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MEASUREMENTS OF NITRIC OXIDE FLUX FROM AN UPPER COASTAL PLAIN, NORTH CAROLINA AGRICULTURAL SOIL

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Abstract—Agricultural soil NO flux measurements (using a dynamic chamber technique) were made from 18 August to 1 September 1993 in the Upper Coastal Plain region of North Carolina in an effort to determine the role of natural emissions of NO on rural atmospheric photochemistry. Overall average NO flux rates increased proportionally to the level of applied fertilizer nitrogen in the agricultural soil. The soybean, cotton, and corn field measurements revealed an average NO flux of 1.79 (range – 1.0–6.9) $\mathrm{ng\,N\,m^{-2}\,s^{-1}}$; 3.77 (range – 0.1–38.0) $\mathrm{ng\,N\,m^{-2}\,s^{-1}}$; and 8.05 (range – 0.5–52.8) $\mathrm{ng\,N\,m^{-2}\,s^{-1}}$ respectively. There was a positive correlation between NO concentration near the soil surface (~50 cm) and NO flux. A significant negative correlation between NO flux and ambient O_3 concentration, however, supports the hypothesis that soil emissions of NO contribute to local production of O_3 in rural areas.

Key word index: Natural emissions, nitric oxide, agricultural soils.

INTRODUCTION

Gaseous oxides of nitrogen ($NO + NO_2 = NO_x$) are trace atmospheric constituents that function directly or indirectly as potentially important greenhouse gases in various global climate change scenarios (Duxbury *et al.*, 1993). NO_x also participates in the production and/or consumption of atmospheric oxidants (e.g. O_3, OH) and is removed from the atmosphere in a series of photochemical reactions that result in the formation of HNO_3, the fastest-growing component of acidic deposition (Logan, 1983). In addition, it has been suggested that NO_x emissions from soils may comprise a significant fraction of the unaccounted source observed in the nitrogen budget of fertilized agricultural soils (Hutchinson and Davidson, 1993).

Measurements of NO_x emission at a variety of locations around the globe (Slemr and Seiler, 1984; Anderson and Levine, 1986; Williams *et al.*, 1987, 1988; Johansson *et al.*, 1988; Johansson and Sanhueza, 1988; Kaplan *et al.*, 1988; Williams and Fehsenfeld, 1991; Hutchinson and Brams, 1992; Valente and Thornton, 1993; Kim *et al.*, 1994) have shown that soil emissions are highly variable both temporally and spatially, and this variation can be substantial. The high variability is due to variations in soil physical, chemical and biological parameters including soil temperature, soil water content, past use (fertilization or domestic animal grazing), vegetation cover, season, surface wind speed, and NO (and possibly NO_2) levels in the air above the soil (Williams *et al.*, 1987; Kim *et al.*, 1994).

Because biogenic emissions from microbial processes in soil are thought to be one of the principal sources of atmospheric nitrogen oxides, it becomes important to determine the magnitude of this source and, if appropriate, to develop control technologies, such as alternative soil management practices, or improved fertilizer formulations and application techniques (Hutchinson and Brams, 1992). Uncertainties in NO_x budgets could cause an incorrect assessment of ozone control strategies. It has been suggested that NO_x emission from soils in rural areas may represent a more significant source of NO_x than was initially estimated (Williams *et al.*, 1988). Since NO_x emission data is used as input for photochemical models, representative estimates of biogenic flux are critical for regional photochemical modeling studies (Kim *et al.*, 1994).

This paper presents results of the measurement of NO_x emissions from an agriculturally-managed soil in the Upper Coastal Plain of North Carolina. These measurements were taken in three different agriculturally managed fields, each containing a crop representing a different level of applied fertilizer nitrogen. The measurements were made using a dynamic chamber technique (Aneja, 1975; Hill *et al.*, 1978; Aneja *et* *al.*, 1979) in order to gain insight into the role of natural emissions of NO$_x$ on rural photochemistry. Observations of ambient O$_3$ complement these measurements.

METHODS AND MATERIALS

Sampling site

Flux measurements were made in three general crop (nonirrigated) fields at the Central Crops Field Laboratory (~105 m MSL) which is owned by the North Carolina Agricultural Research Service and operated by North Carolina State University. The Field Laboratory is located approximately 10 km east–southeast of Raleigh, in the Upper Coastal Plain region of NC. The dominant soil type in each of the fields sampled is Norfolk sandy loam (fine-loamy, siliceous, thermic typic paleudult; Daniels *et al.*, 1984). Each field sampled contained a different row crop (soybean, cotton, or corn) grown using fertilizer rates and management techniques representative of those commonly used by farmers throughout the Coastal Plains region of the southeastern United States.

Soil analysis

Bulk soil chemical properties from each of the three fields were obtained from composite soil samples submitted to the Agronomic Division of the NC Department of Agriculture (Table 1). These included humic matter content based on a 0.2 M NaOH extraction, extractable base cations using a solution composed of 0.2 M CH$_3$COOH, 0.25 M NH$_4$NO$_3$, 0.015 M NH$_4$F, 0.013 M HNO$_3$, and 0.001 M EDTA, and exchangeable acidity using a buffer solution. Effective cation exchange capacity (ECEC; expressed on a volume basis) was obtained by summing extractable cations and exchangeable acidity. Base saturation of the ECEC was determined by (ECEC -exchangeable acidity)/ECEC.

Soil bulk density for the 0–15 cm depth ($n = 10$) was determined using the core method (345 cm^3) near each chamber sampling point in each field (Blake and Harge, 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 using a bucket auger (0–20 cm depth) at the end of each measurement period. Total soil water content was calculated as (initial weight – oven dry (105°C) weight)/oven dry weight. Nitrate and NH$_4^+$ in the 2 M KCl extract (Keeney and Nelson, 1982) was determined using standard autoanalyzer 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). The average values listed in Table 1 are based on numerous soil samples collected over the past ten years at the Central Crops Field Laboratory (D. Cassel, Department of Soil Science, North Carolina State University, personal communication). The amount of N fertilizer applied during the 1993 growing season is based on records maintained by the supervisor of the Central Crops Field Laboratory.

Planting and N fertilizer management

Prior to planting in the spring of 1993, each field received 21 kg N/ha^{-1} as ammonium nitrate fertilizer. This broadcast application was then disked in, prior to preparation of planting beds. Actual planting followed preparation of the seed bed using a ripper-bedder to allow root penetration below a tillage pan that occurs at the 20–30 cm depth. Seeds were planted in the center of each bed, with approximately 1 m spacing between beds. Cotton and corn received two side dressings of N fertilizer during the first portion of the growing season. The side dressing consisted of placing two bands of fertilizer on either side of the crop on top of the beds. No additional N fertilizer was added to the soybeans for the remainder of the growing season.

Flux measurements

Nitric oxide flux was measured using a dynamic chamber technique from five randomly-selected plots (15 m × 15 m) within each crop from 18 August to 1 September 1993. Measurements were taken in the center of the interrow spaces in the soybean crop without destruction of the surrounding canopy. Measurements in the cotton and corn were taken on the center of the beds after removal of plants by cutting the stalks at the soil surface, with minimal disturbance of the surrounding canopy. Soil temperature was monitored with a digital meter attached to a probe buried (5 cm depth) adjacent to the chamber. Air temperature was monitored with a temperature probe placed at chamber-top height, shielded from direct solar radiation. Differences in the air and soil temperatures inside and outside of the

Table 1. Physical and chemical soil parameters determined for each research plot for the soil type: Norfolk sandy loam (fine-loamy, siliceous, thermic typic paleudult).

		Row crop		
Parameter	Unit	Soybean	Cotton	Corn
pH		5.7	6.2	6.0
ECEC[a]	meq/100 cm^3	2.5	3.2	2.7
Base saturation[b]	% (by volume)	84	87	85
Acidity	meq/100 cm^3	0.4	0.4	0.4
Humic matter[c]	% (by volume)	0.5	0.5	0.6
Bulk density	g cm^{-3}	1.73(± 0.08)	1.67(± 0.14)	n.d.
Water content[d]				
"Wilting point"	% (by weight)	2.8	2.8	2.8
"Field capacity"	% (by weight)	10.8	10.8	10.8
N application (1993) growing season	kg ha^{-1}	21	84	173

[a] Sum of extractable base cations.

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

[c] 0.2 *M* NaOH extractable humic matter.

[d] D. Cassel, Dept. of Soil Science, NC State University, personal communication.

chamber were minimal and often within our error of measurement.

Chamber design and operation

The dynamic chamber used in this study is an FEP Teflon-lined (5 mil thick) cylinder (diameter ≈ 27 cm, height ≈ 42 cm, and volume ≈ 25 ℓ) held in place by a stainless steel ring driven into the ground to a depth of ≈10 cm (Fig. 1). Ambient air is pumped through the chamber at a constant flow rate ($Q = 91\ \mathrm{min}^{-1}$), and the air in the chamber is well mixed by a motor driven Teflon stirrer (≈20 cm diameter, 100 rpm). Air samples were collected after reaching steady state conditions (≈30 min of operation) at the inlet and outlet ports of the chamber using Teflon bags (≈10 ℓ). The collection period was typically ≈5 min. The air samples in these bags were then immediately analyzed for their NO and NO_2 concentrations.

Instrumentation

Analysis of the NO and NO_2 concentrations in the air samples was carried out using a TECO 42S chemiluminescent high sensitivity NO analyzer (Thermo Environmental Instruments Inc.), and a LMA-3 Luminol based NO_2 analyzer (Scintrex Ltd.), equipped with a cartridge filter to remove O_3 at the sample inlet. The instruments were periodically calibrated according to protocol using a mixture of 0.109 ppm NO in N_2 and a mixture of 0.116 ppm of NO_2 in N_2 (Scott Specialty Gases Inc., Plumsteadville, PA). Detection limits for these instruments are cited at 50 parts per trillion volume (pptv) for NO (Thermo Environmental Instrument, Inc., 1992) and ≈5 pptv for NO_2 (LMA-3 Operators Manual, 1987). Additional detail concerning the instrumentation are described elsewhere (Kim *et al.*, 1994; Dickerson *et al.*, 1984; Scintrex Ltd., 1989).

Flux calculation

The mass balance for NO in the chamber (Kaplan *et al.*, 1988) is given by

$$\frac{\mathrm{d}C}{\mathrm{d}t} = \left(\frac{Q[C]_0}{V} + \frac{JA}{V}\right) - \left(\frac{LA[C]_f}{V} + \frac{Q[C]_f}{V}\right) + R \qquad (1)$$

where A is the soil surface area covered by the chamber, V the volume of the chamber, Q the flow rate through the chamber, J the emission flux, C the NO concentration in the chamber, $[C]_0$ the NO concentration at the inlet of chamber, $[C]_f$ the NO concentration at the outlet of chamber, L the loss term by chamber wall per unit area assumed first order in $[C]$, and R the chemical production/destruction rate in the chamber. For a well-mixed chamber $[C]_f$ may be assumed to be equal to the NO concentration in the chamber.

Rapid oxidization of NO in the atmosphere requires that the calculated NO fluxes be corrected for possible chemical reactions within the chamber. Generally, three oxidants have a major role in the oxidation of atmospheric NO. They are O_3, HO_2 and RO_2 (Finlayson-Pitts and Pitts, 1986). NO_2 flux (even negative flux) is typically much lower than NO flux from soils (Johansson and Granat, 1984; Slemr and Seiler, 1991) and the low ambient concentrations of NO_2 at the measurement site are not expected to produce significant quantities of NO in the chamber. Thus, R in equation (1) can be written as:

$$\begin{aligned} R &= -(k_1[O_3] + k_2[HO_2] + k_3[RO_2])[NO] \\ &= -\left(\sum_{i=1}^{3} k_i R_i\right) C \qquad (2) \end{aligned}$$

where R_i is each reactant species and k_1 ($= 1.8 \times 10^{-14}\ \mathrm{cm}^3\ \mathrm{molecules}^{-1}\ \mathrm{s}^{-1}$), k_2 ($= 8.3 \times 10^{-12}\ \mathrm{cm}^3\ \mathrm{molecules}^{-1}\ \mathrm{s}^{-1}$) and k_3 ($= 7.6 \times 10^{-12}\ \mathrm{cm}^3\ \mathrm{molecules}^{-1}\ \mathrm{s}^{-1}$) are reaction rates for O_3, HO_2 and RO_2 with NO, respectively. Equation (1) becomes:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = -\left(\frac{Q}{V} + \frac{L}{h} + \sum_{i=1}^{3} k_i R_i\right) C + \left(\frac{J}{h} + \frac{Q[C]_0}{V}\right) \qquad (3)$$

where h (≈42 cm) is the height of the chamber. Solving equation (3) for the NO flux, J, under steady state condition yields:

$$J = h\left\{\frac{Q}{V}(C_f - C_0) + \left(\frac{L}{h} + \sum_{i=1}^{3} k_i R_i\right) C_f\right\} \qquad (4)$$

Surface RO_2 concentrations have been calculated at Scotia, PA (Trainer *et al.*, 1991), at site SONIA near Candor, NC (Hartsell, 1993); and measured at site ROSE, AL (Cantrell *et al.*, 1992). All are similar in magnitude. In this study we assumed an RO_2 concentration of 30 pptv ($7.4 \times 10^8\ \mathrm{molecule\ cm}^{-3}$), which is the value calculated for the average noontime concentration at site SONIA (Kim *et al.*, 1994). The HO_2 concentration was set to 30% of the RO_2 concentration (Trainer *et al.*, 1987, 1991). The near surface O_3 con-

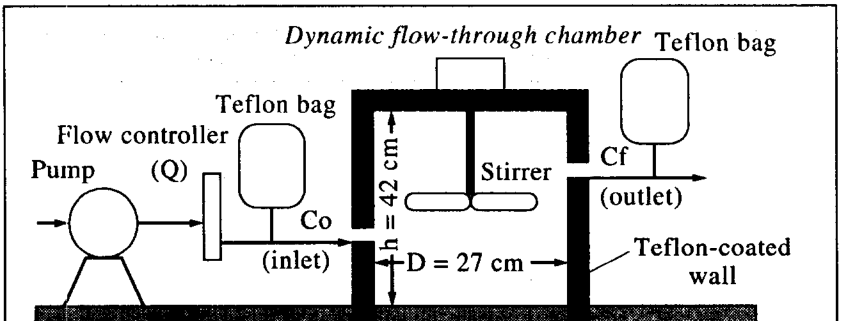

Fig. 1. The schematic figure of the dynamic flow-through chamber. The walls and all internal surfaces are fluorinated ethylene propylene (FEP) Teflon. The chamber height, h = 42 cm; and the diameter, D = 27 cm.

centration used in equation (2) was set equal to the nighttime O_3 average (~ 5 ppbv). This assumption reflects the fact that O_3 concentrations decrease as one approaches the earth's surface. Hourly ambient (10 m) O_3 measurements were taken at the WRAL television transmission tower located approximately 2 km west of the Central Crops Field Laboratory. The average daytime O_3 concentration was 37 ppbv. Wall loss, L, for the Teflon coated wall of the chamber was set equal to 0.02 cm s^{-1}. This value was obtained by taking the difference between the combined surface loss as proposed by Kaplan *et al.* (1988) and the chemical loss in the chamber as calculated by equation (2) (Kim *et al.*, 1994).

Failure to correct for the terms in equation (2) and for L reduces the calculated flux. For the range of paired $[C]_0$ and $[C]_f$ values observed in our study, the maximum reduction possible by excluding the R_i terms is $\sim 50\%$. Removal of the L term from the calculation lowers the NO flux by approximately 5%.

RESULTS AND DISCUSSION

The bulk soil chemical properties were similar between the three agriculturally-managed fields (Table 1), and somewhat typical of soils found in the upper Coastal Plain region of the southeastern United States (low ECEC, low organic matter content, limited available water content; Daniels *et al.*, 1984). The relatively high bulk density values are indicative of the sandy texture of the surface horizon, as is the relatively low water content (Table 1) after drainage of excess water (field capacity; Hillel, 1980). For the soybean field, the soil water content ranged from 1.80% to 7.80% with an average of 3.49 ± 2.44%. The cotton field soil water content ranged from 1.78% to 3.29%, for an average of 2.63 ± 0.74%. Corn field moisture values were 0.58–1.75%, with an average of 1.10 ± 0.60%. There was essentially no rainfall during the measurement period and the three fields were not irrigated. The soil water content for the top 15 cm of the soil, therefore, remained at or below the estimated permanent wilting point (15 bar; Table 1) for this soil type. The cotton and soybean crops survived because their roots were able to access available water in the subsoil. The corn crop, however, had already failed prior to the start of our measurements. Soil temperatures ranged from 23.3 to 32.5°C, with an average of 25.6 ± 1.4°C for the soybean field, and 27.5 ± 7.5°C for the cotton field. The difference in soil temperature between the soybean and cotton fields is due to the maturity of the soybean stand and canopy closure at the time of the measurements. Overall, the NO_x flux measurements for the three fields reflect a period of moisture and heat stress for both the crops and surface 20 cm of the soil.

Overall average NO flux rates increased proportionally to the level of applied fertilizer nitrogen in each of the fields (soybean, 21 kg/ha^{-1}; cotton, 84 kg/ha^{-1}; and corn, 173 kg/ha^{-1}), even though the amount of KCl extractable NH_4^+ and NO_3^- was < 1.5 mg N kg^{-1} for the soybean and cotton fields. For the corn field, KCl extractable NH_4^+ and NO_3^- ranged from 3 to 19 mg N kg^{-1}. The soybean field measurements revealed an average NO flux of 1.79 (range – 1.0–6.9) ng N m^{-2} s^{-1}, the cotton field average NO flux was 3.77 (range – 0.1–38.0) ng N m^{-2} s^{-1}, and the corn field average NO flux was 8.05 (range – 0.5–52.8) ng N m^{-2} s^{-1}. NO flux rates were highest during the mid-morning hours, and decreased for the remainder of the day. This resulted in a negative correlation between soil NO flux and soil temperature, which probably reflects the combination of moisture and heat stress on the soil microorganisms in the top 20 cm of the soil.

NO is rapidly oxidized to NO_2 by reaction with O_3 in the atmosphere, especially during the night.

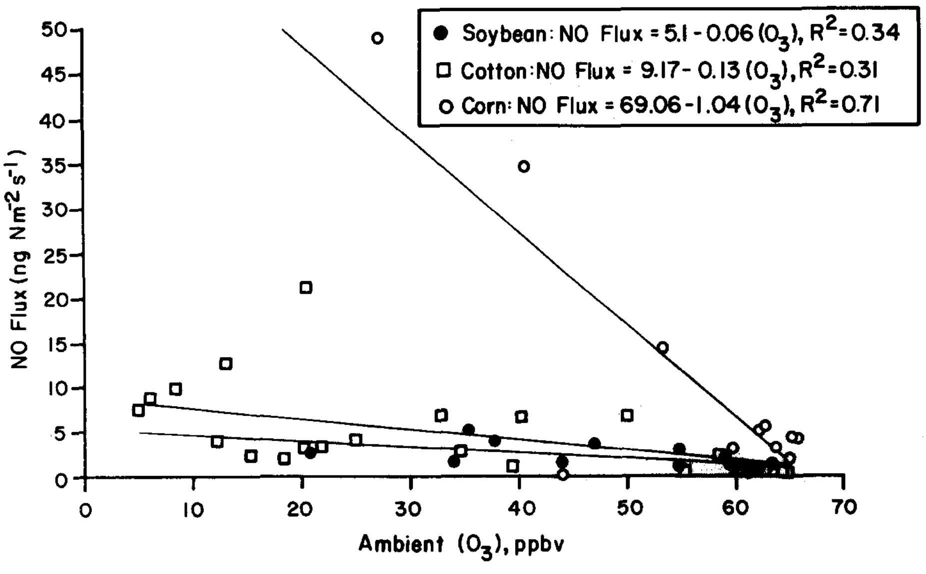

Fig. 2. Soil NO flux vs ambient O_3 concentration (~ 10 m).

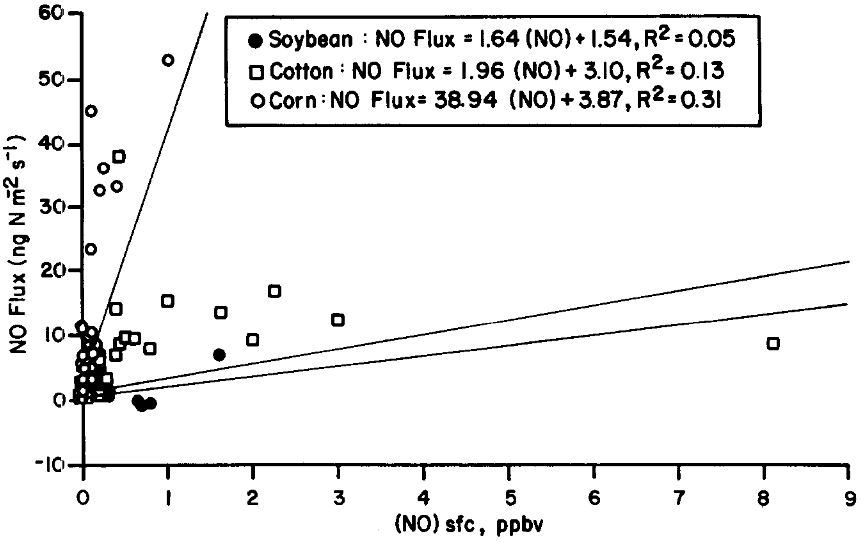

Fig. 3. Soil NO flux vs ambient NO concentration near the surface (~0.5 m).

Therefore, significant concentrations of NO and O_3 are usually not found in the same air mass. Additionally, O_3 does not accumulate during a photochemical air pollution episode until the NO concentration has fallen to low values (Finlayson-Pitts and Pitts, 1986). A negative correlation was observed between NO flux and ambient O_3 concentration in the three crop fields ($R^2 = 0.34$ for soybeans, 0.31 for cotton and 0.71 for the corn field soil, Fig. 2). O_3 regulates the ambient NO concentration and ambient NO concentration is related to NO flux through the NO compensation point (Kim *et al.*, 1994). For this reason, NO flux from soil may also be negatively correlated with ambient O_3 concentration. Moreover, these results suggest that NO emission from the soils increases ambient NO concentrations (Fig. 3).

These results suggest that the flux of NO from agricultural soil appears to be substantially larger than those from a North Carolina nonagricultural soil (average ~1.79 ng N $m^{-2} s^{-1}$; Kim *et al.*, 1994) during summer, even during periods of substantial moisture and heat stress. NO flux increases with increased application of N fertilizer. We are currently performing a comprehensive characterization of NO flux from soils in the Southeast U.S. Nevertheless, these data seem to call into question current methodologies for managed agricultural practices for their role in subsequent ambient air quality.

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