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Nitric oxide emission from intensively managed agricultural soil in North Carolina

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Abstract. Emissions of nitric oxide (NO) were determined from an intensively managed agricultural soil near Plymouth, in the coastal plain of North Carolina, using the dynamic chamber technique. The measurements were made over a soybean field from July 15 to August 15, 1996, as part of the project Natural Emissions of Oxidant Precursors: Validation of Techniques and Assessment (NOVA). A N-containing fertilizer was applied at the middle of the experiment in order to investigate the effect of N-fertilizers on NO emissions and to test the response of instruments. Soil water content was high during the experimental period, with water-filled pore space ranging from 49% to 67%. NO emission during this period ranged between 0.28 and 18.45 ng N m^{-2} s^{-1}, with an overall average of 5.01 ± 3.03 ng N m^{-2} s^{-1}. A normal diurnal pattern with low values at nighttime and high values during the day was observed during the prefertilization period, but a reverse diurnal pattern (high at nighttime, low in daytime) of NO emission variation was found during the postfertilization, closed-canopy period, implying that interaction among canopy development, application of fertilization, and soil parameters may affect the diurnal variation of NO emission from soils. The emissions of NO were related to soil temperature, water-filled pore space, and extractable nitrogen. Application of fertilizer at the middle of the experiment was found to disrupt the normal relations between NO emission and soil temperature and water content seen during the prefertilization period but to enhance the positive relation between NO emission and extractable N. An intercomparison of the dynamic chamber technique with the eddy-correlation technique in this experiment indicates that in spite of large differences in the magnitudes of soil NO emission and the NO flux at 5 m, the two fluxes show similar variations with time and are strongly correlated.

1. Introduction

The oxides of nitrogen, NO_x, (NO_x = NO + NO_2), play an important role in tropospheric photochemistry. They participate not only in the formation of ozone but also in the acidification of precipitation. In the troposphere, ozone is formed by photochemical processes involving NO_x and volatile organic compounds (VOCs) in the presence of sunlight. Tropospheric ozone is an important photochemical air pollutant, which increases respiratory-related diseases, decreases crop yields, and causes other environmental problems. Reducing the 8-hour averaged concentrations of ambient ozone to below 0.8 ppmv is a primary goal of the Clean Air Act (CAA) and its amendments.

It used to be thought that anthropogenic sources were the major sources of NO_x [*Logan*, 1983]. However, recent reports suggest that globally, biogenic emissions of NO are comparable to combustion sources (~20 Tg of NO-N per year) [*Davidson* , 1991; *Davidson and Kingerlee*, 1997; *Aneja et al.*, 1996]. *Hutchinson* [1995] reported that up to 40% of global NO is attributable to emissions from soils. *Williams et al.* [1992], using an empirical model based on the relationship between NO fluxes and soil temperature, estimated that NO_x emissions from soil amount to 14% of combustion sources for the United States and that 66% of soil NO_x emissions come from fertilized agriculture soils. In the southeastern United States, which has large areas of intensively managed agricultural soils, the role of soil NO_x emissions is likely to become more significant in the production of ozone and other oxidants. About 40% of the ozone nonattainment areas in the United States are found in the southeastern United States [*Lindsay et al.*, 1989], which is thought to be NO_x limited, which means that an increase in NO_x emissions into the atmosphere may lead to increased ozone production [*Aneja et al.*, 1996]. Thus measuring and parameterizing the emissions of NO_x are crucial for a better understanding of biogenic NO_x emissions and to developing control strategies for ozone and acidic pollutants in the southeastern United States.

In this paper we will present the results of nitric oxide emission measurements from an intensively managed soybean field in the lower coastal plain of North Carolina. These measurements were made from July 15 to August 15, 1996, and with them we investigated the relationship between NO emissions and controlling parameters such as soil temperature, soil moisture, and soil extractable nitrogen. An intercomparison of the dynamic chamber technique and the eddy-correlation technique in measuring NO fluxes is also discussed.

2. Experiment

2.1. Research Site

The research site is located in the southwest portion of Washington County, approximately 20 km southwest of Plymouth, North Carolina. There were three soil types at the research site: the Conaby muck, the Arapahoe fine sandy loam, and the Portsmouth fine sandy loam. The last is the primary soil

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Table 1. Soil Data for Soybean Field Experimental Site, Plymouth, North Carolina, 1996

Date, 1996	Water Content, %	NH_4^+-N	NO_3^--N	Total Extractable N
July 19	28.90	2.55	3.70	6.25
July 20	27.59	4.14	1.27	5.41
July 22	33.28	2.35	0.52	2.87
July 23	34.62	3.10	1.13	4.22
July 25	34.08	2.82	2.28	5.09
July 26	34.69	4.85	2.34	7.19
July 27	36.42	6.17	2.20	8.37
July 28	32.71	1.84	1.98	3.82
July 29	31.21	3.33	1.23	4.56
July 30	29.07	2.58	1.40	3.98
Aug. 4	36.17	2.22	3.21	5.43
Aug. 5	36.03	3.44	4.37	7.80
Aug. 6	34.97	2.58	3.64	6.22
Aug. 7	33.16	3.41	1.73	5.14
Aug. 8	32.79	3.00	1.41	4.40
Aug. 9	30.44	2.12	0.61	2.73
Aug. 10	30.57	3.24	0.60	3.84
Aug. 11	28.08	4.43	2.13	6.55
Aug. 12	29.96	3.58	0.39	3.97
Aug. 14	30.79	2.58	0.51	3.09
Aug. 15	31.59	3.46	4.88	8.34

type sampled for the experiment, which is characterized as friable and black fine sandy loam with weak medium granular structure. For the top 20 cm of soil the bulk density was 0.83 g cm^{-3}; and the total extractable nitrogen values for each day's measurements can be found in Table 1. The site was a 136-ha continuous cropland with soybean planted during the period of our field sampling campaign (July 15 to August 15, 1996). The soybean plants were 0.2 m in height at the beginning of our experiment and grew to a height of about 1.2 m at the end of the experiment when the soil surface was totally covered by the soybean plants. About 30 kg ha^{-1} N-containing fertilizer (NH_4NO_3) was distributed, in a typical agricultural practice, by an aircraft on the site on July 31 (the middle of the experiment) in order to research the influences of N-fertilizer on NO fluxes. Before fertilization, soybean plants were not dense enough to cover the chamber, and this period is defined as the "open-canopy" period. After fertilization, the chamber was fully covered by soybean plants and this period is defined as the "closed-canopy" period.

Passage of Hurricane Bertha at the experimental site provided excess precipitation to the soil from July 11 to July 13. In addition, smaller amounts of precipitation occurred on days during the experiment period. Consequently, the site was in a wet condition with high water content, ranging between 26.9% and 36.4% (49~67% water-filled pore space (WFPS)), with an average of 32.0 ± 2.88%. High water content may lead to low gas diffusivity in soil, resulting in low NO emissions [*Anderson and Levine*, 1987; *Davidson*, 1991; *Slemr and Seiler*, 1991; *Cardenas et al.*, 1993; *Valente and Thorton*, 1993; *Sullivan et al.*, 1996].

2.2. Dynamic Chamber System

A dynamic flow-through chamber system, illustrated in Figure 1, was used to measure the emission rate of nitrogen oxides from the soil in this experiment. The entire measuring system includes a dynamic flow-through chamber and a temperature-controlled mobile laboratory which houses the analytical instruments and data acquisition system. The open-bottom flow-through dynamic chamber (Figure 1) lined with 5-mil-thick fluorinated ethylene propylene (FEP) Teflon (27 cm in diameter and 42 cm high, with 24.05 L of volume), fits inside of a stainless steel frame, which is driven into the ground to a depth of about 10 cm. The chamber does not enclose the plants. The measurements are made at one location for one day (24 hours) and another location the next day. Throughout the campaign, 23 measurements were made. Ambient air as a carrier gas is pumped through the chamber at a constant flow rate (~4 L min^{-1}). The air inside the chamber is mixed by a variable-speed, motor-driven Teflon impeller and is taken through Teflon tubing (1/4" OD, 1/8" ID) to the analytical instruments (TECO Model 42S NO/NOy analyzer).

A Toshiba laptop computer using Labview Software (National Instruments) is utilized as the data acquisition system; this system yielded 60-s rolling average concentration measurements and then binned and averaged those values every 15 min. All the instruments are housed in a mobile laboratory (modified Ford Aerostar van), which is climate controlled so as to be in the operating range of the instruments. Further details about the dynamic chamber operation and instruments have been discussed by other authors in our Air Quality Group at North Carolina State University (NCSU) [*Kim et al.*, 1994; *Aneja et al.*, 1995].

2.3. Emission Flux Calculation

Emission of analyzed species is calculated from the mass balance equation for the chamber [*Kaplan et al.*, 1988; *Kim et al.*, 1994, *Aneja et al.*, 1995]:

$$\frac{dC}{dt} = \left(\frac{q\,C_{air}}{V} + \frac{J}{h}\right) - \left(\frac{L}{h} + \frac{q}{v}\right) C - R \qquad (1)$$

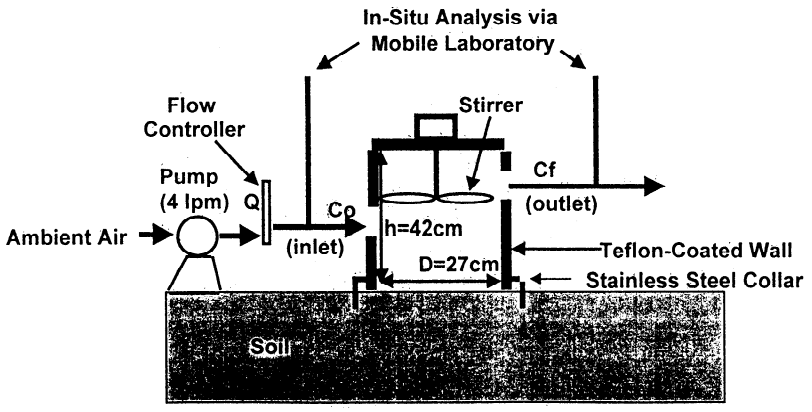

Figure 1. Dynamic chamber system.

where

h internal height of chamber;
J emission flux per unit area;
L rate of loss by chamber wall per unit area;
q flow rate through the chamber;
V volume of the chamber;
C NO concentration in the chamber;
C_{air} NO concentration in ambient air adjacent to the chamber;
R chemical production/destruction rate inside the chamber.

Assuming well-mixed air in the chamber, at steady state conditions (empirically, this chamber needs 15-20 min to reach equilibrium state), the flux J can be determined by

$$\frac{J}{h} = \left(\frac{L'}{h} + \frac{q}{V}\right) C_{eq} - \frac{q\,C_{air}}{V} \quad (2)$$

where C_{eq} is the equilibrium concentration in the chamber. In (2) the total loss term L' is the sum of loss by the chamber wall inside the chamber and chemical reactions of NO with oxidants existing in the carrier gas, such as ozone, and peroxy radicals [*Kim et al.*, 1994; *Aneja et al.*, 1995]. The total loss term here was determined empirically utilizing a method developed by *Kaplan et al.* [1988]. In this method, one plots the value of -ln $[C_{eq} - C)/C_{eq} - C_0)]$ against time (t), where C_0 is the concentration in the chamber at the first equilibrium state achieved at an initial flow rate and C_{eq} is the concentration in the chamber after the flow rate is reduced and allowed to reach a second equilibrium. From the linear regression relationship between the values of -ln $[C_{eq} - C)/C_{eq} - C_0)]$ and time during the experiments, the slope of the line represents the value of $(L'/h) + (q/v)$. Thus the total loss L' in the chamber can be estimated from the linear regression between the value of -ln $[C_{eq} - C)/C_{eq} - C_0)]$ and time with a constant flow rate. This loss term was important in our experiment, amounting up to 25% of NO emission. Values of L' varied from place to place and from one season to another, but there were no significant differences between daytime and nighttime values, and we used an average value of L' in our calculation.

2.4. Soil and Canopy Sampling

Soil temperature is recorded every 15 min using a Fischer Scientific temperature probe inserted 5 cm into the soil adjacent to the chamber. A soil sample is collected from the center of the dynamic chamber at the end of each experimental period (one sample per day), using a bucket auger which removed the top 20 cm of soil. Soil properties such as percentage of water-filled pore space (%WFPS) and total extractable nitrogen were obtained from the collected soil samples. Soybean plant samples were taken once a week during the 1996 summer experiment in order to measure the canopy properties such as plant height and leaf area index. Soil and canopy data are given in Tables 1 and 2.

Table 2. Canopy Data for Soybean Plant at Experimental Site, Plymouth, North Carolina, 1996

Date, 1996	Day of Year	Height, cm	Leaf Area Index
July 4	187		0.50
July 18	201	51.17	2.73
July 25	208	68.80	3.87
Aug. 1	215	82.93	4.40
Aug. 8	222	106.17	5.45
Aug. 15	229	118.37	5.00
Aug. 22	236	121.33	5.19
Aug. 29	243	121.53	4.80
Sept. 19	264	114.53	2.21

Leaf area index is the ratio of leaf to the sampling soil area.

3. Results and Discussion

3.1. NO Emissions

Measured soil NO emission rates over the soybean field during the period of the experiment were low, ranging from 0.28 to 18.45 ng N m^{-2} s^{-1}, with an overall average of 5.01 ± 3.03 ng N m^{-2} s^{-1}. *Anderson and Levine* [1987] reported an average value of 4 ng N m^{-2} s^{-1} for the NO emission rate from a soybean field in Virginia during a 3-month measurement period, with extremes of 0.7 and 9.4 ng N m^{-2} s^{-1}. Figure 2 shows the daily mean and median values of NO emission plotted with daily maximum and minimum values. Application of N-fertilizer at the middle of the experiment (July 31) led to about a tripling of NO emission, which lasted approximately a week and then dropped to normal values before increasing again after August 12.

The increase of NO emission following fertilization is less than the 10-100 times increase often reported in the literature [*Yienger and Levy*, 1995]. Heavy rains following the fertilization may have limited NO emission due to water-logging or may have washed away some of the fertilizer. Data could not be collected for 4 days immediately following fertilization due to heavy rains and relocating the mobile lab (Figure 2).

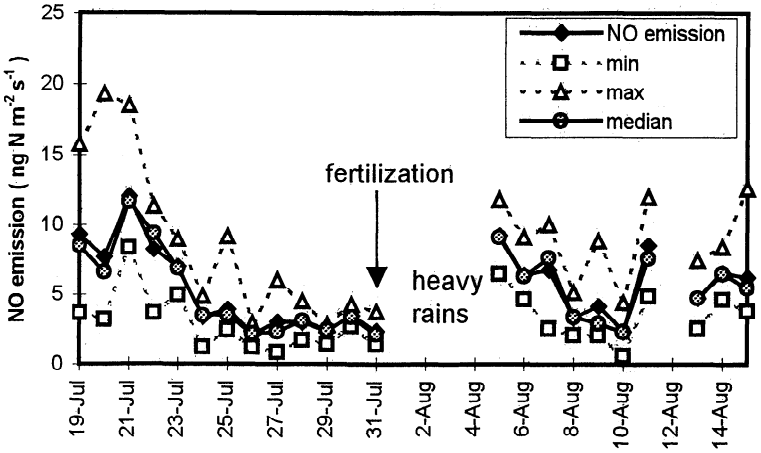

Figure 2. Daily statistics of NO emissions during the experiment.

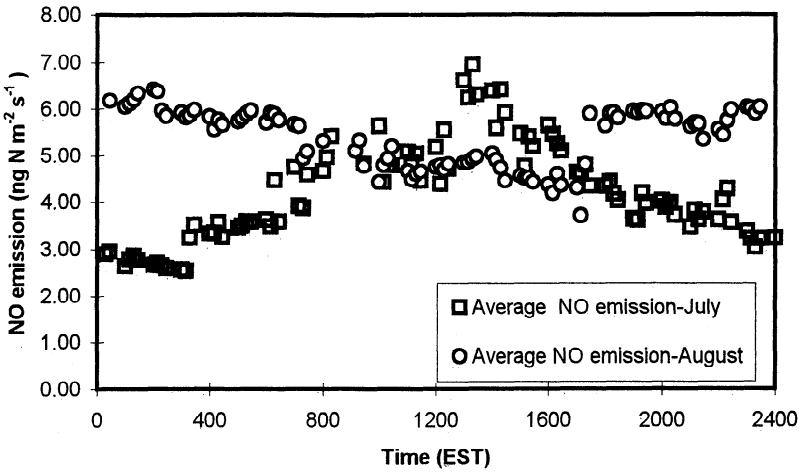

Figure 3. Diurnal variations of NO emissions in July and August.

Figure 3 shows the composite diurnal variations of NO emission in July (prefertilization) and August (postfertilization). An interesting finding is that diurnal variations are quite different in these two periods. During the prefertilization period the peak in NO emissions appeared in midday (around 1400 LT), while minimum values occurred after midnight. This is consistent with a previous study [*Sullivan et al.*, 1996]. However, in August or during the postfertilization period, we have an opposite diurnal trend, with high emissions at night and low emissions during the day. For the sake of simplification we call the postfertilization diurnal variation a U pattern, and we call the prefertilization diurnal variation an inverted-U. Recall that the postfertilization period was also the "closed-canopy" period, in which the chamber was fully covered by soybean plants. Some observations have shown decreased emissions of NO_x due to the presence of plants [*Johansson and Granat*, 1984; *Williams et al.*, 1987; *Anderson and Levine*, 1987; Slemr and Seiler, 1991]. The plants may alter nutrient

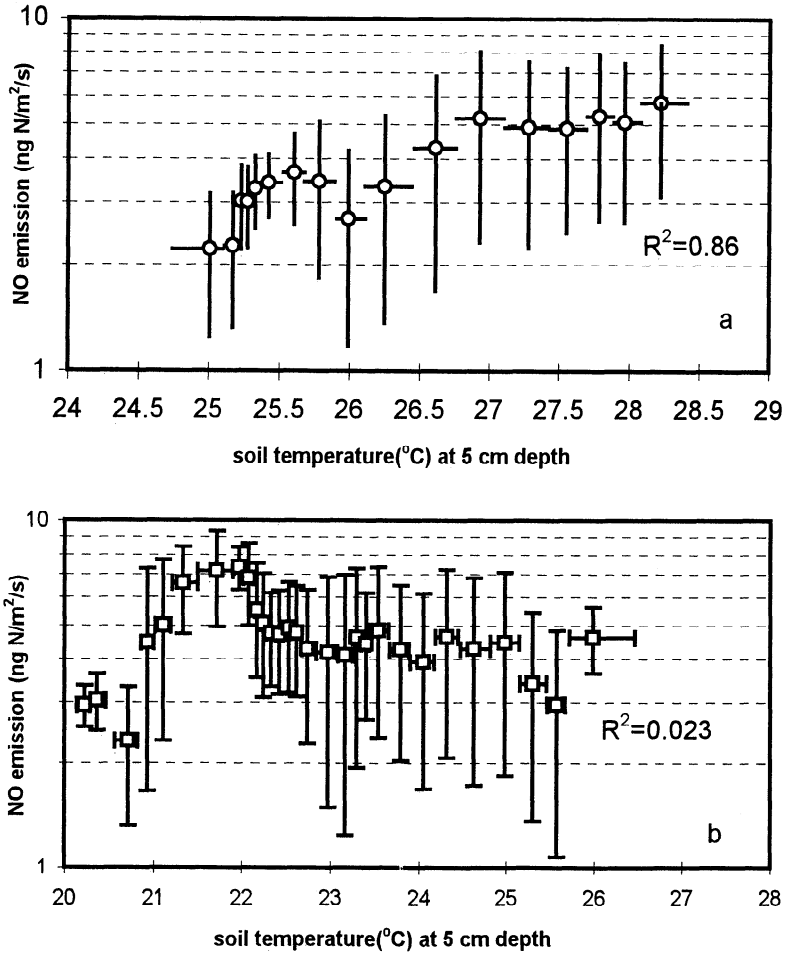

Figure 4. NO emission versus soil temperature in (a) July (prefertilization) and (b) August (postfertilization).

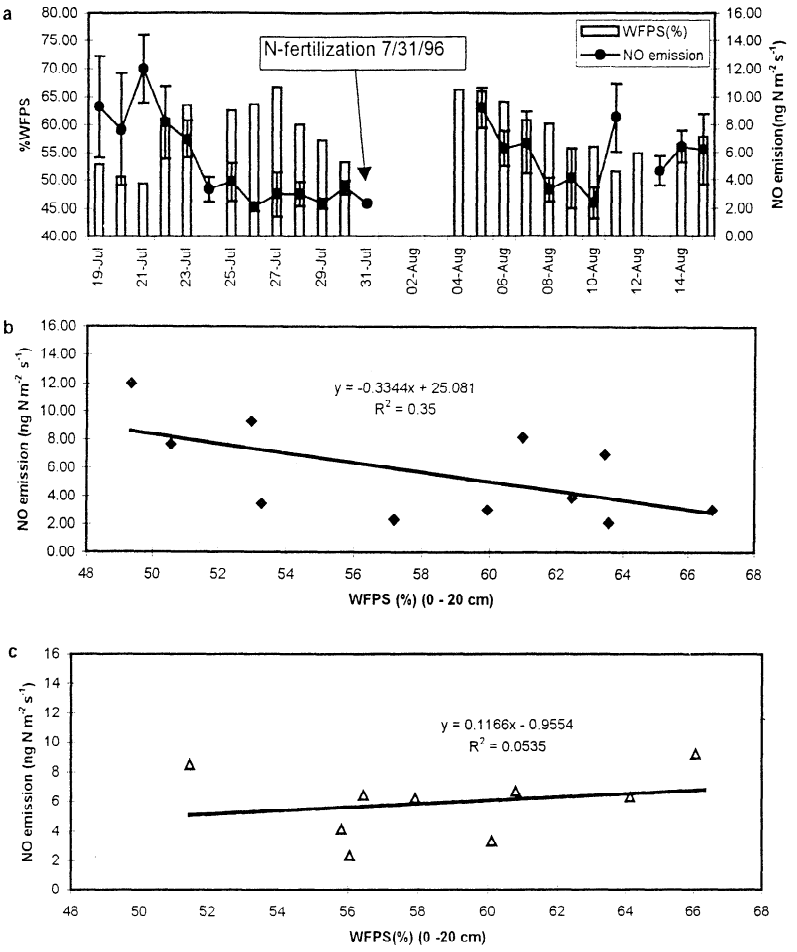

Figure 5. (a) NO emissions versus percent of water-filled pore space. Vertical bars are standard deviations of NO emissions. (b) Prefertilization NO emission plotted versus %WFPS. (c) Postfertilization NO emission plotted versus %WFPS.

levels, soil temperature, soil moisture, and other soil parameters compared with those for bare soils. Since the diurnal variations of these soil parameters are not available, we are unable to relate them to the diurnal patterns of NO emission. However, we can hypothesize that the diurnal U pattern of NO emission has some relationship with the rapid growth of plants following fertilization and heavy rains.

3.2. Effects of Soil Parameters

3.2.1. Soil temperature. Soil temperature is an important parameter since it can greatly affect the microbial processes in the soil environment. Previous measurements of NO_x emissions over different land-use types have shown a strong temperature dependence [*Williams et al.*, 1988; *Slemr and Seiler*, 1991; *Williams and Fehsenfeld*, 1991; *Valente and Thorton*, 1993; *Aneja et al.*, 1998]. NO_x emission increases with soil temperature almost exponentially within a certain range (15°-35°C) [*Williams et al.*, 1992]. In our experiment, however, a strong dependence (R^2 = 0.86) of NO soil emission on soil temperature was observed only during the prefertilization period (July), as shown in Figure 4a. In Figures 4a and 4b, vertical and horizontal bars represent the standard deviations of NO emission and spans of soil temperatures, respectively. The soil temperature/NO emission relationship during the postfertilization, closed-canopy period is much more complex. The average NO emission increases with temperature, reaches a maximum value at about 21.5°C, and then decreases and levels off with no significant relationship to temperature. This may be due to the application of fertilizer at the end of July and heavy rains after fertilization, resulting in an increase of soil water content as well as the growth of soybean plants. Ultimately, the results indicate that factors other than soil temperature have significant influences on NO emission, such as soil water content and nutrient levels. The complex relationship between NO emission and soil temperature also suggests that the application of a soil emission model, in which soil temperature is the only predictor [e.g., *Williams et al.*, 1992], would be highly questionable, especially in the southeastern United States. Further improvements in biogenic NO emission modeling should be based on more extensive data in this region.

3.2.2. Soil moisture. Many studies suggest that large quantities of NO_x are emitted from soils with intermediate moisture levels, whereas emissions from dry (moisture stressed) and wet (saturated) soils are generally lower [*Anderson and Levine*, 1987; *Slemr and Seiler*, 1991; *Williams and Fehsenfeld*, 1991; *Valente and Thornton*, 1993]. *Davidson* [1991] concluded that the optimal water-filled pore space (WFPS) for NO emissions from soils ranges from 30% to 70%. Soil moisture in the soybean field during the experimental period was found to be very high, with %WFPS ranging from 49% to 67%, while NO emission rates were quite low. Figure 5a shows daily

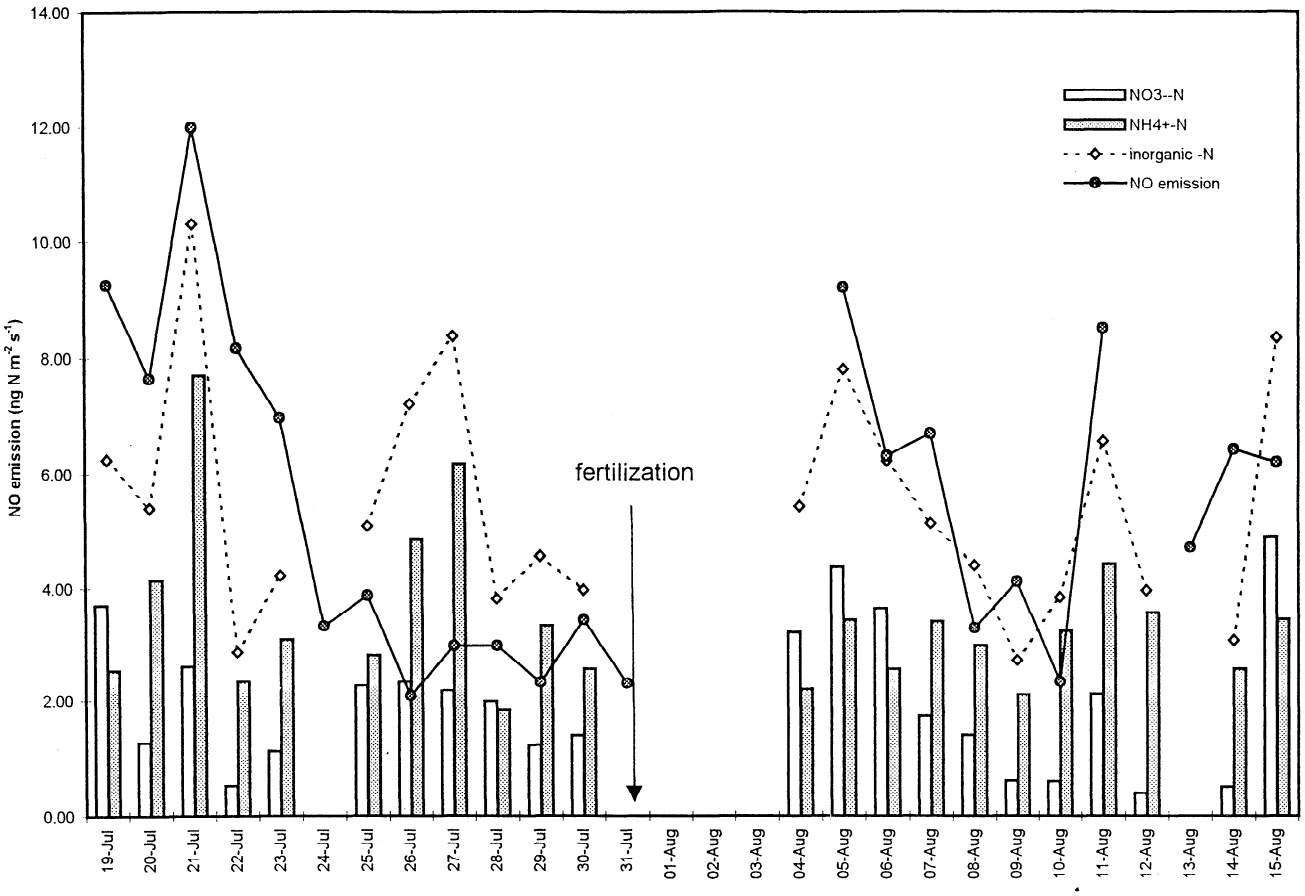

Figure 6. Daily variations of NO emissions (ng N m^{-2} s^{-1}) versus soil extractable N (mg kg^{-1}).

variation of NO emission versus %WFPS. We can see that before the application of N-fertilizer on July 31, NO emission decreases with increasing %WFPS and then increases with decreasing %WFPS. This negative correlation between NO emission and soil moisture is more clearly seen in Figure 5b and is similar to that reported by other investigators [*Davidson*, 1991]. *Davidson* [1991] hypothesized that NO emissions increase with increasing %WFPS until around 50% and then decrease with further increase in %WFPS. Our results partly support Davidson's hypothesis. *Cardenas et al.* [1993] also observed a decreasing NO emission at high soil moisture (%WFPS > 50%). This decrease in NO emissions during high soil moisture is because the abundance of water in pore spaces of soil under wet conditions hinders the diffusion of NO through the soil. Further, the production of NO in soil is hindered under high moisture conditions. However, the application of N-fertilizer on July 31 changed the negative relationship (R^2 = 0.35) between NO emission and soil moisture during the prefertilization period to an insignificant correlation, implying that fertilizer applications may also have significant effects on processes governing soil NO emissions. Dependence of NO emission on soil temperature and soil moisture being significantly altered by fertilization suggests that current NO soil emission-soil temperature/soil moisture models are not applicable after recent applications of nitrogen-containing fertilizers. Because of the limited number of data points used in obtaining the regression relations in Figures 5b and 5c, these may not be extended beyond the limited range of soil temperature and moisture conditions observed in the experiment.

3.2.3. Soil extractable nitrogen. The nutrient level of the soil is also a critical controlling parameter of soil NO emission. Several experiments have been conducted to research the dependence of NO emission on soil extractable nitrogen (N) [*Williams et al.*, 1988; *Bawkin et al.*, 1990; *Davidson et al.*, 1991; *Slemr and Seiler, 1991*; *Skiba et al.*, 1992; *Cardenas et al.*, 1993; *Serca et al.*, 1994; *Aneja et al.*, 1998]. It is reported that an increase of extractable N will generally enhance soil NO emission. In order to investigate the effect of fertilizer on NO emission from soil, about 30 kg/ha^{-1} N-fertilizer was applied to the soybean field on July 31 (the middle of the experiment). There was a heavy rain after fertilization so that NO concentration measurements were interrupted until August 5. Daily variations of total extractable nitrogen in the form of NH_4+ and NO_3^- are plotted with NO emission in Figure 6. An increase of total extractable N following the application of fertilizer was observed, reaching a maximum on August 5. NO emission also had a similar trend of increase as discussed earlier. Thus enhanced NO emissions due to an increase of extractable N were observed in our study, similar to previous reports [*Williams et al.*, 1988; *Bawkin et al.*, 1990; *Davidson et al.*, 1991; *Slemr and Seiler*, 1991; *Skiba et al.*, 1992; *Cardenas et al.*,1993; *Serca et al.*, 1994; *Aneja et al.*, 1998]. An opposite relationship between soil extractable N and NO emission is observed between July 22 and July 26. We can also observe from Figure 6 that the variation of extractable N is more due to the variation of NO_3^- - N than to the variation of NO_4^+ - N. Likewise, *Sanhueza et al.* [1990] and *Cardenas et al.* [1993] observed a similar high dependence of NO emission on nitrate-nitrogen in natural savannah and forest soils. Variations of NO

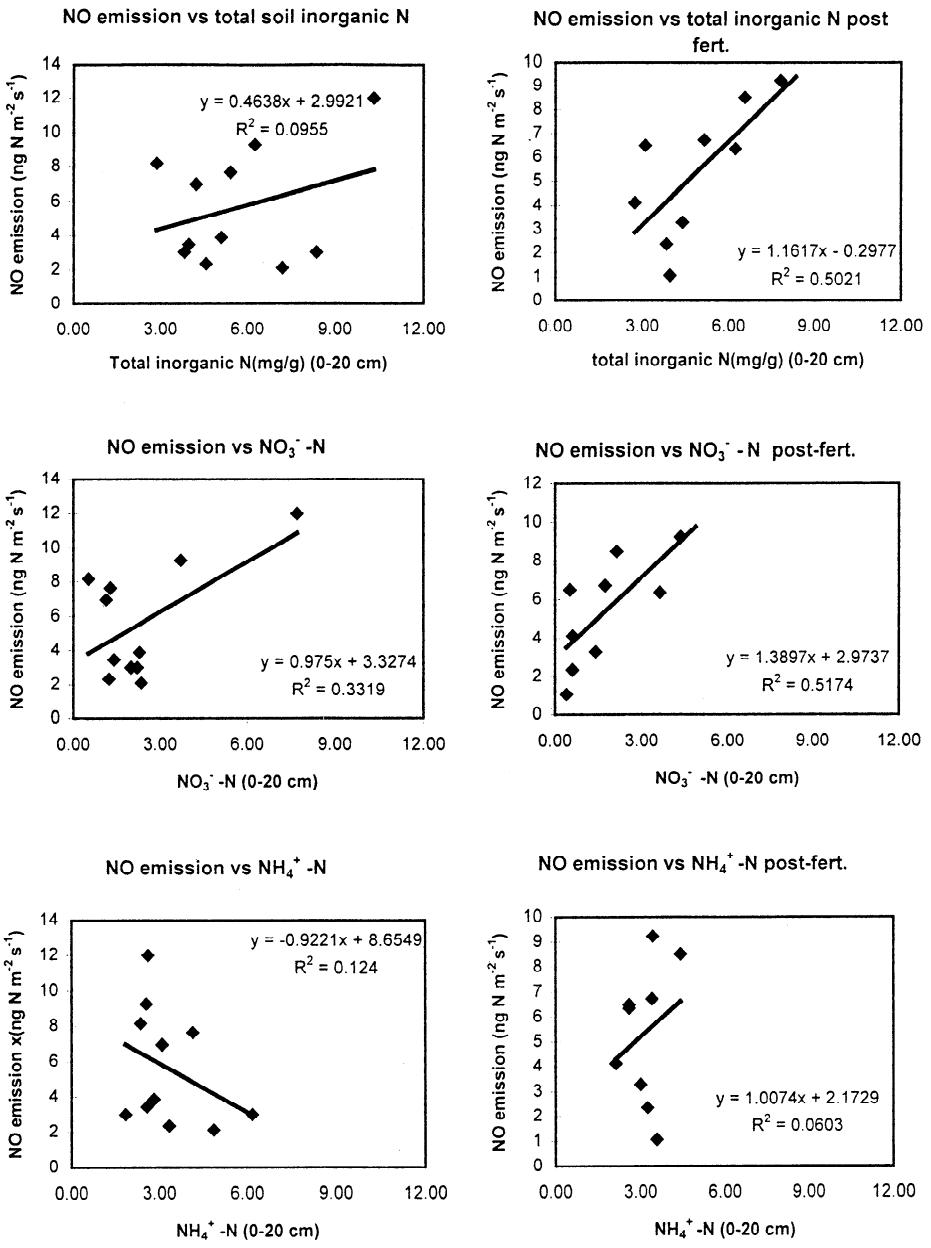

Figure 7. Relation between NO emission and soil extractable N for the prefertilization and postfertilization periods.

emission with extractable N, NO_3^- - N, and NO_4^+ - N before and after fertilization are plotted in Figure 7. We can see the increase of NO emission with soil $NO_3^- - N$ (R^2 = 0.33 and 0.52, respectively). The correlation between NO emission and is much weaker or insignificant both before and after fertilization (R^2 = 0.12 and 0.06, respectively). Fertilization appears to enhance the positive correlation between NO emission and total extractable N; the best-fit linear regression relations and correlation coefficients between the NO emission and different forms of extractable N are given in Figure 7. The results discussed above suggest that NO emission is dependent on complex interactions among soil parameters (temperature, moisture, extractable nitrogen, etc.) rather than on a single factor.

3.2.4. Intercomparison. Figure 8 is a graph of NO fluxes calculated at a 5-m height utilizing the eddy-correlation technique [*Gao et al.*, 1996] and a graph of soil NO emissions determined by the dynamic flow-through chamber technique. In spite of differences in their magnitudes (note the different scales used for these), the two show qualitatively similar variations with time. The values of NO soil emission are greater than the NO fluxes at 5 m, which implies that some of the NO might have been converted to NO_2 through reactions with ozone and peroxy radicals by the time it reaches the 5-m height level. The correlation coefficient between the two sets of measurements is about 0.69, even though not all times during this intercomparison period (July 23-31) had suitable wind direction for intercomparison. There were also times when the two measurements could not be made simultaneously and hence cannot be compared. The two techniques appear to give consistent structure values of NO fluxes in this experiment. This paper analyzes the characterization of NO emission from soils and its relations with controlling parameters based on field measurements over a soybean field in summer 1996.

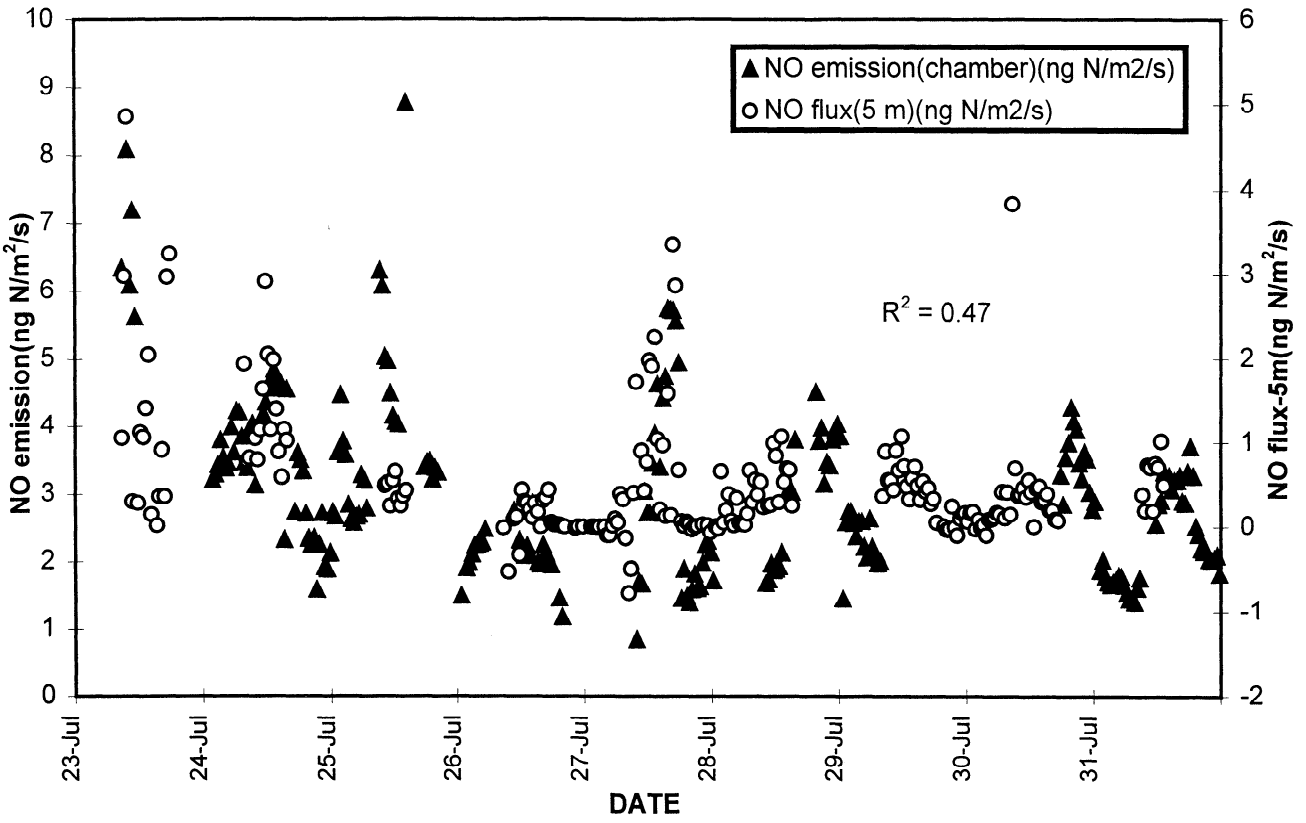

Figure 8. Intercomparison of NO fluxes at 5 m with soil NO emissions (July 23-31, 1996, Plymouth, North Carolina, soybean field).

4. Summary and Conclusions

Before fertilization, our experimental results support the following established results: (1) strong correlation between NO emissions and soil temperature, with NO emission increasing exponentially with soil temperature; (2) negative correlation between NO emission and %WFPS under wet conditions, with water-filled pore space higher than 50%; (3) NO flux increases with soil nitrate level. Application of N-fertilizer was found to disrupt the above relations between NO flux and soil temperature and soil moisture seen during the prefertilization period but to enhance the positive correlation between NO emission and soil nitrate level. The NO emission/soil temperature relationship was more complex, but weak. No significant positive relation between NO emission and soil moisture was observed during the postfertilization, closed-canopy period. These results suggest that NO soil emission depends on the interaction of several controlling parameters such as soil temperature, soil moisture, extractable N, etc., instead of a single factor. More extensive measurements are needed in different regions to gain a better understanding of the interaction, in order to model and parameterize NO emissions. Last, an intercomparison of the dynamic chamber technique with the eddy-correlation technique in this experiment indicated that the soil emissions are much higher than the fluxes at 5-m level, but the diurnal variation of fluxes by the two techniques is similar. Some of the NO emission from the soil is likely to be converted to NO_2 through fast reactions with ozone and peroxy radicals, resulting in a smaller NO flux at 5 m.

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