Measurement of nitrogen oxide emissions from an agricultural soil with a dynamic chamber system

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Abstract. Biogenic soil emissions of nitric oxide (NO) were measured from an intensively managed agricultural row crop (corn, *Zea mays*) during a 4 week period (May 15 through June 9, 1995). The site was located in Washington County, near the town of Plymouth, which is in the Lower Coastal Plain of North Carolina. Soil NO flux was determined using a dynamic flow-through chamber technique. The measurement period was characterized by two distinguishing features: an application of nitrogen (N) fertilizer at the midpoint of the experiment and a nontypical rainfall pattern. Average NO flux prior to the application of N fertilizer was 31.5 ± 10.1 ng N m^{-2} s^{-1}, and more than doubled (77.7 ± 63.7 ng N m^{-2} s^{-1}) after the application of a side-dressing of N fertilizer. Average soil extractable nitrogen values did not change significantly following application of the side-dressing of N fertilizer. We attribute this failure to detect a significant difference in soil extractable nitrogen following N fertilization to the method in which the fertilizer was applied, the subsequent rainfall pattern, and the technique of soil sampling. NO flux followed the same diurnal trend as soil temperature, with maximum NO emissions coinciding with maximum soil temperature, and minimum NO emissions coinciding with minimum soil temperature. NO flux was found to increase exponentially with soil temperature, but only after fertilization. Due to subsurface irrigation practices employed by the farmer, changes in soil water content were minimal, and no relation could be drawn between soil water content and NO flux. Simultaneous measurements of NO$_y$, NO$_2$, and NO emissions revealed that NO and NO$_2$ emissions represent 86 and 8.7%, respectively, of NO$_y$ emissions leaving the soil. Simultaneous NO flux measurements made by a closed box flux technique, at the same site, revealed no statistically significant differences between the two different methodologies for measuring NO flux.

1. Introduction

Nitric oxide (NO) plays an important role in tropospheric photochemistry. Increasing NO emissions, in the presence of hydrocarbons and sunlight, are thought to be the cause of increased regional levels of tropospheric ozone and other photochemical oxidants [*Logan*, 1985; *Penkett*, 1988; *Aneja et al.*, 1996a]. *Yienger and Levy* [1995] developed an empirically based model to estimate soil NO$_x$ (= NO + NO$_2$) emissions on a global scale. They have reported that anthropogenic land use is having a significant impact on global soil NO$_x$ emissions and that soil emissions can account for up to 75% of the total NO$_x$ budget, depending on location and time of year.

Although there have been many experiments conducted that have measured NO emissions from various soil types [*Slemr and Seiler*, 1984; *Johansson and Granat*, 1984; *Williams et al.*, 1988; *Johansson and Sanhueza*, 1988; *Kaplan et al.*, 1988; *Williams and Fehsenfeld*, 1991; *Hutchison and*

Brams, 1992; *Kim et al.*, 1994; *Aneja et al.*, 1995], relatively few have included intensively managed agricultural soils, or continued measurements for substantial periods of time [*Anderson and Levine*, 1987; *Williams et al.*, 1988; *Shepherd et al.*, 1991; *Skiba et al.*, 1992; *Valente and Thornton*, 1993; *Sullivan et al.*, 1996; *Aneja et al.*, 1996b]. Previous measurements of soil emissions from other research groups confirm that there is great spatial and temporal variability in NO flux. For example, *Sullivan et al.* [1996] and *Aneja et al.* [1995] reported average summertime NO fluxes of 21.9 ng N m^{-2} s^{-1} and 8.1 ng N m^{-2} s^{-1}, respectively, for corn planted at the same location for 2 years in a row in the Upper Coastal Plain of North Carolina. Additionally, *Johansson and Sanhueza* [1988] reported that soil NO emission rates can vary by a factor of 2-3 within a 50 m^2 plot.

In the southeastern United States, which is NO$_x$ limited, an increase in NO$_x$ emissions is believed to produce a corresponding increase in O$_3$ levels [*Fehsenfeld et al.*, 1993; *Aneja et al.*, 1996a]. O$_3$ negatively affects human health, as well as ecological systems, such as crop yield. Studies show that prolonged exposure to high ozone levels causes persistent functional changes in the gas exchange region of the lungs. Additionally, ozone plays a critical role in controlling the chemical lifetimes and the reaction products of many atmospheric species [*National Research Council*, 1991]. Gaseous nitric acid (HNO$_3$), the end product of NO reactions in the atmosphere, combines with either aerosols or water in the atmosphere and is removed via rain, snow, or other deposition processes, as acidic deposition.

The primary objective of this study was to characterize NO flux from an intensively managed row crop (corn) in the Lower

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Coastal Plain of North Carolina and to attempt to relate this flux to environmental parameters such as soil temperature, soil extractable nitrogen, and soil water content. This research site was also the site of Project NOVA 1995 [Natural Emissions of Oxidant Precursors: Validation of Techniques and Assessment) [*Aneja*, 1994]. This multi-scientific-agency project was designed to conduct side-by-side comparisons of different NO flux methodologies, namely, chamber techniques and micrometeorological techniques. This paper will also present the results of an intercomparison of soil NO flux values as measured via the North Carolina State University Air Quality Groups' dynamic flow-through chamber and the NASA Langley Research Center, Hampton, Virginia, Groups' static chamber. The knowledge gained from this site will help to further characterize biogenic soil emissions from the southeastern United States, and may help to explain elevated O_3 concentrations in this region.

2.   Methods and Materials

2.1. Physiographic Location

Flux measurements were made on a private farm located in Washington County, in the Lower Coastal Plain region of North Carolina, approximately 20 km southeast of Plymouth (124.63°W, 48.30°N, 43 m mean sea level (MSL)), and 120 km from the Atlantic Ocean (Figure 1). Washington County is situated between two major river basins, the Roanoke River basin and the Pungo River basin, and has a level topography, ranging from 5 to 50 m above sea level. A naturally high water table inhibits drainage, slows the mineralization of soil organic matter, and leaves the surface soil layer black as compared to lighter colored soils in the region, which are well drained. The soil at the research site is classified as a Portsmouth fine sandy loam soil (Thermic Typic Umbraquult; black fine sandy loam, weak medium granular structure, very friable [*Tant*, 1991]).
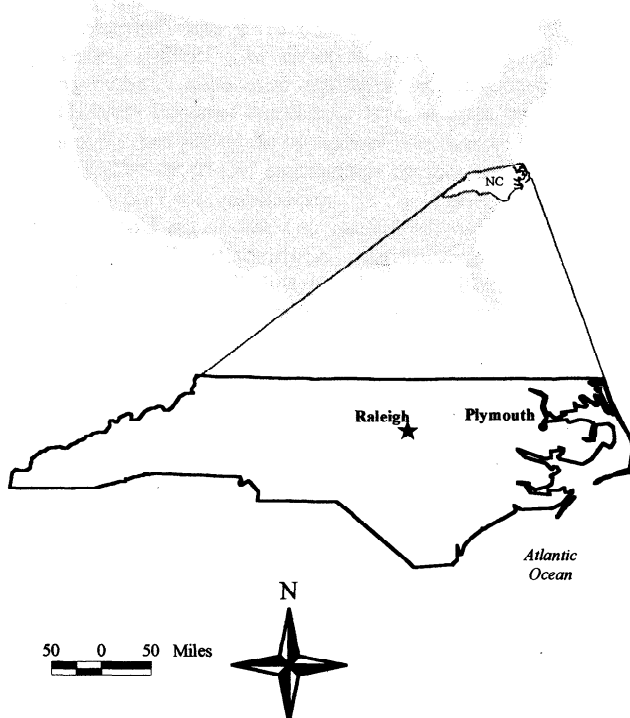

Figure 1. Map of North Carolina indicating research site of Plymouth.

Farming in this region is made possible by a series of ditches and canals that are interconnected and drain into Albemarle Sound. Most farmland is drained by a network of parallel ditches, 1 m deep and 50 m apart, that drain into larger canals, which in turn, empty into several main canals. Most major highways follow these main canals. Beginning in the late 1970s, flash-board risers were installed at exit points on most farms to prevent field runoff via ditches and smaller canals from emptying directly into the main canals and thus into Albemarle Sound. This measure has proven successful in limiting nutrient loading into the Sound and has also been used by individual farmers as a means of subsurface irrigation. During periods of moisture stress, water from deep wells is pumped into the ditch-canal system on individual farms, eventually raising the water table.

The research site itself consisted of approximately 136 hectares (ha) of continuous cropland (corn, *Zea mays*), 1067 m wide and 1280 m long. The site is accessible by a canal road off North Carolina Route 99/45, which lies approximately 2 km to the northeast. Measurements using our technique were confined to the northeast edge of the field. Subsurface irrigation by the farmer was used once during our measurement period.

2.2. Planting and Fertilization

The corn crop was planted on April 12, 1995. The land was treated with a pre-emergent herbicide, and then the corn seed was drilled into soybean stubble (no-till planting) left from the previous fall. The crop was fertilized at planting with 73 kg nitrogen (N) ha^{-1}. Approximately 9 kg N ha^{-1} was applied at planting, 5 cm below the seed. The remainder was applied as a 30% N solution, containing equal parts of urea, ammonia, and nitrate, which was broadcast across the field after planting. The final addition of fertilizer, 102 kg N ha^{-1}, was applied on May 20, 1995, also as a 30% N solution of equal parts urea, ammonia, and nitrate. This final side-dressing was applied as a thin (approximately 2 cm) liquid band down the center of the interrow. A portion of the corn field was not fertilized with the additional N fertilizer to allow comparison of NO flux from fertilized and unfertilized areas.

2.3. Sampling Scheme

The daily sampling scheme consisted of measuring ambient concentrations of NO, NO_y and NO_2, at ground level, and from the exit port on the dynamic flow-through chamber. Daily soil flux measurements consisted of placing the chamber on a stainless steel collar, which had been inserted into the soil the previous evening. The chamber was placed on the collar at approximately 0530 hours and flushed with ambient air for at least 1 hour before data collection began at 0630. This technique ensured that the concentrations within the chamber reached steady state prior to data acquisition and allowed time for daily calibration of the instruments. Gas sampling ended at approximately 1800. The stainless steel collar was then relocated to another interrow position selected at random within a 10 m radius of the mobile laboratory, in preparation for the next day's measurements. This procedure allowed a minimum of 12 hours to dissipate any effect on soil NO flux due to soil disturbance with insertion of the stainless steel collar.

2.4. Dynamic Flow-Through Chamber

A dynamic flow-through chamber lined with 5 mm thick fluorinated ethylene propylene (FEP) Teflon was used to measure NO, NO_2, and NO_y flux from the soil. The translucent
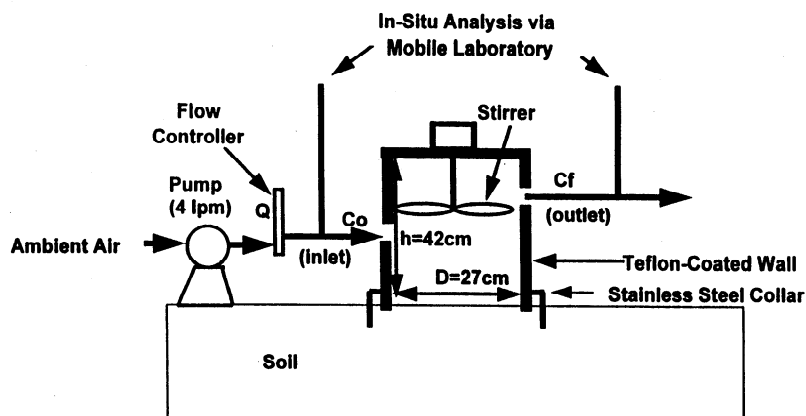
Figure 2. Schematic of dynamic flow-through chamber. The chamber fits inside of a stainless steel collar which is placed in the soil the previous day to minimize soil disturbances.

chamber, 27 cm in diameter, and 42 cm high (volume equal to 24.05 L), fits gas-tight inside of a stainless steel metal ring, which is driven into the ground to a depth of ~10 cm (Figure 2). Ambient air, which is used as a carrier gas, is pumped through the chamber at a constant flow rate (~ 4 L/m). The air inside the chamber is mixed by a variable-speed, motor-driven Teflon impeller. Teflon tubing (1/4 inch outside diameter, 1/8 inch inside diameter) is used to connect the chamber and analytical instrumentation. The entire measuring system, from the inlet port on the chamber to the point where the gas stream is subsampled for analysis, is coated by either Teflon, or gold, or is composed of stainless steel to minimize further chemical reactions with the sample stream. Sample lines connecting the chamber and instrumentation do not exceed 10 m. The NO detection instruments drew 1 L/m, which resulted in a sample residence time in the sample lines of approximately 5 s.

Experiments were conducted to determine if the mixing speed of the Teflon impeller altered soil NO flux measurements. Varying the speed between 20 and 100 revolutions per minute (rpm) did not produce any significant changes in the NO flux. The impeller was set to 70 rpm for the remainder of the experiment. The size of the outlet port on the chamber ensured that there were no substantial pressure differences between the outside atmosphere and the air within the chamber. Research conducted on similar chambers using a tilting water manometer indicates that pressure differences were below detection limits (0.2 mm H_2O) [*Johansson and Granat*, 1984]. Condensation of water vapor in the Teflon lines between the chamber and analytical instrumentation was observed during the afternoon hours. To overcome this problem, the sample line was disconnected and flushed with zero grade air. Although the process took only 4-5 min, concentration measurements were delayed approximately 30 min to allow the system to once again reach steady state. Condensation within the sample lines was no longer a problem after the instruments were converted to measure NO_y concentrations in addition to NO. The instrument conversion involved moving the molybdenum converter, which is heated to 325°C, to the exit port of the chamber. All measurements after May 25 were taken with the molybdenum converter at the exit port of the chamber.

2.5. Temperature-Controlled Mobile Laboratory

All instrumentation was housed in a temperature-controlled mobile laboratory. The mobile system consisted of a modified Ford Aerostar van with a 13,500 BTU air-

conditioning unit. The temperature inside the van was maintained at or below the operating range of the instruments. Power for the air-conditioning and all of the detection instruments was standard 110 V ac installed at the research site.

3. Oxides of Nitrogen Measurement

Nitric oxide (NO) concentrations were measured using a Thermo Environmental Instruments Incorporated (TECO) model 42S chemiluminescence, high-sensitivity NO analyzer [*Thermo Environmental Instruments, Inc.*, 1992]. A multipoint calibration was conducted prior to, and at the midpoint of, the measurement period. Each day, zero and span checks were conducted. A cylinder of 0.109 ppmv NO in N_2 (Scott Specialty gases) and zero grade air (National Welders) were used for zeroing, spanning, and calibrating of the TECO instrument.

The reactive nitrogen compounds (NO_y) were measured using a modified TECO model 42S. With the assistance of the North Carolina Department of Environmental Health and Natural Resources (DEHNR-Division of Air Quality), the instruments were modified so that the molybdenum converter was relocated from inside the instrument to the sample exit port on the dynamic chamber. After modification, the same TECO 42S instrument could measure both NO and NO_y.

Nitrogen dioxide (NO_2) concentrations were measured with a Unisearch Associates Incorporated LMA-3 chemiluminescence NO_2 instrument. The instruments were calibrated prior to and at the midpoint of the experiment, according to written protocols [*Scintrex Ltd.*, 1989]. Additionally, zero and span checks were performed prior to each set of daily measurements. The same mixture that was used to calibrate the NO instruments (0.109 ppmv NO in N_2 - Scott Specialty Gases) was used to calibrate the NO_2 instruments. A TECO 146, Dynamic Calibration System was used to titrate a mixture of NO with an abundance of ozone [*Thermo Environmental Instruments, Inc.*, 1986]. Using the reaction $NO+O_3 \rightarrow NO_2+O_2+h\nu$, a known quantity of NO_2 was delivered to the LMA-3.

3.1. Automated Data Collection

A Toshiba laptop computer and Labview software (National Instruments) were used as an automated data acquisition system. The system recorded 60-s rolling average concentration measurements and then binned and averaged

these values every 15 min. The 15-min binned averages were stored and used later in all flux calculations. At frequent intervals, we recorded the concentrations from the LED readout on the front panel of the instruments. These recorded values were checked against computer recorded values to ensure the systems' accuracy. No significant discrepancies were noted between the instrument display and the computer stored values.

3.2. Flux Calculations

The NO and NO_y fluxes were calculated from a mass balance equation [Kaplan et al., 1988; Kim et al., 1994]:

$$\frac{dC}{dt} = (\frac{q[C_{air}]}{V} + \frac{J}{h}) - (\frac{L}{h} + \frac{q}{V})[C] \qquad (1)$$

where h is internal height of the chamber (42 cm), J is emission flux per unit area (ng N m^{-2} s^{-1}), L is total loss in the chamber per unit area assumed first order in [NO] (cm s^{-1}), q is flow rate through the chamber (L/m), V is volume of the chamber (24.05 L), C is NO concentration in the chamber (ppbv), and C_{air} is NO concentration in the ambient air immediately adjacent to the chamber (the inlet of the chamber) (ppbv).

Assuming the chamber is well mixed, the concentration [C] measured can be assumed to be the same everywhere within the chamber. Additionally, at steady state conditions, the change of concentration, with respect to time, will be zero. Equation (1) reduces to

$$\frac{J}{h} = (\frac{L}{h} + \frac{q}{V})C_{eq} - \frac{qC_{air}}{V} \qquad (2)$$

C_{eq} is the concentration measured at the outlet of the chamber. During most of the measurements, the NO concentrations in the ambient air (C_{air}) adjacent to the chamber were less than 1 ppbv.

In equation (2), the total loss term L is the sum of the loss of NO through reactions with the chamber walls and chemical reactions of NO with existing oxidants in the carrier gas, such as O_3 and peroxy radicals [Kim et al., 1994; Aneja et al., 1995]. The total loss term was determined empirically (five experiments were conducted throughout the day and night) utilizing a method developed by Kaplan et al. [1988]. This method plots the value of -ln $(C_{eq} - C)/(C_{eq} - C_o)$ against time (t). C_o is the NO concentration in the chamber when NO reaches the first equilibrium state at an initial flow rate. C_{eq} is the NO concentration in the chamber after the flow rate is reduced and allowed to reach a second equilibrium. From the linear relationship between the value of -ln $(C_{eq} - C)/(C_{eq} - C_o)$ and time during the experiment, the slope is found to represent $(L/h) + (q/V)$. The total loss in the chamber was estimated to be 0.924 cm min^{-1}. The value of L/h (=0.022 min^{-1}) agrees with those found by Kim et al. [1994], and was used in equation (2) to calculate the NO flux during the experimental period.

3.3. Soil Temperature and Soil Analysis

Soil temperature was recorded every 15 min using a Fischer Scientific temperature probe inserted 5 cm into the soil, adjacent to the chamber. Comparisons were made during the first week of the experimental period to see if there were any significant temperature differences between the soil inside the chamber and the soil outside the chamber. Temperature differences were negligible, which agrees with results obtained by other researchers [Kim et al., 1994; Sullivan et al., 1996; Aneja et al., 1996b].

A soil sample was taken from the center of the dynamic flow-through chamber footprint at the end of each measurement period. Samples were taken with a bucket auger which removed a soil core to a depth of 20 cm. Soil properties for the research site, such as percent water-filled pore space (%WFPS), pH, and total extractable nitrogen, were obtained from the bucket auger samples. The %WFPS is an expression of soil water content and can be expressed as the percentage of pore spaces in the soil filled with water.

Soil bulk density, which is the weight of the soil solids per unit volume of total soil, and soil particle density, are used to determine the %WFPS of the soil [Troeh and Thompson, 1993]. Soil bulk density was measured for the surface soil horizon (10 cm depth) using the core method (345 cm^3) [Blake and Hartge, 1986]. Particle density for most soils is usually assumed to be 2.65 g cm^{-3}; however, particle density will differ from this value for soils with relatively high organic matter content. The particle density for the surface soil horizon at our research site was determined to be 2.3 g cm^{-3}.

The total extractable nitrogen was calculated by summing the extractable fractions of ammonium (NH_4^+) and nitrate (NO_3^-) determined from the soil samples. Extractable NH_4^+ and NO_3^- were determined using a 1 M KCL soil extract (expressed on a weight basis) [Keeney and Nelson, 1982] and standard autoanalyzer techniques [Lachat Instruments, 1990]. Soil water content (SWC) was calculated as

SWC = [initial weight - dry weight (24 h at 105°C)]
          /dry weight (24 h at 105°C).

4. Results and Discussion

4.1. Site Characterization

All soil flux measurements reported here were obtained between May 15 and June 9, 1995. Rainfall patterns during this period were marked by the passage of the remnants of Hurricane Allison over the site on June 5. Prior to this event, there had been limited rainfall, with thunderstorms occurring on May 19 and June 3. Neither of these events left any standing water in the field, as opposed to the heavier rains (12 cm of rainfall) which occurred on June 5, leaving portions of the field flooded for up to 2 days. The only significant deviation in the SWC of the field, which can be expressed as %WFPS, occurred after the passage of the remnants of the hurricane. The average %WFPS for the entire measurement period was 48.7% ± 8.3% (Table 1). The measured %WFPS increased to 68.4% 2 days after passage of the remnants of the hurricane. During the remainder of the measurement period, weather at the site was dominated by high-pressure systems with southerly winds.

Extractable nitrogen (1 M KCl) was present in the soil throughout the measurement period, and although N fertilizer was applied to the field at the midpoint of the experiment, there was not a corresponding increase in the amount of extractable N (Table 1). The lack of a discernible difference in extractable nitrogen after side-dressing with N, as would be expected, is due to a combination of three factors: method of fertilizer application, rainfall distribution, and our soil NO flux measurement technique. The side-dressing with N was applied as a thin concentrated liquid band (2 cm wide) down the center of the interrow (1 m width). During application, the applicator hoses would drag across the soil surface, sometimes being deflected from the center of the interrow. As a result, the concentrated fertilizer band could not be assumed to always be present in the center of the interrow. Once the liquid band

Table 1. Data Summary for the Plymouth, North Carolina (May 15 - June 9, 1995), Measurement Period

	Soil Temperature,* °C	Total Extractable Nitrogen,[†] mg N / kg dry soil	% WFPS,[‡]	NO Flux, ng N m^{-2} s^{-1}
Corn (all measurements)				
Average	24.2	51	35.2	50.8
Standard deviation	3.2	26	6.3	47.7
Minimum	16.4	23	27.9	4.2
Maximum	34.2	116	49.7	264.7
Corn (before side-dressing)				
Average	23.5	49	34.7	31.5
Standard deviation	3.7	21	6.0	10.1
Minimum	16.4	27	27.9	7.6
Maximum	32.7	94	43.4	41.9
Corn (after side-dressing)				
Average	24.8	52	35.7	77.7
Standard deviation	2.3	31	7.0	63.7
Minimum	20	23	27.9	4.2
Maximum	34.2	116	49.7	264.7

All NO flux data, and soil temperature data were computed from 15 min binned averages.
*5 cm soil depth adjacent to dynamic flow-through chamber.
[†]1 N KCl extractable NH$_4^+$ + NO$_3^-$; 0-20 cm depth.
[‡]Percent water-filled pore space; 0-20 cm depth.

dried, it was not possible to determine where the band was located at a particular sampling position. The fertilizer applied as the liquid band remained on the soil surface for a week following application due to a lack of any measurable rainfall. Since the chamber footprint (27 cm diameter) was less than half the width of the interrow, random placement of the chamber meant that it was possible to miss the portion of the interrow that had received the additional N fertilizer. The extractable *N* values in Table 1 for the period after application of the side-dressing of N fertilizer suggest that many of the flux measurements recorded were from portions of the field not directly impacted by the additional application of N fertilizer.

Soil temperatures during the experiment ranged from 16.4 to 34.2°C with an average of 24.2 ± 3.2°C (Table 1). Daily average soil temperatures increased throughout the research period, with all values between the 15 and 35°C optimum range for NO emissions proposed by *Williams and Fehsenfeld* [1992a]. The crop remained in a vegetative

growth stage throughout the experiment and changed in height from 58 to 173 cm at the close of the measurement period.

4.2. NO Flux

Measured soil NO flux ranged from 4.2 to 264.7 ng N m^{-2} s^{-1}. The overall average of the 15 min NO flux measurements for the experimental period was 50.8 ± 47.7 ng N m^{-2} s^{-1} (Table 1). Figure 3 displays a cumulative frequency plot for all of the composite hourly averaged NO flux values. This plot shows that, although there were periods when the flux exceeded 200 ng N m^{-2} s^{-1}, these relatively extreme values represent less than 3% of all observations. The plot further reveals that 80% of the observations were below 67 ng N m^{-2} s^{-1} and 50% of the observations were below 37 ng N m^{-2} s^{-1}. Additionally, over 65% of the observations fell between 15 and 50 ng N m^{-2} s^{-1}.

The average NO flux increased dramatically after the side-dressing of N fertilizer on May 20, 1995. The average NO flux
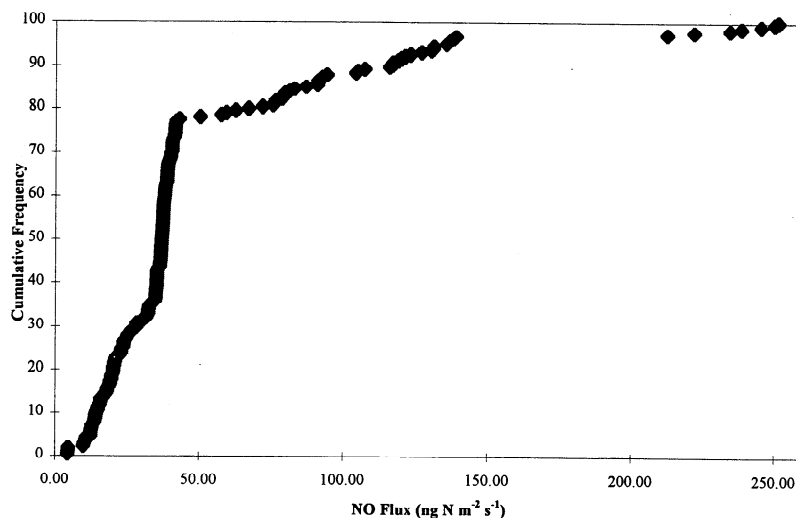

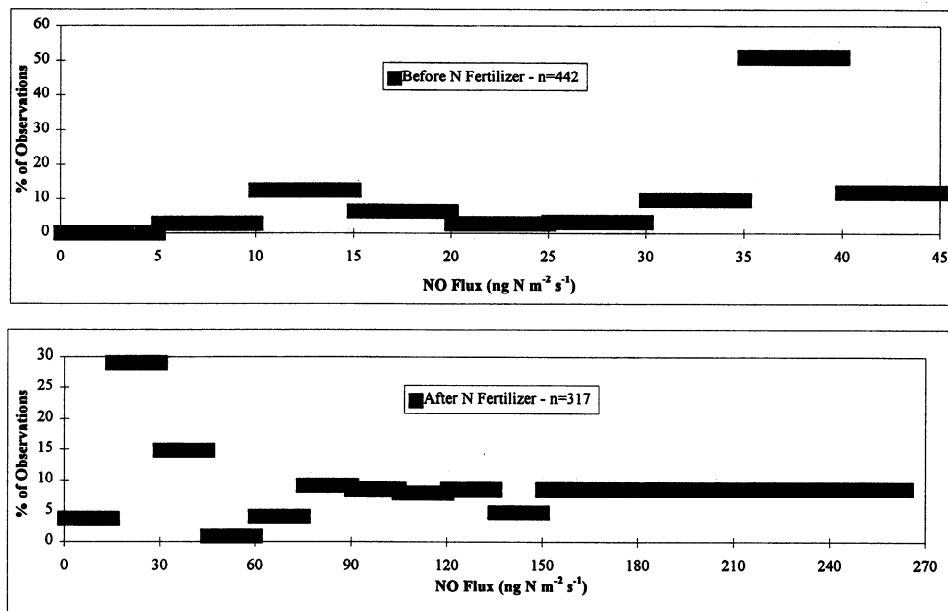**Figure 3.** Frequency plot of the composite hourly averaged NO flux measurements.

Figure 4. Population distribution of 15 min NO flux measurements for 8 day period prior to N fertilizer (top) and 8 day period after N fertilizer (bottom).

prior to this side-dressing was 31.5 ± 10.1 ng N m^{-2} s^{-1}, with a range of 7.6 to 41.9 ng N m^{-2} s^{-1} (Table 1). The average flux from those portions of the field which received the side-dressing of fertilizer was 77.7 ± 63.7 ng N m^{-2} s^{-1} with a range of 4.2 to 264.7 ng N m^{-2} s^{-1}. A shift in the overall population distribution of NO flux values from before fertilization to after fertilization can be seen in Figure 4. Both measurement periods contained approximately the same percentage of observations between 0 and 30 ng N m^{-2} s^{-1} (~ 30%), although for the period prior to N fertilization the majority (72.6%) of the measurements fell between 30 and 45 ng N m^{-2} s^{-1} and for the period after N fertilization the majority (52.3%) of the measurements were greater than 45 ng N m^{-2} s^{-1}. Some of the variation present in the NO flux within each measurement period can be explained by Figure 5, which is a graph of the daily average NO flux (0900 - 1700) throughout the entire research period. Daily soil NO flux measured prior to

application of the band of N fertilizer was essentially constant, except for the passage of a thunderstorm on May 19, which decreased soil NO emissions. Daily soil NO flux after application of the additional N fertilizer are much more variable, with one day (May 30) accounting for the majority of measured NO flux values greater than 150 ng N m^{-2} s^{-1} (Figures 3 and 5). The data in Figure 5 also suggest that surface application of N fertilizer resulted in NO flux becoming much more susceptible to daily changes in other parameters, as noted by the decline in NO flux on succeeding days as compared to daily NO flux measured prior to May 26. The two peaks in daily soil NO flux after May 26 are consistent with the passage of rain events and the conclusion by *Yienger and Levy* [1995] that "pulses" of soil NO flux induced by rain events can account for more than 20% of total soil NO emissions. However, we are not certain as to why no such peaks were observed prior to May 26. The decrease in
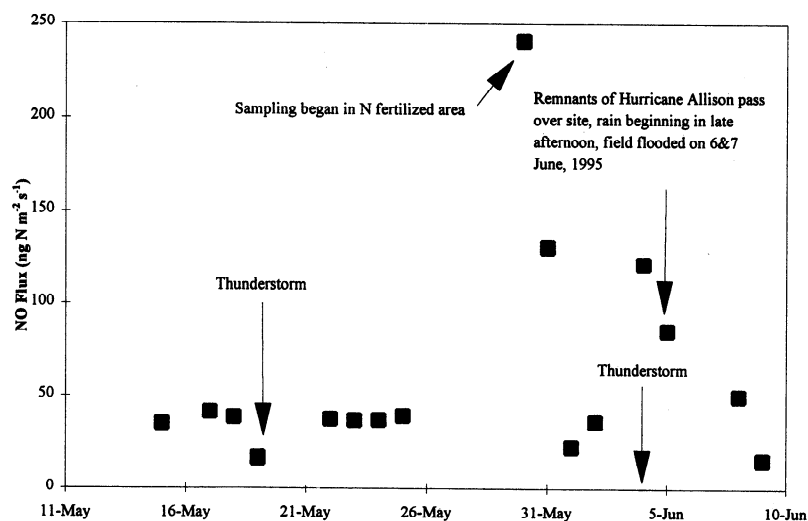

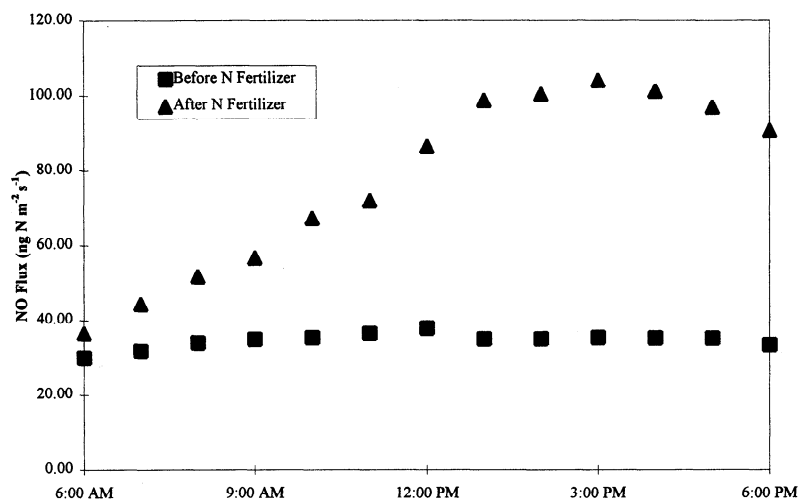**Figure 5.** Daily average NO flux (0900 - 1700) versus day of experiment.

Figure 6. Hourly averaged flux values for the time periods prior to and after the final application of nitrogen fertilizer.

soil NO emissions due to the heavy rains on June 5 and 6 is consistent with the results of other researchers who have reported a decrease in soil NO emissions due to reduced diffusivity of NO through the water-logged soil pores [*Cardenas et al.*, 1993].

The difference in soil NO flux before and after fertilization can also be seen in Figure 6, which is a graph of the composite hourly averaged flux for periods prior to and after the application of fertilizer. The range of NO flux observed during the duration of this study coincides with values reported by other researchers. Table 2 lists values of NO flux reported by other researchers, who measured NO emissions from corn using chamber techniques.

A diurnal trend, in which NO emissions peaked in the afternoon and diminished throughout the evening hours, was evident throughout the experiment (Figure 7). The rise in NO flux during the morning hours coincided very well with the increase in soil temperature, as did the gradual decline in soil NO flux with the gradual decline in soil temperature during the late afternoon and evening hours. This strong relationship between NO flux and temperature has been reported by other researchers [*Johansson and Granat*, 1984; *Johanson*, 1984; *Williams et al.*, 1988; *Shepherd et al.*, 1991; *Slemr and Seiler*, 1991; *Valente and Thorton*, 1993; *Sullivan et al.*, 1996; *Aneja et al.*, 1996b].

Table 2. NO Emissions Obtained by Various Research Groups Using Chamber Techniques

Flux, ng N m^{-2} s^{-1}	Source
5.56 – 239	*Williams et al.* [1987]
5.84 – 67	*Anderson and Levine* [1987]
-0.5 – 106.2	*Aneja et al.* [1995]
7.1 – 106.2	*Sullivan et al.* [1996]
8 – 188	*Valente and Thorton* [1993]
36.4 – 54.7	*Jambert et al.* [1994]
	This paper
4.2 – 264.7	Range for entire research period
7.6 – 41.9	Range before fertilizer side-dressing
4.2 – 264.7	Range after fertilizer side-dressing

All measurements were made from corn crops.

4.3. NO$_y$ Flux

Soil NO$_y$ flux was measured during the latter half of the experimental period, from May 30 to June 9, 1995. The same diurnal trend which appeared in the NO emission profile was evident in the NO$_y$ profile. NO$_y$ is important because it consists of the reactive atmospheric nitrogen compounds (NO$_y$ = NO + NO$_2$ + NO$_3^-$ + HNO$_3$ + HNO$_2$ + PAN + organic nitrates + HO$_2$NO$_2$) [*Fehsenfeld et al.*, 1987]. The range of the calculated NO$_y$ fluxes during this period was 2.09x10^{-10} to 2.16x10^{-8} mol NO$_y$ m^{-2} s^{-1}. NO$_y$ was measured in conjunction with NO and NO$_2$ in order to determine if any other reactive nitrogen compounds were being emitted by biogenic soil processes.

Figure 8 is a graph of the composite daytime averaged flux of NO and NO$_y$ versus time of day. The composite average flux of NO represents ~86% of the composite average flux of NO$_y$. Measurements of NO$_2$ concentrations made during this period indicate a flux range from 0 to 15.73 ng N m^{-2} s^{-1}, with an average flux of 6.19 ng N m^{-2} s^{-1}, which is approximately 8.7% of the total NO emitted and agrees with other reports that <10% of the NO$_x$ (NO+NO$_2$) emitted by the soil is in the form of NO$_2$ [*National Research Council*, 1991]. The average NO emissions during this time period was 71.56 ng N m^{-2} s^{-1}. The results for this research site indicate that 86% of NO$_y$ is made up of NO and 8.7% is present in the form of NO$_2$, leaving 5.3% of the emitted NO$_y$ unaccountable. Our results can not confirm or deny whether this unaccounted NO$_y$ is due to instrument uncertainty or if there are other reactive nitrogen compounds, other than NO$_x$, being emitted from the soil (i.e., NO$_3$, HNO$_3$, HNO$_2$, PAN, organic nitrates, or HO$_2$NO$_2$).

Figure 9 shows the apparent relationship between NO and NO$_y$ at night. Although this graph only represents one diurnal experiment, it appears that the two graphs begin to converge during the late evening/early morning hours. This suggests that the unaccounted reactive nitrogen compounds being emitted during the day, drop to a minimum at night.

4.4. Environmental Controls on NO Flux

The results presented in Figure 7 show a strong temperature dependence of hourly soil NO flux on soil temperature. However, the overall relationship between soil temperature and soil NO flux, when summarized on a daily scale was
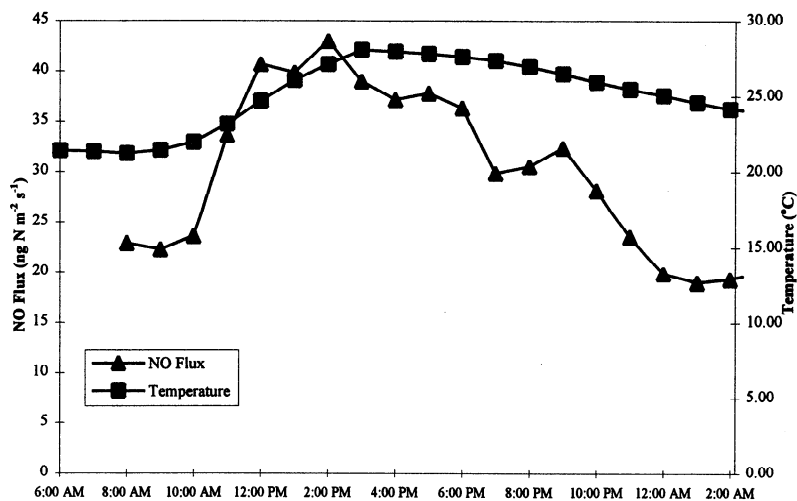
Figure 7. NO flux versus time of day and temperature for diurnal experiment conducted on June 2, 1995.
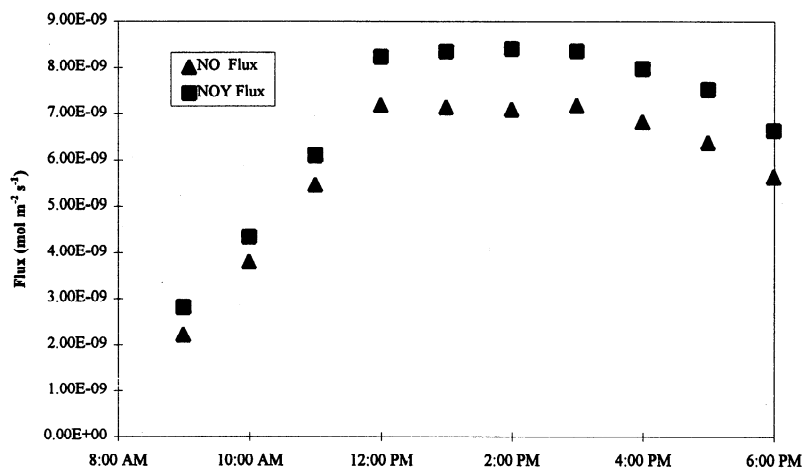

Figure 8. Composite daytime hourly averaged flux of NO and NO_y versus time of day.
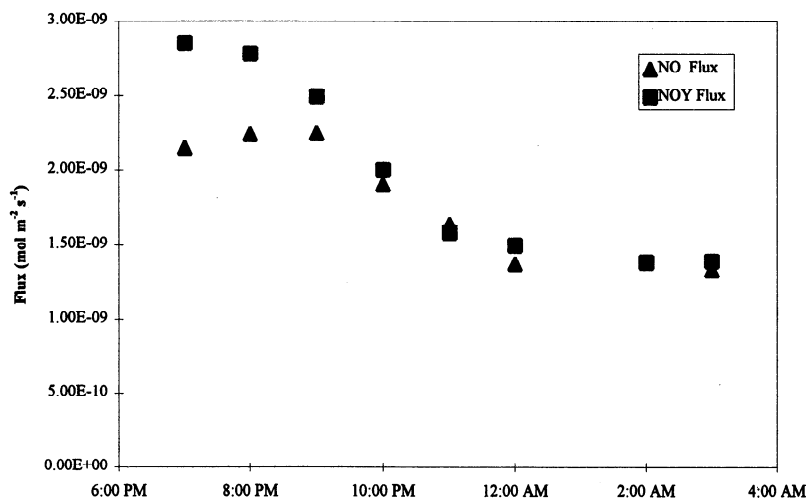

Figure 9. Composite nighttime hourly averaged flux of NO and NO_y versus time of day.

essentially nonexistent for soil NO flux measured prior to N fertilizer application ($R^2 = 0.10$; Figure 10). After N fertilizer application, the exponential dependence on soil temperature improved ($R^2 = 0.34$). However, when we removed one data point from the regression, which occurred during the period when the field was flooded by the passage of the remnants of

the hurricane, we found an even stronger exponential dependence on soil temperature ($R^2 = 0.58$), which is consistent with the observations of other investigators [*Williams et al.*, 1988; *Sheperd et al.*, 1991; *Slemr and Seiler*, 1991; *Williams and Fehsenfeld*, 1991; *Stocker et al.*, 1993; *Sullivan et al.*, 1996; *Aneja et al.*, 1996b]. The lack of a
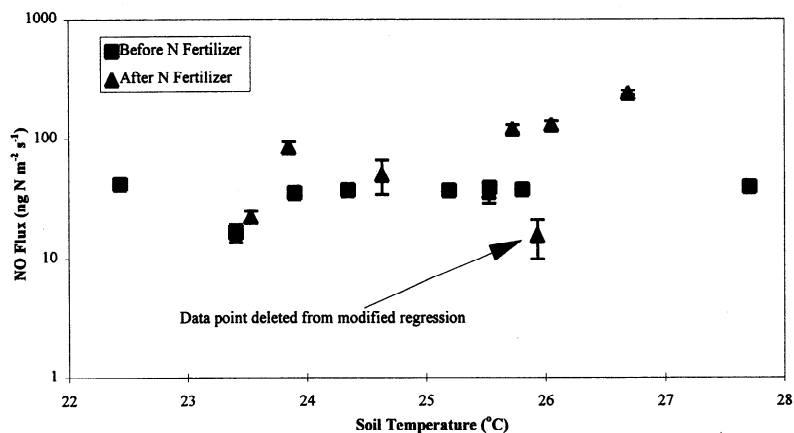
Figure 10. Daily average NO flux (0900 - 1700) versus daily average soil temperature. Data were segregated into periods before and after N fertilizer application. Vertical lines indicate one standard deviation of NO flux. $R^2 = 0.58$ for the time period after the N fertilizer was applied to the field (neglecting the one marked data point).

relationship between soil NO flux and soil temperature prior to the addition of N fertilizer may be due to other factors, such as optimum soil water content in the surface soil horizon. Our data suggest that the exponential dependence of soil NO flux on soil temperature may only be observed in intensively managed agricultural row crops when excess amounts of extractable N are present in the top few centimeters of soil. In the future, soil sampling schemes to estimate extractable N may need to be altered in order to measure the distribution of extractable N with depth in the top 20 cm of the soil.

4.5. Total Extractable Nitrogen and Soil Moisture

Figure 11 is a graph of the daily averaged NO flux versus %WFPS and total soil extractable nitrogen, segregated into periods before and after the N fertilizer was applied. Although
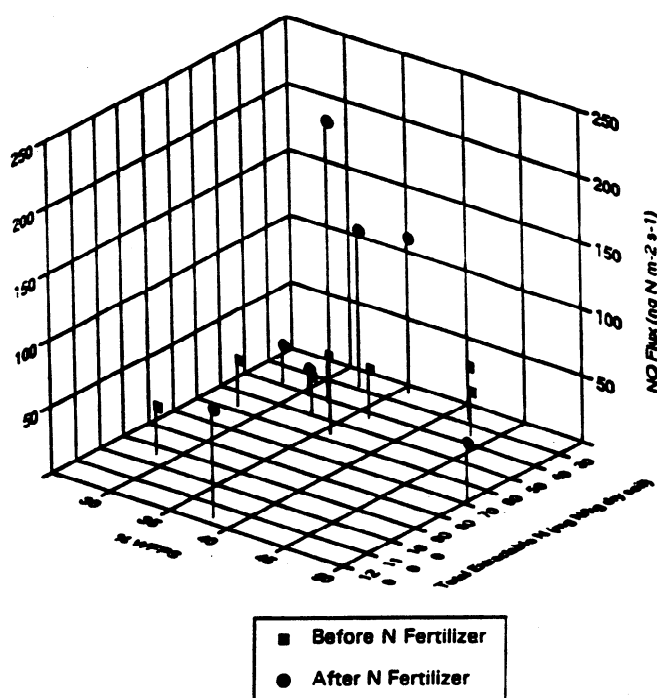

Figure 11. Daily averaged NO flux (0900 - 1700) versus percentage water filled pore space and the total extractable nitrogen. Soil data are from the 20 cm soil core taken from the center of the chamber footprint at the end of each experimental period.

the organic and inorganic nitrogen content of soils has been shown to affect the emissions of NO, a relationship between extractable N and soil NO flux is not evident in our data [*Slemr and Seiler*, 1984; *Anderson and Levine*, 1987; *Williams et al.*, 1987; *Davidson*, 1992a,b; *Hutchison and Brams*, 1992; *Hutchison and Davidson*, 1993]. In fact, the highest soil NO fluxes were obtained from soil with the lowest content of extractable N. This suggests that some other parameter was controlling soil NO flux. Within the range of optimum SWC for soil NO flux, reported to be between 30% and 70% WFPS, changes in %WFPS are not expected to produce a significant change in the NO flux [*Linn and Doran*, 1984; *Davidson and Swank*, 1986; *Parton et al.*, 1988; *Davidson*, 1991]. There were only 3 days in which the %WFPS existed outside this optimum range, precluding any statistical corroboration of the impact of %WFPS on soil NO flux using our data set.

4.6. Intercomparison of Dynamic and Static Chambers

The research conducted in Washington County, North Carolina was part of a larger research effort known as Project NOVA 1995. The North Carolina State University (NCSU) Air Quality Group and NASA Langley Research Center, Hampton, Virginia, both participants of Project NOVA, measured NO emissions from the soil using two different chamber techniques.

The NASA research group used a closed box flux technique (static chamber), in which NO fluxes were calculated using the mixing ratio of NO (ppbv) versus time [*Anderson and Levine*, 1987]. Their measurement technique consisted of placing the chamber collars in the soil, several days prior to the experiment. The collars were arranged in groups of four, approximately 1 m apart, in a square pattern in two adjacent interrows. There were four of these groupings positioned throughout the field. Whereas the NASA Group primarily sampled from the same sites throughout the measurement period, the NCSU Air Quality Group sampled from a different randomized position in the field each day. A typical measurement period for the NASA group involved 1 hour at three or all four of the positions, with sampling from each of the four collars at the individual sites. Nighttime measurements, between 1800 and 0600, were also conducted so that diurnal comparisons could be made between the two chamber techniques. Experimental constraints limited nighttime comparisons to 60 of the total 460 simultaneous measurements. Therefore we have chosen to neglect these
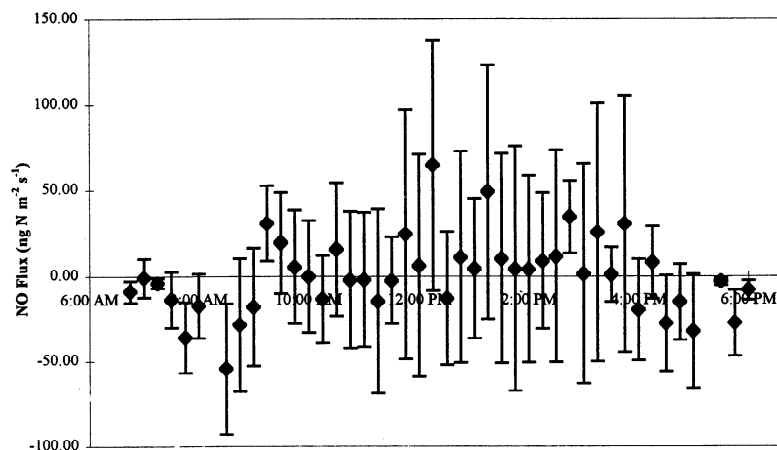
Figure 12. Difference of NO flux between two chamber techniques (NCSU Air Quality Group - NASA Group) versus time of day. Vertical lines indicate one standard deviation of the NO flux measurements made from both chamber techniques.

nighttime measurements in the statistical analysis due to the limited number of data points. However, the limited data during the nighttime period does show that the NASA group measured NO flux consistently higher than the NCSU Air Quality Group.

Figure 12 is a difference plot of the composite averaged fluxes calculated by the NCSU Air Quality Group and the NASA Research Group versus time during NOVA 1995. Differences between the 400 measurements were calculated, and the resulting Δflux were analyzed with the SAS statistical package. Due to time series activity in the data, a procedure called PROC ARIMA (autoregressive integrated moving average) was used to model the data and test the hypothesis that the mean of these differences was zero meaning that both chamber methods yield statistically identical values [*SAS Institute, Inc.*, 1988]. The statistical model which best fit the data consisted of a mean parameter and two autoregressive parameters. The SAS output produced a T-ratio = 0.15 for MU, the mean of the differences. This value indicates that there is not enough statistical evidence to reject the hypothesis that the mean of the differences is zero. Therefore, as the hypothesis fails to be rejected, the conclusion must be that there was no statistical difference between soil NO flux as measured using the two chamber methods (dynamic and static) at the Plymouth, North Carolina, research site.

5. Conclusions and Recommendations

The research conducted at a corn field in Plymouth, North Carolina, provided an opportunity to measure oxides of nitrogen emissions and the environmental variables which may control them, for a continuous 4 week period. During this measurement period we were also able to investigate how the application of N fertilizer affects NO emissions. Utilizing a dynamic flow-through chamber technique to measure NO emissions, the average flux was found to be 31.5 ± 10.1 ng N $m^{-2} s^{-1}$ before the N fertilizer was applied and 77.7 ± 63.7 ng N $m^{-2} s^{-1}$ after the N fertilizer was applied. Although NO flux did follow the same diurnal pattern of soil temperature throughout the research period, we were only able to detect the exponential relationship between daily NO flux and soil temperature, as observed by other researchers, for the period after side-dressing with N fertilizer. We believe that the addition of N fertilizer was responsible for the increased levels of NO flux from this agricultural field. However, the fact that average extractable nitrogen values did not change

significantly between before and after fertilization brings into question the exact location of the biogenic processes responsible for soil NO emissions. Our hypothesis is that the processes responsible for NO emissions are concentrated in the top few centimeters of the soil surface. Our current soil sampling method, which removes a soil core 20 cm deep, could have diluted the concentration of extractable nitrogen present near the soil surface. Future research should consist of 5, 10, 15, and 20 cm deep soil cores so that the dilution effect can be analyzed, and therefore weaken or solidify the relationship between N fertilizer and NO emissions.

These results also demonstrate that the emission of NO from intensively managed agricultural soils might be an important source of atmospheric NO concentration in the rural southeastern United States.

The intercomparison conducted between the two chamber flux methodologies revealed, as other researchers have also found, that there is great spatial variability in soil emissions and the quantification of these emissions is complicated by the high spatial variability exhibited by many microbial processes [*Parkin*, 1993; *Sullivan et al.*, 1996]. Although individual data points between the two chamber techniques can differ substantially, depending on the location within the field, the hypothesis is that many observations of randomized locations in an agricultural field will produce a statistically equivalent average flux value between the two methodologies. In fact, through a statistical intercomparison, we have confirmed this hypothesis for NO flux measurements at Plymouth, North Carolina.

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