NITRIC OXIDE EMISSIONS FROM ENGINEERED SOIL SYSTEMS

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ABSTRACT: Sophisticated laboratory equipment and procedures are developed and used in controlled experiments to measure nitric oxide (NO) emissions ranging from 42 to 75 ng $N/m^2 \cdot s$ from sludge-amended soil of concern to environmental engineers because nitric oxide emitted to the troposphere is a precursor to troublesome ozone formation and also of concern to agricultural engineers because valuable nitrogen as fertilizer is lost from the soil. Water-filled pore space is confirmed to be of critical importance to NO flux, and the upper layers of soil are determined to contribute the larger portion of the NO fluxing from the soil to the troposphere. More than 42% of the total NO flux comes from the top 1 cm of soil, with NO contributions decreasing exponentially with soil depth and very little if any tropospheric NO contributed from soil at a depth of 20 cm or greater. The results are discussed in terms of microbiological, chemical, and soil transport processes that influence NO flux from sludge-amended soil.

INTRODUCTION

Nitrogen oxide (NO) emissions from unamended and engineered soils can adversely impact local and regional air quality in the lower troposphere and can directly impact public health and vegetation as subsequent ozone (O_3) formation; accumulation leads to pulmonary congestion, disorientation, altered breathing, headaches in humans, and decreased crop yields. In addition, these emissions are a direct economic concern because nitrogen valued as fertilizer is lost from the soil. Consequently, these emissions are studied here to gain a better understanding of their net formation, transport, and transformation in the form of NO flux from the soil. With the ability to measure nitric oxide emissions under controlled conditions in the laboratory, it can be possible in the future to gain a better understanding of the mechanisms responsible for NO formation, transport, and transformation with a view to the control of NO emissions from soil into the lower troposphere.

Whether or not increased NO emissions lead to ozone problems in the lower troposphere is dependent on other important atmospheric variables, most notably the NO_x and volatile organic compounds ratio. However, the southeast United States as well as other parts of the country appear to be NO_x limited with volatile organic compounds already in abundance in the lower levels of the troposphere. Consequently, various sources of NO emissions have been studied, and their daily and seasonal variations noted in urban lawns, public parks, forests, and non-sludge-amended agricultural settings (Davidson et al. 1993; Aneja and Robarge 1996; Aneja et al. 1997a,b). Furthermore, the importance of the movement of rural NO and O_3 into urban airsheds is well documented (Lindsay et al. 1989; Aneja et al. 1996; Baumgardener and Edgerton 1998).

In the lower troposphere any increase in NO can lead to an increase in the concentration of photochemical oxidants, particularly O_3, which will in turn adversely affect human health, animals, and plants. The Office of Technology Assessment estimates that high O_3 concentrations cost the United States between \$1 billion and \$5 billion annually in added human health costs and reduced crop yields. The impacts are not limited to the United States: between 10 and 35% of the world's total grain production occurs in regions of the northern midlatitudes where nitrogen fertilizer is being applied to the land with O_3 concentrations high enough to decrease crop yields (Chameides et al. 1994). Thus the $NO \rightarrow O_3$ pollution associated with soil-atmosphere interactions is a problem, which is truly global in nature (Jacobs et al. 1993).

Application of nitrogen-containing fertilizers, including municipal wastewater treatment sludge applied to human food and nonfood chain land, is a practice followed throughout the United States that can lead to the utilization of the nitrogen by crops but could also lead to ozone pollution. For example, previous research documents that soil NO emissions increase in direct proportion to the nitrogen application rate in non-sludge-amended soils (Aneja et al. 1996). Globally, by the year 2025, the continuing usage of nitrogen fertilizer could lead to soil-biogenic NO_x emissions approaching 20 T_gN (Yienger and Levy 1995; Aneja and Robarge 1996).

The focus of this research is on land spreading municipal wastewater treatment sludge. Much of the sludge produced nationwide is not contaminated with harmful heavy metals or persistent organics and thus is potentially useful; it is used as a nitrogen fertilizer and soil conditioner. More than 6,000,000 dry metric tons of municipal sludge are generated annually in the United States with nearly 30% spread or injected into the land. In the future more sludge will be produced as the necessary by-product of the growing number and increased efficiency of municipal wastewater treatment systems. Additionally, the practice of land spreading municipal sludge could become more prevalent as local decision makers strive to control sludge disposal costs while taking advantage of its nitrogen content, potentially compounding the $NO \rightarrow O_3$ problems associated with the application of nitrogen-containing fertilizers to soil.

Thus the objectives of this research can be summarized as follows: (1) Develop laboratory equipment and procedures to study NO emissions from unamended and engineered soil systems under controlled conditions; (2) conduct controlled laboratory experiments, for a range of soil moistures, to study NO flux from unamended soil and sludge-amended soil; (3) compare the laboratory results to previous observations of NO flux made during field studies of non-sludge-amended agricultural soils under uncontrolled environmental conditions; and (4) discuss the findings in terms of factors responsible for the formation, transformation, and transport of NO in soil.

EXPERIMENTAL EQUIPMENT AND MATERIALS

The laboratory equipment used in these experiments was designed and fabricated based on information obtained at Duke University, Durham, N.C., during 17 years of laboratory tests on fluid flow through soil (Peirce et al. 1986, 1987a,b,c; Manila and Peirce 1994; Ormeci and Peirce 1999) coupled with information obtained during field observations made by

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researchers at North Carolina State University, Raleigh, N.C. (Aneja et al. 1995, 1996). The newly designed dynamic flow test chamber illustrated in Fig. 1 is a cylindrical test vessel constructed of chemically inert materials. Viton O-rings maintain an airtight fitting between the glass cylinder and the Teflon top and bottom plates. Teflon tubing is connected to the chamber with threaded Teflon fittings. Reactions taking place within the chamber are thus limited to those reactions taking place in the soil in the chamber, as the result of interactions between the samples and the test materials. A homogeneous headspace above the soil is maintained with a Teflon mixer rotating at 60 rpm.

This test chamber is configured in the test system seen in Fig. 2 to permit a regulated 2.0 L/min constant flow of zero-grade air (National Welders Inc. zero-grade air: 0% hydrocarbons, 0% moisture, 0% NO) into the test chamber with subsequent continuous extraction of headspace gases by the NO analyzer's gas pump. The NO analyzer is the Thermo Environmental Instruments Incorporated Chemiluminescent High Sensitive Model 42S (sampling each 10 s, mean reported each 60 s, with a sensitivity of 50 parts per thousand by volume). This pump is fixed at 1.5 L/min with inflow zero-grade air provided at 1.7 L/min to maintain a small positive pressure in the test chamber to ensure that ambient atmospheric gases containing NO do not leak into the test chamber and alter the system.

All NO reaching the analyzer thus is assumed to be the net result of NO produced, transformed, and transported through the test soil/headspace interface. The NO analyzer is capable of measuring oxides of nitrogen from sub-parts per billion by volume (ppbv) to 200 ppbv. The minimum detectable limit for NO is 0.50 ppbv and the precision is ±0.50 ppbv. The analyzer is calibrated following the guidelines prescribed by the vendor.

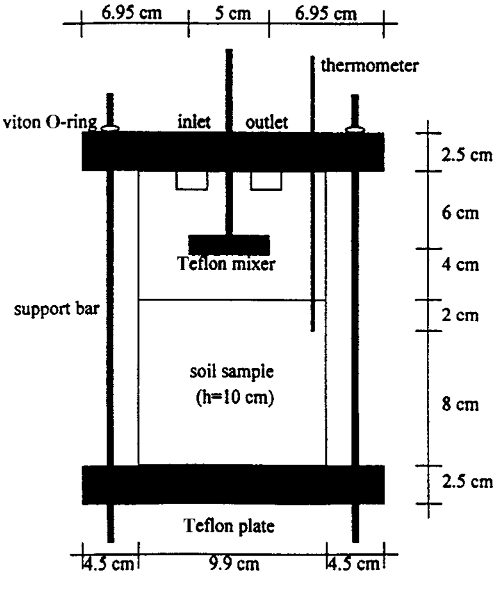

FIG. 1. Dynamic Test Chamber

The mass balance for NO in the chamber is calculated as

$$\frac{dC}{dt} = \left[\frac{Q[C]_0}{V} + \frac{JA}{V}\right] - \left[\frac{LA[C]_f}{V} + \frac{Q[C]_f}{V}\right] + R \tag{1}$$

where C = NO concentration in the chamber (as measured by the analyzer as ppbv); $[C]_0$ = NO concentration at the inlet of the chamber ($[C]_0 = 0$ with the use of the zero-grade air); $[C]_f$ = NO concentration at the outlet of the chamber ($[C]_f = C$ with complete mixing in the gas headspace); A = measured surface area of the soil column; V = measured volume of the gas headspace above the soil sample; J = flux of NO from the soil (ng $N/m^2 \cdot s$); L = loss of NO on the chamber and exit tube walls (first order with C and calculated $L = 0.02$ with the use of the Teflon/glass system); and R = chemical production/destruction rate for NO in the chamber and exit tubes (assumed to be zero for the seconds of residence time in the test system). When the test chamber reaches steady state the change of [NO] with time is zero and the NO flux is controlled by the microbiological/chemical formation and transformation of NO in the soil as well as the transport of NO through the soil prior to the fluxing. Eq. (1) simplifies to

$$J = [C]_f \left[\frac{Q}{A} + L\right] \tag{2}$$

North Carolina Piedmont soil was obtained and aggregated from the first 30-cm plow layer at randomly selected sites within an agricultural field located in central North Carolina. 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 though not during the past 12 months. The nitrogen content of the soil is estimated at total Kjeldahl nitrogen (TKN) = 2,200 mg/kg dry weight; other characteristics of this unamended soil are summarized in Table 1.

Anaerobically digested sludge was obtained from a 7.8-mgd municipal waste water treatment facility located in central North Carolina. This facility utilizes a sequence of unit operations including the following: screen, primary clarifier, trickling filter, activated sludge, secondary separation, and final disinfection of the treated water prior to discharge to a receiving stream. Approximately 30,000 gpd of sludge from the primary clarifier and secondary separator are combined and anaerobi-

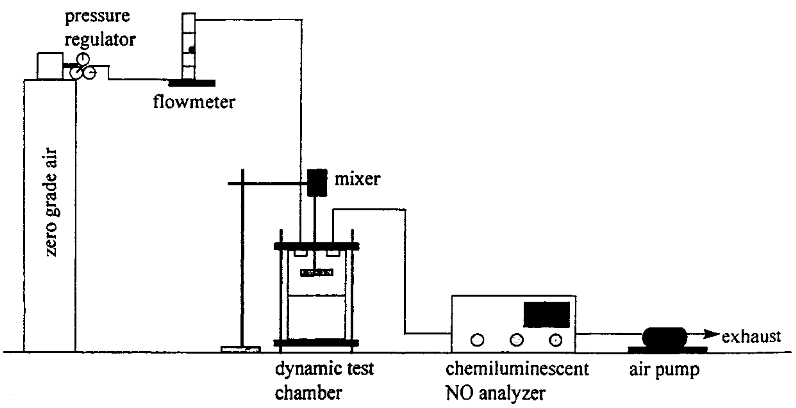

FIG. 2. Experimental System

TABLE 1. Characteristics of Non-Sludge-Amended Soil

Characteristic (1)	Value (2)
Humic matter[a]	0.18%
Weight/volume[a]	1.28
CEC[a]	5.6
CEC occupied by bases[a]	88.0
pH[a]	6.3
TKN[b]	474
Ammonia-N[b]	<28.6 (below detection)
Nitrate-N[b]	<28.6 (below detection)

Note: CEC = cation exchange capacity.
[a] North Carolina Department of Agriculture, 1999.
[b] Burlington Research Laboratory 1999.

TABLE 2. Characteristics of Anaerobically Digested Municipal Wastewater Treatment Sludge

Component (1)	Value (mg/kg dry weight) (2)
As	3.0
Cd	2.5
Cr	37
Cu	327
Pb	50
Hg	3.1
Mo	3.1
Ni	13
Se	<0.59
Zn	762
TKN	94,000
Ammonia-N	25,400
Nitrate-N	<249
Total P	42,000
Total solids	2.6%

cally digested to produce approximately 25,000 gpd for land spreading. The characteristics of this sludge as it exits the facility are summarized in Table 2.

EXPERIMENTAL DESIGN AND PROCEDURES

Unamended soil and sludge-amended soil samples at three different moisture contents [3, 20, and 40% water-filled pore spaces (WFPS)] were studied in the laboratory at 22°C. Identical experimental procedures were followed for each soil-WFPS combination tested in duplicate with the NO flux from each soil sample determined using (1).

Prior to each NO experiment the soil was prepared following standard procedures developed at Duke University designed to produce homogeneous soil samples (control and sludge-amended) from which NO flux measurements could be taken and compared. All soil from the field site was stored in airtight plastic containers at 10°C. The soil was passed through a No. 10 U.S. Standard sieve (2-mm openings) to achieve a uniform particle-size distribution for all experiments. Immediately, the soil was air dried for 24 h to approximately 3% WFPS. The goal was to produce soil with similar particle size and moisture characteristics from which samples could be taken for controls and for amending prior to the NO flux experiments. This preparation process uniformly released moisture and possibly nitrogen from the soil. Individual soil samples (~1 kg) were then taken from this homogeneously prepared soil and either designated as a control or sludge-amended soil and brought to the desired water content.

Soil samples were amended with distilled deionized water or with municipal wastewater treatment sludge as prescribed in the experimental design. The sludge was incorporated into the respective soil samples at an application rate of 30 lb N/acre appropriate for high yield production of grain crops on sandy loam soil with appropriate irrigation (Tucker et al. 1999). Desired soil moisture content was then achieved through either air-drying or a spray bottle irrigation.

The WFPS is the metric used here to define the moisture content of the different soil samples and is a potentially useful measurement for at least three reasons. Initially, it indicates the amount of water available to support microbial activity in the different soil samples. Second, WFPS indicates the air/water ratio in the soil and thus contributes to the availability/unavailability of oxygen that controls the mix of aerobic/anaerobic microbial activity. WFPS also indicates the potential for pore spaces to transport NO gas from the lower levels of the soil to the troposphere either relatively rapidly by diffusion/advection through air-filled pore spaces or relatively slowly by diffusion through WFPS. WFPS is determined as

$$\%\mathrm{WFPS} = (Q_v/TP)100 \tag{3}$$

where Q_v = percent volumetric water content

$$Q_v = (\%Q_m)(P_b) \tag{4}$$

TP is total soil porosity

$$TP = (1 - P_b/P_p)100 \tag{5}$$

P_p is soil particle density

$$P_p = 2.65\ \mathrm{g/cm^3}$$

P_b is soil bulk density

$$P_b = 1.3\ \mathrm{g/cm^3}$$

and Q_m is gravimetric water content measured in grams.

The WFPS of the soil collected in the field was determined to be 18%. Thus the soil samples were air-dried at 20°C to obtain soil samples at lower WFPS, irrigated with spray bottles, and permitted to equilibrate over 24 hours to obtain soil samples at higher WFPS.

Each soil sample was then placed into a test chamber in two sequential 5.5-cm layers to achieve the target 10-cm-high sample once a standard 1-kg mass had been placed on top of the soil column for 1 h. The dynamic test chamber was sealed with hand-tightened wing nuts, and all necessary connections were made to the zero-grade air source, the mixer, and the NO analyzer. The soil-WFPS combination was determined and recorded just prior to and immediately after each experiment. Additionally the temperatures in the headspace of the test chamber and the soil sample were monitored throughout selected experiments and observed to be near 22°C (room temperature) throughout those experiments. Room temperature was maintained near 22°C.

RESULTS

Eq. (1) was used to relate measurements of NO concentrations in the headspace of the test chamber to the NO flux from the soil samples. The results of the different experiments are summarized in Table 3. The NO flux results in Table 3 are

TABLE 3. NO Flux from Soil

Soil sample (1)	WFPS (%) (2)	pH (3)	NO flux (ng N/m$^2\cdot$s) (4)
Unamended soil	2.1	6.13	2.0
	19.2	5.96	3.0
	38.3	6.18	17.0
Sludge-amended soil	3.7	7.82	42.0
	20.7	7.54	30.0
	36.8	7.96	75.0

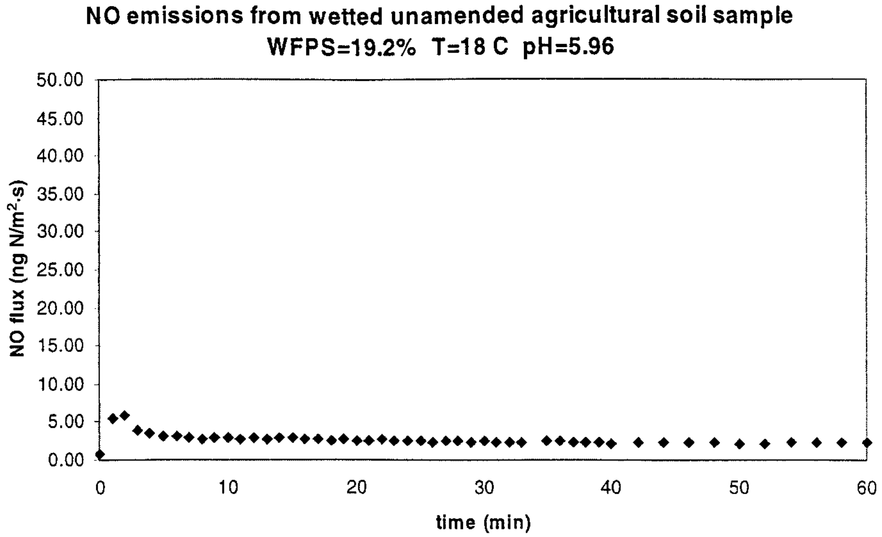

FIG. 3. NO Flux from Unamended Soil

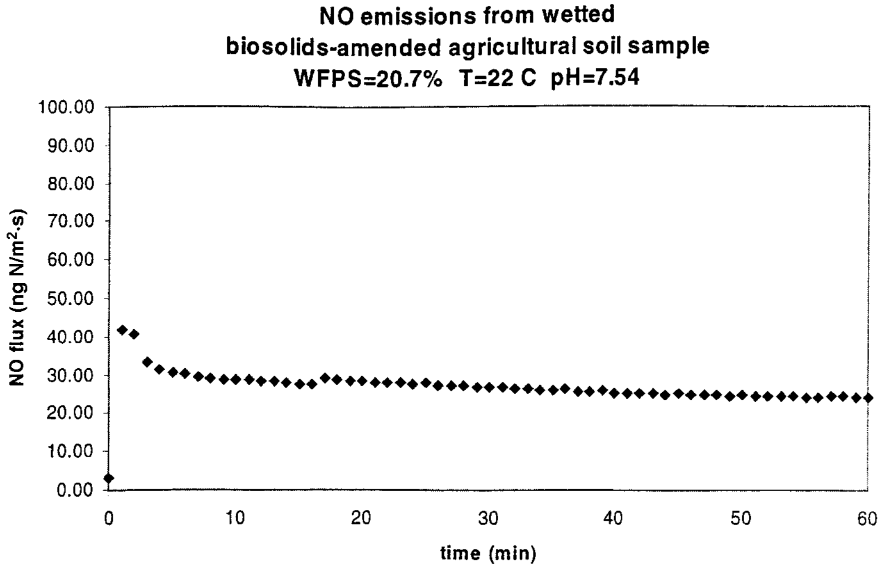

FIG. 4. NO Flux from Sludge-Amended Soil

reported at a standard 30 min into each experiment as seen in representative Figs. 3 and 4. NO flux observations from duplications of each experimental combination varied <1%.

The dynamic test chamber is an active, essentially closed, reactor never really approaching a steady state except in general terms of its flow dynamics. To make standard comparisons across all experiments, 30 min of testing time was selected to represent approximately 60 residence times of zero-grade gas passing through the headspace of the chamber. The decrease (slight, <1%) in NO flux with the passage of time is attributed to many changes taking place in the reactor, but most notably the drying observed in the upper levels of the soil sample as dry zero-grade air continually was input to the headspace of the test chamber as the analyzer pump continually extracted gaseous samples from the headspace for NO analysis.

DISCUSSION

Nitrogen oxide formation, transformation, and transport in chemically fertilized (non-sludge-amended) soil, including direct application of ammonia or nitrate, is well defined in the literature, and thus its anthropogenic perturbations to the various components of the biogeochemical nitrogen cycle are reasonably well understood. In particular, the mineralization, nitrification, and denitrification processes in chemically fertilized soils have been widely studied in the past (Aneja et al. 1997b). However, the composition and characteristics of sludge-amended soils are very complex and very different from chemically fertilized soils in terms of basic concerns [e.g., microbiology (organic content and microbial populations), chemistry (form, availability and transformation of nitrogen), and mechanics of transport (soil porosity, pore size distribution, and NO transport within the soil matrix)]. This complexity and uncertainty of sludge-amended soil systems prevent the transfer of the understanding of NO emissions from ordinary agricultural land to an understanding of NO emissions from land receiving sludge. It is erroneous to make the leap of faith and assume that these two vastly different nitrogen sources will perturb the biogeochemical nitrogen cycle in a similar manner. NO formation, transformation, and transport through sludge-amended soil is highly unpredictable and thus is studied here for the first time.

Factors Contributing to NO Flux

A wide range of factors contribute to the microbiological, chemical, and transport processes in soil, sludge, and sludge/soil mixtures that form, transform, and transport NO to the soil/troposphere interface. The most important factors include moisture, temperature, pH, microorganism population(s), nitrogen source, application rate, as well as plant root structure. For example, based on the temperature range conducive to metabolism and growth in sludge, bacteria are classified as seen in Table 4. Similarly, the growth of bacteria in sludge and soil generally is limited to pH conditions between 4 and 9, with optimal metabolism and growth occurring between pH 6.5 and 7 (Benefield and Randall 1980). The target pH for crop production is between 6 and 6.5 (Tucker et al. 1997); thus anticipated maximum NO flux could occur in the agriculturally preferred range. The effects of moisture are studied and reported here; future research is indicated to address how the other factors influence NO flux from unamended and engineered soils.

NO from Sludge Amended Soil

The observed higher NO flux from the sludge-amended soil is not surprising; the soil samples amended with municipal sludge contain more nitrogen than the unamended soil samples, and the additional nitrogen is available for conversion to NO. However, the enhanced NO flux from sludge-amended soil is a result of complex changes in pH, temperature, microorganism population(s), water in the soil that is available for NO production and transformation, as well as nitrogen source and application rate. For example, the chemical decomposition of dissolved NO_2 under acidic conditions can be suggested as $2H^+ + 2NO_2 \rightarrow 2NO + NO_3 + H_2O$ and/or $2H^+ + 2NO_2 \rightarrow NO + NO_2 + H_2O$. Similarly, microbiological respiratory decomposition can be summarized as $NO_3 \rightarrow NO_2 + NO$. The study of a range of factors, including pH, temperature, microorganism population(s), water in the soil that is available for NO production and transformation, as well as nitrogen source and application rate, individually and in concrete, is outside the scope of this research project. Further research must be conducted to compare the mechanisms responsible for NO production in sludge-amended soil to those mechanisms available in chemically fertilized soil and in unamended soil.

Comparison to Field Observations

In field studies of a variety of (non-sludge-amended) agricultural lands under uncontrolled environmental conditions, NO was observed to move from the soil in eastern North Carolina and elsewhere into the lower levels of the troposphere and contribute to the formation of troublesome ozone (Slemr and Seiler 1984, 1991; Penkett 1988; Kim et al. 1994; Aneja et al. 1995, 1996, 1997a; Sullivan 1995). The information presented in Table 5 suggests that the NO fluxes seen during this research are within the range of field observations that reflect seasonal and other environmental variations.

Soil Moisture

The results of the controlled laboratory experiments reported here confirm previous observations made during uncontrolled field investigations reported in the literature: moisture content clearly has an important effect on NO flux from soil (Aneja and Robarge 1996; Aneja et al. 1997a; Ormeci et al. 1999). When dry soil is wetted even slightly, NO flux increases drastically. Nitrifying (obligate aerobe autrophs) and denitrifying (anaerobic heterotrophs) bacteria are able to survive extreme drought conditions and can become active as soon as the soil is wetted (Conrad 1990; Davidson et al. 1993). As WFPS increases from these dry to wetter conditions, NO flux seems to reach a plateau until soil moisture is considerably above field capacity and NO flux decreases. Extreme wetting of the soil stimulates the denitrification processes in the soil thus contributing to NO production. However, large increases in soil moisture decrease the oxygen available in the soil pore spaces and thus begin to limit the activation of the obligate aerobe nitrifying bacteria. This biological nitrification can be a greater contributor to NO than can be denitrification (Conrad 1990; Hutchinson et al. 1993). The results reported in Table 3 indicate that the 3% WFPS was slightly above the lower threshold for enhanced NO flux, whereas the 40% WFPS was slightly below the upper threshold for decreased NO flux as seen in Fig. 5.

TABLE 4. Temperature Ranges Influencing Growth of Bacteria in Municipal Sludge (Benefield and Randall 1980)

Classification (1)	Temperature range for reproduction (°C) (2)	Optimal range (rapid growth, 12–24 h) (°C) (3)
Obligate psychrophile	−5–20	15–20
Facultative psychrophile	−5–35	30–45
Mesophile	15–50	30–45
Obligate thermophile	45–75	55–75
Facultative thermophile	40–74	45–55

TABLE 5. Field Observations of NO Flux

Field use (1)	NO flux (ng N/m^2·s) (2)	Reference (3)
Soybean	3.8	Aneja et al. (1995)
Soybean	1.2–3.0	Sullivan (1995)
Cotton	1.8	Aneja et al. (1995)
Cotton	0.6–8.0	Sullivan (1995)
Corn	5.6–239	Williams et al. (1987)
Corn	8.1	Aneja et al. (1995)
Urban parks	1.4–16.1	Aneja et al. (1997b)

To further complicate the analysis in relatively dry soil, NO gas transport occurs as NO diffuses through the air in the pore spaces. As water fills the pore spaces, the NO gas transport occurs as NO diffuses much more slowly through the water than through the air. Consider the simplest case where the soil is assumed to be homogeneous in all three dimensions. The soil is bounded at the soil-atmosphere interface where $z = 0$. With the important processes at steady state, the diffusion equation for the vertical transport of [NO] in the pore spaces of the soil is given as

$$F = -Dd[\mathrm{NO}]/dz \quad (6)$$

where F = vertical flux of NO to the atmosphere; and D =

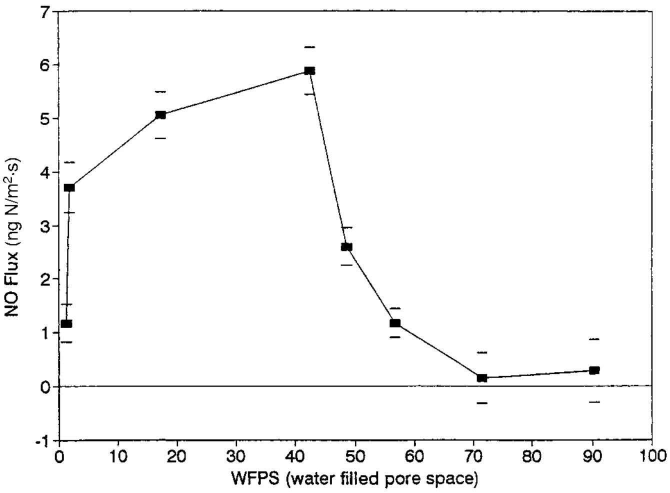

FIG. 5. NO Flux Related to WFPS in Non-Sludge-Amended Soil

diffusivity of NO in the pore spaces. NO diffusivity in air is 0.18 cm^2/s, much faster than NO diffusivity through air, which is on the order of 10^5 cm^2/s (Weast et al. 1984; Galbally and Johansson 1989). Thus, both the production and soil transport of NO are inhibited at much higher WFPS.

Changes in pH

The pH of the soil and sludge-amended soil samples were not controlled during the experiments; thus only general statements on the importance of pH can be made with reference to previous research. Soil pH can affect the chemical and microbiological processes contributing to NO production in the soil. Under acidic conditions NO_2 and other forms of nitrogen including HNO_2 tend to decompose and produce NO, which becomes available for transport to the troposphere. This chemodenitrification is suggested as a primary source of NO in such soils (Galbally 1989). Increased NO production in higher pH ranges can be attributed to both the chemical decomposition of N compounds and more active microbiological processes that produce NO. Previous research indicates that NO from nitrification can be enhanced by increasing soil pH as the total number of Nitrosomonas and Nitrobacter increase (Chase et al. 1968). This previous research helps explain to some extent the NO flux observations from the different samples studied in the laboratory.

NO Contributions from Underlying Soil Layers

To understand the NO contributions from underlying layers of soil, additional laboratory experiments were conducted with unamended soil samples of different thicknesses in the test chamber: 1, 3, 6, and 10 cm. Expressing flux from each thickness as a percent of the total flux observed from the 10-cm sample, the contribution of NO from soil above each depth is summarized in Fig. 6. Note that 42% of NO is contributed by the top 1 cm of the soil with the contribution of each succeeding lower layer decreasing exponentially as

$$Y = B \cdot e^{-kx} \qquad (7)$$

where Y = contribution of NO from each layer (%); x = depth of the soil (cm); and B (=49.7) and k (=0.17) = fitted values with $R^2 = 0.94$. The extrapolation of the data using (7) suggests that very little if any NO is produced in soil depths below 20 cm: $Y \sim 1\%$ at depth of 20 cm and $Y \sim 0$ at a depth of 100 cm. These results highlight the importance of selected factors that control the formation and soil transport of NO in the experiments reported and discussed here. Closer to the surface of the soil samples more oxygen is available for aerobic microbiological activity; water for microbiological and chemical NO production is available in quantities that enhance NO formation but do not preclude NO transport to the soil surface; and shorter distances with shorter transport times and consequently fewer opportunities for NO transformation prior to flux are found.

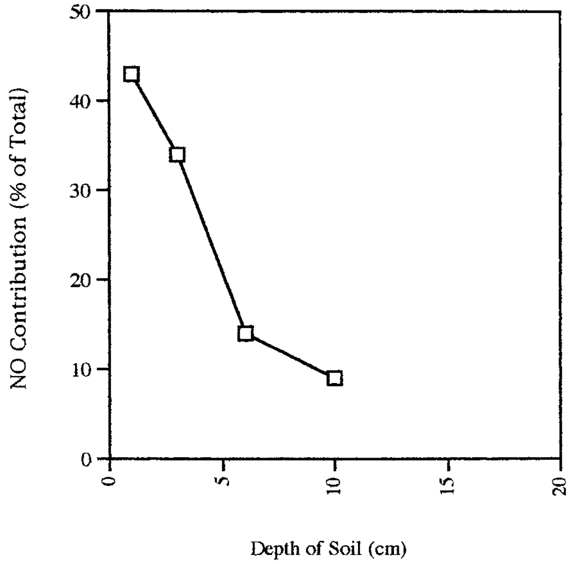

FIG. 6. Contributions of NO from Different Depths of Soil

Ozone Control Strategies

Previous research indicates that chemical and microbiological decomposition of nitrogen in soil contributes to the availability of the NO as a precursor to the formation of the O_3 in the lower levels of the troposphere (Chase et al. 1968; Muller et al. 1980; Linn and Doran 1984; McKinney et al. 1984; Williams et al. 1987; Kaplan et al. 1988; Ronen 1988; Galbally 1989; Conrad 1990; Drury et al. 1992; Davidson et al. 1993; Hutchinson et al. 1993; Aneja et al. 1995). With nitrogen oxides available in the troposphere, ozone can readily be formed as $NO + H_x - C_y + O_2 \rightarrow O_3 + \text{Carb} + H_2O$ and/or $NO_2 \rightarrow NO + O\ (h\nu)$ with $O + O_2 \rightarrow O_3$. Other previous research suggests that O_3 management strategies in the southeast United States and other parts of the country that focus on NO emissions will be more effective in decreasing O_3 concentrations in the lower levels of the troposphere than will be O_3 management strategies, which focus on decreasing anthropogenic emissions of volatile organic compounds (Slemr and Seiler 1991). In addition, ozone nonattainment events occur when NO/O_3 plumes from a variety of sources intersect and produce a cumulative ozone concentration in excess of an ambient air quality standard. Consequently, all sources of NO emissions, including NO from chemical fertilizer and sludge-amended soil, must be studied and accounted within an airshed.

CONCLUSIONS

With the development of sophisticated experimental equipment and procedures the results of this research suggest how complex factors act together to produce NO flux to the troposphere. NO flux from unamended soil and soil amended with municipal wastewater sludge is the result of complex interactions among microbiological, chemical, and mechanical transport factors that produce the NO in the soil and subsequently transform and transport it to the soil-atmosphere interface. The importance of soil WFPS and nitrogen source and form are focused on and discussed here in terms of changes in NO production and transport through the soil. Specific conclusions of the research are as follows:

1. Newly designed sophisticated experimental equipment and procedures can provide insight into very small (ppbv) changes in NO flux as complex experimental conditions are controlled and changed in the laboratory. The laboratory results are reproducible and are generally consistent with observations made during uncontrolled field studies of non-sludge-amended soils.
2. Sludge-amended soil tends to flux more NO to the troposphere than unamended soil: 42 ng $N/m^2 \cdot s$ compared to 3 ng $N/m^2 \cdot s$ for 3% WFPS. Enhanced NO flux from sludge-amended soil is suggested to be a result of complex changes in WFPS, pH, temperature, microorganism population(s), as well as nitrogen content and form.
3. Soil water content, as measured by WFPS, is extremely important in the formation, transformation, and soil transport of NO. At low WFPS (<2%), NO flux is all but precluded. In midrange WFPS (>2 and <40%), NO flux reaches a plateau. At high WFPS (>50%), NO flux de-

creases with increasing WFPS. Microbiological activity requires water, but too much water closes the soil pore spaces. Pore spaces filled with water limit the diffusive transport of NO.

4. The results generally support the findings of previous research focused on field observations of agriculture soil under uncontrolled environmental conditions (Chase et al. 1968; Davidson et al. 1993; Hutchinson et al. 1993; Aneja et al. 1995, 1996). For example Aneja et al. (1996) reported NO fluxes in the range of 3–8 ng $N/m^2 \cdot s$ for agricultural soil in eastern North Carolina. The ranges of NO flux reported here for non-sludge-amended soil are between 2 and 17 ng $N/m^2 \cdot s$.
5. The upper layers of soil contribute the larger portion of the NO flux from the soil to the troposphere. More than 42% of the total NO comes from the top 1 cm of soil, with soil depths >20 cm contributing very little if any NO to the troposphere. These respective source layers of NO reflect important oxygen, water, and transport factors that lead to NO movement from the soil to the lower levels of the troposphere.
6. Future research is suggested to better understand the factors involved with the formation, transformation, and soil transport of NO, particularly in sludge-amended soils. Future research should consider pH, temperature, microorganism population(s), water in the soil that is available for NO production and transformation as well as nitrogen source and application rate, the changing vertical soil moisture profile, and plant root uptake of nitrogen. Connections between NO flux from sludge-amended fields and O_3 formation in regional airsheds must be studied. The goal must be to develop this understanding to the point where NO flux to the atmosphere can be controlled thus conserving nitrogen in the soil for plant utilization while limiting NO as a precursor to troublesome O_3 formation in the lower troposphere.

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APPENDIX II. NOTATION

The following symbols are used in this paper:

A = measured surface area of soil column;
B = fitted constant;
C = NO concentration in chamber (as measured by analyzer);
$[C]_f$ = NO concentration at outlet of chamber;
$[C]_0$ = NO concentration at inlet of chamber;
J = flux of NO from soil;
k = fitted constant;
L = loss of NO on chamber and exit tube walls;
P_b = soil bulk density;
P_p = soil particle density;
Q_m = gravimetric water constant measured (g);
Q_v = percent volumetric water content;
R = chemical production/destruction rate for NO in chamber and exit tubes;
TP = total soil porosity;
V = measured volume of gas headspace above the soil sample;
x = depth of soil (cm); and
y = contribution of NO from each layer of soil.