Soil Nitric Oxide Emissions: Lab and Field Measurements and Comparison

Ross M. Tabachow,[1] Paul A. Roelle,[2] J. Jeffrey Peirce,[1,*] and Viney P. Aneja[3]

[1]Department of Civil and Environmental Engineering
Duke University
Durham, NC 27708
[2]Air Force Combat Climatology Center
Asheville, NC 28801
[3]Department of Marine, Earth and Atmospheric Science
North Carolina State University
Raleigh, NC 27695

ABSTRACT

Equipment and procedures are developed and implemented to measure nitric oxide (NO) emissions from unamended and municipal wastewater treatment plant biosolids-amended soil in controlled laboratory experiments and *in situ* field experiments. NO plays an important role in the formation of tropospheric ozone. Minimization of NO flux from soil is advantageous, protecting air quality as well as conserving valued nitrogen fertilizers. Controlled laboratory and *in situ* field measurements of soil NO flux were conducted on similar soil types under similar water-filled pore space (WFPS) and temperature conditions. The difference in NO emissions between the lab and the field measurements was statistically significant within the WFPS range (18.1 to 45.3%) and temperature range (12 to 28°C) studied. The soil NO flux measured in the lab ranged from 2.5 to 62.9 ng-N/m^{2}s) compared to 2.8 to 128.1 ng-N/(m^{2}s) for field measurements. The NO flux from biosolids amended soil was significantly higher than unamended soil. Temperature relationships modeling NO flux for the lab and field experiments are developed and compared to the EPA's BEIS2 model.

Key words: lab tests; field tests; nitric oxide; soil emissions; tropospheric ozone; biosolids; BEIS2; modeling

INTRODUCTION

CONTROLLED LABORATORY EXPERIMENTS and *in situ* field experiments are used for the determination of gaseous emissions from soil. Scientists, engineers, researchers, regulators, and the public use the information gathered from both lab and field experiments in determining public policy as it affects air pollution. The objective of this research is to compare lab and field measurements of nitric oxide (NO) emissions from soil under similar soil temperature and water-filled pore space (WFPS) conditions. Relationships for lab and field mea-

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*Corresponding author: Department of Civil and Environmental Engineering, Duke University, Box 90287, Durham, NC 27708-0287. *Phone*: 919-660-5210; *Fax:* 919-660-5919; *E-mail:* peirce@duke.edu.

surements of soil NO emissions are developed and compared to an existing model.

NO is the subject of on-going studies due to its importance in the production of tropospheric ozone and to its importance as soil nitrogen (N) is lost to the atmosphere and not available for plant uptake/growth. NO is an important precursor to ozone (O_3) formation in the lower atmosphere that can lead to undesirable air quality and detrimental effects on human health. Tropospheric ozone formation leads to pulmonary congestion, disorientation, altered breathing, headaches in humans, and decreased crop yields. Consequently, NO emissions are studied here to gain a better understanding of their net formation, transport, and transformation in the form of NO flux from soil.

NO production is initiated by both biotic and abiotic processes (Jousset *et al.,* 2001). Globally, the use of nitrogen fertilizers could lead to soil-biogenic NO_x emissions approaching 6.9 TgN/year (6.9×10^{12} g of N/year) (Yienger and Levy, 1995). Lee *et al.* (1997) in a compilation of results from numerous researchers, suggests soils contribute between 10 to 35% of the total global NO budget. Nitrogenous gas emissions resulting from *N* fertilization is influenced by the soil properties, climate, and agricultural practices. The soil properties and climate are largely uncontrollable variables. Additionally, soil properties, climate, and agricultural practices vary widely, and are the source of much of the inconsistencies in published *N* gaseous emissions from *N* fertilizer data (Debrenczeni and Berecz, 1998).

Laboratory and *in situ* field studies are used here to consider the influence of municipal wastewater treatment plant biosolids (biosolids) amended soil compared to nonamended agricultural soil on NO emissions with varying temperature and moisture content. Municipal wastewater treatment facilities generate biosolids that require management or disposal. Disposal of biosolids is a major economic factor in wastewater treatment (Viessman and Hammer, 1993), and has been estimated to comprise half the total cost of wastewater and biosolids treatment and disposal (Bryan, 1995). More than 6,000,000 dry metric tons of municipal biosolids are generated annually in the U.S. (Peirce and Aneja, 2000). According to a U.S. Environmental Protection Agency (1999) (EPA) report, 41% of all biosolids produced in the United States are beneficially reused via land application to provide a source of nutrients for plant uptake. In the future, more biosolids will be produced as a necessary byproduct of the growing number of and increased efficiency of municipal wastewater treatment systems. Additionally, the practice of land-spreading biosolids could become more prevalent as local decision makers strive to control biosolids disposal costs while taking advantage of its ni-

trogen content, potentially compounding the NO $\rightarrow O_3$ problems associated with the application of nitrogen-containing fertilizers to soil.

Researchers attempt to observe the world through field experiments, while lab experiments under controlled conditions attempt to mimic real-world conditions. Experimental researchers of NO flux from soils to the troposphere tend to focus on either lab or field experiments. Frequently, modeling and analysis of NO flux data does not discriminate between the data collection methods. Researchers have attempted to use lab and field data to develop models that predict NO emissions (Galbally and Johansson, 1989). Although researchers have compared various types of lab methodologies (Bollmann *et al.*, 1999) and various field methodologies (Denmead and Raupach, 1993; Christensen *et al.*, 1996), a comparison of laboratory vs. field measurements of NO flux from soils has not been completed. The objectives of this research can be summarized as follows: (1) examine in a controlled laboratory environment and an *in situ* field environment the NO flux from unamended and biosolids-amended (BSA) soil; (2) discuss the effects of temperature and WFPS on NO emissions; and (3) compare the results of laboratory vs. field measurements of soil NO flux. Other soil characteristics, including pH, soil texture, indigenous microbial populations, and organic matter, are not considered in this analysis.

EXPERIMENTAL PROCEDURES

The laboratory equipment used in the lab experiments was designed and fabricated based on information obtained at Duke University, Durham, NC, during 17 years of laboratory tests on fluid flow through soil (Peirce *et al.*, 1986; Ormeci *et al.*, 1999; Tabachow *et al.*, 2001), coupled with information obtained during field observations made by researchers at North Carolina State University, Raleigh, NC (Aneja *et al.*, 1995; Aneja and Roelle, 1997; Roelle *et al.*, 1999).

Laboratory procedures

Soil samples were collected using an 8.26-cm (3.25″) diameter auger at a maximum depth of 30 cm below grade. Each soil sample consisted of approximately 3,000 g of soil, and was continuously refrigerated at a temperature of 4°C in an airtight bag until needed. Each soil sample was thoroughly mixed with a stainless steel trowel and sieved to achieve a uniform particle size through a No. 10 U.S. Standard Sieve (2-mm openings). Soil samples were allowed a maximum holding time of 30 days before being discarded. Each laboratory NO emissions experiment was conducted on a separate batch of soil.
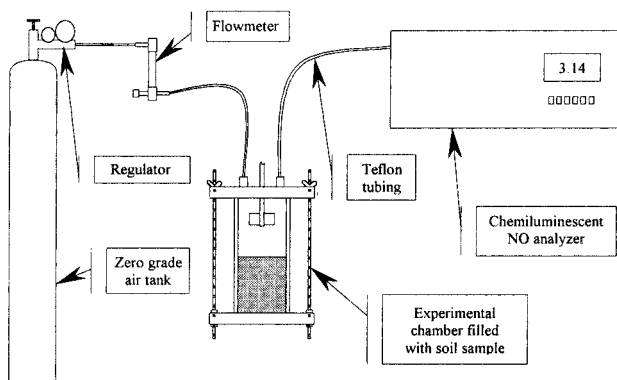
Figure 1. Laboratory experimental setup using dynamic test chamber. Glass column of test chamber is 9.8 cm in diameter by 20.5 cm in height.

The laboratory soil column (Fig. 1) was loaded to a height of 11 cm (approximately 1000 g of soil) and compacted for 1 h using a 1-kilogram weight. Dependent on the desired soil temperature, the entire loaded soil column was left at room temperature or placed in an incubator set at 15°C or 28°C during compaction. After compaction, the 1-kilogram weight was removed and the Teflon top was inserted onto the test chamber and secured with wing nuts. Connections were made to the zero-grade air, the Teflon™ stirrer, and the NO analyzer. The entire soil column plus tubing connections was placed back into the incubator at 15°C or 28°C or left at room temperature for the duration of the experiment.

The laboratory dynamic flow test chamber consists of a glass column enclosed by top and bottom nonreactive Teflon plates incorporating Viton O-rings to maintain an airtight fitting. All gasses enter and exit the test chamber via the Teflon top plate through three circular connection holes. A continuous flow of zero-grade air (0% hydrocarbons, 0% moisture, 0% NO) is used for all laboratory experiments at a constant flow rate of 1.25 liters per minute (L/min) based on research performed by Rammon and Peirce (1999). A Teflon stirrer is used to thoroughly mix the zero-grade air with gaseous soil emissions within the headspace of the test cell. The stirrer is operated continuously at an approximate rate of 100 rpm. The test chamber maintains a slight positive pressure throughout the experimental sequence with the influent flow rate of zero-grade air higher than the effluent flow rate to the NO analyzer; this avoids the migration of NO from the ambient atmosphere into the test cell through the ball-bearing stirrer connector. Excess gas within the test chamber is allowed to escape the chamber via the ball-bearing stirrer connector. The NO Analyzer used in the laboratory research is a Thermo Environmental In-

struments Model 42S Chemiluminescence Low Level NO-NO$_2$-NO$_x$ Analyzer. The NO Analyzer has a range of 0 to 200 parts per billion by volume (ppbv). The sample flow rate into the analyzer averages approximately 1 L/min.

Field procedures

NO flux and soil physical/chemical data was collected from the field episodically during summer 1999 (June–August), winter 2000 (February–March), and spring 2000 (May–June). The *in situ* field measurements were conducted using a temperature-controlled mobile laboratory consisting of a modified van with a 13,500 BTU air-conditioning unit (Fig. 2) ensuring that the temperature inside the van was maintained within the operating range of the instruments. Power for the air-conditioning and all of the detection instruments is standard 11-V AC installed at the research site. NO concentrations are measured using the same Thermo Environmental Instruments Model 42S Analyzer as used in the laboratory experiments. A laptop computer in conjunction with a Campbell Scientific Micrologger is used as an automated data acquisition system. The system records 60-s rolling average concentration measurements, and then bins and averages these values every 15 min. The 15-min binned averages are stored and used in all flux calculations. A 26-liter dynamic chamber system used in the field portion of this study is described further in Roelle *et al.* (1999), and is similar in design and operation to the laboratory chamber. The field chamber was placed on the stainless steel collar, which had been inserted into the soil the previous evening. Any vegetative matter from the soil surface was removed at least 1-week prior to NO measurements. Before data collection, the chamber was flushed with zero-grade air for at least 1 h beginning at 8:00 a.m. This technique ensured that the NO concen-
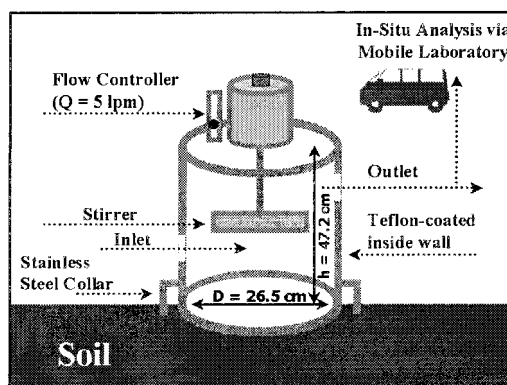

Figure 2. Field experimental setup using dynamic flow-through chamber system.

tration within the chamber reached steady state prior to any data acquisition, and allowed for the instruments to undergo their daily calibrations. Daily experiments ended at approximately 5:00 p.m., and the stainless steel collar was relocated to a random location within a 10-m radius of the mobile laboratory in preparation for the next day's experiment. This procedure allowed a minimum of 16 h for any effect on soil NO flux, due to soil disturbances caused by the insertion of the stainless steel collar, to dissipate. Soil temperature was recorded every minute, and these values were binned and averaged every 15 min using a Campbell Scientific soil temperature probe (accuracy ±3%) inserted 5 cm into the soil adjacent to the chamber.

WFPS and soil temperature

WFPS is an index of the moisture content of soil, and is the ratio of volumetric soil water content to total porosity of the soil. WFPS is useful in indicating the air/water ratio in soil as well as the amount of water available to support microbial activity in soil (Ormeci *et al.*, 1999). Therefore, WFPS is potentially useful in discussing the transfer of NO to the atmosphere via diffusion through water-filled pore spaces, a relatively slow process, or rapidly via advection in air-filled pore spaces. Diffusion is highly variable in rate, depending on the concentration gradient and soil pore structure.

The WFPS parameter was targeted in laboratory experiments for a maximum of 45% WFPS based on research performed by Ormeci *et al.* (1999), which suggests an exponential decline in NO emissions at WFPS >45% attributed to limited advective NO gas transport as pore spaces are filled with water and to decreased nitrifying activity. The WFPS of the agricultural soil samples in the field ranged from approximately 20 to 45%. In the lab, the WFPS was adjusted by either air drying the soil or wetting the soil. Soil was air dried at room temperature in either a stainless steel pan or spread on a thick sheet of nonabsorbent paper.

The soil temperature measured in the field ranged between 12°C (55.4°F) and 28°C (82.4°F). To adjust soil temperature in the laboratory experiments, soil samples were placed in a low-temperature incubator or allowed to equilibrate to room temperature for a minimum of 24 h prior to running an experiment. The soil pH was determined by a potentiometric method based on a 2:1 water to soil ratio by weight.

Biosolids amendment of lab and field soil

Biosolids samples were collected from a municipal wastewater treatment plant (WWTP) in the Piedmont region of North Carolina that incorporates anaerobic di-

Table 1. Characterization of biosolids from WWTP performed by Burlington Research, Burlington, NC.

Parameter	Mean concentration
TKN	80,300 mg/kg dry weight
Ammonia-N (NH_3-N)	23,090 mg/kg dry weight
Nitrate-N (NO_3-N)	<250 mg/kg dry weight
Total phosphorus	37,350 mg/kg dry weight
Percent solids	3.4%

The mean concentrations are of bimonthly analyses performed between January 1998 and November 1998. TKN = total Kjeldahl nitrogen.

gesters and digested sludge storage and thickening tanks as the major biosolids treatment processes to produce Class B biosolids. Biosolids were collected from the purging faucet of a digested sludge storage tank outlet. The biosolids were discarded 2 weeks after collection due to concerns about the biosolids' stability, specifically potential biological and chemical changes in the biosolids composition (Droste, 1997). The 29.5 million liters per day WWTP produces approximately 95,000 liters per day of biosolids for land application. The characteristics of the biosolids as it exits the facility are summarized in Table 1. The biosolids were also analyzed for metals with the results on a dry weight basis as follows: arsenic (2.8 mg/kg), cadmium (1.8 mg/kg), chromium (29.5 mg/kg), copper (342 mg/kg), lead (48.5 mg/kg), mercury (2.9 mg/kg), molybdenum (5.7 mg/kg), nickel (8.4 mg/kg), selenium (2.0 mg/kg), and zinc (509 mg/kg).

A target *N* application rate of 100 pounds of plant available *N* per acre (lbs-PAN/acre) (112 kg-N/ha) was selected for biosolids amended soil to closely approximate *N* amendment application rates in standard agricultural practice. Biing-Hwan (1995) reports in an U.S. Department of Agriculture study that nitrogen application rates for corn, cotton, wheat, and soybeans are approximately 130, 90, 60, and 25 lbs-N/acre (146, 101, 67, 28 kg-N/ha), respectively. To achieve an application rate of 112 kg/PAN/ha in laboratory experiments, 105 mL of biosolids were added to each kg of air-dried soil, and the soil was allowed 24 h to equilibrate to the lab experimental temperature. Because biosolids were not applied to the crop during the field measurement period, fertilization was simulated by applying 400 mL of biosolids, which is equivalent to 112 kg-PAN/ha based on the area of the chamber footprint, onto the soil surface 30 min prior to initial NO measurements, which continued throughout the day. This biosolids application method used in the field studies mimics agricultural biosolids application via spraying onto the soil surface at this and other sites. Field studies on biosolids amended soils were

conducted during the spring and summer measurement campaigns to represent the actual times when crops would receive biosolids applications.

Calculation of NO flux

For both laboratory and field observations, the NO fluxes were calculated from a mass balance equation (Kaplan *et al.*, 1988; Kim *et al.*, 1994):

$$\frac{d[C]_f}{dt} = \left(\frac{Q[C]_o}{V} + \frac{JA}{V} \right) - \left(\frac{LA'}{V} + \frac{Q}{V} \right)[C]_f + R \quad (1)$$

where $[C]_o$ is the NO concentration at the inlet of the chamber (ng-N/m^3); $[C]_f$ is the NO concentration in the chamber (ng-N/m^3) measured by the analyzer in ppbv; A' is the surface area of the experimental setup, including glass column and Teflon tubing, in contact with the headspace atmosphere (m^2); A is the chamber cross-sectional area (m^2); V is the volume of the chamber headspace (m^3); Q is the air flow rate through the chamber (m^3/s); J is the NO emissions from soil, flux per unit area [ng-N/(m^{2}s)]; L is the total loss term encompassing loss of NO on the chamber wall and in tubing, assumed first-order reactions in NO concentration (m/s); and R is the chemical production/consumption rate for NO in the chamber [ng-N/(m^{3}s)]. The lab and field test chambers and all supporting apparatus are composed of chemically inert materials (e.g., glass, Teflon, and stainless steel). Therefore, NO production and NO consumption reactions taking place within the test chamber are not the result of test cell material and gaseous product interactions, and $R = 0$. Influent into the test chamber is free of NO, with the inflow air consisting solely of zero-grade air; therefore, $[C]_o = 0$. The stirrer acts to continuously mix the gasses within the chamber and $[C]_f$ is assumed to be equal to the NO concentration everywhere in the chamber headspace. The total loss term, L, represents the loss of NO through reactions with the chamber walls and tubing and with existing reactive oxidants. The influent air into the chamber is zero-grade air, and thus existing oxidants are assumed to be negligible. The total loss term was determined experimentally and was determined to be negligible (results not shown). Equation (1) is used to relate the NO concentration measured by the NO analyzer (in ppbv) into a NO flux value [in ng-N/(m^{2}s)].

Site characterization

All soil flux measurements reported here were obtained from an active agricultural field located in the Piedmont region of North Carolina (Table 2). The field experiments were conducted on-site while soil was collected and analyzed at an off-site lab. The crops recently grown at this field are small grains including Hallmark Orchard Grass and Kenland Red Clover. This crop historically has been harvested at least twice per year. The field generally experiences a warm, temperate climate receiving rainfall throughout the year, with a frost-free season extending from April into October. The mean monthly air temperature is 5.2°C in January and 24.2°C in July. The field has been amended with unidentified fertilizers, herbicides, and pesticides through the past 10 years, although not during the 12 months prior to these experiments. Biosolids amendment typically occurs twice per year, and all soil collection and field measurements occurred at least 1 month after amendment. The soil samples used in the laboratory experiments were collected a minimum of 30 m from any border of the field to avoid soil field boundary conditions. The *in situ* field measurements were performed immediately adjacent to the laboratory soil collection location.

Table 2. Characterization of the top 30-cm of the lignum silty loam.

Soil parameter	Result	Analytical laboratory
pH	6.3	N.C. Dept. of Agriculture
Soil class	Mineral	N.C. Dept. of Agriculture
Humic matter content	0.18%	N.C. Dept. of Agriculture
Cation exchange capacity	5.6 cmolc/kg soil	N.C. Dept. of Agriculture
Recommended nitrogen application rate	80–100 lbs-N/acre	N.C. Dept. of Agriculture
Bulk density	1.27 g/cm^3	Duke University
Particle density	2.44 g/cm^3	Duke University
Ammonia-N	<28.6 mg/kg dry weight	Burlington Research, NC
Nitrate-N	<5.7 mg/kg dry weight	Burlington Research, NC
Nitrite-N	<5.7 mg/kg dry weight	Burlington Research, NC
Total Kjeldahl nitrogen	474 mg/kg dry weight	Burlington Research, NC

The silty loam Lignum soil is classified as a clayey, mixed, thermic Aquic Hapludults (Dunn, 1977), and this particular soil has been analyzed in the laboratory and field over the past 5 years. Soil texture was estimated to be 60% sand, 23% silt, and 17% clay, sandy loam. Lignum series soils are moderately well-drained, slowly permeable, and are typically found on uplands with slopes of 0 to 3% (Dunn, 1977).

RESULTS AND DISCUSSION

The comparison of lab vs. field measurements of soil NO flux depends on measurement of the same soil under similar WFPS and soil temperature conditions. Lab measurements allow for manipulation of environmental variables such as WFPS, temperature, pH, nitrogen amendment, and soil texture (Day, 1965). Field measurements offer realistic measures of NO emissions directly from the soil surface, but do not allow for control and manipulation of environmental variables. Therefore, field measurements need to be taken over a greater time to encounter a range of environmental conditions compared to lab measurements. An accurate comparison of lab vs. field measurements requires that similar WFPS and temperature data be matched. A total of 12 lab experiments completed on separate soil samples and 16 field measurements completed at varying on-site soil locations are compared under a set of six distinct environmental conditions. For this research, lab and field NO fluxes were compared if the WFPS was within ±5%, and the soil temperature was within 5°C, based on previous research on significant differences in NO emissions with varying soil temperature and pH (Tabachow *et al.*, 2001). A large amount of data from both lab and field measurements were not included in these results as neither the WFPS nor temperature could be matched to the corresponding lab or field measurements.

Laboratory results

All laboratory experiments were conducted for a minimum of 30 min, with steady-state conditions typically observed within 20 min. NO analyzer readings were recorded every minute. The NO concentration measured by the analyzer reaches steady state within a few minutes and the change of NO with time approaches zero (Fig. 3). At steady state, the NO flux is controlled by biological and chemical NO production and by NO transport in the soil. The NO flux from soil measured in the lab ranged from 2.5 to 62.9 ng-N/(m²s) with the WFPS ranging between 18.1 and 45.4%, and the pH varied from
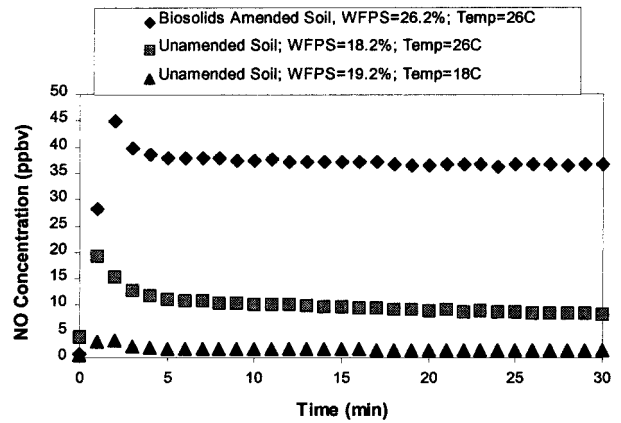

Figure 3. Typical NO emissions concentration vs. time curve measured in the laboratory: three experiments.

5.9 to 6.3. The lab NO flux measurements were observed to be reproducible with all duplicate experiments, conducted on separate soil samples, reproducible within ±3 ng-N/(m²s) of one another.

Field results

NO flux from soil measured in the field ranged from 2.8 to 128.1 ng-N/(m²s) with the WFPS ranging between 19.3 and 43.2%, and the pH varying from 5.5 to 6.4. All lab and field experiments exhibited variability within the range reported by other NO flux researchers (Kaplan *et al.*, 1988; Olivier *et al.*, 1998). The NO concentration measured by the analyzer in the field reaches steady state within several minutes, and the change of NO with time approaches zero (Fig. 4).
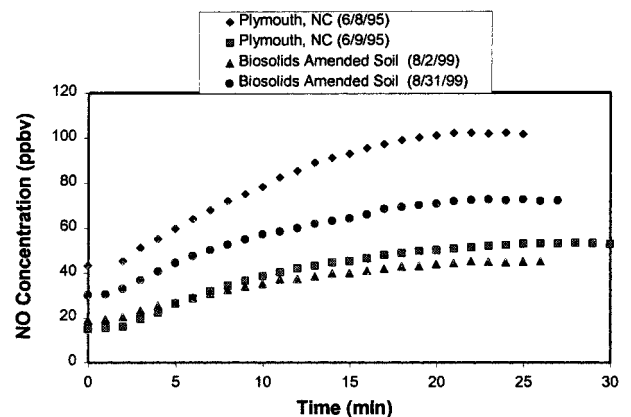

Figure 4. Typical NO concentration vs. time curve measured in the field (North Carolina soil during summer months): four experiments.

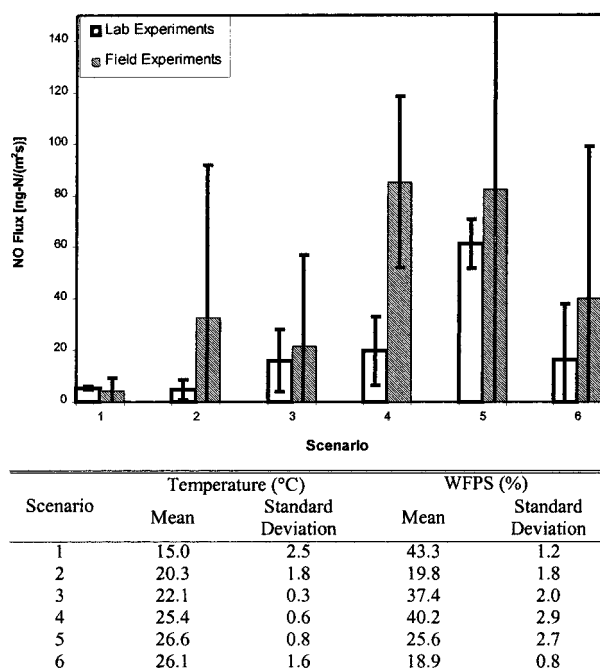| Scenario	Temperature (°C)		WFPS (%)	
	Mean	Standard Deviation	Mean	Standard Deviation
1	15.0	2.5	43.3	1.2
2	20.3	1.8	19.8	1.8
3	22.1	0.3	37.4	2.0
4	25.4	0.6	40.2	2.9
5	26.6	0.8	25.6	2.7
6	26.1	1.6	18.9	0.8

Figure 5. NO flux measured in lab and field experiments. Error bars represent 95% confidence intervals. Biosolids amended (BSA) soil experiments, shown on the far right, were conducted at 27°C with WFPS varying between 22.3 and 29.4%.

DISCUSSION

Comparisons of the NO flux from laboratory and field measurements were made using ANOVA based on a 0.05 level of significance. The mean NO flux for unamended and biosolids amended soil measured in the laboratory is 17.3 ng-N/(m^{2}s) as compared to 49.9 ng-N/(m^{2}s) for measurements made in the field. Data from the lab and field studies, based on the various soil temperature and moisture conditions studied, is plotted in Fig. 5. Of the six measurement comparisons seen in Fig. 5, based on ANOVA, a significant difference in NO flux between the lab and field measurements was observed in only one scenario (mean temperature 22°C, WFPS 38%), and the field and lab data showed reasonable agreement. The NO fluxes measured during laboratory and field experiments are shown to be within the 95% confidence interval ranges under all but one of the scenarios studied. The 95% confidence interval ranges of laboratory and field measurements of soil NO flux from the same soil under varying WFPS and temperature conditions indicate that the laboratory measurements successfully mimic the field measurements. Field experiments provide observations of the real world, and the agreement of lab and field ex-

periments indicate that lab experiments are a good indication of conditions in the real world.

Several field and laboratory studies have focused on the dependence of NO emissions on the nitrogen content of the soil. Research has shown that seemingly homogeneous soils can differ significantly in nitrogen content, and NO emissions can vary by more than an order of magnitude (Williams and Fehsenfeld, 1991; Valente *et al.*, 1995; Roelle *et al.*, 1999). Researchers conducting similar studies have reported on the effects of the soils' organic and inorganic nitrogen content on NO emissions, and in general, have found that soils with higher inorganic *N* content produce higher NO emissions (Davidson, 1991; Cardenas *et al.*, 1993; Potter *et al.*, 1996; Sullivan *et al.*, 1996; Roelle *et al.*, 1999). This study did not evaluate the nitrogen content of the soil; however, it can be assumed that immediately following biosolids application, the nitrogen content in both the lab and field soils was not rate limiting. Laboratory vs. field measurements of NO flux from biosolids amended soil showed no statistically significant difference in the measurement method. For biosolids amended soil, the mean NO measured in the laboratory was 61.2 ng-N/(m^{2}s) compared to a mean of 82.3 ng-N/(m^{2}s) measured in the field. This finding may indicate that nitrogen content of the soil is a critical parameter that must be considered when conducting lab and field nitrogen trace gas emission studies. For the combined results of lab and field experiments, the mean NO flux for unamended soil is 29.6 ng-N/(m^{2}s) compared to 73.8 ng-N/(m^{2}s) for BSA soil. The NO flux from unamended vs. BSA soil was seen to be significantly different based on ANOVA analysis at a 0.05 level of significance.

Considering the significant spatial and temporal variability observed in field measurements of NO, it is not surprising that the difference between lab and field measurements for some WFPS and temperature conditions was statistically significant (Williams *et al.*, 1992; Valente *et al.*, 1995). What researchers have reported to be imbedded within this variability is that NO responds in similar trends to changes in the soil parameters. The effects of soil moisture, reported as WFPS, on NO emissions is well documented in existing literature (Drury *et al.*, 1992; Ormeci *et al.*, 1999; Tabachow *et al.*, 2001). Statements regarding the effect of WFPS on NO emissions cannot be made from the data presented within this research due to the relatively small number of samples and the variability of WFPS encountered in the field experiments. Tabachow *et al.* (2001) observed increasing WFPS was found to promote NO emissions within the range of WFPS studied (3–40%).

The dependence of NO on these various soil proper-

ties is difficult to parameterize. Several studies have examined thousands of individual NO flux measurements, and have attempted to model the NO emissions with mixed results (Sullivan, 1995; Matson *et al.*, 1997; Aneja *et al.*, 2001). Due to its consistent correlation to NO emissions and ease in evaluation, soil temperature is the parameter often used in emission processing models to estimate NO emissions that are then typically used in air-quality models. Williams *et al.* (1992) describes a temperature and land-use algorithm, referred herein as the Williams' model, which is now part of the Environmental Protection Agency's Biogenic Emissions Inventory System (BEIS2), which is given by:

$$\text{NO Flux [ng-N/(m}^2\text{s)]} = A * \exp(0.071 * T_{soil}) \quad (2)$$

where A is the experimentally derived coefficient associated with land use categories; and T_{soil} is the soil temperature (°C). To examine similar exponential relationships between lab and field data sets, the protocol used by Thornton *et al.* (1997) was adopted to create relationships for the field and laboratory study results that are comparable to the Williams' model. In the protocol used by Thornton *et al.* (1997), soil temperatures are segregated, and the corresponding fluxes were averaged to produce one mean NO flux for each temperature span. This approach is found to adequately develop an empirical model because many data points are clustered around a specific range of temperatures, and binning the data prevents the regression from being skewed towards the data with the greatest number of measurements. The field and lab empirical model relationships are:

Field: NO Flux [ng-N/(m²s)]
$$= 1.07 * \exp(0.14 * T_{soil}); \quad R^2 = 0.81 \quad (3)$$

Lab: NO Flux [ng-N/(m²s)]
$$= 1.50 * \exp(0.14 * T_{soil}); \quad R^2 = 0.86 \quad (4)$$

The developed exponential relationships for the lab and field were compared to the relationship developed by Williams *et al.* (1992) to predict NO emissions at varying ambient temperatures (15°C, 22°C, and 28°C) (Fig. 6). An A coefficient of 3.56 was used in the Williams' model, which is the land use coefficient for rye crops. The relationship developed from the lab data predicted the highest NO flux, followed by the relationship developed from the field data. The Williams model predicted the lowest NO flux compared to laboratory and field measurements.

CONCLUSIONS

1. Laboratory and field measurements are shown to be comparable under all but one of the environmental
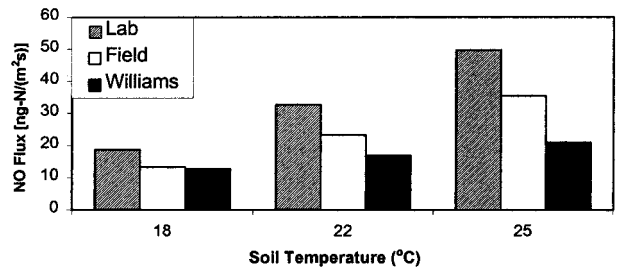

Figure 6. NO flux vs. soil temperature modeled via three exponential relationships using the Williams' model [A = 3.56 μg-N/(m²h), which is representative of rye], laboratory ($n = 89$) and field ($n = 837$) data sets.

conditions studied. Five of six scenarios showed no statistically significant difference in the NO flux measured from the lab vs. the field for comparable WFPS and temperature conditions. Researchers and scientists attempt to observe the world through field experiments, while lab experiments under controlled conditions attempt to mimic the real world. The laboratory and field measurements of soil NO flux from the same soil under varying WFPS and temperature conditions indicates that the laboratory measurements successfully mimic the field measurements. Therefore, lab experiments are a good indication of conditions in the real world.

2. Laboratory and field measurements should be seen as complementary rather than alternatives with each technique having a special role (Denmead and Raupach, 1993). Lab experiments permit replication and minimization of interferences from environmental variables such as WFPS, temperature, pH, sunlight, and wind velocity. Lab experiments are useful when relationships between the flux of NO and soil, chemical, or microbiological factors are to be investigated. Field experiments permit measurements over a diurnal cycle, incorporate seasonal flux differences, and mimic land treatment conditions. Field experiments are very effective for quantification of fluxes at the landscape level (Christensen *et al.*, 1996).

3. Statistically significant differences were not observed for NO emissions measurements from biosolids-amended soil in lab vs. field. For the biosolids amended plots, reasonable agreement between the lab and field studies indicates that the soil nitrogen content should be considered in future studies. The NO flux from biosolids-amended soil was significantly higher than unamended soil.

4. Relationships are developed for both laboratory and field measurements, and these relationships are compared to the Williams *et al.* (1992) model. The lab and

field relationships based on actual NO measurements indicate that the Williams' model may underestimate the NO flux from soil.

Topics of future research suggested by this research are: (1) use of molecular methods to identify and quantify the types of microorganisms responsible for NO production; (2) compare lab vs. field measurements for other soil types and other gases such as CO_2 or NH_3; and (3) adaptation of atmospheric fate and transport models to consider NO and O_3 interrelationships at the regional airshed level.

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