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Measurement of Soil NO_x Emissions in Central Pennsylvania

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Soil emissions of NO and NO_2 were measured at forest and agricultural sites in Pennsylvania. The strong dependence of NO emissions on soil temperature observed in earlier studies was also found in these measurements. The large variation in the measured NO flux at these sites indicated that variables other than soil temperature play an important role. In the present study the strong correlation between the NO flux and the soil nitrate level suggests that the level of available nitrate in the soils may affect NO emission. In this connection it should be noted that the application of chemical pesticides, as well as nitrate-containing fertilizer, may influence these results. In these studies, NO_2 accounted for a minor fraction (6%) of the nitrogen oxide emissions. Laboratory studies designed to investigate the influence of certain environmental and experimental factors on NO emissions under controlled conditions were also conducted. These results also indicate that temperature has a large effect on soil NO emissions, while flush gas humidity and carbon dioxide level exert little, if any, effect.

INTRODUCTION

Nitrogen oxide ($NO + NO_2 = NO_x$) emissions from soils are recognized as being a significant source of atmospheric NO_x [*Logan*, 1983, and references therein]. However, the magnitude of this source is subject to considerable uncertainty. For example, *Hahn and Crutzen* [1982] estimate that soils may represent between 0% and 29% of the total global source. *Stedman and Shetter* [1983] indicate a soil source of NO_x that is between 13% and 50% of the global total, while *Logan* [1983] estimates that between 7% and 30% of the global total NO_x source arises from microbial activity in soils.

At the time that those estimates were published, only one set of soil NO_x emissions data was in the literature [*Galbally and Roy*, 1978]. Since then, several other studies have been conducted [*Johansson*, 1984; *Johansson and Granat*, 1984; *Slemr and Seiler*, 1984; *Delany et al.*, 1986; *Anderson and Levine*, 1987; *Williams et al.*, 1987]. These studies were conducted at different regions around the globe and under a wide variety of climatic and soil conditions. As a consequence, the data exhibit considerable variability and do little to reduce uncertainties in NO_x soil source strength estimates.

In order to substantially improve the estimates it is necessary to produce a data base that reveals factors, such as temperature, soil type, soil moisture, *p*H, and soil nitrate and/or ammonium, that influence soil emissions. The objective is to generate algorithms that relate NO emissions to these factors in order to obtain estimates of NO emission as a function of location and season. In addition, a precise knowledge of the dependence of NO emissions on these factors gives insights into the biogenic mechanisms responsible for the NO generation. Because of the variability of these factors in nature and the complexity of the biogenic response to them, additional field studies, as well as investigations under controlled laboratory conditions, are required.

During the summer of 1986 the soil emissions of NO and NO_2 were measured at two sites in central Pennsylvania. The first site was in an uncultivated, ungrazed forest clearing. The second site was in an agricultural area where the soils were altered by the methods and treatments common to modern agriculture. These results are compared with an extensive data set collected at a Colorado site [*Williams et al.*, 1987] and are discussed in terms of the chemical and physical factors influencing the soil at these sites. Laboratory experiments were also conducted. These were performed to investigate the influence of certain environmental variables, such as flush gas moisture content, carbon dioxide levels, and temperature, on NO emissions from a potting soil.

EXPERIMENTS AND RESULTS

Field Measurements

The field measurements were carried out at two locations in central Pennsylvania near State College. Both locations are operated by Pennsylvania State University.

Detailed descriptions of the measuring equipment and the experimental arrangement have been given previously [*Parrish et al.*, 1987] and will be outlined only briefly here. Nitric oxide is measured via chemiluminescent reaction with ozone. The instrument used in this work has a detection limit of 2 pptv (parts per trillion by volume) NO for an integration time of 10 s. Nitrogen dioxide is measured by photolytic conversion to NO followed by chemiluminescence detection. The detection limit for NO_2 is 10 pptv for a 10-s integration time. Ancillary measurements included ambient air temperature, ambient dew point, wind speed and direction, pressure, solar radiation, precipitation, and ambient ozone (model 49, Thermo Electron Corporation, Waltham, Massachusetts).

Measurements of soil emissions were performed via a chamber method. Stainless steel frames (approximately 0.1 m^2) were driven into the ground to a depth of approximately 10 cm. A Teflon-lined chamber (approximately 27 L in volume)

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TABLE 1. Soil Characteristics of the Pennsylvania Field Sites

	Scotia	Rock Springs	
		Wheat Field	Corn Field
pH	5.9 (0.52)	6.7 (0.2)	6.2 (0.5)
Organic matter, %	2.4 (1.0)	2.4 (1.0)	2.0 (0.1)
Texture	sandy loam	clay loam	clay loam
Soil mixture, %	7.3 (1.6)	9.8 (1.3)	8.7 (0.9)
Soil temperature, °C	27.5 (2.8)	27.1 (4.3)	22.7 (1.6)
NO_2^- N, ppm	<0.1	<0.1	<0.1
NH_4^+ N, ppm	16.7 (7.8)	7.8 (2.1)	9.2 (4.8)
NO_3^- N, ppm	0.75 (0.56)	4.8 (1.3)	40.6 (58.9)

Values in parentheses are the standard deviations.

was placed over the frame and held in place by means of a grooved collar which mated to a lip on the frame. Zero air flush gas flowed through the chamber, providing mixing within the enclosure and eliminating complications arising from ambient NO_x and ozone. Measurements by *Goldan et al.* [1987], using a similar chamber, indicated a negligible pressure gradient (< 0.01 torr) across the chamber wall. The flush gas flow rate was nominally 4 L/min STP but was occasionally varied for determination of possible uptake effects. Also, the chamber has provision for the insertion of a gas line which carries NO calibration gas. This standard addition experiment also was performed in order to determine possible uptake effects. The NO level in the chamber was monitored until a steady state level was achieved (after about 20–30 min). This steady state level was used to calculate the soil emission. A correction for soil uptake of NO, which was not necessary in previous studies [*Williams et al.*, 1987], was required here and is discussed later. At the end of each measurement, soil temperature, both inside and outside of the frame, and the air temperature inside the enclosure were recorded. The soil temperature was measured using a chromel-alumel thermocouple. This thermocouple was shielded and inserted approximately 5 cm into the soil. The estimated uncertainty in this temperature was no greater than 1 K. During the period of the measurement there was no significant change in the soil temperature. Soil moisture levels were monitored by measurement of weight loss of soil samples on drying. These values are reported as percent dry weight. The analysis of the soil samples was done by the Soil Testing Laboratory, Colorado State University, Fort Collins.

In addition to the enclosure flux determinations, measurements of soil NO emissions were also made via a gradient technique. This method has been described elsewhere [*Parrish et al.*, 1987] and will only be outlined here. During nighttime hours the major sink for NO in the atmosphere is reaction with ambient ozone. If conditions can be selected such that a spatially uniform soil NO source provides the only input to atmospheric NO, then one can relate the decrease in NO with height to that soil source and atmospheric sink. This relationship can be obtained by making some reasonable assumptions about the vertical mixing in the atmosphere where, during nighttime hours when these measurements were made, there is little convective turbulence.

The model that we employ assumes that this vertical mixing can be described by an eddy diffusion parameter that increases linearly with height. With the only atmospheric sink for NO being reaction with ozone and the only source being the soil, by knowing the vertical mixing behavior the model can predict the nighttime gradient of NO. Standard gradient curves are generated by the model for different regimes of source and sink strengths. Then the measured NO gradient is compared with these standard curves until a best fit is obtained. Adjustment of the fit for differences in ozone levels and temperatures and pressures that are measured simultaneously with the NO gradient allows the model to produce a value for the net NO soil emission for those conditions.

This gradient method has been extensively intercompared with our enclosure technique at a Colorado grassland site [*Parrish et al.*, 1987]. Excellent agreement between these two independent methods was obtained over a three order of magnitude range of soil NO emissions.

Scotia. The first site is approximately 4 mi (6.4 km) west of State College. In the early 1960s a clearing within a mixed coniferous-deciduous forest was established by removal of approximately 18–24 in (45–60 cm) of topsoil and vegetation. Since then, low shrubs, grasses, and small trees have been reestablished, but the area is still free of thick forest. A number of soil samples were taken for analysis. These data, shown in Table 1, indicate that this soil is a somewhat acidic and reasonably well drained sandy loam that contains moderate amounts of ammonium nitrogen but low levels of nitrate and nitrite nitrogen.

At this site, six small areas were demarked for study by insertion of the enclosure frames into the ground. These frames were placed such that bare ground, as well as small amounts of vegetation, were included for study. The total area spanned by the six frames was approximately 25 m^2. At the Scotia site and at the Rock Springs site (see below) most of the frames were placed in the ground at least 24 hours prior to starting measurements. This time period for equilibration of the frame with the soil-plant system appeared to be adequate, since over the measurement period no systematic trend could be found in the data from any given frame.

Soil emissions were measured at the Scotia site from July 25 to July 30, 1986. Table 2 presents a summary of the data collected from each of the six frames. The NO flux ranged from 0.18 ng N m^2 s^{-1} to 4.10 ng N m^{-2} s^{-1}, while the average NO soil emission for all 32 data points was 1.20 ng N m^{-2} s^{-1}. The flux of NO_2 averaged 0.077 ng N m^{-2} s^{-1}. The soil temperatures ranged from 23.2°C to 33.5°C. Soil moisture, as noted in Table 1, averaged 7.3%.

Rock Springs. The second location, Rock Springs, is an experimental farm that is managed by the Department of Agriculture of the Pennsylvania State University. Soil emissions were measured from two distinct sites. The first was a field of corn planted using a typical no-till method. Aside from the live corn stalks, the field was bare of other vegetation. This field was fertilized in June 1986 with urea (15 kg ha^{-1}) and NH_4NO_3 (15 kg ha^{-1}). The second sampling site was a wheat field that had been recently (within 1 week) harvested. In addition to the wheat stubble in that field, there were also small grasses and weeds growing. This field had been last fertilized in 1985. Analyses of soil parameters at these sites are also shown in Table 1. The soil in both the wheat field and the corn field is a clay loam and is slightly more alkaline and moist than soil at the Scotia site. The average soil temperature of the wheat field is comparable to that at the Scotia site but is higher than that of the corn field because of shading by the corn stalks, which were 6–8 feet (2–3 m) tall at this time. The ammonium nitrogen in these two fields is comparable but is lower than that at the Scotia site by about a factor of 2. The

nitrate nitrogen levels, however, are much higher and considerably more variable than those at the Scotia area. Moreover, the nitrate levels in the corn field are, on average, a factor of 10 higher than those in the wheat field. Finally, the corn field was subject to the application of a wide spectrum of pesticides, including herbicides (Atrazine, Roundup, Bladex), an insecticide (Furadan), and a germination inhibitor (Dual).

A map of the Rock Springs site is shown in Figure 1. At this site, seven frames were placed in each of the two fields. In the corn field, frames were placed in between corn rows as well as in small open areas away from the corn plants. Since the wheat field appeared to be somewhat uniform, the frames were placed in rows without regard to any distinct forms of vegetation. The newly harvested wheat field also provided a very uniform fetch of at least 100 m for 180° about the gradient tower (see Figure 1). The NO gradient was measured at 50- and 200-cm heights continuously from sunset to sunrise between August 6 and August 15. Occasionally, the enclosure was used to simultaneously measure the NO flux from a single frame in the wheat field. Because of the close proximity and consequent interference of the strong corn field NO source, only three periods of light and steady wind from the south to the west quadrant were amenable to calculation of the gradient flux from the wheat field by the gradient method. These results are shown in Table 3.

Emissions of NO from the wheat field were as low as those from Scotia and the most uniform of all three sites. Table 2 summarizes the data from each of the seven frames that were located in this field. The NO flux ranged from 0.21 ng N m^{-2} s^{-1} to 3.8 ng N m^{-2} s^{-1}, and the average of the 119 data points was 1.2 ng N m^{-2} s^{-1}. The average flux of NO_2 was 0.071 ng N m^{-2} s^{-1}. The maximum and minimum soil temperatures at this site were 34.9°C and 17.2°C. Average soil moisture was highest in the wheat field at 9.8%. Also shown in Table 2 are nitrate and ammonium nitrogen levels for four individual frames. These samples were taken from within the frame area at the end of the study. The uniformity of the flux measurements is reflected in the soil nitrogen levels.

TABLE 2. Summary of Data for All Pennsylvania Sites

Frame	NO Flux*, ng N m^{-2} s^{-1}	NO_2 Flux*, ng N m^{-2} s^{-1}	Nitrate, ppm	Ammonium, ppm
		Scotia		
1	0.56 (0.18)	0.031	0.8†	17†
2	1.4 (0.43)	0.072	...	...
3	2.1 (1.4)	0.015	...	...
4	0.45 (0.19)	...	...	...
5	0.22 (0.04)	0.14	...	...
6	0.76 (0.58)	...	...	...
		Rock Springs Wheat Field		
1	0.86 (0.43)	0.069 (0.057)	4	5
2	0.67 (0.26)	0.032 (0.033)	6	10
3	1.7 (0.62)	0.15 (0.24)	...	...
4	1.3 (0.79)	0.070 (0.068)	4	6
5	1.4 (0.62)	0.045 (0.020)	...	...
6	1.4 (0.50)	0.044 (0.046)	3	8
7	1.5 (1.1)	0.088 (0.068)	...	...
		Rock Springs Corn Field		
1	178 (83)	4.4 (3.7)	50	7
2	26 (14)	2.7 (2.5)	6	6
3	99 (47)	0.75 (0.84)	165	16
4	9.4 (2.2)	0.23 (0.12)	17	6
5	133 (42)	0.46	176	22
6	212 (64)	27	...	...
7	4.5 (2.5)	1.1	...	...

*Average value (standard deviation).
†Site-wide average.

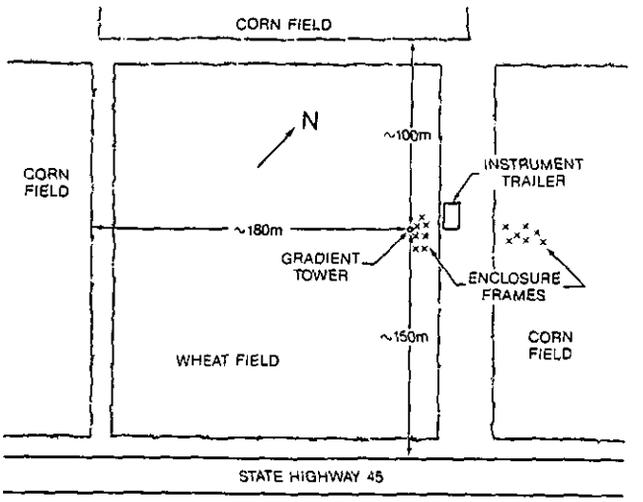

Fig. 1. Schematic diagram of the Rock Springs site. The small crosses correspond to the frames that were used to collect the chamber flux data.

In contrast, NO emissions from the corn field were, on average, much greater and showed much larger spatial and temporal variability. These data, associated with the seven frames located in the corn field, are shown in Table 2. The maximum flux measured at this site was 338 ng N m^{-2} s^{-1}, the minimum flux was 1.6 ng N m^{-2} s^{-1}, and the average of the 89 data points was 94 ng N m^{-2} s^{-1}. In contrast to the wheat field data the frame-to-frame averages in the corn field differed by as much as a factor of 50. The average NO_2 emission was 3.8 ng N m^{-2} s^{-1}. The average soil moisture was 8.7%. Table 2 also shows soil nitrogen levels from five separate frames. In this instance the soil ammonium levels were relatively constant, while the soil nitrate levels varied widely. This variation is reflected as well in the soil NO emissions.

Laboratory Studies

A series of laboratory tests were conducted in order to identify the role played by various environmental and experimental factors in controlling NO emissions from soils. These studies utilized an environmental chamber (Percival, model I-35LLX) that is capable of controlling light intensity and temperature. This chamber has been used in a similar application to study the emission of sulfur species from biogenic sources [*Fall et al.*, 1988]. The experimental arrangement used for these studies is shown in Figure 2 and was designed to

TABLE 3. Results of Gradient Flux Measurements

	Time, EST	Soil Temperature, °C	Flux, ng N m^{-2} s^{-1}
Aug. 6	0245–0345	19	1.09
Aug. 14	2200–2300	19	1.33
Aug. 15	0030–0130	18	0.84

The average of the wheat field enclosure measurements for 19°–24°C is 0.92 ± 0.52 ng N m^{-2} s^{-1}.

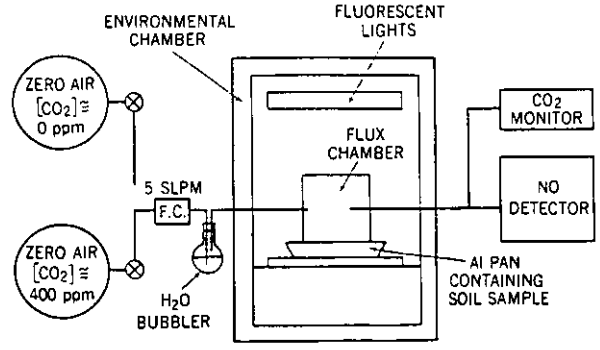

Fig. 2. Laboratory system used to assess the effects of various environmental factors on NO emissions from a potting soil. The environmental chamber is capable of controlling temperature and lighting.

simulate the enclosure method used to collect the field data. Samples of a potting soil (Baccto, Michigan Peat Company, Houston, Texas) were placed in aluminum pans of approximately 3 inches (7.5 cm) depth. The pan was placed in the environmental chamber, and adequate time was given for the soil to equilibrate with the internal conditions of the chamber. The enclosure used to measure the NO emissions was then placed on the soil sample (no frame had been installed), and the NO flux was determined. The NO detector used in this work was a commercial NO analyzer (model 14B/E, Thermo Electron Corporation, Waltham, Massachusetts) that was modified using the approach of *Delany et al.* [1982].

The results from the chamber tests can be summarized as follows:

1. Emissions of NO were measured at different temperatures. These data are shown in Figure 3. When plotted as log (flux) versus temperature, an excellent correlation ($r^2 = 0.9996$) is obtained.

2. The influence of humidity was investigated by placing a bubbler containing deionized water in line with the flush gas. The emission of NO was measured with dry air and with water-saturated air. At 4 L/min STP, the level was 81.1 ng N m^{-2} s^{-1} for dry air and 103 ng N m^{-2} s^{-1} for moist air, a difference in flux of 27%.

3. The effect of carbon dioxide was investigated by using zero air with (~400 ppm) and without CO_2. The average value of three runs with CO_2 was 177 ± 5.3 ng N m^{-2} s^{-1}, and the three-run average without CO_2 was 170 ± 7.9 ng N m^{-2} s^{-1}. Interestingly, the level of CO_2 in gas exiting the chamber was roughly the same (~ 550 ppm) regardless of the CO_2 level of the flush gas entering the chamber.

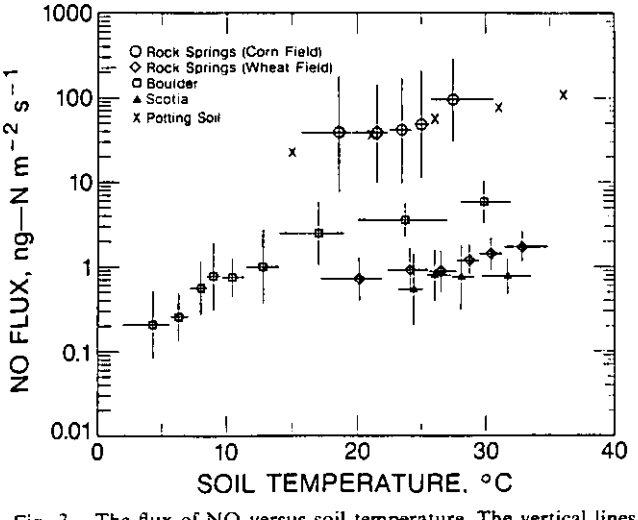

Fig. 3. The flux of NO versus soil temperature. The vertical lines represent the standard deviations of the average NO flux measured over the soil temperature range spanned by the horizontal bars.

DISCUSSION

Field Studies

Enclosure measurements. The flux of NO from soils depends strongly on temperature. This has been previously noted [*Johansson and Granat*, 1984; *Johansson*, 1984; *Slemr and Seiler*, 1984; *Williams et al.*, 1987; *Anderson and Levine*, 1987]. The relationship that we have observed is shown in the data presented in Figure 3. This plot contains the measurements that were made at a grassland site in Colorado [*Williams et al.*, 1987], the results from the Pennsylvania sites, and the data from the laboratory study. Although the magnitude of the emissions from the different locations varies considerably, the dependence of the emission on soil temperature at all locations is similar. This suggests that the biogenic mechanisms responsible for the emissions are common to all locations. The species diversity of nitrifying and denitrifying bacteria has been studied [*Focht and Verstraete*, 1977, and references therein], and these organisms have been found in a wide variety of environments. The biochemical pathways of nitrification and denitrification have similarly been investigated [*Focht and Verstraete*, 1977; *Chalamet*, 1985], and common features among many organisms have been noted. For example, while the optimum temperature for denitrification may vary from one area to another, the rate of denitrification increases by approximately a factor of 2 for every 10°C increase in temperature [*Haynes and Sherlock*, 1986]. This is consistent with the temperature relationships that are shown in Figure 3. It is then not unexpected that similar behavior is observed in the emission of NO, with respect to temperature, at widely different locations.

The most obvious factor that may account for the difference observed in the magnitude of NO flux recorded at these locations, as well as the degree of variability in emissions between frames within a single location, lies in the level and variability of the nitrogen content of the soils. The two largest components of inorganic (hence readily available) soil nitrogen are nitrate and ammonium. Figure 4 shows the relationship between flux and soil nitrate. At the Rock Springs site, soil samples were taken from selected frames. For the two field studies at this site the nitrate concentration from a soil sample in each frame is plotted versus the average NO flux emitted by the soil enclosed by the frame for a temperature range between 20°C and 30°C. In the case of the Scotia and Boulder sites the nitrate levels were recorded from several soil samples taken at the site. The average of these nitrate concentrations is plotted versus the average NO flux exmitted at the site for soil temperatures between 20°C and 30°C. The 26°C data point from the laboratory study is also shown. The correlation between NO emission and soil nitrate is clearly evident in these data. There was no obvious correlation between NO emission and soil ammonium levels (data not shown).

Other investigators have noted that addition of nitrate fertilizers to soil can stimulate NO emissions. *Johansson and Granat* [1984] noted that addition of calcium-nitrate-to-agricultural soils increased NO fluxes threefold. Similar stimu-

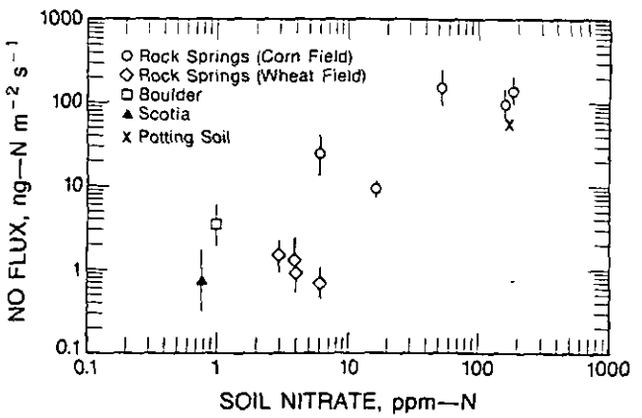

Fig. 4. The flux of NO versus the nitrate content of soil. Symbols shown in the legend also correspond to those in Figure 3. At the Rock Springs site, soil samples were taken from within individual frames. At the Scotia and Boulder sites, samples of soil were taken, and a site-wide average was computed. The NO flux is an average over a temperature range of 20°–30°C.

lations have been reported for forest soils treated with nitrate nitrogen [*Johansson*, 1984; *Kaplan et al.*, 1988]. In contrast, there are reports that show little correlation of NO fluxes with soil nitrate levels [*Slemr and Seiler*, 1984; *Anderson and Levine*, 1987]. Clearly, more information is needed on the dynamics of nitrogen cycling in soil populations of denitrifying and nitrifying bacteria, the major biological sources of soil NO fluxes. Since denitrifiers (and possibly nitrifiers) can also act as a sink for NO [*Knowles*, 1982], the models for the regulation of net NO fluxes from soil will need to consider (1) the population dynamics of these groups of bacteria, (2) the role of heterotrophic nitrification and aerobic denitrification [*Knowles*, 1982], (3) the available inorganic and organic nitrogen species, and (4) the physical variables (e.g., temperature and soil moisture) that influence soil emissions. Finally, while pesticides were applied to the corn field, no tests (such as pesticide amendments to the soil) were performed to determine the effects of these compounds on emission of NO. Information does exist regarding pesticide effects on soil biological activity [*Somerville and Greaves*, 1987], but the complexities involved in such systems are substantial. More research is needed in this area.

Although the soil moisture levels encountered during this study were always adequate to support NO emission, no simple relationship between emission of NO and soil moisture could be discerned from the data. Laboratory studies by *Anderson and Levine* [1986] indicated that NO emission should take place over a wide range of soil moisture conditions, provided that the biogenic entities responsible for the emissions are not stressed by lack of water and that the soils are not water saturated. Field studies [*Williams et al.*, 1987; *Anderson and Levine*, 1987; *Slemr and Seiler*, 1984] have noted that NO emissions are suppressed in dry soils; however, subsequent irrigation produces very large increases in flux. It is likely that these observations are related to the principal nitrogen transformation processes that occur in soils, that is, nitrification and denitrification. While both processes contribute to the emission of NO from soils [*Focht and Verstraete*, 1977], they occur optimally under widely different conditions (soil nitrogen content, aerobic versus anaerobic regimes, *p*H, etc.), and it is probable that the soil moisture level is an important (possibly controlling) factor in determining which process is dominant. For example, under dry conditions the soil becomes aerated, which promotes nitrification, while denitrification occurs primarily under anaerobic conditions. In any case, the relationship between emission of NO and soil moisture is complex and warrants further study.

In the present studies, NO_2 levels in the enclosures were also measured. In an earlier study [*Williams et al.*, 1987] it was noted that NO_2 was emitted and also rapidly removed by the soil-vegetation system contained by these enclosures. The net recovery of NO_2 from the enclosure depended strongly on factors such as the wetness of the vegetation. Calibrated flows of NO_2 that passed through the enclosure indicated that there was only a small loss of NO_2 to the walls. A similar situation was noted with regard to the NO_2 measurements made in Pennsylvania, although systematic experiments of uptake of NO_2 (similar to those for NO, see below) were not conducted. Measurements made at the wheat field before and after removing vegetation from within a frame indicated that the removal caused large increases in NO_2 levels. In one case a factor of 8 was noted, and in a second case the emissions of NO_2 were a factor of 56 higher. For the corn field, which was already free of vegetation except for the cornstalks, the NO_2 levels were quite varied. Although they were much higher in magnitude ($\times$ 100) than the wheat field NO_2 levels, as a percentage of NO emissions they were lower (4% as opposed to 6%). Only a few NO_2 measurements were made at Scotia, and these results were similar to those of the wheat field. Overall, at the Pennsylvania sites the soil emissions of NO_2 averaged about 6% of the NO emissions.

Gradient measurements. Because chamber measurements were not made concurrently with the few gradient flux data points that were measured, direct comparison of measured NO fluxes between the gradient and the chamber techniques is not possible. What has been done is to compare the average of the gradient flux determinations to the average of all wheat field enclosure measurements for the temperature range of interest. Based on this analysis, the average gradient flux is about 28% greater than the average chamber flux (see Table 3). However, it is possible that, even with this carefully selected set of gradient flux determinations, there is still some interference in these measurements by NO from the corn field. Nevertheless, the agreement is quite good and provides independent confirmation of the measured NO emission rates.

Deposition measurements. The method by which the NO emission (as determined by the enclosure) is calculated assumes no less of NO due to uptake by the soil [*Parrish et al.*, 1987]. The validity of this assumption is evaluated by tests and checks which are used to determine whether any uptake of NO occurs in the chamber during measurements. If significant loss of NO occurs, then the emission rate is determined by inclusion of an uptake component in the calculation (see the appendix, equation (1)). This emission rate, then, reflects the gross rate of NO release from the soil. The uptake component is estimated by determining the variation of NO emission with chamber flush gas flow rate or by performing a standard addition of NO to the chamber and measuring the amount recovered. The procedures for calculation of this loss term via these two approaches are shown in the appendix.

We assume here that the deposition of NO occurs via a single-step process that can be described by a surface resistance and that the inverse of this term is an upper bound to the deposition velocity. However, because it is unlikely that mixing in the chamber is similar to mixing in the atmosphere,

TABLE 4. Calculated Deposition Velocities

	Frame	Soil Temperature, °C	Flow, L/min (STP)	NO_{eq}, ppbv*	NO Standard Addition, ppbv	Recovered NO, ppbv	r^{-1}, cm/s
			Wheat Field Flow Variation Experiments				
Aug. 6	W1	···	3.93	0.91			0.089
Aug. 6	W1	26.9	9.67	0.54			
Aug. 6	W2	···	3.93	0.59			0.048
Aug. 6	W2	···	9.67	0.31			
Aug. 7	W6	···	3.93	2.55			0.0057
Aug. 7	W6	···	9.67	1.08			
Aug. 7	W7	···	3.93	0.94			0.098
Aug. 7	W7	···	9.67	0.57			
Average							0.060 (±0.042)
			Corn Field Flow Variation Experiments				
Aug. 5	C4	25.3	3.93	12.6			0.073
Aug. 5	C4	···	9.67	7.17			
Aug. 5	C5	28.8	3.93	322			0.00014
Aug. 5	C5	27.3	9.67	131			
Average							0.037 (±0.052)
			Wheat Field Standard Addition Experiments				
Aug. 8	W1	23.1	3.93		3.17	2.67	0.014
Aug. 8	W1	28.7	3.93		3.17	1.09	0.15
Aug. 8	W2	28.4	3.93		3.17	1.94	0.050
Aug. 13	W2	23.1	3.93		3.17	1.77	0.062
Aug. 8	W3	27.8	3.93		3.17	1.93	0.050
Aug. 13	W3	20.6	3.93		3.17	1.76	0.063
Aug. 7	W6	···	1.93		6.56	4.94	0.013
Aug. 7	W6	···	3.93		3.22	2.86	0.0099
Aug. 6	W6	29.6	3.93		3.22	2.18	0.037
Aug. 7	W6	···	9.67		1.31	1.04	0.051
Aug. 7	W7	32.3	1.93		6.56	2.65	0.057
Aug. 7	W7	···	3.93		3.22	1.87	0.057
Aug. 7	W7	···	9.67		1.31	0.84	0.11
Average							0.055(±0.039)

*Equilibrium mixing ratio of NO at the end of the enclosure flux measurement in parts per billion by volume.

the surface resistance values reported here are applicable only for the experimental conditions under which they were determined [*Galbally and Roy*, 1980]. Nevertheless, it is interesting to compare the value determined in this work (Table 4) to those reported in the literature. Laboratory measurements by *Judeikes and Wren* [1978] showed NO deposition velocities of 0.19, 0.13, and 0.21 cm/s over sandy loam, adobe clay, and cement, respectively. *Granat and Johansson* [1983] measured NO deposition to spruce and pine trees in winter, as well as to snow (melting to −14°C). These results indicated deposition velocities of no more than 0.03 cm/s. *Gravenhorst and Böttger* [1983] report a deposition velocity of 0.02 ± 0.015 cm/s for NO over soil. The average of the inverse surface resistance values reported in this work is 0.055–0.060 cm/s for the wheat field and 0.037 cm/s for the corn field. These values are in the range of those measured previously.

Because it was not possible to obtain NO uptake measurements for all conditions and for all of the study areas in the wheat and corn fields, the soil NO emission data reported here have been corrected for an average uptake. These corrections are 73% for the wheat field data and 46% for the corn field data and are comparable to the variability observed in the emissions measured from the individual frames (see Table 2). That these average corrections are reasonable can be seen by comparison of data from the enclosure and gradient methods, where the disagreement between these two independent techniques is not more than 30%. Unfortunately, no uptake measurements were conducted at the Scotia site, so these data are presented in their uncorrected form.

With measurements of both NO emission and NO uptake, the net NO emission from a site can be estimated. However, because the reaction of NO and ambient O_3 is fast, a fraction of the emitted NO is converted within minutes to NO_2. While we have an estimate of NO_2 emission at these sites, we have no quantitative measure of NO_2 uptake, and without this information we cannot make any estimate of net NO_x flux. We intend to address this point in future work.

Laboratory Studies

A systematic influence on soil NO emission is seen from the variation of soil temperature (cf. Figure 3). In laboratory studies, as well as in the field measurements, the flux of NO is highly correlated with soil temperature. The dependence of NO emissions on temperature obtained from measurements made on potting soil in the laboratory is very similar to those relationships recorded from natural soil samples. This is illustrated in Figure 3 and adds further evidence in support of a common biogenic mechanism.

The NO emission from the laboratory soil sample was large. Likewise, the nitrate level in the sample was substantial and fits well with the trends of NO emission versus soil nitrate level shown in Figure 4.

The effect of flush gas water vapor level on NO flux was small (27%), and there was no significant variation in NO level with variation of the CO_2 level in the flush gas. Thus it is reasonably clear that for NO flux measurements in the field that use enclosures and artificial air mixtures as flush gases, neither the moisture content nor the CO_2 level of the flush gas will significantly bias the data.

CONCLUSIONS

From the data that we have collected at the sites in Pennsylvania and Colorado, as well as from the laboratory studies, only a few parameters have been identified that have a large impact on the emission of NO from soil. The similarity seen in the relationship between soil temperature and NO emission for the various data sets is remarkable in light of the diverse nature of the soils over which the emissions were measured. The correlation between soil nitrate and NO emission is important, for this relationship may provide insight into the processes which occur in the soil that are responsible for the production of NO. Our data indicate that soil nitrate may be a significant factor with respect to NO emission, but a larger data base is necessary in order to confirm this. Yet another factor which affects soil NO flux is soil moisture. From the data that we have collected there is, as yet, no clearly defined, simple relationship between these two parameters. Another potential influence on soil NO flux is the application of pesticides and other chemicals to agricultural soils. Large areas in the United States and other areas of the globe are subject to the use of fertilizers and biocides. These practices may have a great impact on soil NO sources, especially in rural areas.

APPENDIX: METHODS FOR CALCULATION OF SURFACE RESISTANCE

Standard Addition Method

In order to calculate a loss term from a standard addition of NO to the chamber, the following must be assumed: (1) the chamber atmosphere is well mixed, (2) the only loss is uptake of NO by soil, and (3) the soil emission is constant over the course of the measurement. Then for a flux measurement the NO concentration in the chamber is described by

$$\frac{d(\mathrm{NO})}{dt} = \frac{E}{h} + \frac{Q}{V}(\mathrm{NO})_{IN} - \frac{r^{-1}}{h}(\mathrm{NO}) - \frac{Q}{V}(\mathrm{NO})$$

where E is the emission from the soil to the chamber, r is the surface resistance, Q is the volume flow rate of the flush gas, h is the chamber height, V is the chamber volume, and $(\mathrm{NO})_{IN}$ is the nitric oxide level in the flush gas. If the flush gas is zero air, $(\mathrm{NO})_{IN}$ is zero and at steady state:

$$0 = E - r^{-}(\mathrm{NO})_{ss} - \frac{Q}{A}(\mathrm{NO})_{ss} \qquad (1)$$

where A is the area of the enclosed soil surface and $(\mathrm{NO})_{ss}$ is the measured NO level in the chamber at steady state. For a flux determination with a standard addition of NO to the flush gas, the NO concentration in the chamber is described by

$$\frac{d(\mathrm{NO})}{dt} = \frac{E}{h} + \frac{Q}{V}(\mathrm{NO})_c - \frac{r^{-1}}{h}[(\mathrm{NO})^1 + (\mathrm{NO})_{ss}] - \frac{Q}{V}[(\mathrm{NO})^1 + (\mathrm{NO})_{ss}]$$

where $(\mathrm{NO})_{IN}$ equals $(\mathrm{NO})_c$, which is the (known) standard gas concentration added, and $(\mathrm{NO})^1$ is the increase in the measured NO level in the chamber when the standard addition is made. At steady state,

$$0 = E + \frac{Q}{A}(\mathrm{NO})_c - r^{-1}[(\mathrm{NO})_{ss}{}^1 + (\mathrm{NO})_{ss}] - \frac{Q}{A}[(\mathrm{NO})_{ss}{}^1 + (\mathrm{NO})_{ss}] \qquad (2)$$

Subtracting (1) from (2) yields

$$0 = \frac{Q}{A}(\mathrm{NO})_c - r^{-}(\mathrm{NO})_{ss}{}^1 - \frac{Q}{A}(\mathrm{NO})_{ss}{}^1$$

Therefore

$$r^{-1} = \frac{Q}{A}\left[\frac{(\mathrm{NO})_c - (\mathrm{NO})_{ss}{}^1}{(\mathrm{NO})_{ss}{}^1}\right] \qquad (3)$$

In practice, once a flux measurement has reached a steady state point, the NO calibration standard is added, and a new steady state level is reached. Once r^{-1} is evaluated, (1) yields the emission rate E.

Flow Variation Method

By using equation (1) for two different flow rates and combining them to eliminate E (assumed constant), one derives the following equation for the surface resistance:

$$r^{-1} = \frac{Q_B(\mathrm{NO})_{ss}{}^B - Q_A(\mathrm{NO})_{ss}{}^A}{A[(\mathrm{NO})_{ss}{}^A - (\mathrm{NO})_{ss}{}^B]} \qquad (4)$$

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