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Seasonal variations of nitric oxide flux from agricultural soils in the Southeast United States

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ABSTRACT

Fluxes of nitric oxide (NO) were measured from the summer of 1994 to the spring of 1995 from an intensively managed agricultural soil using a dynamic flow through chamber technique in order to study the seasonal variability in the emissions of NO. The measurements were made on a Norfolk sandy loam (Fine-Loamy, Siliceous, Thermic Typic Paleudult) soil located at an agricultural research station in the Upper Coastal Plain region of North Carolina. Soil nitric oxide fluxes from 3 crops, representing 3 levels of fertilizer application (corn, 168 kg N ha^{-1}; cotton, 68 kg N ha^{-1}; and soybean, 0 kg N ha^{-1}), were measured in each season (summer, fall, winter, and spring). Additional measured soil parameters included soil temperature, soil water content (expressed as percent water filled pore space, %WFPS), and extractable nitrogen. The greatest NO flux observed in each crop occurred during the summer (June to August) measurement period (corn, 21.9 ± 18.6 ng N m^{-2} s^{-1}; cotton, 4.3 ± 3.7 ng N m^{-2} s^{-1}; and soybean, 2.1 ± 0.9 ng N m^{-2} s^{-1}). NO flux decreased in each crop through the fall months to a minimum flux in the winter. Application of fertilizer during the spring months once again produced substantial NO flux, but not as high as during the summer months. Over 80% of NO flux from the three crops measured occurred in the summer months with an estimated 5% of the nitrogen applied as fertilizer emitted as NO in a year's time. The corn crop, which had the highest amount of applied fertilizer, had the highest average yearly NO flux (7.0 ± 4.8 ng N m^{-2} s^{-1}) followed by cotton and soybean in order (1.7 ± 1.2 ng N m^{-2} s^{-1} and 1.0 ± 0.3 ng N m^{-2} s^{-1}, respectively). NO flux from soil tracked soil temperature very closely throughout the year, especially through the summer and spring months. However, NO flux measured under a cotton canopy decreased when soil temperature was >25°C and soil moisture content was <20%WFPS. Overall, the data support the assumption that in the Southeast United States, which has naturally emitted VOC's and large acreages of fertilized soils, NO emissions from agricultural soils may result in the formation of tropospheric ozone, especially during the summer months when NO emissions are highest.

1. Introduction

Nitric oxide (NO) plays a key role in regulating the atmospheric concentrations of ozone (O_3) and the hydroxyl radical in the earth's troposphere (Logan et al., 1981). When the atmosphere is in a pseudo-photostationary state, NO reacts with O_3 to form nitrogen dioxide (NO_2) and oxygen (O_2). The pseudo-photostationary state can be disrupted by radicals formed in the reaction of hydroxyl radicals with volatile organic compounds (VOCs). NO then reacts preferentially with these new formed radicals leading to an accumulation

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of O_3. Whether or not increased NO emissions lead to ozone destruction or ozone formation is dependent on other atmospheric variables such as the NO_x/VOC ratio. The southeastern United States is thought to be NO_x limited, which means an increase of NO emissions into the atmosphere will likely lead to increased O_3 production (SOS, 1993; Aneja et al., 1996). This becomes evident in that 40% of the ozone non-attainment areas in the United States are found in the southeastern United States (Lindsay et al., 1989). NO produced in certain areas may also convert to nitric acid (HNO_3), which is the fastest growing component of acid precipitation. As the southern states continue to grow in industrial strength, the problem of acid rain will likely increase. Thus in the southeastern portion of the United States, it has become crucial for O_3 control strategies and acid rain prevention to measure and parameterize the emissions of NO from all sources.

The predominant amount of NO emitted into the atmosphere is assumed to be anthropogenic in nature, but a recent report (Watson et al., 1992) has suggested that as much as 50% of NO_x ($NO+NO_2$) emitted into the global atmosphere may be from natural sources (principally lightning and emission from soil). The portion of natural sources attributable to NO emissions from soils has been in dispute with estimates of this value ranging from 15% (Logan, 1983) to 40% (Hutchinson, 1995). It is likely that the upper estimate is closer to the truth as published field measurements and inventories of NO emissions continue to show substantial NO emissions from soil, especially from tropical savannas (Poth et al., 1995), tropical forests and successional pastures (Keller and Reiners, 1994; Davidson, 1991), and intensively managed agriculture (Anderson and Levine, 1987; Bowman, 1990; Williams et al., 1992; Valente and Thornton, 1993). Using an empirical model of soil-biogenic NO_x emissions, Yienger and Levy (1995) have estimated that the strongest emitters are agriculture, grasslands, and tropical rain forests, accounting for 41%, 35% and 16% of the annual budget, respectively. By including "pulsing" (the release of a large burst of NO following wetting of a very dry soil) in their model, Yienger and Levy calculated that 1.35 TgN NO_x of the estimated annual above-canopy emissions of 5.5 TgN are associated with seasonal events that occur over a relatively brief period of time but with fluxes that are 10–100× above background levels.

Serca et al. (1994) have shown that NO fluxes from rain forest soils followed a wetting/drying cycle with maximum flux coming immediately after the rainy season but before the drought season. Shepherd et al. (1991) seemed to confirm this cycle in an agricultural soil by studying the seasonal variation of NO flux on a bare fertilized soil in Ontario, Canada. Their results show a clear seasonal cycle in NO fluxes which seemed to follow nutrient levels in the soil. This work is consistent with the observations of Davidson (1992 a,b) on the pulsing of NO from the wetting of dry soil. Poth et al. (1995) recorded NO flux in excess of 200 ng-N m^{-2} s^{-1} for recently burned tropical savanna following addition of water. Fluxes did not return to control levels until a year later, indicating that the effect of burning on enhanced soil NO emissions lasted longer than single rain events. Several researchers have attempted to study the seasonal variation of NO flux from soils (Anderson and Levine, 1987; Shepherd et al., 1991; Jambert et al., 1994; and Serca et al., 1994). In general, these researchers have found that the majority of NO flux occurs during the summer months due to higher soil temperatures. Anderson and Levine (1987) noted that 76% of all NO flux in a year occurs between the months of May and October. However, these same researchers have also pointed to other factors which may become important in predicting the flux of NO from soils on a seasonal basis. These include soil water content and available N, as well as soil temperature (Nägele and Conrad, 1990; Baumgärtner and Conrad, 1992; Hutchinson et al., 1993; Parsons and Keller, 1995). In the case of the southeastern United States (U.S.), the reaction of NO flux to moisture stress (drought) and applied fertilizer may be significant (Aneja et al., 1995). The interactions between soil temperature, soil moisture, and applied fertilizer may drastically alter the relationship between NO flux and soil temperature (Aneja et al., 1995). This fact was acknowledged by Yienger and Levy (1995) in the development of their empirical model, as they noted that the strong exponential temperature dependence of soil NO flux (Williams and Fehsenfeld, 1991) becomes weaker in very dry soils (Stocker et al., 1993).

Application of N-containing fertilizers, however,

exerts the dominant influence on soil NO emission from intensively managed agricultural soils. Yienger and Levy (1995) have calculated that with continuing usage of N fertilizer, global soil-biogenic NO_x emissions will approach 6.9 T_gN with agricultural soils accounting for more than 50% of the global natural source by the year 2025. Shifts in the use of nitrogenous fertilizers on a global basis will have a significant impact on a number of trace gas emissions from agriculture (Matthews, 1994). Yienger and Levy's estimates are consistent with Galloway's et al. (1995) projections that the anthropogenic N-fixation rate will increase by 60% by the year 2020, primarily due to a combination of fossil-fuel combustion and fertilizer use. A number of researchers have observed that fertilization of agricultural soils leads to increased fluxes of NO (Williams et al., 1988; Bawkin et al., 1990; Davidson et al., 1991; Shepherd et al., 1991; Slemr and Seiler, 1991; Skiba et al., 1992; and Serca et al., 1994). In areas where there are naturally emitted VOC's (i.e. isoprene) and large acreages of fertilized soils, increases in tropospheric ozone may be likely as ozone is formed from both anthropogenic and biogenic fluxes of VOC's and NO. These conditions exist throughout much of the southeastern United States. As a result it is important to quantify and parameterize the NO flux from crop lands in the southern portion of the United States. The primary objective of this study, therefore, was to measure the flux of NO throughout the year to assess the seasonal variability in the emissions of NO from an intensively managed agricultural soil. The secondary objective of the study was to determine the relationship between NO flux and certain soil parameters (soil temperature, percent water filled pore space, and applied N fertilizer) and how the flux of NO varied with these soil parameters during an entire year.

2. Materials and methods

2.1. Sampling site

Soil NO flux measurements were made on three crops (corn, cotton, and soybean) in Summer 1994, Fall 1994, Winter 1995, and Spring 1995. The measurements were made at Clayton, NC on the North Carolina Department of Agriculture research station located approximately 14 miles southeast of Raleigh, NC. The dominant soil type in each of the fields sampled is a Norfolk sandy loam (Fine-Loamy, Siliceous, Thermic Typic Paleudult; Daniels et al. 1984). The average pH of the crop soils studied ranged from 5.7 to 6.2 while the soil bulk densities of the fields varied slightly from 1.67 g cm^{-3} to 1.70 g cm^{-3}. The wilting point of the soils was 2.8% soil moisture content (by weight) and field capacity of the soils was measured at 10.8% soil moisture content (by weight) (D. Cassel, Department of Soil Science, North Carolina State University, personal communication). Fertilizer was applied only during the spring and summer months in keeping with the planting and harvesting schedule of the Clayton, NC research station. The crops studied received 168 kg N ha^{-1}, 68 kg N ha^{-1}, and 0 kg N h^{-1} of fertilizer respectively for the corn, cotton, and soybean fields.

2.2. Sampling seasons

Table 1 summarizes the dates for each season in which flux measurements were made on the soils of three crops at Clayton, NC. Average values of environmental variables measured at the same time of the flux measurements are also listed as well as the physiological growth stages of the crops at the time of the flux measurements. The differing growth stages between crops (e.g., complete versus vegetative) illustrates a changing demand for nitrogen between crops during each set of measurements.

The corn crop was planted in early April, almost a full month before the cotton crop. The corn crop received a broadcast application and two side dressings of fertilizer during its growing season. The cotton crop received the same broadcast fertilizer application as the corn crop, but only one side dressing application of fertilizer. Fertilizer application was completed at least three weeks prior to measurements of NO flux. The soybean crop was planted in late May and received no fertilizer application. All three crops were harvested in late September or early October.

After the crops were harvested, the crop stubble was leveled using a mower and the residue was disked into the surface soil. Winter wheat was then planted as a cover crop. The winter wheat grew sparsely over the fields and never exceeded 5 cm in height during any of the fall or winter sampling periods. By the fall sampling period, the

Table 1. *Sampling periods for NO flux measurements and average values of soil parameters measured during NO flux experiments; all the soil NO flux measurements were made at Clayton, NC on corn, cotton, and soybean crops*

	Sample dates	Growth stage	Soil temp. (a)	Air temp.	% water content (b)	% WFPS (c)	Extract. nitrogen (d)
Corn							
late summer	29 Aug–1 Sep '93	failed crop	NA	35.0	1.1	5	9.6
mid summer	7 Aug–11 Aug '94	complete	23.8	24.5	4.4	21	7.9
early fall	21 Nov–3 Dec '94	fallow	11.1	11.1	8.6	41	5.2
mid winter	10 Feb–17 Feb '95	fallow	4.3	4.4	11.7	55	1.1
early spring	29 Mar–4 Apr '95	pre-plant	15.5	17.4	5.4	26	29.1
Cotton							
late summer	23 Aug–28 Aug '93	bole formation	27.5	28.2	2.6	12	1.5
mid summer	12 July–26 Jul '94	flowering	27.3	29.0	3.7	17	13.4
early fall	24 Oct–2 Nov '94	post-harvest	14.1	12.9	6.1	29	3.2
mid winter	18 Jan–27 Jan '95	fallow	3.4	5.4	8.3	39	1.6
Soybean							
late summer	18 Aug–22 Aug '93	vegetative	25.6	29.7	3.5	17	0.7
mid summer	31 Jul–4 Aug '94	vegetative	25.1	26.4	7.6	36	6.0
early fall	7 Nov–18 Nov '94	fallow	17.8	12.9	6.9	33	31.3
mid winter	31 Jan–8 Feb '95	fallow	2.1	5.4	7.8	37	4.7

(a) Units of air and soil temperature are degrees Celsius.
(b) Amount of water contained per unit mass of dry soil (105°C).
(c) % water filled pore space (%WFPS), the amount of soil pore space occupied by water.
(d) Units of extractable nitrogen (nitrate and ammonium) are mg N kg dry soil^{-1}.
(e) Summer 1993 data collection by Aneja et al. (1995).
(f) NA = not available.

corn and soybean fields had been mowed and disked, but the cotton field still had standing stubble. The soybean and corn fields had just been planted with the winter wheat cover crop. During the winter measuring period all fields had been mowed and disked and the winter wheat was approximately 2 cm tall and growing only in small patches across the field. A spring measurement was done on the corn field approximately two weeks after the broadcast fertilizer application for the summer 1995 growing season. The amount of fertilizer applied to the corn field was 27 kg N ha^{-1}. After application, the fertilizer was disked in prior to preparation of the planting beds.

3. NO flux measurements

NO flux measurements were made for four days in each crop during each season. The NO flux measurements were accomplished using an open bottom continuously stirred dynamic flow through chamber system (Aneja et al., 1995). The dynamic chamber used in this study is an FEP Teflon-lined (5 mil thick) cylinder (diameter $\approx$ 27 cm, height $\approx$ 42 cm, and volume $\approx$ 25 ℓ) held in place by a stainless steel ring driven into the ground to a depth of $\approx$ 10 cm. Ambient air is pumped through the chamber at a constant flow rate (Q = 9 ℓ min^{-1}), and the air in the chamber is well mixed by a motor driven Teflon stirrer ($\approx$ 20 cm diameter, 100 rpm). Analysis of the chamber NO concentration was carried out in-situ by using a Thermal Environmental Instruments Incorporated (TECO) Model 42S chemiluminescent high sensitivity NO analyzer (Thermal Environmental Instruments, Inc., 1992). A multi-point calibration was executed before each seasonal measurement intensive period and the

instrument was zeroed and then spanned to 15 ppbv before each experiment. The NO analyzers and calibration equipment were placed in a mobile laboratory where the instruments were temperature controlled (30 ± 2°C). Air samples were collected from the chamber after steady state was achieved (≈ 30 min) at the outlet port of the chamber through a PFA (perflouroalkoxy) Teflon sample line (i.d. = 3.175 mm) directly attached to the TECO Model 42S NO analyzer. The sample line was approximately 15 m long, thus the maximum residence time of the sample in the line was 70 s.

The night before each experiment, the chamber was inserted into the soil. Ambient air was passed through the chamber during the twelve hours before the experiment to prevent NO accumulation in the chamber that might have effected NO production in the soil and to minimize any effect due to placement of chamber in the soil.

The flux of NO was calculated from the concentration of NO measured in the chamber via a mass balance (Aneja et al., 1995). Because zero air was used as a flush gas in the flux experiments, a simplified form of the flux equation at steady state is

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

where:

A = soil surface area covered by the chamber
Q = flow rate through the chamber
J = emission flux of NO from the soil
$[C]_f$ = NO concentration at the outlet of the chamber
L = loss term by chamber wall per unit area assumed first order in $[C]_f$ (Kaplan et al., 1988)

4. Soil parameters

Several soil parameters (soil temperature, soil water content, and total extractable nitrogen) were measured at the same time as the NO flux measurements. Soil temperature was measured via a digital meter attached to a probe buried (5 cm depth) adjacent to the chamber. Air temperature was evaluated utilizing the same digital meter with an air temperature probe hanging off of the chamber surface. Total soil water content was calculated as (initial weight — oven dry (105°C) weight)/oven dry weight. Nitrate (NO_3^-) and ammonium (NH_4^+) in a 2 M KCl soil extract (Keeney and Nelson, 1982) were determined using standard auto analyzer techniques (Lachat Instruments, 1990). Total soil water content at 15 bar 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). 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 NH_4^+ and 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 day.

5. Results and discussion

5.1. Seasonal fluxes of NO

The majority of NO flux from soils occurs during the summer months (Table 2). Relatively little NO flux occurs in the fall and winter months and only after fertilizer is applied in the spring season do fluxes of NO again reach significant levels. Anderson and Levine (1987) estimated that 76% of the flux from soybean and corn crops occurred in the months between May and October. Each of the crops studied in this paper also achieved a maximum NO flux during the summer. The % of total yearly flux attributable to summer fluxes for all the crops measured was 77%. The % contribution of each crop's summer flux to its yearly flux was 67%, 83%, and 77% for soybean, cotton, and corn, respectively.

Skiba et al. (1993) enhanced NO production from a freely drained sandy loam soil with addition of $(NH_4)_2SO_4$. Mean NO flux was 20.7 ng N m^{-2} s^{-1}, which is comparable to the summer average daily flux for corn (21.9 ng N m^{-2} s^{-1}) fertilized with NH_4NO_3 in this study (Table 2). The addition or presence of NH_4^+ has also been found to stimulate NO production in tropical pastures (Parsons and Keller, 1995), and tropical savannas (Poth et al., 1995) as well as other intensively managed agricultural soils (Valente and Thornton, 1993). Nitrification is considered the dominant soil process in the production of

Table 2. *Flux summary table for each crop in each season*

		Soybean	Cotton	Corn
average daily flux [a]				
	winter	0.3 (0.3)[e]	0.2 (0.1)	0.0 (0.1)
	spring			6 (2.0)
	summer	2.1 (0.9)	4.3 (3.7)	21.9 (18.6)
	fall	0.7 (0.3)	0.7 (0.4)	0.2 (0.1)
average yearly flux [b]		1.0 (0.3)	1.7 (1.2)	7.0 (4.8)
amount of fertilizer applied to each field [c]		0	68	168
% of fertilizer used returned as NO flux	summer	N/A	1% (see note 1)	4% (see note 2)
	entire year	N/A	4%	5%

[a] Units of daily flux are ng N m^{-2} sec^{-1}, per crop.
[b] Units of yearly average flux are ng N m^{-2} sec^{-1}, per crop.
[c] Units of applied fertilizer are kg N ha^{-1} yr^{-1}.
[d] All values calculated from flux measurements taken during 6:00 AM to 6:00 PM.
[e] Numbers in parentheses are one standard deviation.
[f] N/A: not applicable.

Note 1: % of fertilizer used during the summer season returned as NO flux is equal to average summer flux of NO divided by the amount of N fertilizer applied.
Note 2: % of fertilizer used during the entire year returned as NO flux is equal to the sum of N average NO fluxes divided by the amount of N fertilizer applied.

NO in the presence of NH_4^+ in aerobic soils. However, Baumgärtner and Conrad (1992) observed that stimulation of NO emissions by the presence of NH_4^+ was not uniform across a range of soil types, although flux rates were highest during the summer months. This lack in uniformity in response for aerobic soils to the presence of NH_4^+ may be due to such soil factors as pH (Nägele and Conrad, 1990) or degree of soil genesis (Baumgärtner and Conrad, 1992). While such observations have significance for unmanaged soils in differing ecosystems, it can be assumed that intensively managed agricultural soils will be amended to produce optimum crop yields. Under these conditions, it is reasonable to assume that additions of NH_4^+-based fertilizers (including urea) will enhance NO production in soils.

In this study, corn, with the largest amount of applied fertilizer, had the largest average yearly flux at 7.0 ± 4.8 ng N m^{-2} s^{-1} (Table 2). This value is comparable to the combined mean NO flux from corn observed by Valente and Thornton (1993) for their summer (27.0 ng N m^{-2} s^{-1}) and fall (2.85 ng N m^{-2} s^{-1}) measurements on a silt loam soil. The summer measurements for soybean, cotton and corn are also comparable to the range of soil NO flux observed by Anderson and Levine (1987) from agricultural sites in Virginia and Colorado, and for the tabulated mean NO flux values for other wet and dry biomes, such as savannas and forests (Yienger and Levy, 1995).

By taking a ratio of the average yearly flux in each crop to the fertilizer amount applied to that crop over a year period, an estimate for the amount of nitrogen based fertilizer returned to the atmosphere as NO flux can be obtained. For the crops studied in this paper, the % of nitrogen in fertilizer returned to the atmosphere as a NO flux is 4% for the cotton crop and 5% for the corn crop. Similar estimates can be obtained for corn from the observations of Valente and Thornton (1993). Anderson and Levine (1987) calculated that only 0.8% of the applied fertilizer was lost as NO-N, suggesting that our estimates are high. Yienger and Levy (1995), however, have calculated that the present NO_x contribution from fertilizers globally is approximately 2 T_gN annually. Using

Galloways et al. (1995) estimate of fertilizer production of approximately 80 $T_g N\ yr^{-1}$, yields a value of approximately 2.5% for fertilizer-N returned to the atmosphere as NO flux. This value is comparable to our calculated values.

5.2. *Daily trends of NO flux*

The change in the daily flux pattern for each season in the 3 different crops can be seen in Fig. 1. Each data point in this figure represents the average flux for a particular crop at a certain time of day ($n=4$ days) for each season measured. It is evident that the fluxes of NO are strongest during the summer season. The reason for the higher fluxes in the summer is two fold. First, the crops are fertilized during the spring and summer months, therefore there is a "pool" of readily available nitrogen from which the soil microbes responsible for NO production can draw. The influence of fertilizer application amounts on NO flux is evident in the change in scales on the y-axes in Fig. 1. The greatest NO flux occurred in the most fertilized crop (corn); the second highest NO flux was recorded in the crop which had an intermediate amount of fertilizer applied (cotton); and the soybean crop which had no applied fertilizer yielded much less NO flux. Second, the greater soil temperature in the summer months leads to increased NO production in the soil. Several researchers have found the NO flux from soils to vary exponentially with soil temperature (Williams et al., 1988; Shepard et al., 1991; Slemr and Seiler, 1991; Valente and Thorton 1993; Kim et al., 1994; and Aneja et al., 1995). As such, the higher temperatures representative of summer conditions would increase the flux of NO from soils even if the fields were not fertilized. In each crop measured, the combination of fertilizer application and higher temperatures during the summer months results in fluxes at least 2 orders of magnitude greater in summer months than in any other season.

During the winter and fall months, NO flux was substantially reduced, and the order for the crop with the highest NO flux reversed with soybean and cotton having higher average flux rates than corn. The reduction in NO flux is due in part to a decrease in soil temperature, and an increase in soil water content (Table 1). The incorporation of the crop stubble together, with the increase in soil water content, would also favor denitrification (Baumgärtner and Conrad, 1992), at least at microsites within the soil matrix. The reason for the relatively higher soil NO flux rates for the soybean and cotton fallow as compared to corn is less obvious. Incorporation of crop residue and decay of the root mass represents a recycling of fertilizer N back into the soil. Even though soybean is a legume, the crop residue from cotton and corn represents a significant return of N to the soil. The incorporated residue, therefore, is a potential pool of N that could influence NO flux during mineralization by soil microbes. One factor limiting this process, however, is the carbon to nitrogen ratio of the incorporated organic matter. Soybean residue has a relatively low carbon to nitrogen ratio (15:1) compared to cotton (32:1) and corn (50:1) (Troeh and Thompson, 1993). As such, microbial demand for N will be substantially higher during mineralization of the corn and cotton residue than for the soybean residue, effectively limiting release of NH_4^+, and possibly, indirectly limiting NO production.

6. NO flux versus soil parameters

6.1. *Soil temperature and NO flux*

In this study we monitored NO flux from the same fields for an entire year, allowing the relationship between soil temperature and NO flux to be examined over a relatively wide range of temperatures (0°C to 35°C). As has been reported by other researchers (Williams et al., 1988; Shepard et al., 1991; Slemr and Seiler, 1991; Valente and Thornton, 1993; Kim et al., 1994; Aneja et al., 1995), we observed an exponential relationship between NO flux and soil temperature for the majority of soil temperatures measured during the summer and fall (15°C to 35°C) as illustrated in Fig. 2. Each point in Fig. 2 represents an average daily NO flux plotted against the corresponding mean daily soil temperature on the day NO emissions were measured. Only the data for the soybean crop is shown in Fig. 2 to facilitate demonstrating the exponential relationship between NO flux and soil temperature. The combined data set for all three crops is shown in Fig. 4 with the added variable of percent water filled pore space.

The lack of a response to an increase in soil temperature (Fig. 2) below a threshold of 15°C is

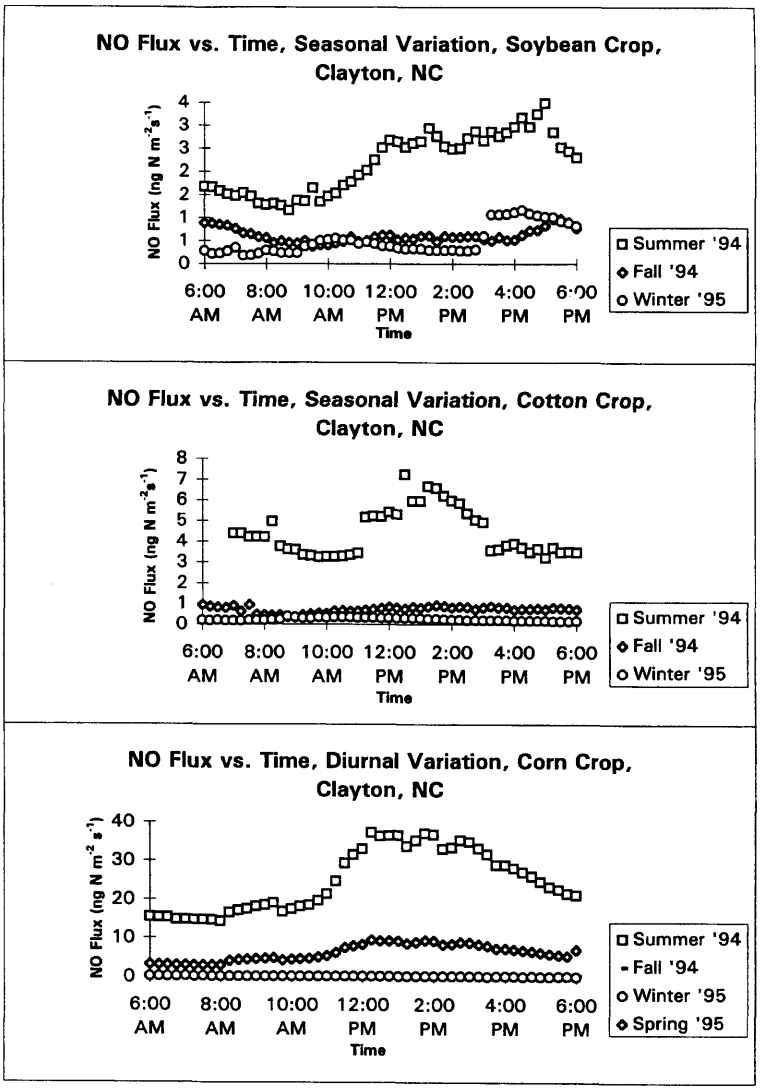

Fig. 1. Daily trends of NO flux for each crop in each season. Each point represents an average of 4 measurements in each season.

consistent with the observations of Valente and Thornton (1993), and support Yienger and Levy's (1995) modeling assumption that NO flux is exponentially related to soil temperature in wet soils from >10°C to 30°C. Above 15°C, we noted a rapid increase in NO flux with increase in soil temperature for both soybean and corn, but not for cotton (Fig. 4). For cotton, there tended to be no clear response in NO flux with increase in soil temperature from >15°C to 25°C, and a decrease in NO flux at soil temperatures >25°C. We also observed a substantial degree of variability in NO flux within a crop at any given soil temperature. These variations are undoubtedly due to soil variability in NO flux, but may also be due to other influences such as daily changes in soil water content. Skiba et al. (1992) reported a strong correlation between NO emissions and soil surface

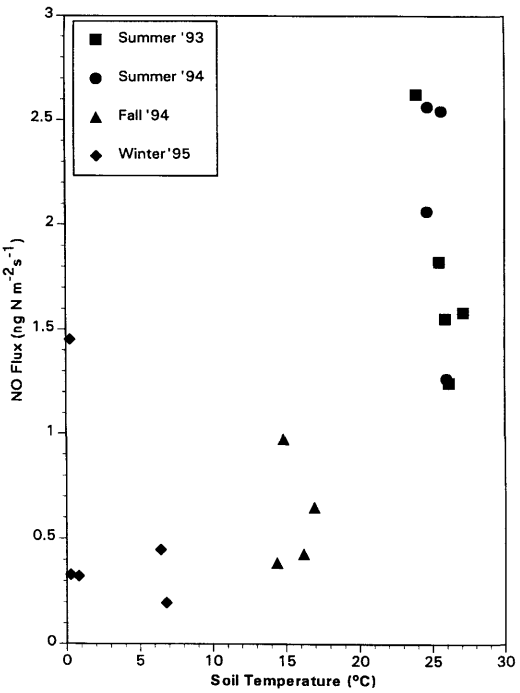

Fig. 2. Average daily flux from the soybean crop plotted against average daily soil temperature measured on the day of emission measurements. Summer '93 data collected by Aneja et al. (1995).

temperature (3 cm depth, $r^2=0.74$) for both a sandy loam and a clay loam soil, and concluded that observed variations were random in nature and that there was no systematic relationship with crop type or season. Poth et al. (1995), however, noted a poor relationship ($r^2=0.25$) between NO emissions and soil temperature (2 cm depth) for burned grassland savannas. While this may represent an extreme case, it does serve to illustrate that other soil factors can have a dominating influence on NO emissions besides soil temperature.

Williams et al. (1992) accounted for the variation in soil NO flux from different ecosystems by incorporation of a curve fitting parameter (since labelled A) which is considered associated with a given land use category. Application of this parameter has proven useful in categorizing the relationship between soil NO flux and soil temperature, but there is still a substantial amount of variability in calculated A terms for a given ecosystem, as tabulated by Yienger and Levy (1995; Tables 4, 5). We chose not to calculate A terms from our data, both because of the limited number of data points in our data set and the uncertainty regarding the assumption of a positive response in NO emissions with continued increase in soil temperature. As pointed out by Yienger and Levy (1995), close inspection of the extensive data set provided by Valente and Thornton (1993; Fig. 7) suggests no continued positive response above a given temperature. For the purposes of their global soil-biogenic NO_x model, Yienger and Levy chose 30°C as the optimal temperature above which they assumed soil NO flux was no longer dependent on soil temperature. The data summary provided by Valente and Thornton, however, does not allow for resolution of closely related temporal trends such as our data set. Thus it is not possible to determine whether their observations at temperatures >30°C actually reflect a decrease in soil NO flux with increase in soil temperature such as we observed for cotton (Fig. 4). It is evident from their data that the highest NO emission rates for corn fell between 24°C and 30°C (65 to 108 ng-N $m^{-2}\ s^{-1}$), while emission rates at >30°C range only from 20 to 52 ng-N $m^{-2}\ s^{-1}$. The results presented by Valente and Thornton (1995) for a pasture ecosystem are less clear, as the NO emission rates they reported ranged from 30 to 80 ng-N $m^{-2}\ s^{-1}$ up to a temperature of 35°C.

6.2. *Soil water content and NO flux*

A plot of the average daily flux from cotton over an entire year versus WFPS estimated from soil samples taken on the same day the flux was measured is shown in Fig. 3. The overall trend in Fig. 3 is for flux to decrease with increase in WFPS. This agrees with the model suggested by Davidson (1991) that predicts NO as the dominant N gas released from soils when WFPS $<60\%$. As noted by Williams and Fehsenfeld (1991), there is an interaction between soil temperature and soil moisture content that has a significant effect on NO emissions. Our combined data for soybean, corn, and cotton (Fig. 4), demonstrates that when soil moisture does not limit microbial activity or NO diffusion through the soil, that soil NO flux will increase with increase in soil temperature and appear to be somewhat independent of WFPS. Stocker et al. (1993) observed a strong linear relationship between the flux of NO_y and soil temperature (-3°C to 34°C) for a grassland site

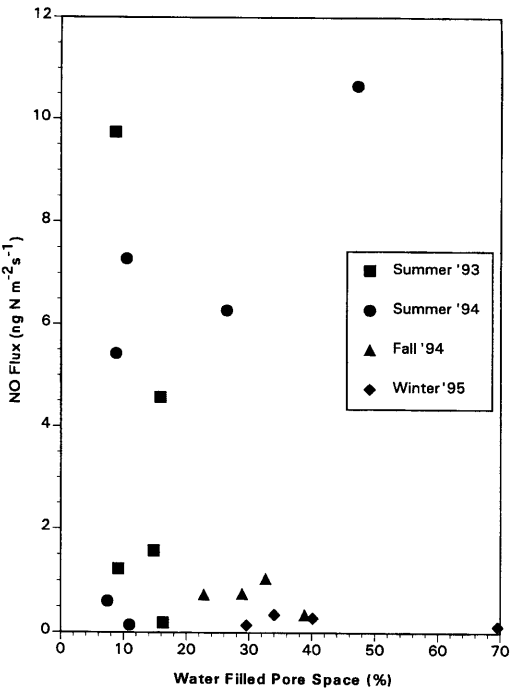

Fig 3. Average daily flux from the cotton crop plotted against % water filled pore space calculated from soil water content taken on the same day as the flux measurement. Summer '93 data was collected by Aneja et al. (1995).

when the surface soil was relatively wet. When the soil was dry, however, there was a marked decrease in NO_y flux above 30°C to 35°C. Similar decreases in NO soil flux at low soil moisture contents have been reported by Williams et al. (1987), Johansson et al. (1988), and Williams and Fehsenfeld (1991) for a variety of different ecosystems.

We observed a decrease in NO flux for cotton when soil temperatures exceeded 25°C and WFPS <20%. Since cotton is planted later than corn at our research site, our summer measurements for cotton coincided with critical periods of physiological development (bole formation or flowering, Table 1) when the crop would be most susceptible to periods of moisture stress. Because of the sandy loam texture at our site, the amount of available water in the surface rooting zone is limited, and soil moisture stress is common in July and August when rainfall is limiting. Our observations for cotton agree very well with soil NO flux as a function of soil temperature reported by Cardenas et al. (1993) for a grassland savannah site (sandy loam soil texture) in Venezuela. These investigators observed a linear decrease in NO soil flux between 24°C to 44°C when soil moisture content <2% (WFPS=10%), and an overall decrease in NO flux when WFPS <30%.

We did not record a decrease in soil NO flux for soybeans at higher (>25°C) soil temperatures. This may be an influence of tillage, since all these crops are planted using a ripper-bedder technique, which allows root penetration below a tillage pan that often forms in this soil type. The soybean crop is very efficient at exploiting the opportunity to reach soil water in the underlying subsoil made available by use this tillage technique. The soybean canopy also reaches closure during the vegetative growth stage and provides more shading of the soil as compared to cotton and corn. The combination of these two factors may have acted to limit the effects of low soil moisture content on soil NO flux from the soybean crop.

6.3. NO flux and total extractable nitrogen

A number of published field studies have reported a positive relationship between soil NO and extractable N (NH_4^+, NO_3^-, or $NH_4^+ + NO_3^-$). This relationship has been shown to exist across a number of different ecosystems including tropical rain forests, abandoned pastures and secondary forests (Keller and Reiners, 1994), tropical savannas (Poth et al., 1995), northern forests (Johansson et al., 1988; Williams and Fehsenfeld, 1991), as well as agricultural lands (Skiba et al., 1992; Valente and Thornton, 1993). A positive response to N additions across a range of soil types has also been recorded using disturbed soil cores (Baumgärtner and Conrad, 1992), and in glasshouse studies using fixed soil beds (Skiba et al., 1993). We observed no obvious trend in soil NO flux and extractable N ($NH_4^+ + NO_3^-$) when we plotted the average daily flux from each crop against total extractable N for soil samples collected on the same day as the flux measurements (Fig. 5, data for cotton and soybean not shown). Lack of a positive trend in NO emissions in our data is probably due to the relatively short time period allocated to each set of measurements as compared to the rate of change in soil extractable N, and to the interaction of soil temperature and soil moisture content. Skiba et al. (1992) concluded, based on a significant correlation between

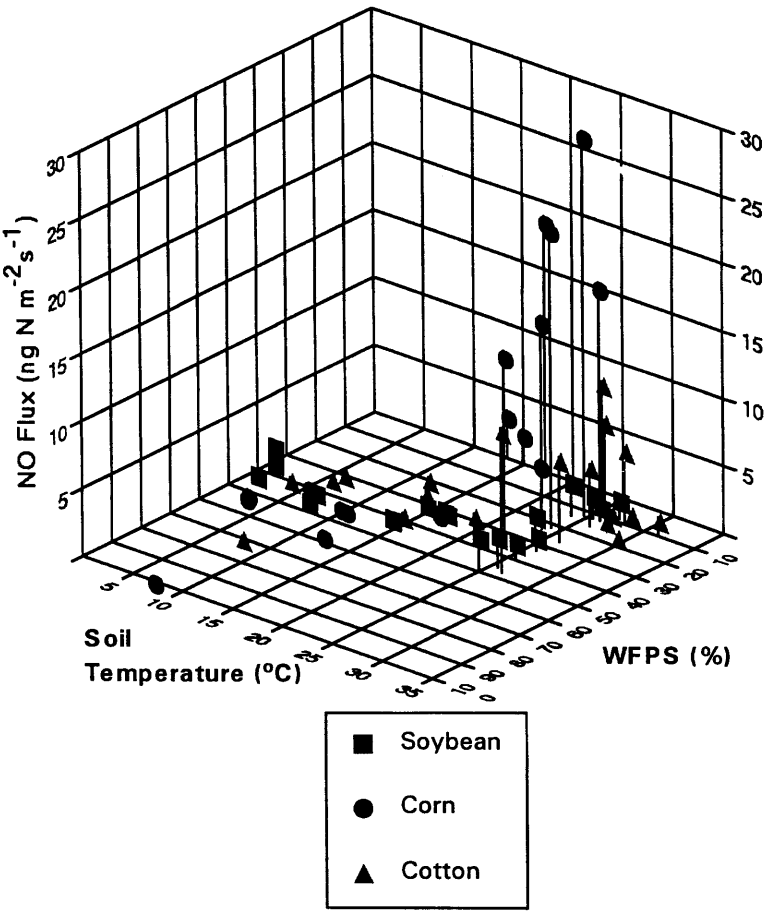

Fig 4. Plot of NO flux versus % water-filled pore space (%WFPS), and soil temperature. Each point represents soil water content, averaged NO flux, and averaged soil temperature for the day soil water content was measured.

NO flux and soil-available NH_4^+ ($r^2=0.89$) and NO_3^- ($r^2=0.86$), that extractable N was the dominant soil variable controlling NO emissions when compared to soil moisture content, soil temperature and soil type. While our data supports this general trend in that the highest soil NO flux for the spring and summer months is associated with the crop receiving the highest application of N fertilizer (i.e., corn, Table 2), it appears that both soil moisture content and soil temperature become important controlling variables following N application. Cardenas et al. (1993) noted large enhancements in NO emission following addition of nitrate solutions to an acidic tropical savannah soil. However, these pulses of NO flux only lasted for a period of a day. Overall they observed that, for soil moisture contents, $<20\%$, WFPS $<70\%$, soil NO flux increased with N addition, unless soil moisture content became limiting (i.e., during the dry season NO flux decreased despite N additions). Our data suggest, that for the remainder of the growing season following N fertilizer applications, it is the interaction of extractable N, soil moisture content, soil temperature, and N partitioning into the crop (especially the below ground root mass) that dictates soil NO flux from intensively managed agricultural soils.

7. Uncertainty in soil flux values

The data we present in Table 2 compare favorably with other published results using enclosed

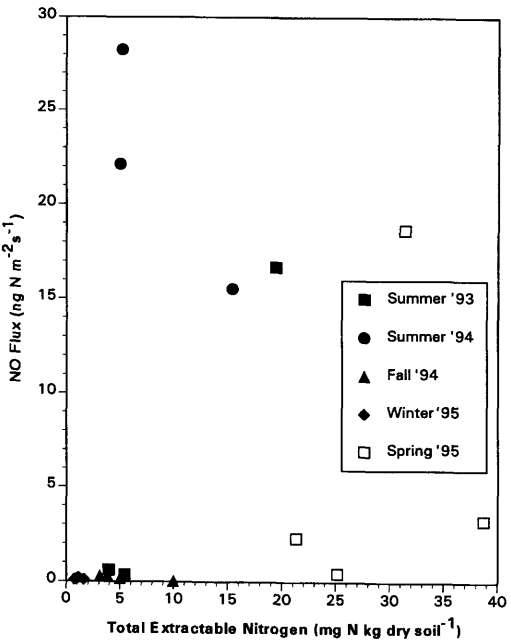

Fig 5. Average daily flux from the corn crop plotted against total extractable nitrogen calculated from soil collected on the same day as the flux measurements. Extractable nitrogen includes ammonium and nitrates. The soil sample was taken immediately after removal of the chamber. Summer '93 data was collected by Aneja et al. (1995).

chamber techniques to measure soil NO flux from intensively managed agricultural soils (Anderson and Levine, 1987; Valente and Thornton, 1993). The data also supports, in general, the assumptions made by Yienger and Levy (1995) in the formation of an empirical model of global soil-biogenic NO_x emissions, except for the possible negative influence of soil moisture stress above a critical soil temperature. Yienger and Levy, as well as others (Williams et al., 1992), assumed an optimal soil temperature for NO flux of 30°C for both wet and dry soils (i.e., soil NO flux becomes independent of soil temperature above 30°C). Our results for cotton indicates, at least for dry soils, that assuming an optimal soil temperature for NO flux is in error, and that the interaction of increasing soil temperature and soil moisture stress will decrease NO emissions. Our conclusion in this regard is consistent with the observations of Cardenas et al. (1993), and supports the implication of Yienger and Levy (1995) that there is a critical need for data in order to include soil moisture content in a model of the soil temperature/flux relationship. Stocker et al. (1993) suggested that soil moisture content itself is not as an important factor controlling NO emissions as the drying of recently wetted soils. Clearly there is a need for controlled field studies that will generate the necessary soil moisture/temperature/flux data to properly characterize the relationship between these two soil parameters and NO emissions. This is particularly true for agricultural regions such as the southeastern United States, which have soil types with limited available water-holding capacity, and droughty conditions during the summer and fall that lead to periods of physiological drought during the growing season.

Our current measurement system prevented measurement of soil NO flux immediately following rain events. If a dry soil is wetted, a large burst in NO flux is often observed (Davidson 1992 a,b). Assigned the terms "pulse" or "pulsing", NO emissions immediately following wetting have been estimated by Yienger and Levy (1995) to account for approximately 24% of the total above-canopy emissions of NO_x. This calculation suggests that our values for soil NO flux, at least for the summer and fall periods, are underestimated possibly by as much as 25%.

Our research site, which is typical of most agricultural fields in North Carolina, is located adjacent to a paved highway with substantial vehicular traffic. We used zero-air to avoid this local source of NO_x, and to avoid introducing ozone into our chamber. Conrad (1994) has recommended not using zero-air to flush flow-through chambers unless the existence of consumption reactions for NO in the soil has not been excluded. This is based on the existence of the compensation concentration, which is the concentration at which the rate of production of NO equals the rate of consumption (net soil NO flux equal to zero) (Conrad, 1994). Skiba et al. (1992) noted a reversal of the normal diurnal variation in NO emissions for soil NO flux values < 0.15 ng-N m^{-2} s^{-1} on ryegrass plots, and < 2 ng N m^{-2} s^{-1} for winter wheat. NO deposition was recorded on the unfertilized ryegrass plot during the day as soil temperature increased from 4°C to 16°C. This data suggests that the winter fluxes reported in Table 2 should in fact be zero or

negative in value. Positive values were obtained because the use of the zero-air carrier gas dilutes the concentration of NO within the chamber to below the compensation point.

The size and magnitude of possible bias in the remaining flux values we report in Table 2 using zero-air as the carrier gas in our chamber is less clear. Baumgärtner and Conrad (1992) have tabulated a range of compensation points for a number of soil types and conditions, but Conrad (1994) cautions that such data must be interpreted with caution as the NO compensation point may change during the period in which fluxes are measured due to changes in both ambient NO concentrations and soil conditions. Data presented by Baumgärtner and Conrad (1992) suggest that NO uptake rate constants increase with decrease in soil moisture content, but the range in soil moisture content reported is limited and does not extend below 14%. It is possible that the data we present in Table 2 contains a positive bias due to our usage of zero-air as the carrier gas in our chamber. We are unable, however, at this time to estimate the magnitude of this bias, other than to say that such bias is probably also present to some degree in other reported NO emissions data gathered using static chambers or flow-through chambers with zero-air as the carrier gas.

An additional uncertainty associated with the data in Table 2 deals with spatial variability in NO emissions. With our experimental design, we were able to monitor, at most, only two positions within the crop canopy for any given day. Thus our ability to assess spatial variability in NO flux on a daily basis was very limited. Valente and Thornton (1993) estimated the spatial variability in NO emissions from the mean of five chambers within a 10×10 m experimental area. Their values, expressed as a percent spatial variability, ranged from 85 to 118 for the summer measurements, and 85 to 110 for the fall measurements for corn, pasture and a forest site. We restricted our measurements to the row position where rooting density is the greatest, and where the maximum amount of N fertilizer was applied (band application). The similarity in our diurnal flux patterns to those of Valente and Thornton (1995), together with the agreement in our estimates of average flux (Table 2), suggest that the limited nature of our sampling design still provided an acceptable estimate of soil NO flux from the three crops studied.

8. Conclusions

The data we present in this paper adds to the growing knowledge of soil NO flux from intensively managed agricultural soils in the southeastern United States. Because this was an observationally based study of NO flux, the data collected was limited to values dictated by conditions when the measurements were made. As a result, it was very difficult to relate soil flux of NO to soil parameters due to the lack of connection between the crops in space and time. Certain combinations of variables, i.e. high soil temperature and high water content, could not be observed. A controlled field study of NO flux, in which the entire range of each soil parameters could be controlled, would elucidate the true relationship between NO flux, soil temperature, %WFPS, and applied nitrogen based fertilizer.

Yienger and Levy (1995) have estimated, using an empirical soil-biogenic NO_x model, that agriculture currently accounts for 41% of soil NO emissions, and that this figure will grow to 50% by the year 2025 based on continued usage of N containing fertilizer. Continued agricultural development in the southeast United States, including use of land disposal for manures from large scale poultry and hog operations, will ensure that agricultural soils will continue to be a significant source of NO in this region of the country. This, coupled with the fact that the southeast United States is an area with naturally emitted VOC's, will undoubtedly result in the formation of tropospheric ozone, especially during the summer months when NO emissions from agricultural soils are the highest.

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