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Effect of Environmental Variables on NO Emissions from Agricultural Soils

By

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Summary

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Nitric oxide (NO) is an important air pollutant which leads to the production of ozone and acidic precipitation. Biogenic emissions of NO are gaining in importance for ozone formation in semi-urban and rural regions of the Southeast United States. Using a dynamic chamber system interfaced to a mobile laboratory for continuous NO analysis, soil emissions of NO were measured over typical row crops in North Carolina during 1994 - 1996. This paper investigates the effect of soil temperature, soil water content and soil extractable nitrogen on soil NO emissions from corn and soybean canopies. Three of five sets of measurements from corn and two of four sets of measurements from soybean displayed an exponential relationship between soil NO emissions and soil temperature. No significant correlation between soil NO emissions and water filled pore space (WFPS) was observed. The best correlation observed between soil NO emissions and total extractable nitrogen (TEN) was found to be linear for soybean (NO emission = 0.67 + 1.43*TEN, $R^2 = 0.34$), and logarithmic for corn (NO emission = 21.20*Ln (TEN) – 27.27, $R^2 = 0.17$). Multiple regression models (Ln (NO emission) = 1.5017 + 0.0786*TEN – 0.0006*TEN^2; $R^2 = 0.58$ for corn; Ln (NO emission) = 77.917 – 6.19*T + 0.1243*T^2 + 0.0068*TEN^2; $R^2 = 0.65$ for soybean) appear to be the best overall model for predicting soil NO emissions.

Introduction

Nitric oxide (NO) is an important air pollutant in tropospheric photochemistry. It participates in the formation of ozone and also in the acidification of precipitation. Biogenic emissions of NO from soils are gaining importance for ozone

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formation since it is estimated that soil emissions are responsible for ~ 40 % of the global NO budget. YIENGER & LEVY 1995 reported that soil NO emissions rank second only to fossil fuel combustion in the global NO budget, and can account for 50 % of the NO_x budget in the remote agricultural areas in the U.S., and even exceed 75 % during summer months. A modeling study by BIAZAR 1995 showed that in rural Giles County of Tennessee, sufficient soil emissions of NO existed to produce about 60 ppbv of ozone in the rural environment without any anthropogenic NO sources. About 40 % of the ozone non-attainment areas in the United States are found in the southeastern United States (LINDSAY & al. 1989). This region is thought to be NO_x limited implying that greater soil emissions of NO will lead to higher ozone production. However, the strength of soil NO emissions is still highly uncertain due to the spatial and temporal variability of these emissions and the limited measurement data that have been available. It is important to accurately quantify the amount of NO emissions from soils in this region in order to develop an effective control strategy for ozone and acidic pollutants. Field measurements are one way to obtain the necessary information concerning NO emissions from soils. The Air Quality Group at North Carolina State University made measurements of NO emissions over different crop fields in North Carolina during different seasons of the year from 1994 – 1996 (ANEJA & al. 1996, SULLIVAN & al. 1996, ROELLE & al. 1999, LI & al. 1999). The objective of this paper is to investigate the correlation between NO soil emissions and three environmental variables (soil temperature at 5 cm depth, soil water content expressed as percent of water-filled pore space, and soil total extractable nitrogen in the top 20 cm), in order to provide the necessary information for developing an empirical model for predicting soil NO emissions.

Materials and Methods

Sampling sites

NO emission measurements from corn and soybean fields at four different locations (Clayton, Kinston, Plymouth, and Reidsville) were made in North Carolina from 1994-1996. The sampling sites, soil properties, crop growth stages and the sampling periods are summarized in Table 1.

Dynamic chamber system and flux equation

A dynamic flow through chamber system was used to measure the emission rate of nitric oxides from the soil. The entire measuring system includes a dynamic flow-through chamber and a temperature-controlled mobile laboratory which houses the analytical instruments and data acquisition system. The open bottom flow-through dynamic chamber and associated flux equation are discussed in detail in ROELLE & al. 1999.

Table 1. NO emissions sampling sites, soil properties, crop growth stage and sampling periods.

Sampling Sites	Soil	Crops	Crops Growth Stages	Sampling Periods
Central Crops Field Laboratory, Clayton, North Carolina	Norfolk Sandy Loam	Corn	Complete	Aug 7-10, 94
		Soybean	Vegetative	Jul 31-Aug 3, 94
Lower Coastal Plain Research Station, Kinston, North Carolina	Rains Fine Sandy Loam	Corn	Maturity	Jun 30-Jul 5, 95
		Soybean	Vegetative	Jul. 10-13, 95
Upper Piedmont Research Station, Reidsville, North Carolina	Pacolet Sandy Loam	Corn	Maturity	Aug. 2-11, 95
Michael Boyd Property, Plymouth, North Carolina	Portsmouth Fine Sandy Loam	Corn	Vegetative	May 15-25, 95
		Corn	Vegetative	May 30-Jun 9, 95 (post-fert)
		Soybean	Vegetative	Jul 15-31, 96
		Soybean	Vegetative	Aug 6-15, 96 (post-fert)

Results and Discussion

Seasonal and diurnal variations of soil NO emissions

Diurnal variations of NO emissions measured from corn and soybean canopies at Clayton, NC for different seasons during 1994-1995 are shown in Fig. 1.

For corn, NO emissions are the strongest during the summer. This is due to higher soil temperature and application of N fertilizer in summer months. The greater temperature leads to more NO production in soil, and N fertilizer provides more available nitrogen for soil microbial processes which are presumed to be responsible for NO production. The second strongest emission occurs during the spring season, again reflecting increasing soil temperature and application of N fertilizer. The emissions during fall and winter seasons are relatively smaller and are essentially negligible. For soybean, the emissions of NO during the summer season are also greater than those during fall, spring and winter seasons as shown in Figure 1b. However, since soybean receives no applied N fertilizer, the NO emissions are less than those from crops receiving high levels of N fertilizer such as corn. Previous studies showed that the summer months contributed about 77 % of yearly NO emissions (ANEJA & al. 1996). ANDERSON & LEVINE 1987 also reported that 76 % of the emission from soybean and corn crops occurred between May and October. Based on these observations, we only use the data measured in late spring and summer (May to August) in this paper.

For corn, the peak in NO emission during the summer season (approximately 35 ng $N/m^2/s$) occurs between the hours of 12 p.m. and 3 p.m., corresponding to the peak in soil temperature. The minimum value in soil NO emissions (15 ng N/m^2/s) occurs at night. This midday maximum and nighttime minimum diurnal pattern also occurs during the spring season (Fig. 1a). For soybean, the peak of NO emissions (approximately 3 ng N/m^2/s) in the summer also occurs during 12 p.m. to 5 p.m. in the afternoon, with a minimum at night. Because the soybean canopy is more dense than that of corn, the amount of solar radiation reaching the soil is reduced, resulting in a 1 to 2 hour lag of the peak soil temperature.

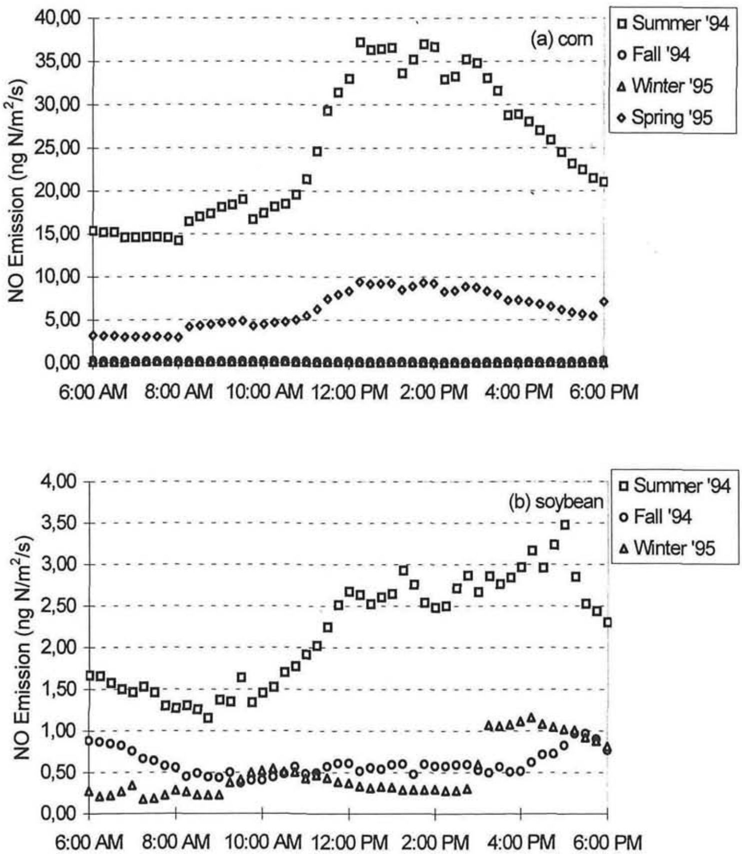


Fig. 1. Diurnal variation of NO emission from (a) corn (b) soybean for different seasons, Clayton, NC.

Effect of soil temperature

The effect of soil temperature on NO emissions from corn and soybean is illustrated in Fig. 2.

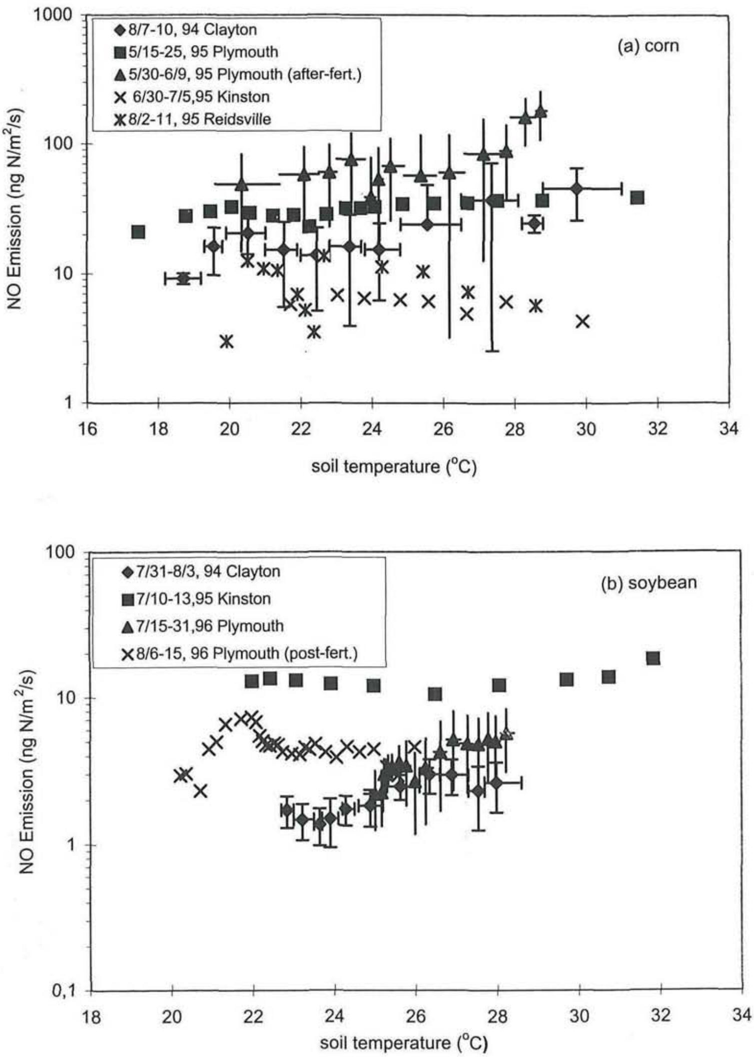


Fig. 2. Effect of soil temperature on NO emission from (a) corn (b) soybean.

Each point in the figure represents a mean of 25, 15-minute averaged data points. Horizontal bars represent the span in soil temperature, and the vertical bar represents the standard deviation in NO emissions for each plotted point. Assuming an exponential relationship with the soil temperature, WILLIAMS & al. 1992a proposed an empirical model for NO emission from soils:

$$\text{NO emission (ng N/m}^2\text{/s)} = A * \exp\{B * T_{soil}\ (^{\circ}C)\} \qquad (1)$$

where A is an indicator for landuse class, associated with the usage of fertilizer; T_{soil} is soil temperature, which is considered to be an important controlling factor since it can significantly influence the microbiological reaction rate and soil gas diffusion rate; and B is an empirical constant with the value of 0.071. In our experiments, only three of five sets of measurements over the corn crop and two of four sets of measurements over the soybean crop show significant positive correlations between NO emissions and soil temperature. The values of A and the coefficient B obtained from the best-fitted regression lines through our experimental data of Fig. 2 are listed and compared to Williams's in Table 2. Two of three values of the factor A for the corn crop are much lower than Williams's but our B values are higher. The other set of data yield a much larger value of A, but smaller B values. Our average values of A=6.0 and B=0.091 for the three data sets are close to the values obtained by Williams & al. 1992 for corn. For soybean, our values for factor A are lower while the B values are higher by a factor of 2~3 than those obtained by Williams et al. for soybean. They also differ considerably between the two measurement periods. Our results suggest that the model parameters A and B are highly variable and that other environmental variables, besides soil temperature, should be considered in developing a more refined model for soil NO emissions in the Southeastern United States.

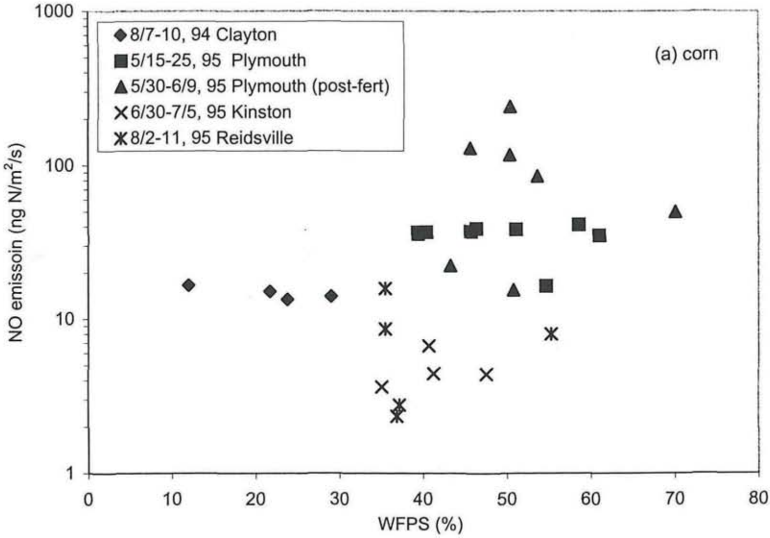
Table 2. Results of linear regression analysis of the logarithm of NO emission versus soil temperature and comparison with those of WILLIAMS & al. 1992a.

	Factor A	Exponential coeff. B	R^2
8/7-10, 94 Clayton corn	1.621	0.1049	0.71
5/15-25, 95 Plymouth corn	13.867	0.0345	0.63
5/30-6/9 Plymouth corn (after-fert.)	2.602	0.1328	0.58
WILLIAMS & al. 1992 corn	9	0.071	N/A
7/31-8/3, 94 Clayton soybean	0.062	0.1379	0.73
7/15-31, 96 Plymouth soybean	0.006	0.2442	0.87
WILLIAMS & al. 1992 soybean	0.2	0.071	N/A

Effect of WFPS

The relationship between percent water filled pore space (% WFPS) and soil NO emissions measured from corn and soybean is shown in Fig. 3.

Most % WFPS values fall in the range of 30-70 % which is believed to be optimal for NO emissions from soils (DAVIDSON 1991). We did not find any significant correlation between % WFPS and soil NO emissions for either of the two (corn and soybean) crops. However, if the Clayton data (WFPS ranged from 12 % to 30 %) are excluded, we can see a general increasing trend of NO emission with increasing % WFPS for corn where WFPS ranged from 35 to 70 %, and a general decreasing trend of NO emissions for soybean where WFPS ranged from 40 to 67 %. In general, the correlation between % WFPS and soil NO emission is weak, and it may not be prudent to consider % WFPS as a predictor in an empirical model for soil NO emission.



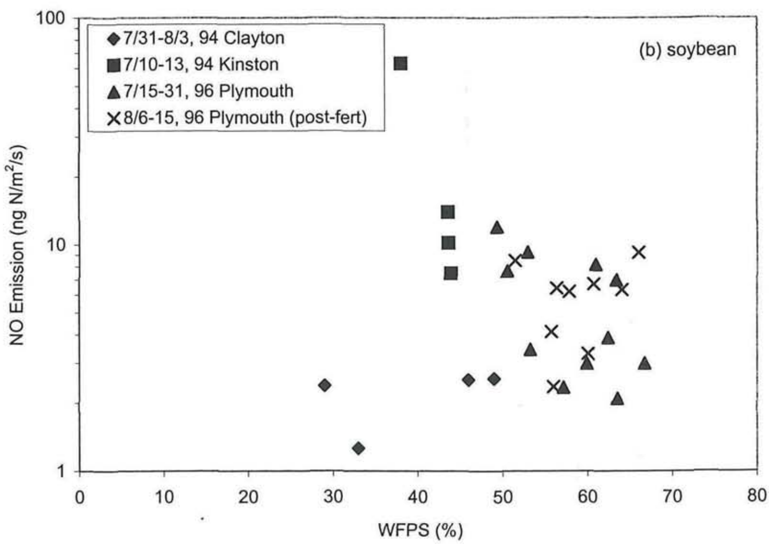


Fig. 3. Effect of WFPS on NO emission from (a) corn (b) soybean.

Effect of total extractable nitrogen

Soil NH^+_4, NO_3^-, or their sum (TEN) might be expected to serve as a useful indicator to predict soil NO emissions due to the positive correlation between TEN and NO emissions (WILLIAMS & al. 1992b). Extractable NH_4^+ and NO_3^- were determined using a 1 M KCL soil extract (expressed on a weight basis) and standard autoanalyzer techniques. As indicated in Fig. 4a, a logarithmic correlation between total extractable nitrogen and soil NO emissions from corn was observed:

$$\text{NO emission} = 21.20 * \text{Ln (TEN)} - 27.27, \quad R^2 = 0.17 \qquad (2)$$

The values of TEN for corn vary from 4 to about 94 mg N/kg dry soil. NO emissions increase dramatically when TEN > 20, but are much less when TEN < 20. For soybean, where TEN < 20 because of no application of fertilizer, the correlation between TEN and soil NO emissions is linear (Fig. 4b):

$$\text{NO emission} = 0.67 + 1.43 * \text{TEN}, \quad R^2 = 0.34 \qquad (3)$$

Multiple regression model

As discussed earlier, soil emission of NO is dependent on multiple soil parameters and the complex interaction among them (soil temperature, water content, total extractable nitrogen, etc.), and it is perhaps unrealistic to expect one of these parameters to control soil NO emissions. To examine the combined effects of three soil parameters: soil temperature, % WFPS and TEN on soil NO emissions, a multiple regression model in the following form was evaluated:

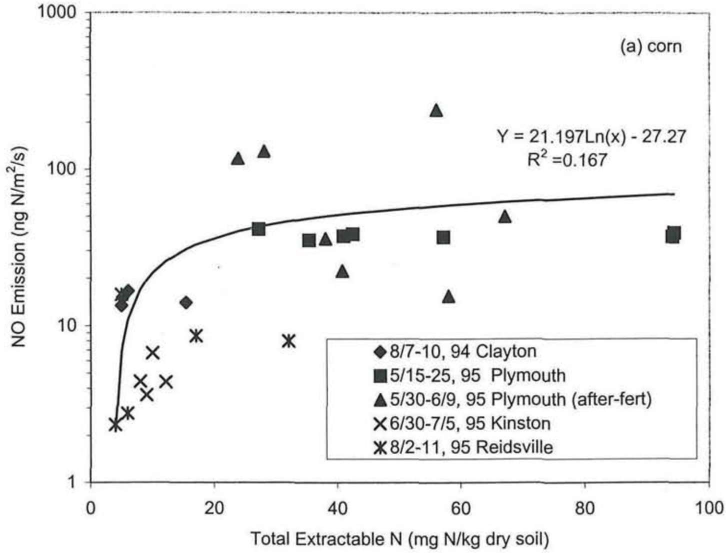
$$\text{Ln (NO emission)} = B_0 + B_1 * T + B_2 * W + B_3 * \text{TEN} + B_4 * T * W + B_5 * T * \text{TEN} + B_6 * W * \text{TEN} + B_7 * T^2 + B_8 * W^2 + B_9 * \text{TEN}^2 + \varepsilon \qquad (4)$$

where on the right-hand side:

Term 0 – Overall intercept of NO emission when other variables are zero
Term 1 – Effect of soil temperature on NO emission
Term 2 – Effect of percent water-filled pore space on NO emission
Term 3 – Effect of total extractable nitrogen on NO emission
Term 4 – Interaction effect between soil temperature and WFPS
Term 5 -- Interaction effect between soil temperature and TEN
Term 6 -- Interaction effect between WFPS and TEN
Term 7 – Effect of quadratic soil temperature on NO emission
Term 8 – Effect of quadratic WFPS on NO emission
Term 9 – Effect of quadratic TEN on NO emission
Term 10 – The error term inherent in each observation
T -- soil temperature in the unit of °C
W -- percent water-filled pore space
TEN -- total extractable nitrogen in the unit of mg/(kg dry soil)

$$(37)$$

The regression coefficients $B_{1\text{-}9}$ are determined from ordinary least squares multiple regression and depict the change in NO emission (ng N m^{-2} s^{-1}) expected from a unit increase in one variable if all other variables are held constant.



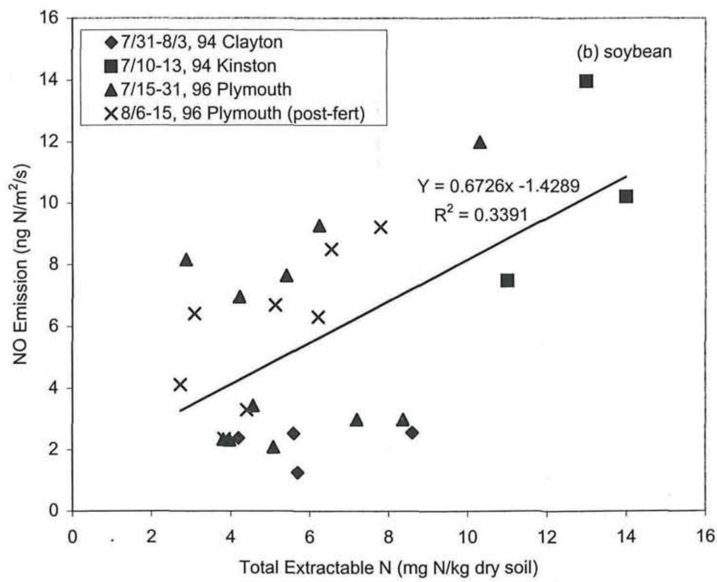
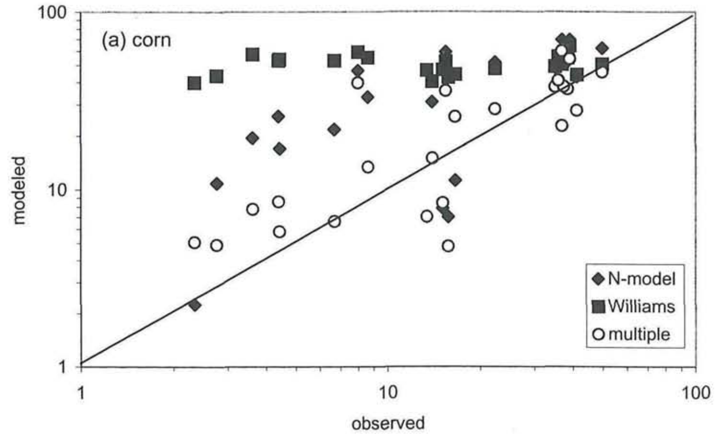


Fig. 4. Effect of total extractable N on NO emission from (a) corn (b) soybean.

Daily averages of NO emissions and soil temperature were computed from 15-minute data; % WFPS and TEN are assumed to be daily averaged, thus there are



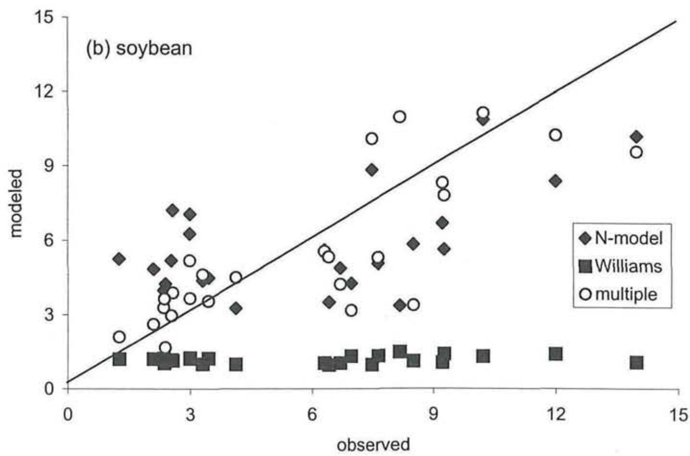


Fig. 5. Comparison of model results with NO emission observation.

two daily-averaged data sets that could be analyzed to test all possible combinations in the regression and the degree of significance for each combination. The SAS package (SAS/ETS 1988) was used for the analysis of the data sets. Variables were discarded in each step of the regression until the remaining variables were at the same level of significance ($P < 0.05$). The final multiple regression models derived using this procedure are as follows:

Corn

$$\text{Ln (NO emission)} = 1.50167 + 0.0786*\text{TEN} - 0.0006*\text{TEN}^2,\ R^2 = 0.58 \quad (5)$$

Soybean

$$\text{Ln (NO emission)} = 77.917 - 6.19*T + 0.1243*T^2 + 0.0068*\text{TEN}^2,\ R^2 = 0.65 \quad (6)$$

For corn, soil temperature, % WFPS, and their quadratic terms, and all the interaction terms were excluded from the final regression model. For soybean, TEN, all the interaction terms, % WFPS and its quadratic term were excluded from the regression model. The relatively large intercept value (77.9) in equation 6 is a direct function of the limited range in T observations (20 to 32 °C) (Fig. 3b). The equation is valid only when T is within this range, thus, the high intercept in Eq. (6) has no specific meaning (since $T \neq 0$). The exclusion of % WFPS from both the multiple regression models implies that it does not exert a significant effect on soil NO emission as compared to soil temperature and TEN.

The predicted observations from the multiple regression models, single linear models (Eq. 2 & 3), and Williams' model (Eq. 1) are compared with actual data in Fig. 5. The Williams' model overestimates soil NO emissions from corn, but underestimates NO emissions from soybean. The tendency for over or under prediction is probably related in part to the values of A and B in equation (1), since differences in the characterization of the sites and the management practices may result in different values of A and B. Failure to account for the effect of TEN may also be another reason for over or under prediction from Williams' model. The single linear models also overestimate soil NO emissions for corn, but not as much as the Williams' model. The multiple regression model is the best predictor of soil NO emissions compared to the other two models.

Summary and Conclusions

Using field data obtained during 1994 – 1996, we examined the effect of environmental controlling parameters on soil NO emissions from corn and soybean in the southeast United States. Only half of the experimental results showed a close correlation between soil NO emissions and soil temperature. The coefficients generated from an exponential fit of the data are different from those reported by Williams (WILLIAMS & al. 1992a). This suggests that the application of Williams' model to North Carolina or other similar regions in the southeastern U. S. is questionable. Soil NO emissions are found to increase with increasing TEN, and are not correlated to % WFPS. Compared to soil temperature and % WFPS, TEN is the most promising predictor for a single-predictor based empirical model of soil NO emission. However, a multiple regression model appears to be the best overall model for predicting soil NO emissions.

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