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Natural Emission of Nitric Oxide from Agricultural Soil of Corn-field in Eastern North Carolina

Deug-Soo Kim[1], Paul Roelle[2] and Viney P. Aneja[2]
[1]Department of Environmental Engineering
Kunsan National University
[2]Department of Marine, Earth and Atmospheric Sciences
North Carolina State University

Abstract

Natural emissions of NOx from soils were measured at an agricultural corn field during 3 weeks of growing season in summer (from May to June) 1995. This experiment was conducted in an effort to characterize the role of soil NOx on tropospheric ozone formation in rural atmosphere, and understand the natural NOx emission mechanism with respect to soil parameters. NO fluxes were measured every 15 minutes as well as soil temperature and soil moisture. NO soil fluxes were ranged from 3.1 ng Nm^{-2} s^{-1} to 259.0 ng Nm^{-2} s^{-1}, and average NO flux during experimental period was found to be 47.6±50.6 ng $Nm^{-2}s^{-1}$ with 732 number of data. Diurnal variation of NO flux was shown clearly with daytime maximum and nighttime minimum. NO fluxes were correlated with soil temperature. Exponential soil temperature dependency of NO fluxes was found with $0.0160°C^{-1}$ of k and $r^2=0.508$, which agrees well to the value estimated at corn fields in eastern United States. The significant increases of NO fluxes from agricultural soil were detected after applying N fertilizers to soil. The mechanisms attributed to this are enhanced biological nitrification and denitrification. In the view of rural ozone formation, the roles of natural NO emissions are very essential, especially in NOx - limited region such as southern United States.

Key word : Natural emission, Nitrogen oxides, Flow-through chamber, NO flux controlling parameter, Soil NO emission.

1. INTRODUCTION

The natural emission of NOx has been underestimated and often misunderstood in the regional or global amount of emission. As we know, the NOx in the atmosphere has very important role in the tropospheric photochemistry, such as the formation of ozone and other phytotoxicant oxidants. These oxidants can negative effects not only human health but also ecological system and crop yield. The final fate of NOx, gaseous nitric acid (HNO_3), combining with aerosol or water in the atmosphere, is removed from atmosphere, and then acidifys the soil and surface water. This phenomenon was called the acidic deposition, and acidification of lake gives many adverse effects on the soil biology and water living systems. Understanding these oxidants distribution in global base, many researchers have been measured soil NOx emission in many other places in North America, Europe, Australia, South America but scarcity of in Asia (Yienger and Levy, 1995). The purpose of these measurements, of course, is understanding of natural emission of NOx from soil for different kind of

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* To whom correspondence should be addressed.

soil surface system. However, still numerous field data will be necessary to understand the natural NOx emission accurately and to predict or analyze ozone distribution.

Williams *et al.*(1992) parameterized soil NOx using their experimental data in North America and estimate natural emission of NOx in US. Yienger and Levy (1995) recently has developed global soil biogenic NOx emission model using most data available measured in different continents. They pointed out important factors which effect on soil NOx emission, which are temperature dependence, moisture dependence, biomass burning stimulation and canopy reduction. The NOx flux from soil was parameterized in terms of those four factors using available worldwide experimental data, and results from model run were being compared to those experimental data. The results were agreement within 50% uncertainty. However, there are certainty and reasonable with this kind of global scale model. Reducing the uncertainty for NOx flux estimation, we need more field data especially in Asia (which has worst data base, but seems to be more effective flux possibility). Models for NOx flux estimation should be able to apply for the different agricultural crop types. In this case, fertilizer types and quantity may be considered as important factors because different amounts of nitrogen fertilizer are applied to different crop fields.

We are attempting to find out the NO flux from different kinds of crop field in North Carolina through next 5 years measurement study, which might be very useful to develop global soil biogenic NOx model and also to understand how the different kinds of crop soils give different level of emission. It is also important to understand the formation of rural oxidants especially ozone in country side. The first year pilot measurement for NO flux was conducted at a corn crop field, Plymouth, N.C. during 3 weeks intensive period in 1995 summer by Air Quality Group of North Carolina State University. The results from the measurement were discussed here with other important soil parameters.

2. EXPERIMENTAL

2.1 Sampling site characteristics

Flux measurements were made at a corn field of Plymouth, North Carolina (124.63°W, 48.30°N, 43 m m.s.l.), which was located in the eastern NC and 4 km inland from Albermerle Sound 10km from Washington, NC. There are no major anthropogenic sources within 100 miles radius from the site: may be defined as a rural agricultural area.

NOx fluxes were measured from randomly different sampling plots for each day within the corn field site during a period from May 16, 1995 to June 9, 1995. The flux plot was moved to the other place within 20 m radius after finishing experiment for the day, which may give us unbiased flux data for the site. Additional measurements included continuous monitoring of the concentrations of NO, NOx and O_3, and meteorological parameters (temperature, wind direction and speed, solar radiation) at 10 m above the ground level. 24 hours experiments were conducted three times to examine the diurnal variation of NOx flux.

2.2 Flux measurement

Initial total soil water content at the start of each flux measurements was determined from soil samples collected using a bucket auger (0~15 cm depth), ~50 cm way from each sampling plot.

Final total soil water content, pH, and elemental nitrogen contents (Robarge and Fernandez, 1986) were obtained from soil samples taken after removal of the sampling chamber. Soil water content was converted to percent water-filled pore space using an average bulk density of 1.30 g/cm^{-3} and assuming a particle density of 2.65 g/cm^{-3}. The soil moistures were ranged from 17.69% to 27.68% during experimental period. Soil temperature measurements were performed by inserting thermometers into the soil adjacent to the sampling chamber and recorded every sampling time.

Flow-through dynamic chamber was used to measure the nitrogen flux from soil. The chamber was Teflon-lined cylinder (27 cm of diameter, 42 cm of height, and 25 *l* of volume). It was placed by a stainless steel frame driven into the ground to a depth of ~10 cm (Fig. 1). Ambient air near the chamber is pumped through the chamber at a constant flow rate of 4 lpm and air inside chamber is well mixed by a motor driven Teflon stirrer (~20 cm diameter, 120 rpm). Air samples were monitored for NO and NOx concentration simultaneously from the air before going into the chamber and after going through the chamber using two separate NO-NOx chemiluminescent analyzers (TECO 42S: Thermo Environmental Instruments Inc.). The instruments were periodically calibrated once a week using multiple dilution with a mixture of 0.109 ppmv NO in N_2 and a mixture of 0.116 ppmv of NO_2 in N_2 (Scott Specialty Gases, Inc.). Detection limits for these instruments are cited at 50 pptv for NO (Thermo Environmental Instrument, Inc., 1992). Additional information concerning the instrumentation is described elsewhere (Kim *et al.*, 1993; Dickerson *et al.*, 1984)

2. 3 Flux calculation

Flux of NO calculated from the mass balance for NO in the chamber (Kim *et al.*, 1994; Kaplan *et al.*, 1988). The mass balance equation is given by

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

where,

h : internal height of chamber; cm

J : emission flux per unit area; ppb cm min^{-1}

L : total loss in the chamber per unit area assumed first order in [NO]; cm min^{-1}

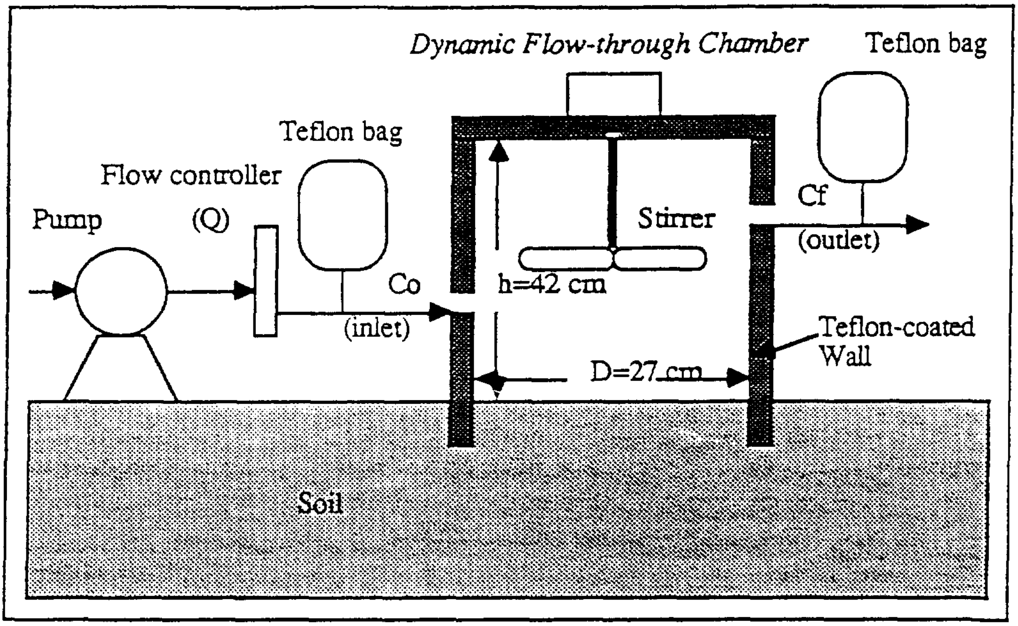

Fig. 1. The schematic figure of the dynamic flow-through chamber. The wall and interfaces are FEP Teflon (refer to Kim et al., 1994).

q : flow rate through the chamber; *lpm*
v : volume of the chamber; *l*
C : NO concentration in the chamber; ppb
C_{air} : NO concentration in ambient air near the ground (i.e., inlet of chamber); ppb.

Assuming well-mixed air in the chamber, general solution of the mass balance equation (1) for C will be

$$C_f=\left(C_o-\frac{\alpha}{\beta}\right)e^{-\beta t}+\frac{\alpha}{\beta} \qquad (2)$$

where,
C_f : NO concentration in chamber at time t after placing the flux chamber;
C_o : NO concentration in chamber at time placing the chamber (t=0);
α : $J/h+qC_{air}/v$;
β : $L/h+q/v$.

Physical meaning of this solution is that the NO concentration in flux chamber reach to an equilibrium concentration, $C_{eq}=\alpha/\beta$, at certain time of period, and enough time period for reaching the equilibrium state was, in both mathematically and empirically, found to be 15 minutes for the chamber used in this research. The NO flux from soil therefore was determined from the equilibrium state NO concentration, C_{eq} in the chamber.

$$\frac{J}{h}=\left(\frac{J}{h}+\frac{q}{v}\right)C_{eq}-\frac{q[C_{air}]}{v} \qquad (3)$$

where C_{eq} is an equilibrium NO concentration in the flux chamber. In most time of experimental period, NO concentrations in ambient air near the ground, C_{air}, were observed less than 1 ppbv, which is one or two order of magnitude less than C_{eq}, and the last term in (3) could therefore be neglected for NO flux calculation.

In equation (3), total loss term, L is the sum of loss by chamber wall reaction with NO in the chamber and chemical reactions of NO with oxidants existing in the pulling air (e.g., ozone, peroxy radicals) due to pull ambient air near ground into the chamber (Aneja *et al.*, 1995; Kim *et al.*, 1994). The total loss term here was determined empirically (five times experiments for day and night) following Kaplans way (Kaplan *et al.*, 1988), which plots the value of $-\ln\frac{(C_{eq}-C)}{(C_{eq}-C_o)}$ against time t. C_o is the NO concentration in the chamber when [NO] reaches the first equilibrium state at low flow rate. (For further detail technical procedures to determine total loss term, *see Kaplan et al.* [1988]). From the linear relationship between the value of $-\ln\frac{(C_{eq}-C)}{(C_{eq}-C_o)}$ and time t for daytime and nighttime experiments, the linearity represents the loss in the chamber which equals to $\left(\frac{L}{h}+\frac{q}{v}\right)$. The total loss in the chamber, L/h, was estimated to be 0.022 $\min^{-1}$ from the linear relationship between the value of $-\ln\frac{(C_{eq}-C)}{(C_{eq}-C_o)}$ and time t with a constant flow rate. This value of L/h was well agree to the loss in Kim *et al.* (1994), and directly used in equation (3) to calculate the NO flux during the experimental period.

3. RESULTS AND DISCUSSIONS

3.1 Daily measurements of NO flux from soil

Many researchers (Jambert *et al.*, 1994; Kim *et al.*, 1994; Sanhueza *et al.*, 1994; Williams and Davidson, 1993; Skiba *et al.*, 1992; Williams and Fehsenfeld, 1991; Kaplan and Wofsy, 1988; Williams *et al.*, 1988, 1991, 1992; Anderson and Levine, 1987; Parrish *et al.*, 1987; Johanson and Granat, 1984; Galbally and Roy, 1978) have been made NO flux measurement from various ecosystems: most of their measurements, however, were made several times a day during a few days or a week, which may not be enough data size to represent the sampling plots.

NO flux measurements from corn crop field were made every 15 minutes by using flow through chamber technique during 3 weeks period in summer season. This experiment is first attempting to measure NO flux from soil for every 15 minutes, continuously with ambient air.

In this section, large number of data (732 data points) are analyzed to discuss NO flux from a corn crop field of NC.

Statistical summary of NO flux data is illustrated in Table 1. Most measurements were conducted during daytime because of difficulties to make measurements during nighttime. Four 24 hours experiments were conducted for showing diurnal variation during this experimental period. However, only three 24 hours data were shown in Table 1, because one 24 hour experiment did not succeed due to rain. The magnitudes of NO fluxes from soil measured are shown to be very fluctuate on each day during experimental period. The ranges of NO flux were from 3.1 to 259.0 ng Nm^{-2}s^{-1}. NO fluxes more than 100 ng Nm^{-2}s^{-1} were measured in daytime after applying fertilizer. On the other hand, NO fluxes before applying fertilizer were mostly less than 45 ng Nm^{-2}s^{-1}. Those big changes in daytimes may contribute to make large difference between day- and night-time average NO fluxes in Fig. 2. However, without considering those large changes, hourly average data set in Table 1 may generally show diurnal trend which has maximum in day and minimum in night. The magnitude of flux may change on each day depending on the soil condition of the day measured, mostly, soil temperature, soil moisture, the level of N in the soil. The role of soil moisture on NO flux was discussed by several researchers (Kim *et al.*, 1994; Valente and Thorton, 1993; Cardenas *et al.*, 1993; Davidson, 1991; Slemr and Seiler, 1991; Anderson and Levine, 1987). It is generally suggested that there is a range of soil moisture for optium NO flux, and excess of moisture leads to moisture stress for soil microbes and decrease in NO flux. The roles of soil temperature and level of N on NO flux were summarized recently to develop an empirical model of global soil-biogenic NOx emission (Yienger and Levy, 1995). Generally, these effects on soil NO flux were positive, which means that increases of these factors increase soil NO flux. Those relationships will be discussed in next section.

The average flux of corn crop field during the experimental period was 47.6 ng N m^{-2}s^{-1} with 50.6 ng Nm^{-2}s^{-1} of standard deviation, whi-

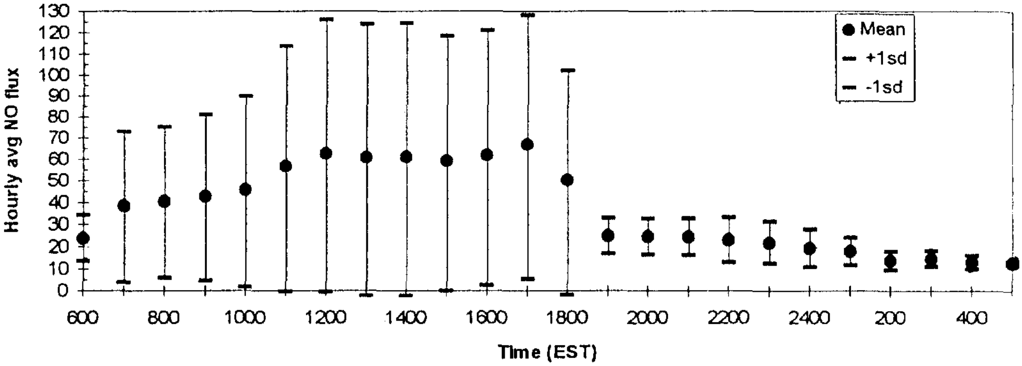

Fig. 2. Composite diurnal variation of hourly averaged NO flux from soil during the experimental period at the site.

Table 1. Summary of hourly averaged NO flux based on 15 minutes flux measurement at the Boyd site. [unit = ng Nm^{-2}s^{-1}]

time	16-May	17-May	18-May	19-May	22-May	23-May	24-May	25-May	30-May	1-Jun	2-Jun	4-Jun	5-Jun	8-Jun	9-Jun	Mean	stdev	N
600		40.44		17.69		32.95	35.08	20.25		25.18					4.56	23.7	10.3	14
700	34.84	40.26	38.06	18.03	36.33	32.02	35.18	20.13	9.98	21.46		88.45	141.53	25.27	4.45	38.2	34.5	47
800	35.00	40.10	37.87	18.57	35.98	36.96	35.76	20.20	9.61	21.44	22.90	96.26	140.33	26.99	4.32	40.5	34.7	56
900	35.10	40.10	38.03	20.69	36.78	36.78	36.74	20.55	8.22	23.87	21.63	114.91	146.98	24.37	8.47	42.6	38.2	56
1000	34.52	40.64	38.31	20.29	37.44	36.49	36.65	23.73	6.47	25.04	28.72	142.76	166.43	37.03	12.70	45.6	44.1	55
1100	34.69	41.04	38.49		37.42	36.60	37.03	24.85	250.74	23.55	38.86	54.28	108.58	50.58	17.10	56.5	56.9	50
1200	35.38	41.13	38.72	14.87	37.31	36.61	37.63	25.90	235.88	25.37	39.47	53.01	177.95	61.34	20.93	62.5	63.3	54
1300	35.22	41.13	38.65	13.30	37.68	36.79	37.37	29.78	236.50	22.38	42.26	50.83	175.07	53.13	21.59	60.5	63.1	55
1400	35.22	41.40	38.79	14.07	37.88	37.06	36.85	32.15	242.71	19.95	40.95	50.61	171.39	62.92	20.43	60.8	63.3	55
1500	35.15	41.58	38.56	15.61	37.76	37.08	36.69	32.40	238.15	19.65	37.63	52.47	142.16	59.64		58.9	59.3	54
1600	35.44	41.26	38.75	15.66	37.14	37.17	36.68	31.50	223.13	19.82	36.91	100.94	147.44			61.7	59.2	52
1700	35.70	41.22	39.04	15.16	36.95	37.22	36.87	30.80	211.90	17.89	38.27	120.03	155.54			66.7	61.3	46
1800		41.16	38.74	13.41	36.86	37.16		204.37	16.56	32.11	126.10	163.26				49.9	52.0	20
1900				14.30			30.40				30.19					25.0	7.9	12
2000				14.19			26.74				32.49					24.5	8.0	12
2100				13.30			29.04				30.31					24.2	8.2	12
2200				11.39			33.74				24.07					23.1	10.1	12
2300				10.30			31.56				23.50					21.8	9.4	12
2400				9.84			29.14				18.73					19.2	8.5	12
100				10.09			23.91				19.57					17.9	6.3	12
200				11.32			10.99				19.08					13.8	4.3	12
300				12.35			13.12				18.37					14.6	3.5	12
400				12.30			13.94									13.1	3.0	8
500				12.79												12.8	0.8	4
avg	35.12	40.88	38.50	14.33	37.13	36.22	31.25	26.02	156.47	21.70	29.82	87.55	159.06	44.62	12.73	36.6	19.0	732
stdev	0.34	0.51	0.36	3.08	0.58	1.69	8.30	5.08	109.97	2.85	8.33	34.16	15.19	16.24	7.49	27.95		
N	11	13	12	23	12	13	23	12	12	13	20	12	12	9	9	206		
Statistical summary using 15 min. measurements(Number of data 732)																		
avg	35.09	40.88	38.49	14.20	37.14	36.38	31.12	25.70	159.15	21.81	29.22	84.13	158.78	43.60	11.54	47.61		
stdev	0.36	0.57	0.39	3.09	0.60	1.58	8.42	4.94	106.64	2.79	8.42	34.19	16.34	17.98	7.01	50.63		
N	38.	47	44	87	45	46	89	45	40	46	86	40	45	19	14	732		

*Hourly data in the table were made from 15 minute average flux measurements.

ch has a same order of magnitude with the value have measured at another corn field site at Clayton, NC (21.9 ng $Nm^{-2}s^{-1}$ and range of 7.1 to 106.2 ng $Nm^{-2}s^{-1}$, Sullivan, 1995). This average NO flux and ranges were found to be much higher than those (1.79 ng $Nm^{-2}s^{-1}$ of average and range of 0.13 to 6.67 ng $Nm^{-2}s^{-1}$) at a fallow agricultural field in the central Piedmont region of North Carolina (Kim *et al.*, 1994). It may think of the role of importance that the change of soil charicteristics by long-term agricultural activity. In Fig. 2, during nighttime, the flux is stay at about 20 ng $Nm^{-2}s^{-1}$, and then it starts to increase as sun rises (around 5:00~6:00 a.m. EST).

The composite hourly mean flux reaches at first peak of 62.5 ng $Nm^{-2}s^{-1}$ around noon and stabilize its level until late afternoon (around 5:00 p.m.). After this time period, it decreases and goes to minimum at late night. The diurnal trend of hourly averaged NO flux seems to be quite related to the trend of soil temperature in a day.

The composite diurnal variation of hourly averaged soil temperature are shown in Fig. 3. The effects of soil temperature on NO flux from soil was empirically modeled in attempting to estimate regional or global NOx emission from different land use because of the limitation of soil NO flux data in field measurements (Yienger and Levy, 1995; Shepard *et al.*, 1991; Williams *et al.*, 1988, 1992). These effects will be discussed.

3.2 Soil temperature and NO flux

It is now vastly known that soil temperature is one of the important controlling factor for NO emission from soil, and empirically suggested that NO emissions exponentially depend on soil temperature of certain range (Yienger and Levy, 1995; William *et al.*, 1992; William and Fehsenfeld, 1991). NO flux was parameterized for United State using field experimental data have measured at different types of soil based on exponential temperature dependence model (Williams et al., 1992; William and Fehsenfeld, 1991). The general form of the emission algorithm was

$$\mathrm{Flux} = A_w \times e^{k(^{\circ}C-1)\times T} \qquad (15^{\circ}C \leq T \leq 35^{\circ}C)$$

where T is soil temperature in degrees Celsius, A_w in ng $Nm^{-2}s^{-1}$ is a factor that is associated with land use (i.e. called a biome fitting parameter) and k is dependency coefficient which is relatively constant across biomes. The actual value of their k was estimated from a weighted average of the slopes of the regression lines obtained from plots of the logarithm of emission versus soil temperature for

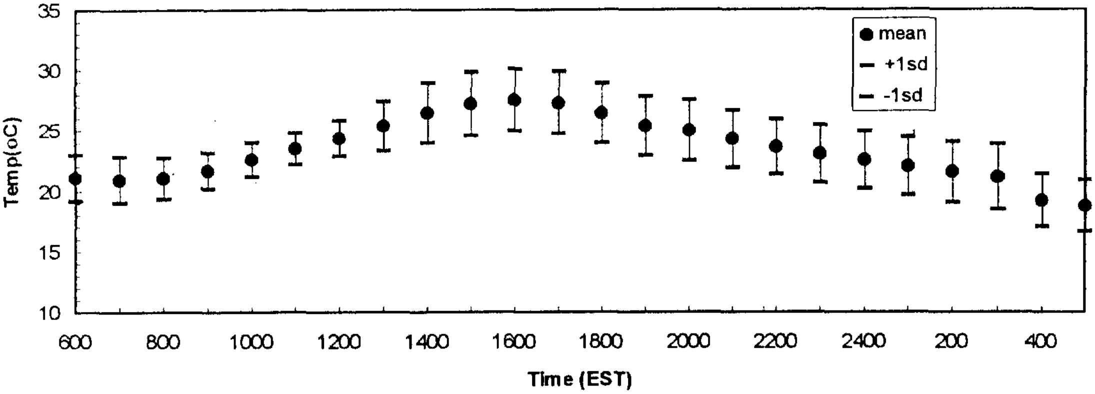

Fig. 3. Composite diurnal variation of hourly averaged soil temperature during the experimental period at the site.

the data sets which they performed at different land use (Williams *et al.*, 1992). This value was 0.071±0.07°C^{-1}.

Above 30°C decrease of soil NO flux or lack of strong exponential temperature has been reported in the southeastern U.S. (Williams and Feshenfeld, 1991) and grassland and agricultural soil in North Carolina (Aneja *et al.*, 1995; Kim *et al.*, 1994). The possibility of a significant moisture stress at the sampling soil, and its possible negative influence on soil micrcobial activity may account for the trend in NO flux with soil temperature. There also appears to be an optimal temperature for biogenic processes above which the temperature dependence weakens or disappear. Yienger and Levy (1995) suggested that applying temperature exponential above 30°C would systematically overestimate emission, and given that some tropical environmentents with over 45°C of soil temperature, the error would be quite large. Compiling most soil NO flux data available in temperate climates between 10°C and 30°C, they calculated the value of k, 0.103±04°C^{-1} (Yienger and Levy, 1995).

Soil temperatures measured at sampling site were ranged from 15°C to 30°C, and diurnal variation was shown in Fig. 3. Logarithm of NO flux versus soil temperature was plotted in Figure 4, and the slope which is k value from data of 732 measurements was found to be 0.160±034°C^{-1} for the corn crop field. Yienger and Levy (1995) summarized the temperature dependence coefficient k for different type of biomes from data reported by many other researchers (Stocker *et al.*, 1993; Valente and Thornton, 1993; Williams *et al.*, 1992; Anderson and Levine, 1987). The range of k was from 0.040°C^{-1} to 0.189°C^{-1}, and the weighted average k was 0.103±0.04°C^{-1}. Comparing k vau-le for this corn crop field measurement to others, it is larger than that estimated in Williams *et al.*(1992) for estimation inventory of U.S. soil NO emission, but still is in the range of the values and very similar to weighted average k value in Yienger and Levy (1995).

A biome fitting parameter, ln (A_w) was calculated for this corn field by applying mean soil temperature (23.4°C) and mean NO flux (47.61 ng Nm^{-2}s^{-1}) in experimental period to an exponential temperature dependence model mentioned above with k=0.160°C^{-1}. The value of ln (A_w) calculated was 0.119 ng Nm^{-2}s^{-1}, which is within a standard error for the estimate of

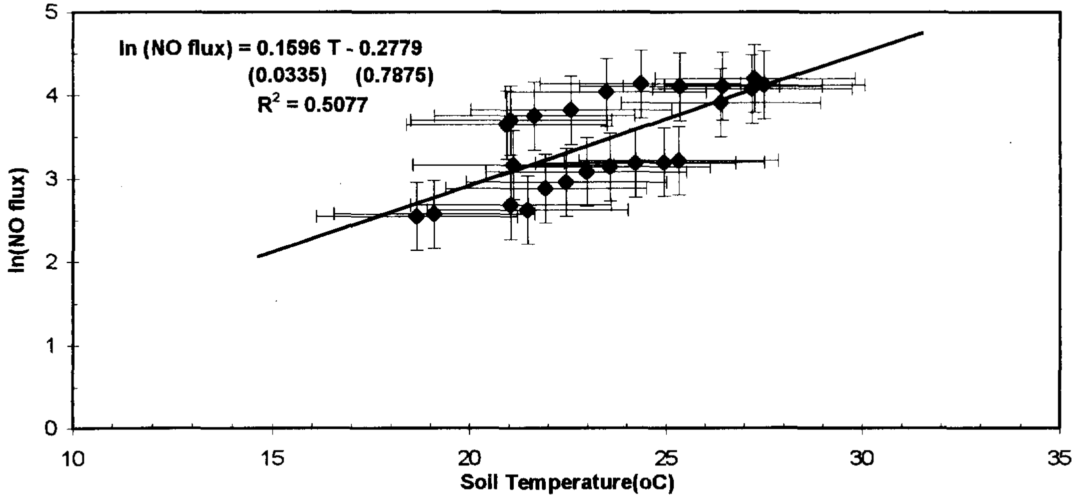

Fig. 4. Plot of ln (NO flux) versus soil temperature. Vertical and horizontal lines indicate one standard deviation of the average NO flux and soil temperature, respectively.

ln (A_w) in fitting funtion of Fig. 4. The biome fitting parameter was larger than the mean value of -1.022 ng $Nm^{-2}s^{-1}$ summarized by Yienger and Levy for wet soil biome. Comparing mean NO flux in this research to others in the U.S, mostly measured at Colorado (mostly grassland, forests and wetlands) by Williams *et al.* (1987, 1991), the mean NO flux in this measurement is two to five times larger than those in their measurements. This large amount of NO flux in sampling site makes to be large a biome fitting parameter, ln (A_w) in our agricultural managed field. The difference may come from the different soil parameters between agricultural areas and natural areas: in this case, role of nitrogen fertilizer may have a significant role. Apperently, their ln (A_w) calculated in corn, cotton and wheat fields were ranged from 1.099 to 2.197 ng $Nm^{-2}s^{-1}$, which resulted from applying fertilizer in the field site (Williams *et al.*, 1992). As fertilization rate increases, both emission of NO and biome parameter from agricultural soil increased. Effects of fertilizer on soil NO flux will be discussed.

3. 3 Fertilizer effects on soil NO flux

It is well described that the use of nitrogen fertilizers in agriculture is a significant source of reactive nitrogen compounds for the atmosphere because of incresses biogenic NOx emission (Jambert *et al.*, 1994; Shepard *et al.*, 1991). In temperate region, gaseous nitrogen compound emission are strongly related to agricultural activities: use of nitrogen fertilizer and farming (Williams *et al.*, 1992). The mechanisms attributed to this are enhanced biological activities, i.e. nitrification and denitrification, depending on the form of fertilizer. In general, there is a positive linear relationship between fertilizer use and nitrogen emission. A number of researchers found emission rates from fertilized soils rivaling those found in urban areas from combustion.

There is now opinion that, eventhough NOx pollution is due mainly to fossile fuel combustion and biomass burning, biogenic NOx dominates over the region of intensive agriculture during the summer season when soil emission are at a maximum (Yienger and Levy, 1995).

A number of amount of fertilizer was applied at the sampling site during middle of the experimental period (25th of May). Sampling days were segrigated before and after fertilizer, and discussed here.

Fig. 5 shows 15 miniutes averaged NO flux plots against time for days before applying fertilizers and after. Big jump of NO flux was shown from the data, which is quite larger emission in after fertilizer than those in before. Before fertilizer, variation of NO flux was relatively small (from 10 to ~40 ng $Nm^{-2}s^{-1}$); however, the variation became very large after fertilizer, upto 250 ng $Nm^{-2}s^{-1}$.

This large veriation of data was not observed before applying fertilizer. Especially, the NO flux measured at 30-May, 4-June, and 5-June were observed significantly high during daytime. As well as soil temperature, about 1 °C higher of the daytime average soil temperature at those 3 days than in other days was observed. It is possible that both effects of temperature and fertilizer increase NO flux significantly at the site. However, daytime soil temperature variations on each days before applying fertilizer was also observed, such kind of large variation of NO flux as after fertilizer was not recorded. It may suggest that this large variation mostly attribute to applying nitrogen fertilizer at the sampling site. Composite hourly average NO flux measured before and after applying fertilizer to the corn field were plotted against time in Fig. 6. Both cases showed similar diurnal variations with higher emission during daytime period. Daytime maximum of hourly averaged NO flux observed after fertilizer (~110 ng $Nm^{-2}s^{-1}$) was significantly higher than the flux observed before fertilizer

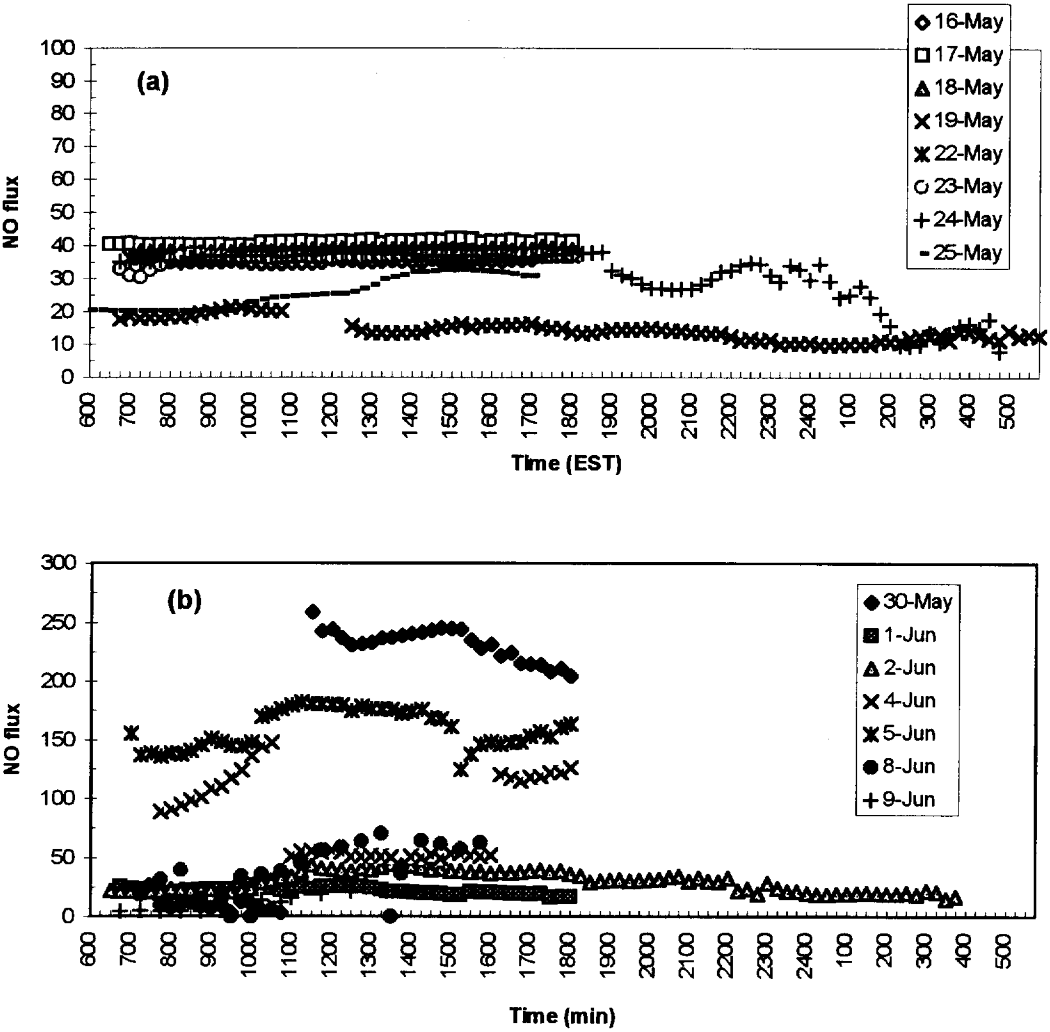

Fig. 5. Composite NO flux measured every 15 minutes (a) before, and (b) after applying fertilizer tothe corn field site during the experimental period.

(~35 ng Nm^{-2}s^{-1}). However, there were much small differences in averages between each case during nighttime.

This small difference during night may come from the lack of nighttime flux data during the experimental period. Table 2 summarized statistics of two different sets of NO flux data for before and after fertilizer. Mean NO flux for before and after fertilizer were 25.9 ng Nm^{-2}s^{-1} and 55.4 ng Nm^{-2}s^{-1}, respectively. In order to examine the significance of the mean difference between before and after fertilizer, t-statistics was used at $\alpha=0.05$. The results were shown in Table 2. Larger t-statistics than t critical value suggests that the difference of mean NO flux observed from two data sets is statistically significant at 95% of confident level. Consequently, there are enough evidence of increase of NO flux after fertilizer and this increase may due to apply nitrogen fertilizer to the agricultural soil.

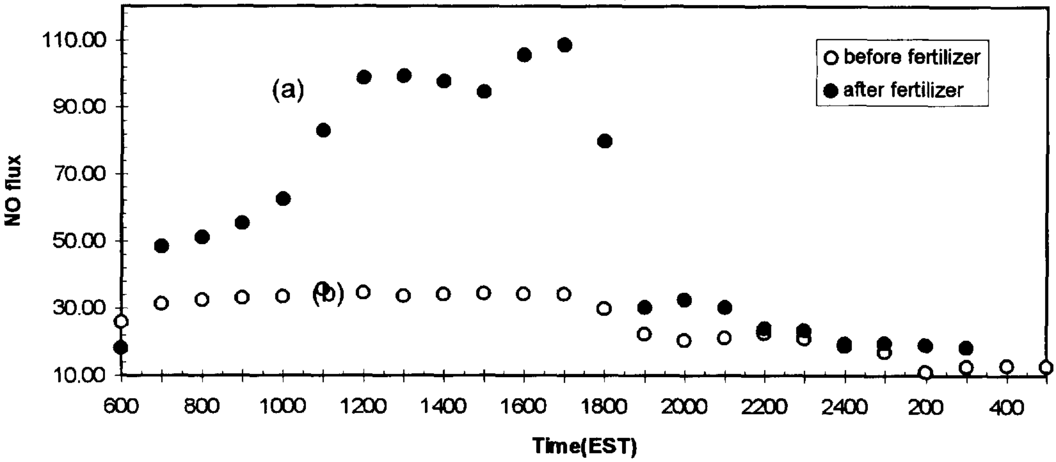

Fig. 6. Composite hourly averaged NO flux measured (a) before, and (b) after applying fertilizer to the corn field site during the experimental period.

Table 2. Summary of statistics of flux data for comparing flux measured before and after applying fertilizer at the corn field.

Flux types	Number of Data	Mean Flux	Standard Deviation
Before fertilizer	442	25.88	8.50
After fertilizer	290	55.42	34.14
t-Statistics*	4.105	t Critical value	1.680 at $\alpha=0.05$

* t-Test implies that there is a significant difference between means of flux measured before and after applying fertilizer at the corn field.

4. CONCLUSIONS

This experiment compiled very discreet (15 minute average) soil NO flux data measured at corn crop filed in North Carolina during intensive 3 weeks period of summer season in 1995. The biogenic emission of NO from agricultural soil were analyzed and discussed in terms of major controlling parameters, i.e. soil temperature and fertilizer applied at the site. Mean flux found here was 47.6 ng $Nm^{-2}s^{-1}$, however it may not represent the average NO flux during the experimental period because of discontinuity of nighttime measurements. Most measurements were made during daytime, and therefore daytime(06:00~18:00) average of NO flux was found to be 53.1 ng $Nm^{-2}s^{-1}$. This value was much larger than those measured temperate wet natural soils in eastern U.S. (Delaney *et al.*, 1986; Anderson *et al.*, 1987; Williams *et al.*, 1987, 1991); it may be thought to attribute applying N fertilizer to the agricultural soil. The NO flux with time showed diurnal variation clearly with maximum in daytime and minimum in nighttime. This trend may follow the diurnal variation of soil temperature. The exponential temperature dependence model was applied to measurement data set, and 0.160°C^{-1} of k was given. The k value was correspond to the averaging k (0.103°C^{-1}) for the temperate wet soils by Yienger and Levy (1995). It was found that there were significant increase of NO flux from soil, and it was mostly due to apply nitrogen fertilizer to agricultural areas. Consequently, without understanding and control of biogenic emission of nitrogen compounds from agricultural soil, there are much higher possibility of global or regional increase of nitrogen compounds in the atmosphere. There are still many uncertainties between nitrogen emission and controling parameters. A number of well designed field measurements at many different soil characteristics, especially in rural and agricurtural areas should be required to estimate more acurate nitrogen emission inventory as well as developing model.

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