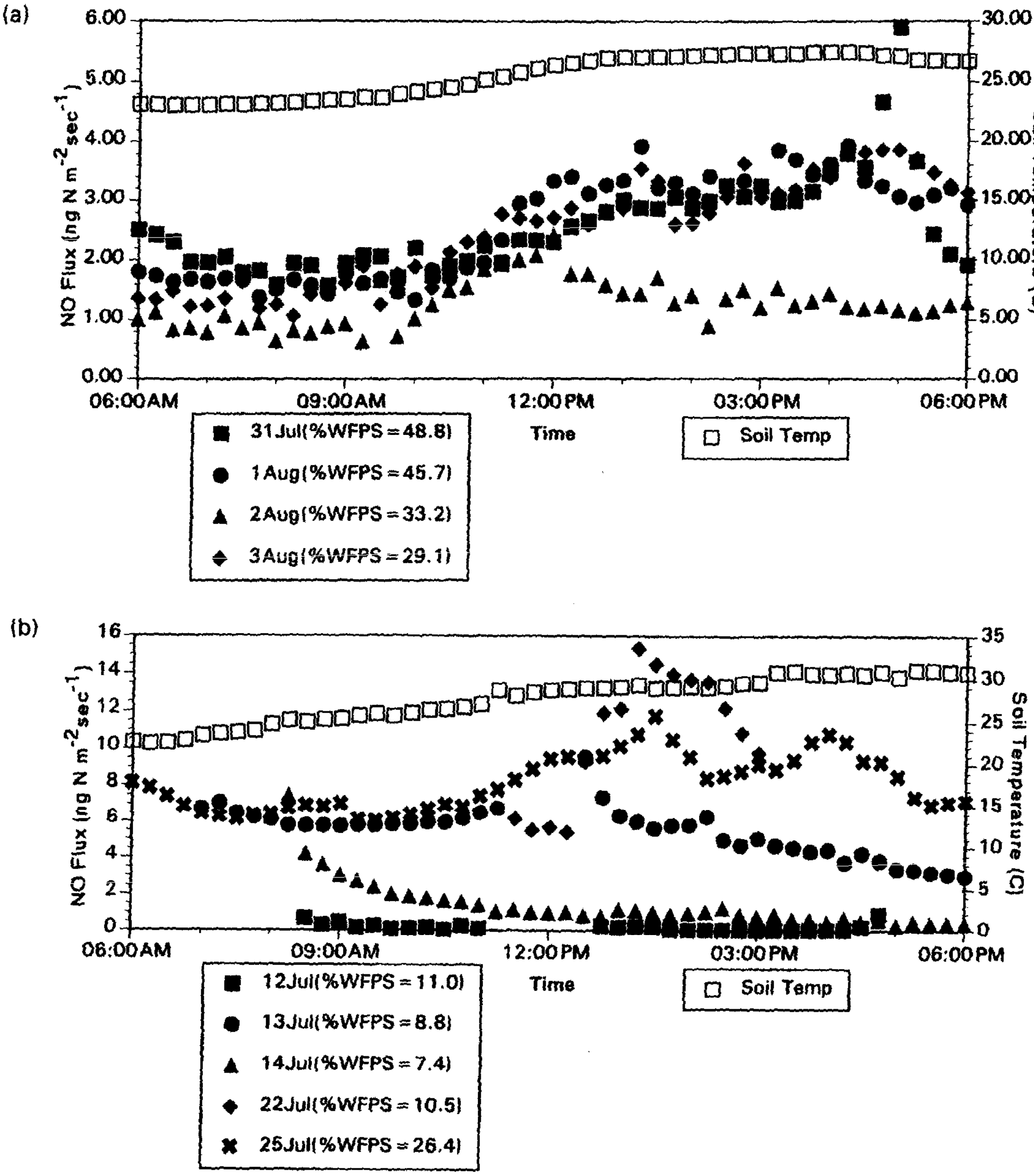

Fig. 4. Graph of NO flux versus time of day for all experiments in a soybean, cotton and corn crops during the summer of 1994. Percent water filled pore space (%WFPS) for each day of measurement can be seen in the legend. Soil temperature is averaged over: (a) four days of measurements in the soybean crop; (b) five days of measurements in the cotton crop; and (c) four days of measurements in the corn crop.

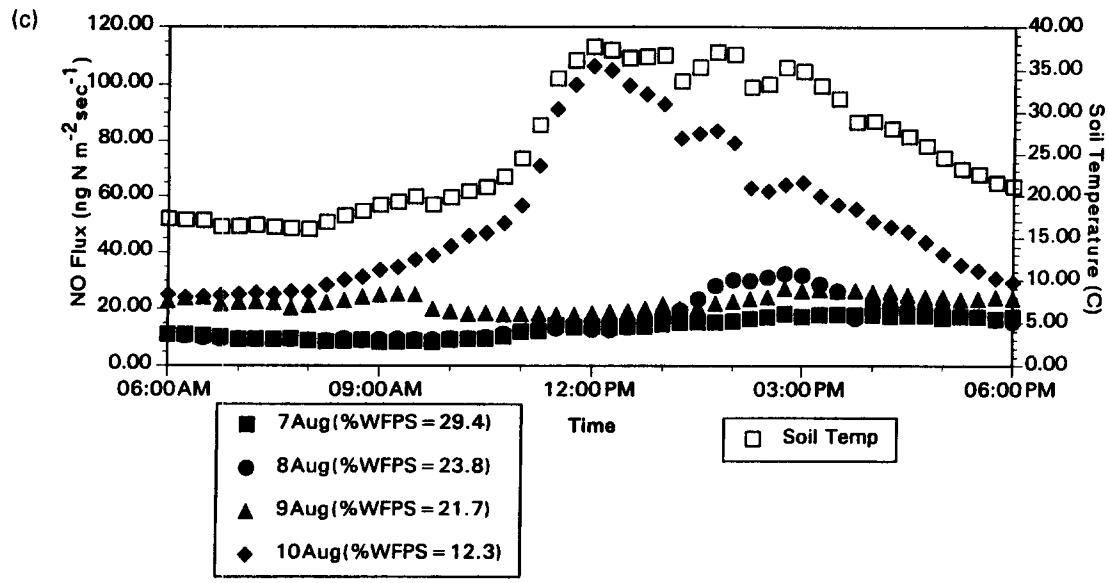

Fig. 4. (Continued.)

Table 2. Results of researchers using chamber techniques on agriculturally managed soils. Units of NO flux are $\mathrm{ng\,N\,m^{-2}\,s^{-1}}$

Crop	Flux ($\mathrm{ng\,N\,m^{-2}\,s^{-1}}$)	Source
Soybean	0.7–9.4	Anderson and Levine (1987)
	3.8	Aneja *et al.* (1995)
	2.1 ± 0.9	This paper
Cotton	1.8	Aneja *et al.* (1995)
	4.3 ± 3.7	This paper
Corn	5.84–67	Anderson and Levine (1987)
	5.56–239	Williams *et al.* (1987)
	27	Valente and Thorton (1993)
	36.4–54.7	Jambert *et al.* (1994)
	8.1	Aneja *et al.* (1995)
	21.9 ± 18.6	This paper

relatively small changes in soil water content may have significant effect on average daily NO flux.

The flux values obtained by this research and other similar measurements on agricultural soils works are summarized in Table 2. In general, there is a reasonable amount of agreement between researchers doing NO flux measurements from agricultural soils. The average flux values listed represent daytime fluxes from varying locations around the globe. The scatter in daily fluxes between researchers can be explained by differing soil moisture, temperatures, and soil types used in the measurements. As each crop differed within the Clayton, NC measurement period, so too did the site characteristics of each of the experiments listed in the table. As each of the measurements studied were observationally based it is reasonable to assume a large scattering of flux values due to differing air–soil systems present in each experiment.

SOIL PARAMETERS

Soil temperature

The effect of soil temperature on emission of NO from agriculturally managed soil was modeled as an exponential function as suggested by several other investigators (Williams *et al.*, 1988; Shepherd *et al.*, 1991; Slemr and Seiler, 1991; Valente and Thorton, 1993). The results of this analysis are presented in Fig. 5. In the soybean and corn crop, NO flux increased exponentially as soil temperature increased [corn, $\log(\text{flux}) = 0.236 + 0.236(T_s)$, $R^2 = 0.73$; soybean, $\log(\text{flux}) = -1.32 + 0.06(T_s)$, $R^2 = 0.74$]. For the cotton crop, NO flux decreased exponentially with soil temperature [$\log(\text{flux}) = 2.28 - 0.06(T_s)$, $R^2 = 0.42$]. The decrease in NO flux with increase in soil temperature is associated with soil moisture stress. The %WFPS in the cotton crop was very low through four of the six days in which NO flux was measured (average %WFPS = 19%). Segregating the NO flux measurements for cotton according to soil water content (Fig. 5) reveals a positive slope with soil temperature [$\log(\text{flux}) = -6.9 + 0.57(T_s)$, $R^2 = 0.86$] when %WFPS > 16%. A decrease in NO flux at high (> 33°C) soil temperature was also observed by Aneja *et al.* (1995) during periods of soil moisture stress. In this study the data demonstrate the strong interaction between soil temperature and soil water content on NO flux in soils with a sandy to sandy loam surface texture.

The dependence of NO flux on temperature also varied by an interaction with soil fertilizer. The flux value in the corn crop increased approximately four times faster than the flux value in the soybean and cotton crops. This phenomenon may be the result of a larger, more easily accessible nitrate source for microbial activity that is heightened by increased fertilizer addition.

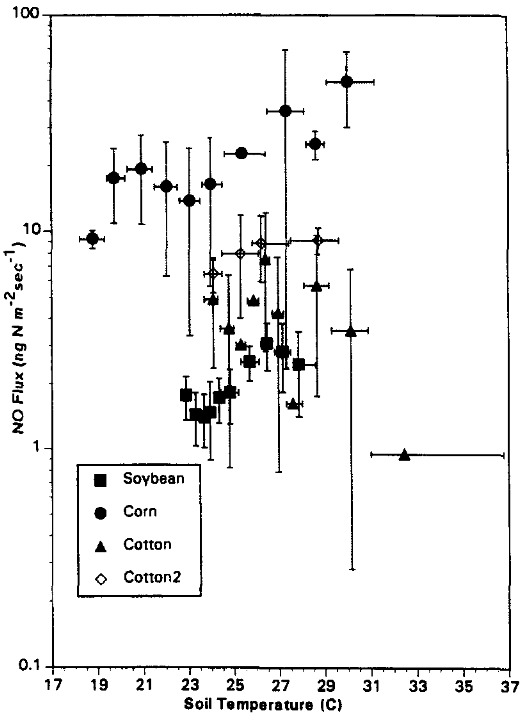

Fig. 5. Plot of NO flux vs soil temperature. Vertical lines indicate 1 standard deviation of the average NO flux, measured over the soil temperature range spanned by the horizontal bars. Points labeled as cotton include all data from the cotton crop. Cotton 2 points include only non-moisture stressed data.

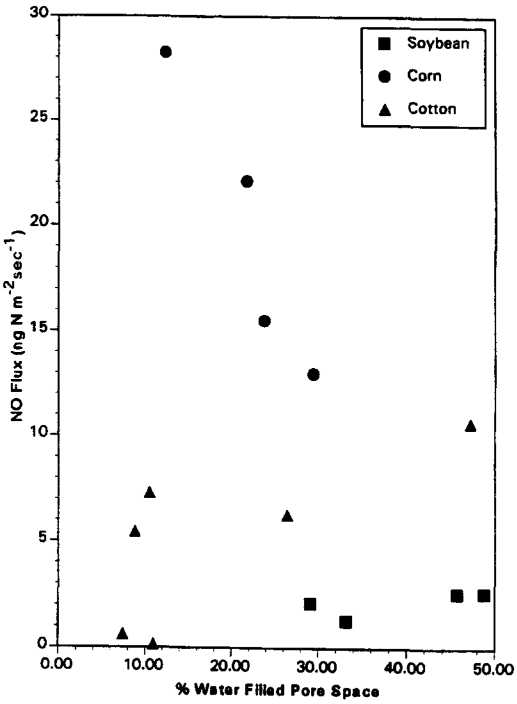

Fig. 6. Average daily NO flux is plotted against percent water filled pore space from the day the flux was measured for the summer of 1994 (12 July–11 August 1994).

Soil water content

As discussed above, the soil water content data from the summer of 1994 in Clayton, NC fall into two definite categories. The soil water content in the soybean crop was consistently above 30%WFPS, whereas the corn and cotton data fall below a %WFPS of 30%. Davidson (1991) proposed an optimum moisture content for maximum NO flux between 30% and 70% WFPS. Within the range of optimum soil water content, changes in %WFPS are not expected to change NO flux significantly. Below a %WFPS value of 30% NO flux is expected to change significantly with changes in %WFPS. Figure 6 partially supports Davidson's (1991) hypothesis. The fluxes from the soybean crop did not increase or decrease significantly within the optimum soil water content proposed by Davidson (1991). Below 30% WFPS, an increase in %WFPS led to larger NO flux in the cotton crop. The first four points in Fig. 6 from the cotton crop were sampled during the soil moisture stress period at the beginning of the summer measurement intensive. A rain event increased the %WFPS in the cotton crop which led to an increase in NO flux. The corn crop NO flux data also showed a dependence of NO flux on soil water content. All four sampling days in the corn crop exhibited %WFPS values below 30%. Each successive measurement in the corn crop had a decreasing %WFPS value (Fig. 3) yet the average daily NO flux for each corn measurement increased. The different effects of soil water content on the corn and cotton crops may be due to interactions of %WFPS with soil temperature (decreased in corn crop) and N fertilizer application. These results seem to suggest that at %WFPS values greater than 30%, soil water content is not a good predictor of NO flux values from this soil type. However, at %WFPS values below the 30% threshold, differing amounts of soil moisture will affect (increase or decrease) NO flux from soils depending on the physiological growth stage of the crop.

Extractable nitrogen

Several researchers have attempted to model soil extractable nitrogen values with NO flux (Williams *et al.*, 1988; Bawkin *et al.*, 1990; Davidson *et al.*, 1991; Shepherd *et al.*, 1991; Slemr and Seiler, 1991; Skiba *et al.*, 1992; Serca *et al.*, 1994). Typically, as in the work of Slemr and Seiler (1991), there is a general increase of NO flux with extractable soil nitrogen. Figure 7 shows the relationship between NO flux measurements from Clayton, NC in the summer of 1994 and extractable nitrogen measurements taken on the same day as the flux measurements. The scatter in the data is due to confounding factors including soil temperature, soil water content, physiological growth stage (nitrogen demand), and fertilizer application.

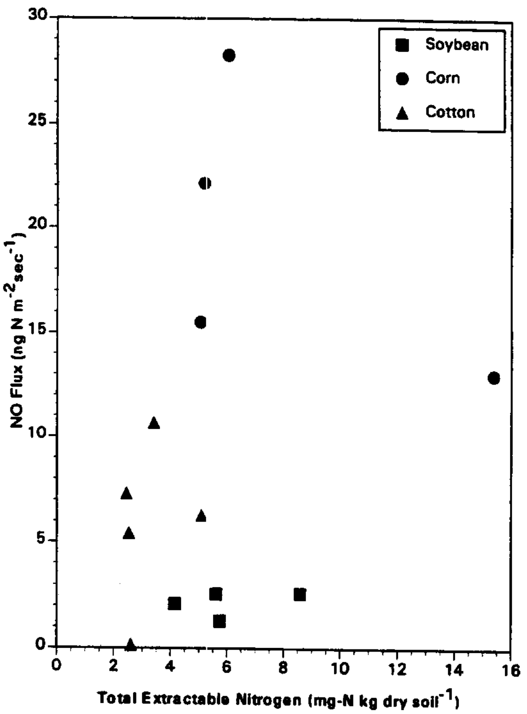

Fig. 7. Average daily flux plotted against total extractable nitrogen calculated from soil collected on the same day as the flux measurements. Extractable nitrogen includes ammonium and nitrate.

CONCLUSIONS

The summer (12 July–13 August 1994) of 1994 presented more typical weather conditions with which to study NO flux than were studied by Aneja *et al.* (1995) at the same sampling site. Utilizing a dynamic flow through chamber technique the average fluxes for corn, soybean, and cotton crops during the summer of 1994 were found to be 21.9 ± 18.6, 4.3 ± 3.7, and 2.1 ± 0.9 $\mathrm{ng\,N\,m^{-2}\,s^{-1}}$, respectively. The daily pattern of NO flux followed the increase of soil temperature throughout the daylight hours, peaking between 1:00 PM to 3:00 PM, if soil microbial activity was not limited by lack of soil water. Measurements in the cotton crop were made during a period of moisture stress with the result that there was no clear pattern of NO flux from the soil. NO flux from the soybean and corn crops varied exponentially with soil temperature. NO flux in the cotton crop yielded no correlation with soil temperature during periods of moisture stress. Above a %WFPS value of 30%, NO flux did not change with differing levels of soil water content. However, as predicted by Davidson (1991), below 30%WFPS, NO flux increased with increasing %WFPS in the cotton crop, but increased NO with a decreasing amount of %WFPS in the corn crop. NO flux increased with increasing extractable nitrogen across the three crops and within each crop. Differing physiological growth stages between each crop, however, influence the amounts of measurable extractable nitrogen by either fixing nitrogen during vegetative growth or adding to available nitrogen in the soil through root decomposition. No one variable or combination of variables (soil temperature, soil moisture, fertilizer amount) explained the differences in the NO flux measurements in each crop and between crop types. Because this was an observationally based study the variables measured were not controlled and a large degree of variation in flux measurements is inevitable. As a result of this natural variation, it is very difficult to explain day-to-day variations in the measurement of NO fluxes.

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REFERENCES

Anderson I. C. and Levine J. S. (1987) Simultaneous field measurements of biogenic emissions of nitric oxide and nitrous oxide. *J. geophys. Res.* **92,** 965–976.

Aneja V. P., Robarge W. P. and Holbrook, B. D. (1995) Measurements of nitric oxide flux from an upper coastal plain, North Carolina agricultural soil. *Atmospheric Environment* **29,** 3037–3042.

Aneja V. P., Kim D. S., Das M. and Hartsell B. E. (1996) Measurements and analysis of reactive nitrogen species in the rural troposphere of southeast United States: Southern Oxidant Study Site SONIA. *Atmospheric Environment* **30,** 649–659.

Bawkin P. S., Wofsy S. C., Wong-Miao F., Keller M., Trumbore S. E. and Maria da Costa J. (1990) Emission of nitric oxide (NO) from tropical forest soils and exchange of NO between the forest canopy and atmospheric boundary layer. *J. geophys. Res.* **95,** 16,755–16,764.

Blake G. R. and Hartge K. H. (1986) Particle density. In *Methods of Soil Analysis, Part 1* (edited by Klute A.), ASA Monograph No. 9. American Society of Agronomy, Madison, WI, Chap. 14.

Cardenas L., Rondon A., Johannson C. and Sanhueza E. (1993) Effects of soil moisture, temperature, and inorganic nitrogen on nitric oxide emissions from acidic tropical savannah soils. *J. geophys. Res.* **98,** 14,783–14,790.

Cassel D. K. and Nielsen D. R. (1986) Field capacity and available water capacity. In *Methods of Soil Analysis, Part 1* (edited by Klute A.), ASA Monograph No. 9, American Society of Agronomy, Madison, Wisconsin, Chap. 36.

Daniels R. B., Kleiss H. J., Buol S. W., Byrd H. J. and Phillips J. A. (1984) Soil systems in North Carolina, North Carolina Agricultural research services. Bulletin 467, North Carolina State University, Raleigh, North Carolina.

Davidson E. A. (1991) Fluxes of nitrous oxide and nitric oxide from terrestrial ecosystems. In *Microbial Production and Consumption of Greenhouse Gases: Methane, Nitrogen Oxides, and Halomethanes* (edited by Rogers J. E. and

Whitman W. B.), pp. 219–235. American Society for Microbiology, Washington, District of Columbia.

Davidson E. A., Vitousek P. M., Matson P. A., Riley R., Garcia-Mendez G. and Maass J. M. (1991) Soil emissions of nitric oxide in a seasonally dry tropical forest of Mexico. *J. geophys. Res.* **96,** 15,439–15,445.

Davidson E. A. (1991) Sources of nitric oxide and nitrous oxide following wetting of dry soil. *Soil Sci. Soc. Am. J.* **56.**

Ehhalt D. H. and Drummond J. W. (1982) The tropospheric cycle of NO_x. In *Chemistry of the Polluted and Unpolluted Atmosphere* (edited by Georgii H. W. and Jaeschke W.), NATO ASI Series, Vol. C96, pp. 219–251. Reidel, Dordrecht, Holland.

Gallbally I. E. and Roy C. R. (1978) Loss of fixed nitrogen from soils by NO exhalation. *Nature* **275,** 734–735.

Jambert C., Delmas R. A., Lobroue L. and Chassin P. (1994) Nitrogen compound emissions from fertilized soils in a maize field pine tree forest agrosystem in the southwest of France. *J. geophys. Res.* **99,** 16,523–16,530.

Johansson C. (1984) Field measurements of emission of nitric oxide from fertilized and unfertilized soils in Sweden. *J. atmos. Chem.* **1,** 429–442.

Johansson C. and Granat L. (1984) Emission of nitric oxide from arable land. *Tellus* **36B,** 25–37.

Johansson C. and Sanhueza E. (1988) Emission of NO from savanna soils during rainy season. *J. geophys. Res.* **93,** 14,193–14,198.

Johansson C., Rhode H. and Sanhueza E. (1988) Emission of NO in a tropical savanna and a cloud forest during the dry season. *J. geophys. Res.* **93,** 7180–7192.

Kaplan W. A., Wofsy S. C., Keller M. and Costa J. M. D. (1988) Emission of NO and deposition of O_3 in a tropical forest system. *J. geophys. Res.* **93,** 1389–1395.

Keeney D. R. and Nelson D. W. (1982) Nitrogen—inorganic forms. In *Methods of Soil Analysis, Part 2* (edited by Page A. L.), ASA Monograph No. 9, American Society of Agronomy, Madison, Wisconsin, Chap. 33.

Kim D.-S., Aneja V. P. and Robarge W. P. (1994) Characterization of nitrogen oxide fluxes from soil of a fallow field in the central piedmont of North Carolina. *Atmospheric Environment* **28,** 1129–1137.

Klute A. (1986) Water retention: Laboratory methods. In *Methods of Soil Analysis, Part 1* (edited by Klute A.), ASA Monograph No. 9, American Society of Agronomy, Madison, Wisconsin, Chap. 26.

Lachat Instruments Co. (1990) Methods Manual for the Quick Chem Automated Ion Analyzer. Lachat Instruments, 6645 West Mill Road, Milwaukee, Wisconsin 53218.

Logan J. A. (1983) Nitrogen oxides in the troposphere; Global and regional budgets. *J. geophys. Res.* **88,** 10,785–10,807.

National Research Council (1991) *Rethinking the Ozone Problem in Urban and Regional Air Pollution*, pp. 351–379. National Academy Press, Washington, District of Columbia.

Parrish D. D., Williams E. J., Fahey D. W., Liu S. C. and Fehsenfeld F. C. (1987) Measurements of nitrogen oxide fluxes from soils: Intercomparison of enclosure and gradient measurement techniques. *J. geophys. Res.* **92,** 2165–2167.

Sanhueza E., Cardenas L., Donoso L. and Santana M. (1994) Effect of plowing on CO_2, CO, CH_4, N_2O, and NO fluxes from tropical Savannah soils. *J. geophys. Res.* **99,** 16,429–16,434.

Serca D., Delmas R., Jambert C. and Labroue L. (1994) Emissions of nitrogen oxides from equatorial rain forest in central Africa: origin and regulation of NO emissions from soils. *Tellus* **46B,** 243–254.

Shepherd M. F., Barzetti S. and Hastie D. R. (1991) The production of atmospheric NO_x and N_2O from a fertilized agricultural soil. *Atmospheric Environment* **25A,** 1961–1969.

Skiba U., Hargreaves K. J., Fowler D. and Smith K. A. (1992) Fluxes of nitric and nitrous oxides from agricultural soils in a cool temperate climate. *Atmospheric Environment* **26A,** 2477–2488.

Slemr F. and Seiler W. (1991) Field study of environmental variables controlling the NO emissions from soil and the NO compensation point. *J. geophys. Res.* **96,** 13,017–13,031.

Southern Oxidants Study Annual Report (1993) (edited by Fehsenfeld F., Meagher J. and Cowling E.), pp. 47–61.

Thermo Environmental Instruments Inc., Instruction Manual Model 42S: Chemiluminescence NO-NO_2-NO_x analyzer. Designated reference method number RFNA-1289-074, Franklin, MA, 1992.

Valente R. J. and Thorton F. C. (1993) Emissions of NO from soil at a rural site in Central Tennessee. *J. geophys. Res.* **98,** 16,745–16,753.

Watson R. L., Meira Fihlo L. G., Sanhueza E. and Janetos A. (1992) Greenhouse gases: sources and sinks. In *1992 IPCC Supplement*, pp. 28–46. Cambridge University Press, New York.

Williams E. J. and Fehsenfeld F. C. (1991) Measurement of soil nitrogen oxide emissions at three North American ecosystems. *J. geophys. Res.* **96,** 1033–1042.

Williams E. J., Guenther A. and Fehsenfeld F. C. (1992a) An inventory of nitric oxide emissions from soils in the United States. *J. geophys. Res.* **97,** 7511–7519.

Williams E. J., Hutchinson G. L. and Fehsenfeld F. C. (1992b) NO_x and N_2O emissions from soil. *Global Biogeochemical Cycles* **6,** 351–388.

Williams E. J., Parrish D. D., Buhr M. P. and Fehsenfeld F. C. (1988) Measurement of soil NO_x emission in Central Pennsylvania. *J. geophys. Res.* **93,** 9539–9546.

Williams E. J., Parrish D. D. and Fehsenfeld F. C. (1987) Determination of nitrogen oxide emission from soils; Results from a grassland site in Colorado, United States. *J. geophys. Res.* **92,** 23,173–23,179.