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Biogenic nitric oxide emissions from cropland soils

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Abstract

Emissions of nitric oxide (NO) were determined during late spring and summer 1995 and the spring of 1996 from four agricultural soils on which four different crops were grown. These agricultural soils were located at four different sites throughout North Carolina. Emission rates were calculated using a dynamic flow-through chamber system coupled to a mobile laboratory for in-situ analysis. Average NO fluxes during late spring 1995 were: 50.9 ± 47.7 ng N m^{-2} s^{-1} from soil planted with corn in the lower coastal plain. Average NO fluxes during summer 1995 were: 6.4 ± 4.6 and 20.2 ± 19.0 ng N m^{-2} s^{-1}, respectively, from soils planted with corn and soybean in the coastal region; 4.2 ± 1.7 ng N m^{-2} s^{-1} from soils planted with tobacco in the piedmont region; and 8.5 ± 4.9 ng N m^{-2} s^{-1} from soils planted with corn in the upper piedmont region. Average NO fluxes for spring 1996 were: 66.7 ± 60.7 ng N m^{-2} s^{-1} from soils planted with wheat in the lower coastal plain; 9.5 ± 2.9 ng N m^{-2} s^{-1} from soils planted with wheat in the coastal plain; 2.7 ± 3.4 ng N m^{-2} s^{-1} from soils planted with wheat in the piedmont region; and 56.1 ± 53.7 ng N m^{-2} s^{-1} from soils planted with corn in the upper piedmont region. An apparent increase in NO flux with soil temperature was present at all of the locations. The composite data from all the research sites revealed a general positive trend of increasing NO flux with soil water content. In general, increases in total extractable nitrogen (TEN) appeared to be related to increased NO emissions within each site, however a consistent trend was not evident across all sites.

Keywords: Nitric oxide; Biogenic emissions; Dynamic chamber; Agricultural soils

1. Introduction

Ozone is produced in the troposphere through photochemical processes involving oxides of nitrogen ($NO_x = NO + NO_2$) and volatile organic compounds (VOCs). Tropospheric ozone is an important photochemical air pollutant which increases respiratory illness, damages crops, and causes other environmental problems. Currently, the only known pathway for the production of ozone is the photolysis of NO_2 ($NO_2 \rightarrow NO + O(^3P)$), which further reacts with O_2 to produce ozone (O_3) by the reaction $O(^3P) + O_2 \rightarrow O_3$. In a pseudo-photostationary environment, the O_3 produced would react with the NO that was generated via the photolysis of NO_2 in the following reaction: $NO + O_3 \rightarrow NO_2 + O_2$. Hence, there is no net production of O_3. However, in the real atmosphere, hydroxyl radicals combine with VOCs to produce new radicals which preferentially react with NO, allowing a net O_3 accumulation.

Recent estimates report that on a global scale biogenic emissions of NO are comparable to anthropogenic sources (~ 20 Tg NO–N yr^{-1}) (Li et al., 1999). Regions such as the southeast US, which comprise approximately 40% of the US non-attainment areas, are classified as NO_x limited and increased emissions of NO into the troposphere are likely to produce increased O_3 concentrations (Fehsenfeld et al., 1993). Over 40% of the ozone non-attainment areas of the US are in the southeast. Therefore, in order to formulate more successful ozone control strategies in the southeast US, the source strength of ozone precursors (i.e., NO) and the parameters which

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control their release must be better understood. An estimate of the global source of biogenic NO emissions conducted by Davidson and Kingerlee (1997) reports a slight improvement over estimates made by Galbally and Roy (1978). In their paper, Davidson and Kingerlee report that further improvements to their estimate will most likely come from an increased biogenic NO dataset and by gaining a greater understanding of the processes which govern the release of NO from the soil. To these ends, the objectives of this study were to increase the NO dataset and to attempt to verify previously reported relationships between NO and environmental variables (i.e., soil temperature, soil water content, applied N fertilizer).

2. Methods and materials

2.1. Field sites and sampling scheme

NO concentration measurements were made from four different agricultural soils (on which corn, soybean, tobacco and wheat were cultivated) during late spring and summer 1995 and spring 1996 (refer to Tables 1 and 2 for research sites, dates, soil parameters and NO flux values). All of the sites, except for Plymouth were operated by the North Carolina State University in conjunction with the North Carolina Agricultural Research Service. All of the sites were managed using practices typical for their respective crops and physiographic locations.

The design of this experiment was to measure soil emissions of NO at four different locations in North Carolina during two different times of the year. Each site was sampled twice, once in the late spring/summer and again the following year in the spring. The measurement locations at each site were essentially the same as the previous season (within a distance of 5 m). The daily sampling scheme consisted of measuring ambient NO concentrations at ground level before entering the dynamic flow-through chamber and immediately after exiting the chamber. A Toshiba laptop computer using Labview software (National Instruments) was utilized as the data acquisition system. The system produced 60 second rolling average concentrations, which were then binned and averaged every 15 min. A daily experiment consisted of placing the chamber on the stainless-steel collar approximately 1 h prior to data acquisition. At the conclusion of each daily experiment, the collar was relocated to a random position within a 10 m radius of the mobile laboratory, allowing a minimum of 12 h for any effect on the soil, due to insertion of the collar, to dissipate. The randomization of the collar and chamber system placement resulted in it being located both in and between the rows of the row crops (corn, soybean, tobacco), however, plants were never inside the enclosure.

2.2. Dynamic flow-through chamber and flux calculation

The technique used to measure NO emissions from soils during this measurement campaign was the dynamic flow-through chamber system in conjunction with a Thermo Environmental Instruments Inc. (1992) chemiluminescence low level NO analyzer. This system is one technique to arrive at gas flux from the soil, although several other techniques exist such as the gradient method, static chambers, and eddy-correlation methods. Each system has its own associated benefits and drawbacks which are summarized by Meixner (1994). Several field experiments have been conducted to examine differences between flux methodologies. Valente and Thorton (1993) and Roelle et al. (1999) reported reasonable agreement between static and dynamic chambers utilized for NO flux measurements at fertilized cotton and corn crops respectively. Similarly, Parrish et al. (1987) reported no systematic differences between a dynamic chamber and micrometeorological techniques for experiments conducted at nighttime. Li et al. (1999) also reported that the intercomparison between a dynamic chamber and eddy-correlation method produced similar diurnal profiles, although the chamber system consistently resulted in higher flux values than the fluxes calculated at 5 m utilizing the eddy-correlation method.

The chamber used in this study was lined with 5 ml fluorinated ethylene propylene (FEP) Teflon to minimize losses occurring on the walls of the chamber. The translucent chamber, 27 cm in diameter, and 42 cm high (volume-24.05 l) fits inside of a stainless steel ring. Which is driven into the ground to a depth of 10 cm. Ambient air, which is used as the carrier gas is pumped through the chamber at a constant flow rate (4 lpm). The sample exiting the chamber travels through Teflon tubing (1/4″ outside diameter, 1/8″ inside diameter) to the detection instruments. The entire system, from the inlet port on the chamber, to the point where the stream is analyzed in the instrument is comprised of Teflon, stainless steel, or gold to minimize further chemical reactions within the sample. The sample lines do not exceed 10 m. The NO detection instruments drew 1 lpm, resulting in a sample residence time of approximately 5 s.

Experiments were conducted to determine if the mixing speed of the Teflon impeller altered soil NO flux values. Varying the speed between 20 and 100 revolutions per minute (rpm) did not produce any significant change in the calculated NO flux. The impeller was set to 70 rpm for the remainder of the experiments. Outlets in the chamber ensured that there were no substantial pressure differences between the outside and inside of the chamber. Research conducted on similar chambers using a tilting water manometer indicated that pressure differences were below detection limits (0.2 mm H_2O) (Johansson and Granat, 1984). A schematic of the dynamic flow-through chamber and associated equations

Table 1
Location, dates, fertilizer application and soil types of the sites where the research was conducted

Crop	Location/ Measurement dates	Fertilization dates	N Applied (amount and how applied)	Soil
Corn	Plymouth, NC N Latitude: 35°43′ W Longitude: 76°42′ 15 May–9 June 1995	April 12 May 20	9 kg N ha^{-1} as 10–20–20/soil injection 64 kg N ha^{-1} as 30% N soln[a]/broadcast 102 kg N ha^{-1} as 30% N soln[a]/side-dressed	Portsmouth fine sandy loam
Corn	Kinston, NC N Latitude 35°18′ W Longitude: 77°34′ 30 June–July 5 1995	April (pre-plant) Mid-May	33 kg ha^{-1} as 10–20–20/soil-injection 157 kg ha^{-1} 30% N soln[a]/side-dressed	Rains fine sandy loam
Corn	Reidsville, NC N Latitude 36°23′ W Longitude: 79°42′ 3–10 August 1995	April (at-planting) Mid-May	56 kg ha^{-1} as 10–20–20/soil-injection 141 kg ha^{-1} NH_4NO_3/side-dressed	Pacolet sandy loam
Corn	Reidsville, NC 14–18 May 1996	April (at-planting)	45 kg ha^{-1} as 10–20–20/soil-injection	Pacolet sandy loam
Soybean	Kinston, NC 10–13 July 1995	None		Rains fine sandy loam
Tobacco	Oxford, NC N Latitude 36°17′ W Longitude: 78°37′ 20–27 July 1995	Mid-May (1 week after transplating) Late-May (2 weeks after transplanting)	45 kg N ha^{-1} as 8–8–24/soil injection 25 kg N ha^{-1} as 15–0–14/side-dressed	Vance sandy loam
Wheat	Plymouth, NC 11–14 April 1996	October (at-planting) February	50 kg N ha^{-1} as 10–20–20/soil injection 100 kg ha^{-1} NH_4NO_3/broadcast	Portsmouth fine sandy loam
Wheat	Kinston, NC 17–20 April 1996	October (at-planting) February	30 kg N ha^{-1} as 10–20–20/soil injection 120 kg ha^{-1} 30% N soln[a]/side-dressed	Portsmouth fine sandy loam
Wheat	Oxford, NC 24–28 April 1996	October (at-planting) February	45 kg N ha^{-1} as 10–10–10/soil injection 95 kg ha^{-1} NH_4NO_3/broadcast	Vance sandy loam

[a]30% N solution contains equal parts urea, ammonia and nitrate.

Table 2
Soil parameters and NO flux for various argicultural soild on which different crops were grown[a]

Location	Crop		Soil temp (°C)	TEN (mg N (kg dry soil)$^{-1}$)	% soil moisture	NO (ng Nm^{-2} s^{-1})
Plymouth	Corn	Avg	24.1	51	21.1	50.9
$N = 16$		Std Dev	3.2	26.2	2.8	47.7
$n = 759$		Min	16.4	24	17.7	4.2
		Max	32.7	116	27.7	264.7
Kinston	Corn	Avg	25.6	9.8	12.4	6.4
$N = 5$		Std Dev	2.6	1.7	1.4	4.6
$n = 203$		Min	21.1	8	10.7	2.1
		Max	32.6	12.1	14	37.2
Kinston	Soybean	Avg	25.8	14.2	12.8	20.2
$N = 4$		Std Dev	3.2	3.4	0.8	19.0
$n = 276$		Min	21.5	11	11.6	1.7
		Max	31.9	19	13.4	96.8
Oxford	Tobacco	Avg	27.4	8	5.6	4.2
$N = 6$		Std Dev	2.2	2.5	2.3	1.7
$n = 285$		Min	23.5	6	2.7	1.0
		Max	32.5	13	8.1	13.0
Reidsville	Corn	Avg	23.0	12.8	11.3	8.5
$N = 4$		Std Dev	2.5	11.9	2.4	4.9
$n = 289$		Min	19.7	4.0	10.0	1.4
		Max	29.0	32.0	15.6	20.5
Plymouth	Wheat	Avg	14.3	9.4	22.7	66.7
$N = 4$		Std Dev	3.2	4.4	1.2	60.7
$n = 229$		Min	5.5	5.3	21.3	2.7
		Max	19.2	13.9	23.8	175.6
Kinston	Wheat	Avg	17.1	3.2	9.4	9.5
$N = 4$		Std Dev	2.9	0.8	2.5	2.9
$n = 166$		Min	9.5	2.2	6.3	4.3
		Max	21.5	4.0	11.7	19.9
Oxford	Wheat	Avg	15.4	1.8	6.9	2.7
$N = 4$		Std Dev	2.4	0.5	1.3	3.4
$n = 187$		Min	10.7	1.3	5.8	0
		Max	19.3	2.4	8.7	25.5
Reidsville	Corn	Avg	19.1	19.7	21.7	56.1
$N = 4$		Std Dev	4.9	13.0	2.4	53.7
$n = 161$		Min	11	8.6	19.8	4.5
		Max	28.4	36.5	24.9	191.9

[a] N is the number of sampling days; n the number of NO concentration measurements; and TEN the total extractable nitrogen.

for arriving at the NO flux can be found in Roelle et al. (1999).

2.3. Temperature and soil analysis

Soil temperature was recorded every 15 min using a Fischer Scientific temperature probe inserted 5 m into the soil, adjacent to the chamber. On average, the soil temperature difference between the inside and outside of the chamber was 0.23 ± 1°C (Sullivan et al., 1996; Roelle et al., 1999). A soil sample (8.3 cm in diameter to a depth of 20 cm) was taken from the center of the dynamic flow-through chamber footprint at the end of each measurement period (1 sample per day) and analyzed for percent soil moisture and total extractable nitrogen.

3. Results and discussion

3.1. Soil temperature

Fig. 1 is an hourly averaged diurnal profile of NO flux versus time of day for each site and crop type. This graph has been split to reflect two different ranges in NO flux so

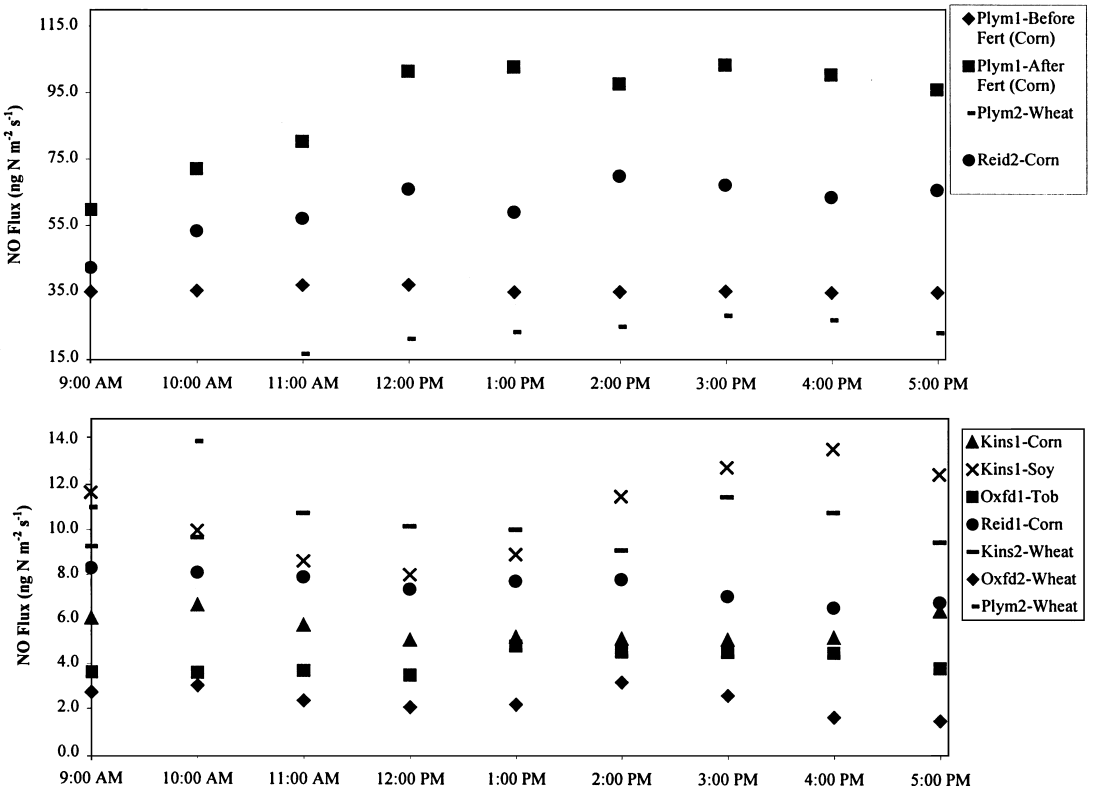

Fig. 1. Hourly averaged NO flux (09:00–17:00) for each measurement site and crop type. Note the change in scale on the vertical axes-graphs have been split so that diurnal trends would be easier to discern. The 1 & 2 attached to each site name indicates the season the site was sampled, 1 = late spring/summer 95; 2 = spring 96.

that diurnal variations can be better discerned. In general, both graphs reveal that maximum NO emissions occur in the afternoon when soil temperatures are typically at a maximum and reduce to lower values in the late afternoon hours when soil temperatures are typically lower. The bottom graph also reveals that several sites have a local maximum of NO emissions in the morning. This morning peak has been observed by other researchers (Johansson and Granat, 1984; Roelle, 1996), however a solid understanding as to the cause of this phenomenon has yet to be determined. It has been hypothesized that this morning peak is a result of plant roots which may exude organic substances in the morning hours which denitrifying bacteria can utilize to produce NO (Johansson and Granat, 1984). Aneja et al. (1995) reported a negative correlation between NO flux and soil temperature, which was explained by a combination of moisture and heat stress on the soil microorganisms in the top 20 cm of soil. This explanation is not sufficient in this study, because although there was a brief period when the correlation was negative, the greatest values of NO flux were in the afternoon, when soil temperatures were at a maximum.

It is generally found that in the range of temperatures between 288 and 308 K, biochemical reactions will rise exponentially with temperature (Warneck, 1988). Several researchers have investigated this relationship, and in fact have observed there to be an exponential dependence of NO flux on soil temperature (Williams and Fehsenfeld, 1991; Sullivan et al., 1996; Thornton et al., 1997; Roelle et al., 1999). The research conducted during this experiment revealed similar results, however, the exponential dependence of NO flux on soil temperature was not consistent at all sites.

Plymouth, NC, during the late spring 1995 experiment displayed some dependence of NO flux on soil temperature [log (NO flux) = 0.083(Soil T) − 0.41; $R^2 = 0.27$] for the entire 16 day period. However, this research site was characterized by an additional application of N fertilizer midway through the experiment allowing the data to be segregated into periods 'before' and 'after' fertilization. For the period before the additional N fertilization, there was virtually no relationship between temperature and flux [log (NO flux) = 0.023(Soil T) + 0.89; $R^2 = 0.10$]. However, for the period after the additional N fertilization (Excluding one day due to the remnants

of Hurricane Allison flooding the field), the relationship increased [log (NO flux) = 0.23(Soil T) − 3.823; $R^2 = 0.58$]. Additionally, there was some dependence of NO flux on soil temperature observed at a soybean crop located in Kinston, NC during the summer 1995 research period when one day was excluded due to heavy rains the previous day (log (NO flux) = 0.45(Soil T) − 11.33; $R^2 = 0.35$). There was also some dependence observed at the tobacco crop in Oxford, NC [Log (NO flux) = 0.09(Soil T) − 2.00; $R^2 = 0.56$]. At the remainder of the research sites, this same exponential dependence on soil temperature was difficult to detect.

Fig. 2 is a composite of the data from each site with hourly averaged soil temperature plotted versus hourly averaged NO flux. This graph and regression analysis reveals a significant improvement in R^2 values for data which was collected at Plymouth and Reidsville, which were being cultivated with corn during approximately 86% of the measurement period. These results are more in line with similar analyses conducted by Thornton et al. (1997), who reported R^2 values of 0.87 for a dataset comprised of approximately 9900 observations, of which 94% were from soils where corn was being cultivated. This deviation from the often-cited relationship between NO flux and soil temperature at Kinston and Oxford suggests that factors other than soil temperature are acting to control the flux of NO. Researchers in California conducting extensive research on a very robust NO data set report that depending on location and time, other variables (i.e. crop type, soil type, water-filled pore space, N content) can have stronger influences than soil temperature on NO flux (Matson et al., 1997). Additionally, Sullivan et al. (1996) reported that differences in a crops growth stage and the age and amount of root biomass further act to influence the NO flux/temperature dependence.

3.2. Total extractable nitrogen

Another variable, which has also been found to control the NO flux, is total extractable nitrogen (TEN) ($NH_4 + NO_3^-$). Fig. 3 is a graph of the total average NO flux (stippled bar) (09 : 00–17 : 00) and TEN on the secondary axis plotted for each research site. Three sampling days were removed from this analysis, which occurred during or immediately after rain events at the site. This graph does reveal a trend of NO emissions responding to increasing and decreasing amounts of TEN, however a consistent relationship was unable to be detected. Researchers conducting similar studies have

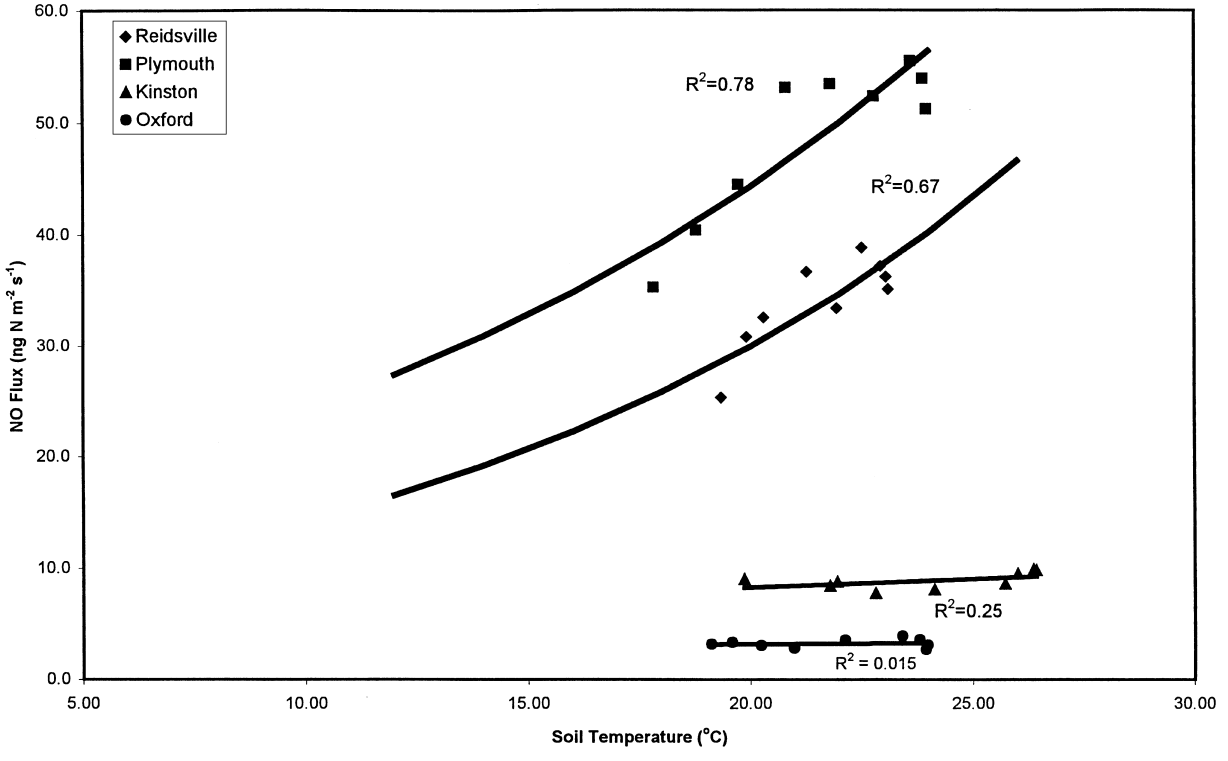

Fig. 2. Hourly averaged NO flux plotted versus hourly averaged soil temperature (at 5 cm depth) for the composite data from the four sites where the data was collected.

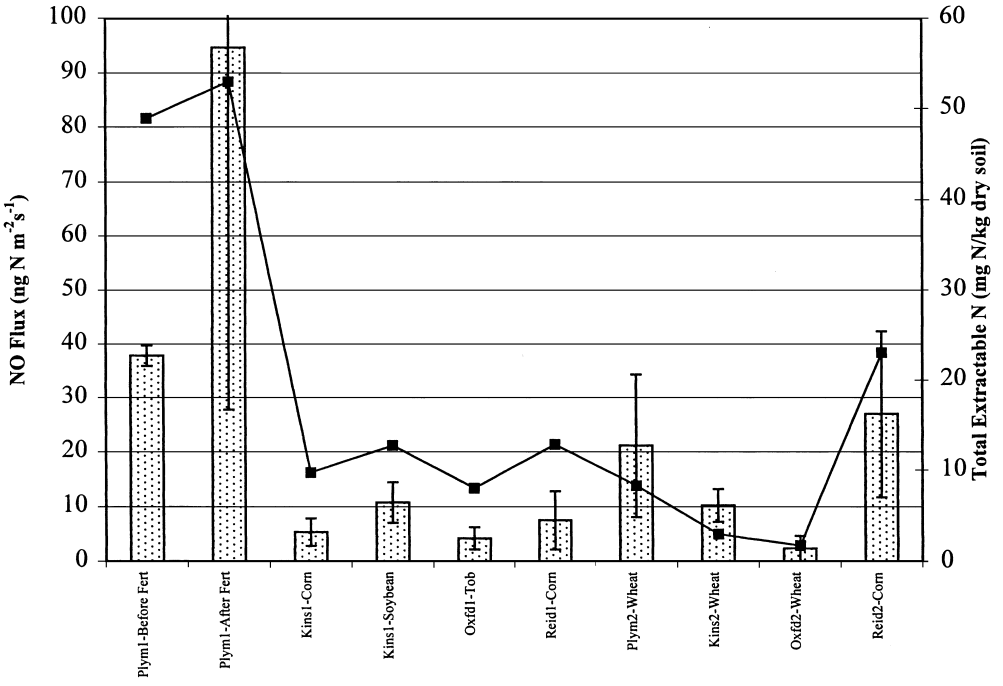

Fig. 3. NO flux between 09:00 and 17:00 (stippled bars) and total extractable N (on secondary axis) plotted for each site. The 1 and 2 attached to each site name indicates the season the site was sampled, 1 = late spring/summer 95; 2 = spring 96. Error bars represent one standard deviation. One sampling day at Kinston1-Soybean, Plymouth2-Wheat, and Reidsville2-Corn, were not included in this dataset due to rainshowers occurring at the site.

reported on the effects of organic and inorganic nitrogen content in soils on NO emissions and in general have found that soils with higher N content produce higher NO emissions (Davidson, 1991a, b; Cardenas et al., 1993; Potter et al., 1996; Sullivan et al., 1996; Roelle et al., 1999). If the research conducted in spring 1995 at Plymouth, NC is taken as an example, it is evident that TEN alone is not controlling the release of NO from the soil. At this site, a small increase in TEN was associated with a much larger increase in NO emissions. A plausible explanation as to the lack of a consistent relationship in our data between TEN and NO emissions could be the result of our soil sampling method. One method of N fertilizer application is to use applicator nozzles which drag across the soil surface (2 cm wide strip of concentrated liquid fertilizer). This application method was used on the corn crop at the Plymouth site. Upon drying, there is no way to discern where exactly this fertilizer band is in the interrow (1 m width). It is possible that the fertilized strip was in the chamber footprint (diameter 27 cm) but our soil core sample (diameter 8.3 cm) missed the band. Further, it is possible that a soil sample, which occurred immediately following fertilization, collected the fertilized strip which had yet to penetrate the soil surface.

Statistical analysis of the data in Fig. 3 reveals a noisy data set with an *R*-squared value of only 0.15. However, this relationship does improve and becomes highly significant ($p < 0.0001$) when those flux values greater than 100 ng N m^{-2} s^{-1} are removed from the regression. The justification for removing 3 (from Spring 95 data set) of the 5 data points greater than 100 ng N m^{-2} s^{-1} is that the data was collected immediately (within 2 weeks) after fertilization. In contrast, at all the remaining measurement sites, there was no data collected within at least one month of fertilization. These results suggest that TEN can be used effectively in NO flux models, although further research will be needed to determine under what physiological and environmental conditions this relationship can be best applied. Sullivan et al. (1996), during a field study with an equivalent experimental design, experienced similar results and reported that the differences in a plants physiological growth stages, during which nitrogen demands of the plants will vary, confound the relationship between NO flux and TEN.

3.3. Soil moisture

The role of soil moisture on NO flux has been examined by several researchers (Cardenas et al., 1993; Valente and Thorton, 1993; Ormeci et al., 1999). Typically, each soil type will have a range of soil moisture which optimizes NO flux. For example, Cardenas et al. (1993)

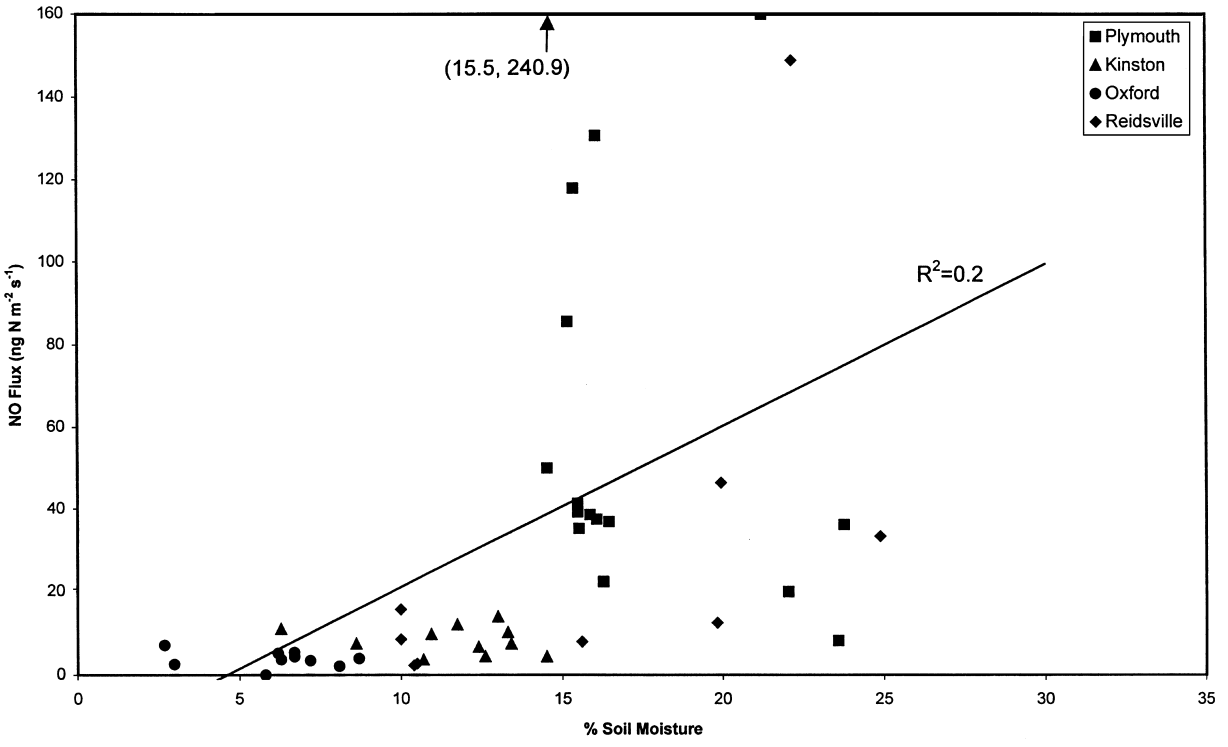

Fig. 4. Average NO flux (09:00–17:00) vs. % soil moisture. Percent soil moisture was determined from a soil sample taken from the center of the chamber footprint at the end of each measurement period. Data have been segregated into sites.

reported that the optimum range of soil water content for sandy loam soils was between 9 and 18%. Moisture values above a soils optimum zone will generally decrease NO flux due to pore spaces filling with water and inhibiting gas transport. Moisture values below a soils optimum zone will generally lead to decreased NO emissions as a result of moisture stress to the soil microbes. Fig. 4 is a graph of the daily averaged (09:00–17:00) NO flux values versus % soil moisture for the four research sites where the experiments were conducted. These results partially support Cardenas et al.'s (1993) research in that NO flux tends to respond positively to increased moisture, and then begins to decrease again at moisture levels greater than 20%. However, it is also evident that with *R*-squared values of 0.2, this variable alone cannot adequately predict NO emissions from biogenic processes. Using the same rationale as in Fig. 3, the data points greater than 100 ng N $m^{-2} s^{-1}$ were removed from the data set and then reanalyzed. However, unlike Fig. 3, this approach only resulted in a slightly better model prediction ($R^2 = 0.3$).

3.4. NO response to soil parameters

Chameides et al. (1988, 1994) have reported on the importance of including both anthropogenic and biogenic NO emissions when attempting to predict the concentrations of tropospheric ozone. One of the methods used in air quality models for estimating soil NO emissions is the Biogenic Emissions Inventory System (BEIS2) model. This model utilizes soil temperature data and an emission factor which is based on crop type, the type and amount of fertilizer applied, and other chemicals applied to the soil (Birth and Geron, 1995). The NO flux is then calculated by:

$$\text{NO flux (ng N m}^{-2}\text{ s}^{-1}) = \text{A EXP}(0.71 * T_s)$$

where A is the experimentally derived coefficient which is dependent on the land use category and T_s is the soil temperature (Williams et al., 1992).

This temperature dependence model has been questioned by several researchers who have found that temperature alone does not adequately explain the flux of NO in their measurements (Matson et al., 1997; Roelle et al., 1999; Li et al., 1999). In fact, Matson et al. (1997) reported that for most crops in their research, percent water-filled pore space (WFPS) was equally as important as temperature in predicting NO emissions.

Table 3 lists Williams' values for A as well as those calculated for this study. The range of soil temperatures (T_s) with the corresponding fluxes produced using the BEIS2 model versus the actual data measured during this study is also on this table. There was reasonable

Table 3
NO emissions for this study and the results using the BEIS2 model for the corresponding range of soil temperatures observed during the study

Crop type	Emission factor (A) (this study) (ng N $m^{-2} s^{-1}$)	Williams' emission factor (A) (ng N $m^{-2} s^{-1}$)	T_{soil} range (°C)	NO flux (using BEIS2) (ng N $m^{-2} s^{-1}$)	NO flux (this study) (ng N $m^{-2} s^{-1}$)
Corn	7	9	11–32.7	20–92	Range: 2–265 Average: 30
Soybean	3	0.2	21.5–31.9	1–2	Range: 2–97 Average: 30
Tobacco	0.6	4	23.5–32.5	21–40	Range: 1–13 Average: 4
Wheat	11	3	5.5–21.5	4–14	Range: 0–176 Average: 26

agreement between A factors for the corn crop, where Williams' A value is 9 ng N $m^{-2} s^{-1}$ and the A value from this study is 7 ng N $m^{-2} s^{-1}$. However, the remaining crops, (soybean, tobacco, and wheat) varied from Williams' model by factors of 15, 6.7, and 3.7, respectively. Research conducted in the San Joaquin Valley in California produced even larger deviations from Williams' model, where these researchers calculated A values for corn between 0.0001 and 0.0005 ng N $m^{-2} s^{-1}$ (Matson et al., 1997). As the table indicates, using the BEIS2 model to estimate NO emissions can produce values different by up to an order of magnitude than the NO emissions that were calculated during this study.

4. Conclusion and recommendations

NO emissions and soil properties were studied from several croplands in order to gain a better understanding of the chemical and physical properties of soil which influence NO flux, and to provide much needed data to the biogenic NO emission dataset. Utilizing a dynamic flow-through chamber, the flux of NO from soil was determined for four different regions and crop types during both spring and summer. NO flux was generally found to follow a diurnal profile with maximum emissions coinciding with maximum soil temperatures. Additionally, several sites displayed a morning peak in NO emissions, which is occasionally observed by some researchers but has yet to be explained. The exponential dependence of NO flux on soil temperature existed at all sites, but to different levels of significance. It was also observed that NO flux did respond to varying amounts of both total extractable nitrogen (TEN) in the soil and soil moisture content.

Although relationships between soil parameters (soil moisture, TEN, soil temperature) were evident, no one variable or combination of variables has yet been found to adequately model the flux of NO from agricultural soils. Parkin (1993) addressed the difficulty in modeling a system with such high variability, yet stressed the importance of continued research, as improved estimates will only be achieved as we gain a greater understanding of the processes causing the variability. The data from this observationally based study raise concerns about the current practice of basing emission estimates solely on temperature and land cover type. Errors in soil emission estimates caused by ignoring the influence of parameters such as soil moisture and TEN, which was pointed out in the comparison of BEIS2 model estimates to actual calculated fluxes, may also hinder the ability of ozone models to simulate VOC/NO_x emission control scenarios. With the addition of this data set reported here, and with data such as reported by Thornton et al. (1997), the scientific community should combine other observational data to build a model which includes a broader set of environmental parameters (i.e., %WFPS, TEN, soil type), which will likely lead to better estimates of NO emissions from agricultural soils.

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References

Aneja, V.P., Robarge, W.P., Holbrook, B.D., 1995. Measurements of nitric oxide flux from an upper coastal plain, North Carolina agricultural soil. Atmospheric Enviroment 21, 3037–3042.

Birth, T.L., Geron, C.D., 1995. Users guide to the personal computer version of the biogenic emissions inventory system (PC-Beis2). EPA-600/R-95-091.

Cardenas, L., Rondon, A., Johannson, C., Sanhueza, E., 1993. Effects of soil moisture, temperature, and inorganic nitrogen on nitric oxide emissions from acidic tropical savannah soils. Journal of Geophysical Research 98, 14783–14790.

Chameides, W., Lindsay, R., Richardson, J., Kiang, C., 1988. The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study. Science 241, 1473–1475.

Chameides, W., Kasibhatla, P., Yienger, J., Levy, H., 1994. Growth of continental-scale metro-agro-plexes, regional ozone pollution, and world food production. Science 264, 74–77.

Davidson E.A., 1991a. Sources of nitric oxide and nitrous oxide following wetting of dry soil. Soil Science Society of American Journal 56.

Davidson, E.A., 1991b. Fluxes of nitrous and nitric oxide from terrestrial ecosystems. In: Rogers, J.E., Whitman, W.B. (Eds.), Microbial Production and Consumption of Greenhouse Gases, Methane, Nitrogen Oxides and Halomethanes. American Soceity for Microbiology, Washington, DC, pp. 219–235.

Davidson, E.A., Kingerlee, W., 1997. A global inventory of nitric oxide emissions from soils. Nutrient Cycling in Agroecosystems 48, 37–50.

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

Galbally, I.E., Roy, C.R., 1978. Loss of fixed nitrogen from soils by nitric oxide exhalation, Nature 275, 734–735.

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

Li, Y., Aneja, V.P., Arya, S.P., Rickman, J., Brittig, J., Roelle, P., Kim, D.-S., 1999. Nitric oxide emission from intensively managed agricultural soil in North Carolina, Journal of Geophysical Research 104, 26115–26123.

Matson, P., Firestone, M., Herman, D., Billow, T., Kiang, N., Benning, T., Burns, J., 1997 Agricultural systems in the San Juaquin Valley: Development of Emission Estimates for Nitrogen Oxides, Technical Report, University of California, Berkeley, Contract Number 94-732.

Meixner, F.X., 1994. Surface exchanges of odd nitrogen oxides. Nova Acta Leopoldina NF 70 (288), 299–348.

Ormeci, B., Sanin, S.L., Peirce, J., 1999. Laboratory study of NO flux from agricultural soil: effects of soil moisture, pH and temperature. Journal of Geophysical Research 104, 1621–1629.

Parkin, T.B., 1993. Spatial variability of microbial processes in soil – A review. Journal of Environmental Quality 22, 409–417.

Parrish, D.D., Williams, E.J., Fahey, D.W., Liu, S.C., Fehsenfeld, F.C., 1987. Measurement of nitrogen oxide fluxes from soils: intercomparison of enclosure and gradient techniques. Journal of Geophysical Research 92, 2165–2171.

Potter, C.S., Matson, P.A., Vitousek, P.M., Davidson, E.A., 1996. Process modeling of controls on nitrogen trace gas emissions from soils worldwide. Journal of Geophysical Research 101, 1361–1377.

Roelle, P.A., 1996. Chemically reactive nitrogen trace species in the planetary boundary layer, MS Thesis, NC State University, Department of Marine, Earth and Atmospheric Sciences, p. 73.

Roelle, P.A., Aneja, V.P., O'Connor, J., Robarge, W., Kim, D.-S., Levine, J.S., 1999. Measurement of nitrogen oxide emissions from an agricultural soil with a dynamic chamber system. Journal of Geophysical Research 104, 1609–1619.

Sullivan, L.J., Moore, T.C., Aneja, V.P., Robarge, W.P., 1996. Environmental variables controlling nitric oxide emissions from agricultural soils in the southeast United States. Atmosopheric Environment 30 (21), 3573–3582.

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

Thornton, F., Pier, P., Valente, R., 1997. NO emissions from soils in the southeastern United States. Journal of Geophysical Research 102, 21189–21195.

Valente, R.J., Thorton, F.C., 1993. Emissions of NO from soil at a rural site in Central Tennesee. Journal of Geophysical Research 98, 16745–16753.

Warneck, P., 1988. Chemistry of the Natural Atmosphere. Academic Press, New York, pp. 422–425.

Williams, E.J., Fehsenfeld, F.C., 1991. Measurement of soil nitrogen oxide emissions at three North American ecosystems. Journal of Geophysical Research 96, 1033–1042.

Williams, E., Guenther, A., Fehsenfeld, F., 1992. An inventory of nitric oxide emissions from the soil in the United States. Journal of Geophysical Research 97, 7511–7519.