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Simultaneous Field Measurements of Biogenic Emissions of Nitric Oxide and Nitrous Oxide

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Seasonal and diurnal emissions of nitric oxide (NO) and nitrous oxide (N_2O) from agricultural sites in Virginia and Colorado were simultaneously determined as a function of soil temperature, percent moisture, and exchangeable nitrate, nitrite, and ammonium concentrations. Nitric oxide fluxes at the Virginia site were significantly correlated ($P < 0.01$) with nitrate concentration, temperature, and percent moisture. At the Colorado site, NO fluxes were both positively and significantly correlated ($P < 0.01$) with temperature and moisture. Nitrous oxide emissions were only observed when percent moisture approached or exceeded field capacity of the soil. Nitric oxide emissions at the Virginia site were observed throughout the entire year with 76% of the annual flux produced between May and October and 24% between November and April. Wintertime fluxes of NO have not previously been reported in the literature. Annual NO emissions at the Virginia site ranged from 0.53 kg(N) ha^{-1} yr^{-1} from unfertilized land to 2.08 kg(N) ha^{-1} yr^{-1} from fertilized land. Of the 196.4 kg ha^{-1} of fertilizer added to the soil site being studied, 0.79% was lost as NO(N), and 1.2% was lost as N_2O(N). A series of diurnal studies demonstrated that variations in NO flux throughout the day were correlated with changes in soil temperature. Nitric oxide was emitted over a broad range of soil moisture conditions, provided that percent moisture did not exceed field capacity of the soil. When field capacity was exceeded, NO fluxes declined whereas N_2O emissions increased. Rewetting of dry soils at the Colorado site resulted in dramatic increases in emissions of both NO and N_2O. Our data suggest that NO is produced primarily by nitrification in aerobic soils whereas N_2O is formed by denitrification in anaerobic soils.

INTRODUCTION

Nitric oxide (NO) and nitrous oxide (N_2O) are both produced by biogenic processes in the soil. Both species are pivotal in the photochemistry and chemistry of the troposphere and stratosphere as well as in the biogeochemical cycling of nitrogen between the biosphere and the atmosphere. In the troposphere, chemically active NO (with an atmospheric lifetime ranging from seconds to minutes before chemical conversion to nitrogen dioxide (NO_2)) leads to the photochemical production of ozone (O_3) and nitric acid (HNO_3), the fastest growing component of acid precipitation [*Logan et al.*, 1981; *Graedel*, 1985]. In addition, NO regulates the photochemical production of the hydroxyl radical (OH), which is the major chemical oxidizer in the troposphere and thus controls the distribution and atmospheric lifetime of almost every biogenic and anthropogenic species [*Logan et al.*, 1981; *Graedel*, 1985]. Nitrous oxide, which is chemically inert in the troposphere (atmospheric lifetime of about 150 years), diffuses up to the stratosphere where about 90% of it is photolyzed by solar ultraviolet radiation, forming nitrogen (N_2) and excited atomic oxygen [$O(^1D)$]. The remaining N_2O (about 10%) reacts with $O(^1D)$, forming either two NO molecules or N_2 and oxygen (O_2). The NO thus formed in the stratosphere causes destruction of ozone which shields the earth's surface from solar ultraviolet radiation [*Turco*, 1985]. The NO_x (NO + NO_2) catalytic cycle is the major chemical destruction mechanism for stratospheric O_3 [*Turco*, 1985]. A portion of the NO formed by the chemical transformation of N_2O in the stratosphere is transported downward, impacting the NO budget of the troposphere (Table 1) [*Levy et al.*, 1980]. This high-altitude source of NO may be more significant than its magnitude implies, since its lifetime in the upper troposphere is longer than that of surface-emitted NO, which is produced in considerably greater quantities [*Liu et al.*, 1980]. In addition to its impact on the photochemistry of the stratosphere and troposphere, N_2O absorbs infrared radiation, thus impacting the climate of the earth/atmosphere system [*Kuhn*, 1985; *Ramanathan et al.*, 1985; *Wang and Molnar*, 1985; *Dickinson and Cicerone*, 1986]. Measurements indicate that atmospheric levels of N_2O are increasing at the rate of about 0.2% per year [*Weiss*, 1981].

It is interesting to note that the calculated thermodynamically equilibrated mixing ratio (mole fraction) of N_2O should be about 2×10^{-19} [*Chameides and Davis*, 1982]. The thermodynamically equilibrated concentration is that calculated by assuming thermodynamic equilibrium with a gas mixture containing 0.78 atm N_2, 0.21 atm O_2, 0.01 atm water vapor, and 3.3×10^{-4} atm carbon dioxide (CO_2) at a temperature of 298°K. The measured mixing ratio of N_2O at the surface is approximately 3×10^{-7}, a trillionfold greater concentration than the calculated thermodynamically equilibrated mixing ratio, suggesting that a significant nonthermodynamic equilibrium source of N_2O exists at the surface, i.e., the biosphere. Biogenic production in soil is the overwhelming source of N_2O and may be a significant source of NO. Other sources include fossil fuel combustion, biomass burning, and atmospheric lightning. For NO there are major uncertainties concerning the magnitude of the global biogenic source, as well as the other sources of NO on a global scale (Table 1). Note that estimates given for the magnitude of the global biogenic source range from zero to 20 Mt(N) y^{-1}. For N_2O, while there is general agreement that biogenic production is the major source on a global scale, there is considerable uncertainty concerning the magnitude of that source. *Stedman and Shetter* [1983] estimate that the biospheric production of N_2O may be as high as 38 Mt N_2O(N) yr^{-1}, which is considerably higher than earlier estimates which range from about 1 to 5 Mt N_2O(N) yr^{-1}.

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TABLE 1. Global Tropospheric Sources of NO

	Baulch et al. [1982]	*Ehhalt and Drummond* [1982]	*Logan* [1983]	*Stedman and Shetter* [1983]	*National Academy of Sciences* [1984]
Surface sources					
Fossil fuel combustion	8.2–18.5	13.5(8.2–18.5)	21(14–28)	20(18–22)	15–25
Biomass burning	10–40	11.2(5.6–16.4)	12(4–24)	5(1.7–15)	1–10
Biogenic production	0–15	5.5(1–10)	8(4–16)	10(5–20)	1–10
Atmospheric sources					
Lightning	3–4	5(2–8)	8(2–20)	3(1.5–6)	2–20
NH_3 oxidation	···	3.1(1.2–4.9)	1–10	1(0.5–2)	≤5
From stratosphere	0.5–1.5	0.6(0.3–0.9)	0.5	1(0.5–2)	0.5–1.5
High-flying aircraft	0.25	0.3(0.2–0.4)			0.15–0.3
Total	22–80	39(19–59)	50(25–99)	40(27.2–67)	20–70

Units are Mt(N) yr^{-1}.

With respect to biogenic production, it is not yet known which of two possible biochemical mechanisms, nitrification or denitrification, is responsible for formation of NO or N_2O or how various soil parameters such as percent moisture, temperature, or concentrations of available substrates affect these emissions. Previous experiments performed in our laboratory have predicted that NO emissions from soil result primarily from autotrophic nitrification and will occur over a wide range of soil moisture conditions, provided that some oxygen is available [*Levine et al.*, 1984; *Anderson and Levine*, 1986]. N_2O, on the other hand, is formed by denitrification, performed by either nitrifiers or denitrifiers and will be emitted primarily under oxygen-limiting conditions [*Levine et al.*, 1984; *Anderson and Levine*, 1986].

Thus far only a very limited number of field investigations of biogenic NO emissions have been performed [*Galbally and Roy*, 1978; *Slemr and Seiler*, 1984; *Johansson and Granat*, 1984; *Johansson*, 1984], mainly at agricultural sites and one at a forest site in Europe. These studies took place over short time spans, primarily during spring and summer, and involved few ancillary measurements. Many more studies of biogenic N_2O emissions have been performed [*Conrad et al.*, 1983; *Ryden*, 1981; *Duxbury et al.*, 1982; *Goodroad et al.* 1984; *Hutchinson and Mosier*, 1979; *Mosier and Hutchinson*, 1981; *Slemr et al.*, 1984; *Blackmer et al.*, 1982; *Folorunso and Rolston*, 1985; *Keller et al.*, 1983]. Most of these studies report a high degree of spatial and temporal variability.

In the present study we will report on simultaneous field measurements of the biogenic production of NO and N_2O from two widely spaced agricultural sites. It was decided to study a few sites intensively rather than to survey a large variety of sites, since we wanted to better understand the underlying mechanisms and factors controlling NO and N_2O emissions. We hoped that such knowledge would help us to explain the high degree of spatial and temporal variability observed by others. Measurements were obtained from agricultural sites in Jamestown, Virginia, and near Boulder, Colorado. The soil at each of the sites was well characterized. In addition to gas emissions, we measured a variety of soil parameters, including temperature, percent moisture, pH, and exchangeable nitrate, nitrite, and ammonium. At the Virginia site, measurements were performed over a full year, during which the sites were normally farmed. The Colorado measurements were obtained during May and July. We also performed a series of diurnal studies under widely different soil conditions both in Virginia and in Colorado.

Field Measurement Sites and Cropping Practices

Nitric oxide and nitrous oxide flux measurements were made at agricultural sites in Jamestown, Virginia, and in Bennett, Colorado, aproximately 97 km east of Boulder. Soils at the Virginia site were classified in the Pamunkey series [*Hodges et al.*, 1984]. They are well drained, sandy loam soils with a slope of 2–6%. The surface layer is approximately 10 cm thick. These soils contain about 2% organic material and are slightly acidic. Field capacity in these soils is approximately 21%. The fields are normally double-cropped. Flux measurements were made at three field sites in Jamestown, from June 1984 to July 1985. The cropping history and fertilization schedule for each of these sites is listed in Table 2. In order to assess spatial variability, measurements were made at three plots in site 1, two in site 2, one in site 3, and four in site 4.

TABLE 2. Cropping and Fertilization History: Experimental Sites

Site	Cropping History	Fertilizer Added, kg(N) $acre^{-1}$
	Virginia Sites	
1	corn, planted April 4, 1984; harvested Sept. 24, 1984	4.5, April 10, 1984 66, May 28, 1984
	barley, planted Oct. 24, 1984; harvested June 1, 1985	9.1, Oct. 8, 1984
2	soybeans, planted June 5, 1984; harvested Nov. 20, 1984	9.1, Oct. 6, 1983 26, March 16, 1984
	corn, planted April 5, 1985; anthesis June 11, 1985	4.5, April 7, 1985
3	grass, uncultivated	none
4	garden, planted April 1985	fertilized in April (amount unknown)
	Colorado Sites	
1	winter wheat, planted Sept. 15, 1984; anthesis, May 20, 1985; senescence, July 12, 1985; harvest, July 20, 1985	25, June 30, 1984
2	fallow, since July of previous year	

1 acre = 0.405 hectare.

Studies were performed at a wheat field site in Bennett, Colorado, during May and July 1985. The soil is a clay loam with 1.8–2.1 m of topsoil and containing approximately 1.4% organic matter. The soil *p*H is slightly basic. Field capacity is approximately 32%. Flux measurements were made in two fields, one fallow and one cropped in winter wheat. The cropping and fertilization history is given in Table 2. Measurements were made at four plots within the wheat field and at one plot in the fallow field.

METHODS

Closed Box Flux Technique

At each of the plots selected for this study, rectangular aluminum collars were inserted into the soil to a depth of at least 3 cm. The collars covered an area measuring 0.407 m^2. The top edges of the collar formed a V-shaped groove into which the flux box could be set. Water in the groove provided a seal for the flux box. The inner surfaces of both the collar and the flux box were coated with Teflon. The flux box was insulated with a closed-cell foam covered with highly reflective aluminized Mylar. The combined volume of the flux box plus collar varied from 165.5 L to 187.3 L, depending upon the depth to which the collar was inserted into the soil. A muffin fan inside the box stirred the air at the rate of 2.97 m^3 min^{-1} at zero static back pressure. A 1.5-cm vent at the top of the box prevented development of a pressure differential when air was pumped out of the box for analysis of NO. Teflon tubing mounted in a bulkhead fitting and extending 20 cm into the box was used for sampling air for NO and NO_x analysis. Fittings with silicone rubber septa were used for removal of box air by syringe for N_2O analysis. Another fitting allowed insertion of probes used to measure the temperatures of both soil and air within the box.

Care was taken to minimize disturbance to soil and vegetation when collars were inserted. Collars were installed at least one week prior to our beginning a series of measurements and remained undisturbed for the duration of the study. The flux box was left in place for a maximum of 16 min for determination of the NO flux and 30 min for the N_2O flux.

Analyses of NO, NO_x, and N_2O

For analysis of NO or NO_x (NO + NO_2), either box air or ambient air was pumped at the rate of 540 mL min^{-1} into a model 1600 chemiluminescence detector (Columbia Scientific Industries, Austin, Texas). The detector was zeroed with ultra zero air monitoring (Scott Environmental Technology, Inc., Plumsteadville, Pennsylvania) and calibrated for NO with a field calibration standard containing approximately 100 parts per billion by volume (ppbv) (10^{-9} vol/vol) NO in N_2 (Scott Environmental Technology, Inc.). The field calibration source was checked every 6 months against a National Bureau of Standards Standard Reference Material (SRM) containing 9.49 ± 0.16 ppmv (10^{-6} vol/vol) NO in N_2. For determination of NO_x, the detector utilizes a copper converter for conversion of NO_2 to NO. The efficiency of this converter, which was periodically checked by titration of a NO standard with ozone (O_3), was greater than 96%. The NO_2 concentration is given as the difference between the NO_x and the NO signals. The detection limit of the instrument is 2 ppbv (twice the signal to noise ratio) using a 60-s time constant. The instrument was powered in the field by a 1600-W generator kept at least 60 m downwind from the sample site. The rise time of the instrument is approximately 225 s with a 60-s time constant and 60 s with a 5-s time constant. Both O_3 and NO_2 concentrations decreased to near zero (2–3 ppbv) during the first 4 min after setting the flux box down on the collar (Figure 1). NO_2 has been shown to be absorbed onto soils [*Prather et al.*, 1973] and to be both absorbed and metabolized by plants [*Hill*, 1971; *Rogers et al.*, 1979]. In a separate set of experiments performed in polluted air (data not given), we observed that NO_2 decreased rapidly from mixing ratios of approximately 50 ppbv to 2 ppbv within 4 min of setting the flux box onto the collar. We concluded that the closed box technique was not suitable for determining NO_2 fluxes. We therefore ignored NO_2 and based all calculations of NO fluxes upon the increase in mixing ratio versus time of NO from 4 min to 14 min after starting the flux measurement. The minimum NO flux that could be measured with this system was 0.5 ng(N) m^{-2} s^{-1} at 298°K.

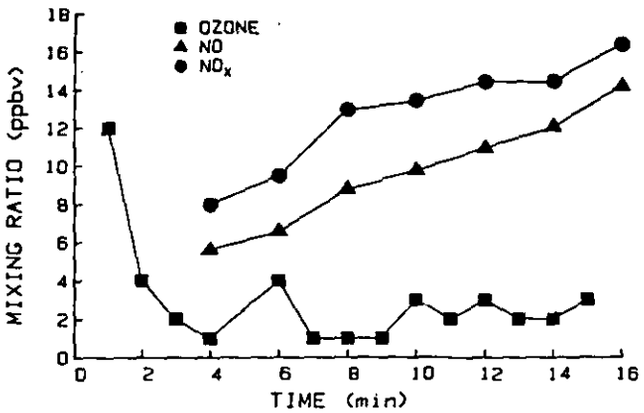

Fig. 1. Typical flux measurement using the closed box method.

Samples for analysis of N_2O were taken through a silicone rubber septum by a 50-mL disposable plastic syringe with a rubber plunger tip. The syringes were fitted with three-way Lexan stopcocks. During leak tests of the syringes, using methane as the sample gas, we observed a 1% loss of gas over a 24-hour period and a 2.8% loss over a 54-hour period. Samples for this study were never kept over 48 hours before analysis. Samples were injected into a gas chromatograph with an electron capture detector. For our Jamestown, Virginia, studies, an F and M model 810 gas chromatograph (F and M Scientific Division, Hewlett Packard Co., Palo Alto, California) equipped with a 2.7 m × 0.3 cm Poropak Q column at 50°C and an ^{63}Ni electron capture detector held at 350°C was used. Carrier gas (5% methane in argon) was supplied at a flow rate of 18 mL min^{-1}. The precision of this instrument was 2.8% (standard deviation/mean) in ambient air. The minimum detection limit with the system used at the Jamestown, Virginia, site was 4 ng(N) m^{-2} s^{-1} at 298°K. Samples taken at the Colorado wheat field site were analyzed by injection into a Hewlett Packard, model 5880A gas chromatograph with a 30 cm × 0.2 cm molecular sieve 5A precolumn and 1.8 m × 0.2 cm molecular sieve 5A analytical column held at 250°C and electron capture detector at 350°C. Nitrogen was used as the carrier gas at a flow rate of 40 mL min^{-1}. The precision of this instrument was 1% (standard deviation/mean). The minimum detection limit with the system as used at the Colorado site was 1 ng(N) m^{-2} s^{-1} at 298°C.

Analysis of Ozone

Samples for analysis of O_3 were passed through a recirculating loop from the flux box through a Dasibi, model 1003-AAS, ozone analyzer (Dasibi Environmental Corp. Glendale, California) and back to the flux box.

Soil and Environmental Analyses

Exchangeable nitrate, nitrite, and ammonium. For analysis of exchangeable nitrate, nitrite, and ammonium, at least five soil samples were taken to a depth of 10 cm in an area surrounding the experimental plots, using either an auger (6.5 cm ID) or a footstep sampler (2 cm ID). The samples were mixed, air-dried if necessary, and passed through a sieve (2 mm opening size). A 20-g sample of sieved soil in 200 mL potassium chloride (KCl, 2 *M*) was agitated on a magnetic stirrer for 1 hour. The extract was decanted, filtered (0.45 μm pore size), and frozen until analyzed. Percent moisture of a parallel sample was determined by gravimetric analysis. Analyses for nitrate, nitrite, and ammonium were performed according to Environmental Protection Agency (EPA) methods 353.2 with cadmium reduction, 353.2 without cadmium reduction, and 350.1 respectively, using a Technicon Autoanalyzer II.

Percent moisture. Samples for analysis of percent moisture were taken as described above and stored in ziplock bags on ice for no longer than 16 hours. Samples were dried to constant weight at 110°C for 24 hours. Percent moisture was reported as percent dry weight.

Measurement of pH. The pH was determined after stirring a 5-g sample of sieved soil in 5 mL of distilled water for 15 min.

Temperature. Soil temperature was measured at a depth of 2.54 cm within the flux box, using an Omega, model 866 thermometer equipped with a thermistor probe. Box temperature was measured 20 cm down inside the flux box using the same thermometer.

Flux Calculations

All of the NO fluxes reported were calculated using the slope of the NO mixing ratio (ppbv) versus time (minutes) from 4 min until 14 min after the flux box was installed onto the collar. During this time the slope was linear. Similarly, N_2O fluxes were calculated from the slope of the N_2O mixing ratio versus time from zero until 30 min after installation of the flux box. All mixing ratios were corrected for the dilution caused by pumping box air into the chemiluminescence detector at 540 mL min^{-1}. For calculations of annual fluxes, the measured fluxes at a particular site were first normalized for time of day, and 24-hour fluxes were calculated, based upon the diurnal variation observed at that site. Monthly and annual averages were computed from the 24-hour diurnally corrected fluxes. No attempt was made to take into account the flux variation due to changes in soil moisture.

Multiple Linear Regression Analysis

Regression analyses were performed on an IBM-XT, using the interactive statistical package Crisp (Crunch Software Corp., San Francisco, California).

RESULTS

Figure 1 shows typical results of a flux box measurement. NO and NO_x mixing ratios increased linearly from 4 to 16 min after installing the flux box. Ozone mixing ratios declined to levels near zero by 4 min after starting the test. Nitrogen dioxide fluxes were not observed in any of our studies, perhaps because nitrogen dioxide tends to stick to surfaces of soil, vegetation, and the flux box itself.

Seasonal Variation in NO and N_2O Fluxes at the Virginia Site

At the Jamestown, Virginia, farm, NO and N_2O flux measurements were made at three sites, whose cropping and fertilization histories are given in Table 2. Results of these measurements are summarized in Table 3 and Figure 2. Fluxes of NO at all three sites followed a similar pattern throughout the seasons, although fluxes were much higher at site 1 during June–July and again in October, due to application of 79.5 kg of fertilizer nitrogen per acre (196.4 kg per hectare). Fertilizer application to site 2 in June 1985 also resulted in increased fluxes at that site. The effect of soil disturbance is shown by the unexpectedly high flux observed at site 3 on October 30. The collar at this site had been accidentally removed and reinstalled 1 week prior to our making the reported flux measurement. This observation emphasizes the need to avoid, as much as possible, disturbance to the experimental plot when making measurements. Nitrous oxide fluxes were observed from sites 1 and 2 (Table 3) only when percent moisture approached or exceeded field capacity (21%).

Statistical Analysis of Virginia and Colorado Data Sets

Measurements of gas fluxes and soil parameters at the Colorado site are summarized in Table 4. Data sets from both the Virginia and Colorado sites were analyzed by stepwise linear multiple regressions in order to determine the relationships between NO flux and various soil parameters, including temperature, percent moisture, and exchangeable nitrate and ammonium concentrations. The numbers of data points used, the calculated regression coefficients, and the coefficients of determination (correlation coefficient squared) are given for each analysis in Table 5. In addition, 95% confidence limits were calculated using the two-tailed *T* test for each of the regression coefficients and are also shown in Table 5.

Analysis of the Virginia data set showed that at site 1 ($n = 93$), nitrate concentrations, moisture, and temperature were all significantly correlated ($P < 0.01$) with NO flux, whereas at site 2 ($n = 72$), only nitrate and temperature were significantly correlated with flux. The coefficients of determination (r^2), which may be used in this case to explain how much of the variation in NO flux is due to changes in nitrate, moisture, and soil temperature [*Snedecor and Cochran*, 1967], varied from 25 to 33%. Thus unknown factors other than the soil parameters considered influenced NO fluxes at the Virginia site.

Soil conditions at the Colorado site were far more stable than at the Virginia site. Flux measurements were made during May when soil percent moisture was high (15–28%, $n = 14$) and again in July when soil percent moisture was low (11–13%, $n = 43$). Fertilizer (anhydrous ammonia) had been applied the previous July, and exchangeable nitrate concentrations did not vary except in the unvegetated collar (explained below). The NO flux was significantly and positively correlated with both temperature and moisture ($P < 0.01$). Percent moisture remained well below field capacity (about 32%) during our study in Colorado, insuring that the soil was sufficiently aerobic to support nitrification. The multiple coefficient of determination for all measurements made in Col-

TABLE 3. Summary of Flux and Soil Data, Virginia

Date	Time	Temperature, °C	Moisture, % Dry Weight	NO_3[a]	NH_4[b]	NO[c]	N_2O[d]
			Site 1, Plot 1				
June							
7	1528	35	18	70	6	5.5	241
13	1304	37	18.2	70	6	13.7	111.5
13	1417	38	18.2	70	6	15.8	111.8
21	1225	33	16	60	3	7.4	
21	1405	32	16	60	3	11.3	
26	1205	29	12.6	50	2	12.6	58
26	1400	31	12.6	50	2	11.6	
July							
3	1300	37	13	45	1.5	11.9	
11	1400	34	15.7	43.3	1.36	19.5	28
17	1255	39	15	50	1	7.2	
19	1405	33	20	64.6	0.18	7.2	85
25	0608	24	18	60	0.2	2.5	
25	0915	23.7	20	60	0.2	5.4	
25	1113	30.3	20	60	0.2	4.9	
25	1315	30.9	20	60	0.2	4.2	
25	1519	31.8	20	60	0.2	6.4	
25	1710	30.8	20	60	0.2	5.2	
25	1940	27.6	20	60	0.2	4.1	
25	2057	24.9	20	60	0.2	3.2	
25	1437	29	18	50	2	1.6	
31	1430	35	18.5	50	2.3	3.7	
Aug.							
7	1510	34	18.5	50	2.3	4.6	40
9	1230	32	18.5	10	4	5.2	
14	1415	31	18.9	8.9	5.7	3.4	
14	1120	30	18.9	8.9	5.7	2.3	38
21	1200	26	16.5	7	3	0.3	
30	1135	29	11.7	15	2	0.8	
Sept.							
6	1400	22	13.1	21.9	2.1	2.9	
19	1210	20	8	5.5	2.3	1.7	
26	1420	31	9	2.7	2.2	2.4	
Oct.							
3	1310	22	10.3	2.6	8.4	7.1	
3	1343	22	10.3	2.6	8.4	6.6	
9	1255	30	9.6	6.1	8.3	12.5	
9	1330	30	9.6	6.1	8.3	10.3	
11	1305	27	9.6	6.1	8.3	15	
30	1310	21	9	37.9	1.9	5.9	
30	1358	21	9	27.9	1.9	6	
Nov.							
8	1308	18	7.8	37.4	1.6	4	
14	1400	13	8.3	46.1	3.2	2.9	
14	1455	14	8.3	46.1	3.2	2.9	
Dec.							
10	1300	10	16.5	13.2	0.72	1.9	
17	1453	15	20.2	2.5	5	2.9	
Feb.							
21	1200	9	20	2	2	1.7	
April							
16	1312	20	20	2.6	1.4	6.8	19.7
May							
30	1400	28.5	11.4	2.6	1.6	2.9	
30	1500	29.1	11.4	2.6	1.6	3	
			Site 1, Plot 2				
June							
7	1554	32	18	70	6	11.9	125
13	1235	36	18.2	70	6	28.1	27.8
13	1442	38	18.2	70	6	67.2	167.4
21	1145	32	16	60	3	29.5	
21	1430	32	16	60	3	33.9	32.6
26	1132	28	12.6	50	2	38.3	
26	1335	28	12.6	50	2	51.6	57
28	1310	29	12.6	50	2	39.8	

TABLE 3. (continued)

Date	Time	Temperature, °C	Moisture, % Dry Weight	NO_3[a]	NH_4[b]	NO[c]	N_2O[d]
			Site 1, Plot 2 (continued)				
July							
3	1300	35	13	45	1.5	52.6	
11	1330	39	15.7	43.3	1.4	44.6	
11	1440	36	15.7	43.3	1.4	38.6	30
17	1230	38	15	50	1	21.9	
19	1345	32	20	64.6	0.2	8	115.3
25	0545	24.1	18	50	0.2	6.2	
25	0855	23.7	23.5	50	0.2	0.001	
25	1055	29.5	23.5	50	0.2	0.001	
25	1300	30.9	23.5	50	0.2	0.001	
25	1500	31.8	23.5	50	0.2	0.89	84.2
25	1650	30.8	23.5	50	0.2	0.45	
25	1920	27.6	23.5	50	0.2	0.41	
25	2117	24	23.5	50	0.2	0.57	127.7
25	1455	34	18.5	50	2.3	4.4	
Aug.							
7	1208	32	18.5	10	4	5.1	
14	1355	33	18.9	8.9	5.7	2.5	
14	1055	29	18.9	8.9	5.7	1	
21	1136	23	16.5	7	3	2.8	
30	1110	30	11.7	15	2	4.7	
Sept.							
6	1340	22	13.1	21.9	2.1	3.3	
19	1145	20	8	5.5	2.3	2.3	
26	1400	31	9	2.7	2.2	4.5	
Oct.							
3	1250	20	10.3	2.6	8.4	9	
3	1328	20	10.3	2.6	8.4	7.9	
9	1235	29	9.6	6.1	8.3	11.4	
9	1315	29	9.6	6.1	8.3	21.6	
11	1250	26	9.6	6.1	8.3	18.4	
30	1230	21	9	37.9	1.9	14.2	
30	1344	21	9	37.9	1.9	14.7	
Nov.							
8	1250	18	7.8	37.4	1.6	4.7	
14	1348	15	8.3	46.1	3.2	5.4	
14	1440	15	8.3	46.1	3.2	5.1	
Dec.							
10	1225	9	16.5	13.2	0.72	0.89	
17	1403	16	20.2	2.5	5	2.4	
Jan.							
14	1425	4	24.5	1.3	0.33	1.4	
Feb.							
21	1335	12	24	2.4	0.3	0.96	
March							
19	1400	13.7	11.8	3.9	1.5	1.38	
April							
16	1230	27.1	18	2.6	1.4	19.9	17.3
May							
30	1420	32.1	11.4	2.6	1.6	3.4	
			Site 2, Plot 1				
June							
28	1231	29	20	18	1.5	3.2	
July							
3	1445	38	20	18	1.5	6.3	
11	1205	34	25.1	18.7	1.64	4.2	
11	1250	36	25.1	18.7	1.64	6	
17	1405	45	23	18	1.3	4.9	
17	1455	46	23	18	1.3	4.3	
19	1520	30	22	2.3	0.19	4.7	
31	1310	29	20	20	2	0.74	
Aug.							
7	1230	33	20.8	20.5	2.4	3.8	
7	1305	34	20.8	20.5	2.4	3.5	
9	1340	34	20.5	20.5	2.4	3.7	
14	1235	32	20.3	8.2	2.3	2.9	
30	1347	35	7.5	20	2.5	3.4	

TABLE 3. (continued)

Date	Time	Temperature, °C	Moisture, % Dry Weight	NO_3[a]	NH_4[b]	NO[c]	N_2O[d]
Site 2, Plot 1 (continued)							
Sept.							
6	1430	22	15	40	3.3	4	
19	1415	25	7.9	1.5	2.3	2.6	
26	1255	33.8	10	2.8	3.3	2.6	
26	1335	32.1	10	2.8	3.3	3.2	
Oct.							
3	1530	22	12.9	5.6	3	5.7	
9	1415	30	11	5.6	1.1	4.2	
24	1355	24	19.4	16.7	2.5	3.5	66.3
30	1450	21	11.5	23.4	2.9	5.8	
Nov.							
8	1455	19	25	20	1	3.3	
Dec.							
10	1507	8	17	3.7	1.1	2.1	
17	1313	15	21.6	11.5	14	3.9	
Jan.							
14	1357	2	19.5	3	0.87	0.74	
Feb.							
21	1530	9	18	3.4	0.6	1.1	
March							
19	1320	12.7	15.9	5.5	0.95	2.6	
April							
16	1500	21.3	18	10	40	3.4	
June							
6	1310	25.3	24	11.3	40	4.8	
11	0557	23.4	18.2	37	1.2	7.3	201.9
11	0934	26.4	18.2	37	1.2	9.1	266.4
11	1210	27.5	18.2	37	1.2	9.9	251.9
11	1522	31.8	18.2	37	1.2	12.9	399.6
11	2110	26	24	37	1.2	3.8	518
Site 2, Plot 2							
June							
28	1116	29	20	20	1.5	2.6	
July							
3	1415	38	20	20	1.5	1.7	
3	1515	38	22	20	1.5	3.1	
11	1140	32	25.1	18.7	1.64	1.9	
11	1230	34	25.1	18.7	1.64	4.2	
17	1340	45	22	2.3	0.19	6.6	
17	1435	46	22	2.3	0.19	6.4	
19	1500	34	22	2.3	0.19	6.3	109
31	1330	30	22	18	2	1.2	
Aug.							
7	1200	31	20.8	20.5	2.4	6.2	
7	1245	33	20.8	20.5	2.4	5.1	
9	1400	35	20	10	2	9.4	
9	1425	34	20	10	2	6.6	
14	1300	33	20.3	10	2	4.8	
0	1327	35	7.5	20	2	3.5	
Sept.							
6	1207	24	15	40	3.3	6.5	
6	1453	23	15	40	3.3	4.9	
19	1310	29	7.9	1.5	2.3	4.8	
26	1225	32.3	10	2.8	3.3	2.8	
26	1315	33	10	2.8	3.3	4.8	
Oct.							
3	1505	23	12.9	5.6	3	4.4	
9	1415	30	11	5.6	1.1	3.5	
24	1320	24	19.4	16.7	2.5	5	
24	1430	24	19.4	16.7	2.5	5.4	
30	1436	21	11.5	23.4	2.9	5.7	
Nov.							
8	1430	17	15	5	1	2.3	
Dec.							
10	1535	8	17	3.7	1.1	4	
17	1257	16	21.6	11.5	14	4.2	
Jan.							
14	1322	3	19.5	3	0.87	0.37	

TABLE 3. (continued)

Date	Time	Temperature, °C	Moisture, % Dry Weight	NO_3[a]	NH_4[b]	NO[c]	N_2O[d]
Site 2, Plot 2 (continued)							
Feb.							
21	1515	10	18	3.4	0.6	0.96	
March							
19	1300	12.5	15.9	5.5	0.95	0.4	
April							
16	1427	21.5	18	10	40	2	160.1
June							
6	1245	24.7	24	11.3	40	4	1453
11	0632	23.6	18.2	37	1.2	6.2	
11	1013	27.2	18.2	37	1.2	8.4	
11	1240	27	18.2	37	1.2	9.4	
11	1553	31.2	18.2	37	1.2	19.2	
11	2140	25.8	25	37	1.2	8.1	
Site 3							
July 25	1201	42	16.7	0.6	1.77	4.4	
Aug. 7	1415	32				1.5	
Aug. 14	1355	36	19.9	7.5	6.7	3.7	
Aug. 16	1300	34				9	
Aug. 21	1330	35	22.5	10	2.3	4.1	
Aug. 21	1145	32	22.5	10	2.3	2.9	
Aug. 28	1239	30	21.1			2.5	
Sept. 6	1235	34	10.3			0.003	
Sept. 13	1310	23	16.1	20.9	2.3	2.1	
Sept. 26	1230	28	6.8	46.1	3.8	2.1	
Oct. 3	1440	32	8	54.3	10.6	0.93	
Oct. 10	1400	22	10.2	7	4.6	6.1	
Oct. 16	1348	30	6.4	8	7.2	4.6	
Oct. 18	1400	28	6.5	8	7.2	3.5	
Nov. 8	1415	21	13.3	9.8	2.8	12.5	
Nov. 14	1355	19	10			1.5	
Nov. 20	1510	15	8.2	36.2	4	4.7	
Dec. 10	1355	12	18			0.003	
Dec. 17	1522	16	18.1	14.7	2	0.64	
Feb. 21	1430	11				0.44	
March 19	1450	15.2	17.6			0.003	
April 16	1355	23.5	18			2.8	
May 30	1535	31.3	14.3			3.9	
June 6	1440	25.8	24			9.3	

[a]Exchangeable nitrate, $\mu g\ g^{-1}$ soil.
[b]Exchangeable ammonium, $\mu g\ g^{-1}$ soil.
[c]Nitric oxide, ng(N) $m^{-2}\ s^{-1}$.
[d]Nitrous oxide, ng(N) $m^{-2}\ s^{-1}$.

orado during May and July was 54% ($n = 63$). However, if during the analysis the data were filtered such that only fluxes within small ranges of percent moisture were considered, the r^2 value for temperature versus NO flux ranged from 60 (moisture range, 11–13%) to 79% (moisture range, 23–30%).

At the Colorado site, nitrous oxide fluxes were observed from the unvegetated sites 2 and 4 in May when soil moisture was high (Table 4). Wheat plants had been removed from these collars 1 week prior to our starting the study. At the vegetated site, no N_2O fluxes were observed during May. It is likely that mineralization of underground vegetation after removal of plants from sites 2 and 4 provided limiting substrates required for denitrification to take place. During July, N_2O was observed only at site 2 after irrigation (Table 4). Site 2, which remained unvegetated throughout the study, had accumulated a higher concentration of exchangeable nitrate than was observed at site 1.

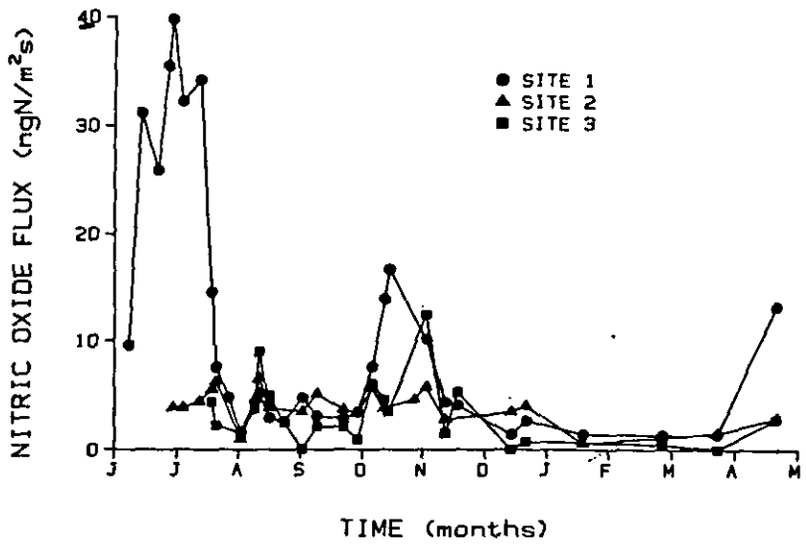

Fig. 2. Seasonal study of NO fluxes—Virginia. Fluxes of NO were measured at three sites in Jamestown, Virginia, from June 1984 to June 1985. Each point represents in most cases an average of three to five flux measurements. Site 1 was fertilized 1 week and site 2 was fertilized 3 months prior to the start of the experiment. Site 3 was unfertilized.

Diurnal Studies

In order to study the relationships between NO or N_2O gas fluxes and soil variables, especially temperature and moisture, under more controlled conditions, we conducted a series of diurnal studies at both the Virginia and Colorado sites. Figure 3 shows the results of a diurnal study conducted during September at three plots within site 4 in Virginia. Measurements were made between 0600 and 2000 local time (LT) of NO fluxes and soil temperatures. Soil moisture was 2.7%, and exchangeable nitrate was 6 μg(N) g^{-1} soil. Increases in NO fluxes generally corresponded to increases in soil temperature although peak fluxes occurred several hours before peak temperatures. The effect of changing surface soil moisture on water-stressed microorganisms may account for this offset in peak overlap. N_2O emissions were not detected from any of the plots.

Figure 4 demonstrates the effect that water saturation of soil has on NO emissions. Nitric oxide fluxes were measured during a diurnal study performed at two plots within site 1 in Virginia during July. The first measurements were made prior to rain (2.54 cm), which occurred between 0600 and 0845 LT. During the storm, plot 1 was exposed to the rain whereas plot 2 was protected. After the storm, soil moisture was 24% at plot 1 and 18% at plot 2. Field capacity at these plots was 21%. Fluxes at plot 2, after the rain, generally corresponded to soil temperature. At plot 1, NO fluxes were very low or not measurable, although some N_2O was emitted (Table 3).

Results shown in Figure 5 demonstrate that NO and N_2O fluxes respond differently to water saturation of soil. Measurements of NO were made at four plots during a diurnal study in site 2, Virginia, in July. Nitrous oxide emissions were determined at two of the plots. The site had been recently fertilized. Exchangeable nitrate was 37 μg(N) g^{-1} soil. Spatial variability in NO fluxes between plots was high, probably due to variations in fertilizer application. Changes in NO and N_2O fluxes corresponded to temperature between 0500 and 1600 LT. Rain (2.54 cm) occurred between 1700 and 1900 LT. Percent soil moisture was 18% before and 25% after the rain. By 2100 LT, NO fluxes had decreased, whereas N_2O fluxes had increased sharply.

A diurnal study was performed in Colorado during July after an extended period of dry weather. Results shown in Figures 6*a* and 6*b* demonstrate what happens when soil which has been dry for an extended period of time is rewetted. At the time of the study, the wheat had already undergone senescence. Site 1 was vegetated; site 2 was unvegetated. On the day following the diurnal study, site 2 was irrigated with 2.54 cm of water. Figure 6*b* demonstrates the dramatic increase in NO flux following irrigation. Nitrous oxide emissions were also observed from site 2 but not site 1. Soil moisture, which was 11% prior to irrigation and 25% following irrigation, did not approach field capacity (approximately 32%). The large increase in NO flux from site 2 was in part due to an accumulation of nitrate from mineralized underground vegetation. Rewetting of this dried soil allowed for renewed microbiological activity and thus increased emissions of NO.

Estimates of Annual Emissions

Calculation of the annual emission of NO expected from moderately fertilized agricultural land in a temperate climate was based upon results of flux measurements made at our Virginia site over a full year. Based upon the diurnal variation observed at the same sites, all observed fluxes were corrected to levels that would appear at 1200 LT. Twenty-four-hour daily fluxes were calculated from these corrected noontime fluxes. Monthly fluxes were determined from the averages of daily fluxes. The annual flux thus corrected for diurnal variability was 65% of the value calculated from the monthly averages of uncorrected fluxes measured between 1100 and 1500 LT. The annual flux ranged from 0.53 kg(N) ha^{-1} yr^{-1} for the unfertilized site 3 to 0.61 kg(N) ha^{-1} yr^{-1} for site 2, fertilized 3 months prior to our beginning the study, to 2.08 kg(N) ha^{-1} yr^{-1} for the moderately fertilized site 1. Fertilizer loss as NO(N) was calculated by subtracting the loss of NO(N) at the unfertilized site from that at the fertilized site. Of the 196.4 kg ha^{-1} of fertilizer added to site 1, 0.79% was

TABLE 4. Summary of Flux and Soil Data, Colorado

Date	Site	Time	Temperature, °C	Moisture, % Dry Weight	NO_3[a]	NH_4[b]	NO[c]	N_2O[d]
May 10	4	1500	27.2	15.6	2.6	0.8	1.65	209.6
	4	1605	23	15.6	2.6	0.8	1.64	213.9
May 12	1	1155	15.5	15.6	2.6	0.8	0.78	
	2	1230	16.5	15.6	2.6	0.8	2.25	233.8
May 14	3	1400	16.3	28	1.6	2.2	1.38	
	4	1430	25.9	28	1.6	2.2	4.44	173.4
	2	1510	23.2	28	1.6	2.2	2.02	
	1	1535	17.2	28	1.6	2.2	2.1	
May 15	3	1300	18.7	24.7	1.6	2.2	3.19	
	4	1315	27.2	24.7	1.6	2.2	5.01	
	2	1345	24.2	24.7	1.6	2.2	2.85	101.6
	1	1430	21.4	24.7	1.6	2.2	3.14	9.7
	2	1630	23.3	24.7	1.6	2.2	2.8	
	3	1655	16.7	24.7	1.6	2.2	1.13	
July 3	1	1645	29.4	13	4.2	2.6	3.83	
	2	1720	29.1	13	4.2	2.6	2.95	
July 4	4	1210	32.1	13	4.2	2.6	1.2	
	3	1235	25.6	13	4.2	2.6	0.83	
	4	1600	39.4	13	4.2	2.6	3.18	
	3	1615	28.3	13	4.2	2.6	2.2	
July 6	4	0455	16.5	11.3	4.2	2.6	0.48	
	3	0515	16.7	11.3	4.2	2.6	0.27	
	2	0550	17	11.3	4.2	2.6	0.001	
	1	0625	17.8	11.3	4.2	2.6	0.36	
	4	0800	20.4	11.3	4.2	2.6	0.62	
	3	0818	18.7	11.3	4.2	2.6	0.46	
	2	0837	25.8	11.3	4.2	2.6	1.41	
	1	0857	21.5	11.3	4.2	2.6	1.26	
	4	1000	28.9	11.3	4.2	2.6	1.71	
	3	1023	21.6	11.3	4.2	2.6	1.32	
	2	1042	34.9	11.3	4.2	2.6	3.92	
	1	1100	27.9	11.3	4.2	2.6	3.17	
July 9	1	0445	20	11	4.6	3.3	0.8	
	2	0520	19.1	11	4.6	3.3	0.74	
	1	0700	20.1	11	4.6	3.3	1.32	
	2	0720	20.8	11	4.6	3.3	1.64	
	1	0900	23.6	11	4.6	3.3	2	
	2	0920	30.8	11	4.6	3.3	4.8	
	1	1100	29.3	11	4.6	3.3	3.14	
	2	1120	34.7	11	4.6	3.3	6.07	
	1	1300	35.7	11	4.6	3.3	4.17	
	2	1325	40.9	11	4.6	3.3	5.55	
	1	1500	33.5	11	4.6	3.3	2.48	
	2	1535	37	11	4.6	3.3	3.45	
	1	1700	34.3	11	4.6	3.3	2.61	
	2	1720	34	11	4.6	3.3	2.99	
	1	1850	30.8	11	4.6	3.3	1.78	
	2	1910	29.7	11	4.6	3.3	2.35	
	1	2025	25.5	11	4.6	3.3	1.95	
	2	2055	24.8	11	4.6	3.3	1.56	
July 11	2	1155	42.5	11	4.6	3.3	4.18	
	1	1225	40.8	11	4.6	3.3	2.45	
	2	1300	37	25	4.6	3.3	9.81	16.3
	1	1330	44.9	11	4.6	3.3	3.08	
	2	1405	35.5	25	4.6	3.3	16.03	24.9
	1	1438	40.6	11	4.6	3.3	3.02	
	2	1510	33.7	25	4.6	3.3	11.36	25.1
	1	1540	34.1	11	4.6	3.3	2.9	
	2	1614	31.1	25	4.6	3.3	6.98	21.7
	1	1645	32.6	11	4.6	3.3	3.17	
July 12	2	1125	31.8	23	17.1	2.4	11.25	18.8
	1	1200	34.9	11	4.6	3.3	2.76	
	2	1430	35.4	23	17.1	2.4	4.22	18.3
	1	1505	35	11	4.6	3.3	2.4	
May 16	fallow	1240	16.3	26.5	1.9	0.8	1.84	
	fallow	1350	17.5	26.5	1.9	0.8	0.92	

[a]Exchangeable nitrate, $\mu g\ g^{-1}$ soil.
[b]Exchangeable ammonium, $\mu g\ g^{-1}$ soil.
[c]Nitric oxide, ng(N) $m^{-2}\ s^{-1}$.
[d]Nitrous oxide, ng(N) $m^{-2}\ s^{-1}$.

lost as NO. The percent of fertilizer loss as $N_2O(N)$ from site 1 during June, July, and August was 1.2%. Since this calculation was based upon a very limited data set, it is subject to a large uncertainty.

Although soil moisture strongly impacts both NO and N_2O emissions, we did not have enough data to incorporate a correction factor for the effect of moisture on annual emissions. No attempt was made to calculate annual emissions of N_2O, since the fluxes observed were extremely variable and sensitive to soil moisture conditions. An accurate estimate of the annual N_2O flux from a given site requires a very large number of data points and more information than was available concerning the day-to-day variation in percent soil moisture.

CONCLUSIONS

Estimates of the global annual biogenic emission of NO from the soil to the atmosphere have thus far been calculated from a very small data base obtained under a very limited variety of conditions. *Galbally and Roy* [1978], using a closed box flux technique, during May and November measured emissions of NO and NO_2 from grazed and ungrazed pastures in Australia. Based upon the assumption that the average of the measured fluxes was representative of globally averaged land emissions, they estimated that the global annual flux of NO was 10 Tg(N) yr^{-1} (1 Tg(N) = 10^{12} g(N)). Although this was an important, pioneering study, the conclusions were based on only 12 flux measurements with no correction for diurnal or seasonal variability.

Lipschultz et al. [1981] projected annual global emissions of NO equal to 14 Tg(N) based upon laboratory measurements of the ratio of NO to N_2O produced by nitrifying bacteria growing in a liquid medium. The ratio of NO to N_2O varied from 1.2 to 5.1. They assumed a global annual flux of N_2O equal to the calculated photochemical destruction rate (about 10 Tg(N) yr^{-1}). *Anderson and Levine* [1986] observed similar NO to N_2O ratios with nitrifier cultures in laboratory experiments. However, they also observed that denitrifying bacteria are capable of producing more N_2O per cell than are nitrifiers and that the ratio of NO to N_2O in denitrifying bacteria can be as low as 0.01. Anderson and Levine made no attempt to estimate the global annual emission of NO from these laboratory studies since sparged bacterial cultures, growing under optimal conditions, do not duplicate soil conditions.

Slemr and Seiler [1984] estimated the emission of NO_x from all soil sources including that from fertilized and unfertilized land as well as from animal excreta to be somewhat less than 11 Tg(N) yr^{-1}. They based these estimates on data obtained during August through October from fertilized and unfertilized sites in Germany and in Spain. Since they utilized the open flux box technique, they were able to measure NO_2 fluxes as well as NO fluxes, and they noted that the NO flux approximately equaled the NO_2 flux. Their estimate of NO_x emissions from unfertilized land took into account diurnal variation. In addition, they make a crude correction for seasonal variation, although all their measurements took place between August and October. They assumed that land areas poleward of 30° latitude contribute NO_x to the atmosphere only over a 6-month period.

Johansson and Granat [1984] determined NO and NO_2 emissions from fertilized and unfertilized land in Sweden between April and July and again in September. They compared the open to the closed box flux techniques and concluded that the closed system was more reliable. Their estimates of annual

TABLE 5. Multiple Regression Analysis: No Flux Versus Soil Parameters

Site	Number of Measurements	Soil Variables	Regression Coefficient[a]	Standard Error Regression Coefficient	r^2
Colorado (all plots)	43	temperature[b]	0.14 (0.04)	0.02	0.60
	14	temperature[c]	0.56 (0.18)	0.08	0.79
	63	temperature and moisture	0.22 (0.06) 0.25 (0.08)	0.03 0.04	0.54
Virginia					
Site 1	93	temperature	0.57 (0.34)	0.17	
		moisture	−0.75 (0.52)	0.26	
		nitrate	0.13 (0.12)	0.06	0.25
Site 2	72	temperature	0.07 (0.06)	0.03	
		nitrate	0.12 (0.04)	0.02	0.33

[a]95% confidence limits given in parentheses.
[b]Data filtered—soil moisture 11–13%.
[c]Data filtered—soil moisture 23–30%.

NO emissions, corrected for diurnal variation, range from 0.2 kg(N) ha^{-1} to 0.6 kg(N) ha^{-1} for unfertilized and fertilized sites, respectively. They assumed zero emission during winter. In addition to these measurements, *Johansson* [1984] determined emissions of NO from fertilized and unfertilized forest soils in Sweden during June and August to September. Assuming zero emissions during winter, *Johansson* [1984] calculated an annual flux of 0.04 kg NO(N) ha^{-1} from unfertilized sites. Utilizing their own flux estimates for arable and forested land and those of *Galbally and Roy* [1978] for temperate grasslands and assuming that tropical rain forests as well as savannahs and tundras emit less NO than cultivated land, they estimated a global annual NO flux of 0.2–3.2 Tg NO(N), far less than that estimated by others.

It is clear that more information concerning the critical parameters that control NO and N_2O emissions is required before such extrapolations can give accurate estimates of global annual biogenic NO or N_2O emissions. In our studies we observed a strong diurnal variation for NO. The annual NO flux corrected for diurnal variation was 65% of the flux calculated without taking diurnal variation into account. In virtually all of our measurements, soil was a source of NO to the atmosphere. Ambient concentrations of NO during our studies were generally 5 ppbv or less.

Significant NO emissions were observed during all seasons, including winter. This is the first report, to our knowledge, describing wintertime fluxes. The NO emitted between May and October accounted for 76% of the annual flux, whereas 24% of the total NO was emitted between November and April. Thus winter months should not be ignored when calculating annual emission rates.

Microbiological activity (as opposed to abiological production) was responsible for production of both the NO and N_2O observed at our field sites. *Chalk and Smith* [1983] have suggested that chemodenitrification (the nonenzymatic decomposition of nitrite) is the major source of the NO emitted from soils. However, in all of our soil analyses, nitrite concentrations were less than 0.5 $\mu g\ g^{-1}$ soil. In addition, soil from our experimental sites failed to produce either NO or N_2O after it had been autoclaved at 121°C for 30 min.

We observed NO fluxes ranging from 0.53 kg(N) $ha^{-1}\ yr^{-1}$ for unfertilized land to 2.08 kg(N) $ha^{-1}\ yr^{-1}$ for fertilized land. *Galbally and Roy* [1978] observed a range of 0.5–1.1 kg(N) $ha^{-1}\ yr^{-1}$ for ungrazed and grazed grassland; however,

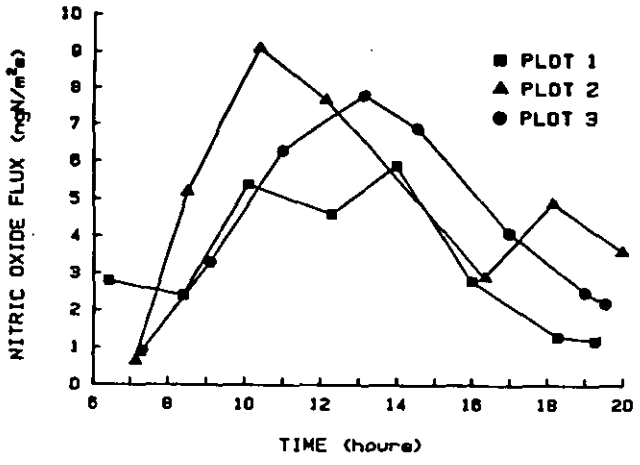

Fig. 3a. Nitric oxide fluxes at three plots.

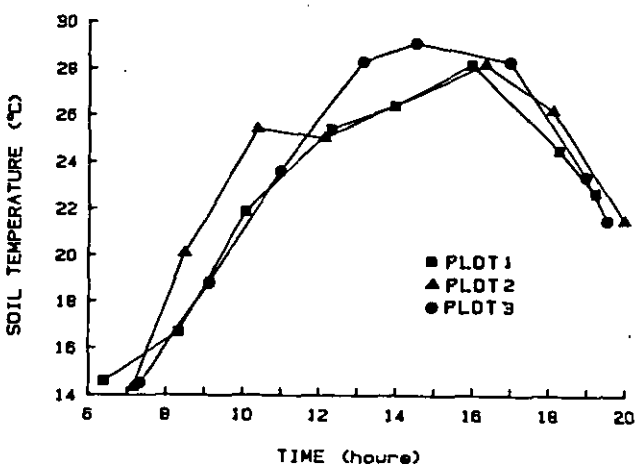

Fig. 3b. Soil temperatures at the same three plots.

Fig. 3. Effect of soil temperature on NO fluxes during a diurnal study—Virginia. Measurements were made between 0600 and 2000 LT of NO fluxes and soil temperatures at three plots in site 4, Jamestown, Virginia. Soil moisture at this site was 2.7%. The concentration of exchangeable nitrate was 6 $\mu g(N)\ g^{-1}$ soil.

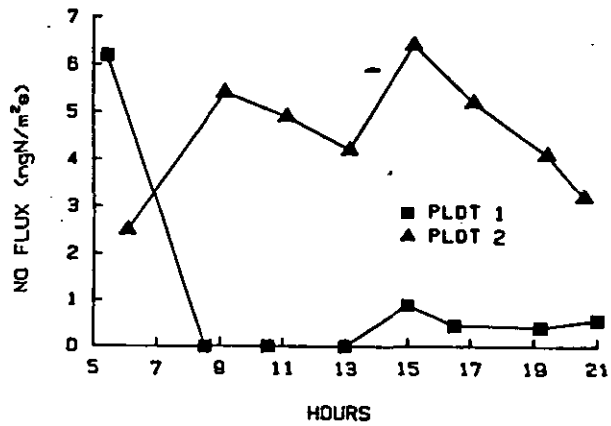

Fig. 4a. NO fluxes.

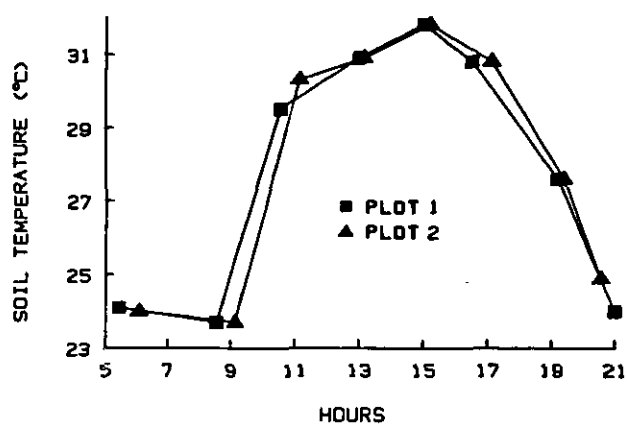

Fig. 4b. Soil temperatures.

Fig. 4. Effect of water saturation on NO fluxes during a diurnal study—Virginia. Measurements of NO fluxes, soil moisture, and temperature were performed at two plots in site 1, Jamestown, Virginia, during July 1984 between 0500 and 2100 LT. The first measurements were made prior to rain (2.54 cm) which occurred between 0600 and 0845 LT. During the storm, plot 1 was exposed, and plot 2 was protected from the rain. Soil moisture was 24% at plot 1 and 18% at plot 2. Field capacity was approximately 21%.

they made no correction for diurnal or seasonal variation. *Slemr and Seiler* [1984] observed emissions of 0.7 kg(N) ha^{-1} yr^{-1} for unfertilized soils. Finally, *Johansson and Granat* [1984] observed fluxes of 0.2 kg(N) ha^{-1} yr^{-1} for unfertilized and 0.6 kg(N) ha^{-1} yr^{-1} for fertilized arable land. In addition, *Johansson* [1984] reported an average annual flux of 0.04 kg(N) ha^{-1} from unfertilized forest soils. The fluxes reported by Johansson are lower than those reported by others perhaps because of the lower average land/air temperatures occurring during his study. The percent fertilizer loss as NO(N) reported in our study at an agricultural site was 0.79%, whereas Johansson observed a loss of 0.35% from forest soils.

A strong dependence of flux on temperature was noted in this study as well as in reports by *Slemr and Seiler* [1984] and by *Johansson and Granat* [1984]. Similarly, all of these studies reported a strong influence of soil moisture on NO emissions. The effect of moisture on NO and N_2O emissions depends upon field capacity of the soil and upon the time interval between wetting and drying. In our study we observed that saturated soil did not produce NO. Gas emission from soil is an integrated result of both production and loss mechanisms. Results of laboratory studies [*Anderson and Levine*, 1986; *Lipschultz et al.*, 1981] confirm that both NO and N_2O production are strongly impacted by the availability of oxygen. Loss mechanisms are not as well understood. Based upon available information, the results of this study suggest that NO is produced primarily by nitrification, an aerobic process. On the other hand, as reported in this study and by *Slemr and Seiler* [1984], NO fluxes increased dramatically when soil that had been dry for a prolonged period of time was wetted, provided that the soil did not become saturated. At our Colorado site we observed a large increase of nitrate within our unvegetated collar during July, apparently resulting from mineralization of underground vegetation left behind when wheat plants were pulled from the soil in early May. The dry period during June and July depressed microbiological activity, resulting in an accumulation of nitrate.

We found that it was difficult to compare emissions from

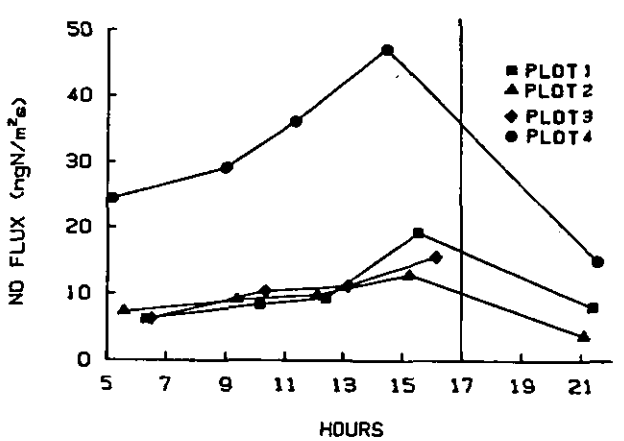

Fig. 5a. NO fluxes.

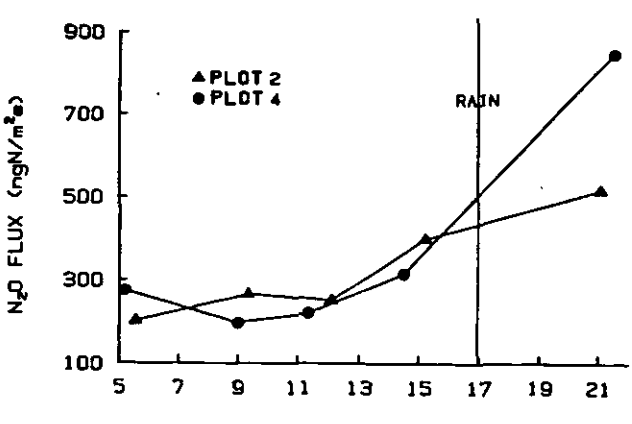

Fig. 5b. N_2O fluxes.

Fig. 5. Effect of water saturation on NO and N_2O fluxes during a diurnal study—Virginia. Measurements were made at four plots in site 2, Jamestown, Virginia, during July 1985. The site had been recently fertilized. Exchangeable nitrate was 37 μg(N)/g soil. Rain (2.54 cm) occurred between 1700 and 1900 LT. Soil moisture was 18% before and 25% after the rain.

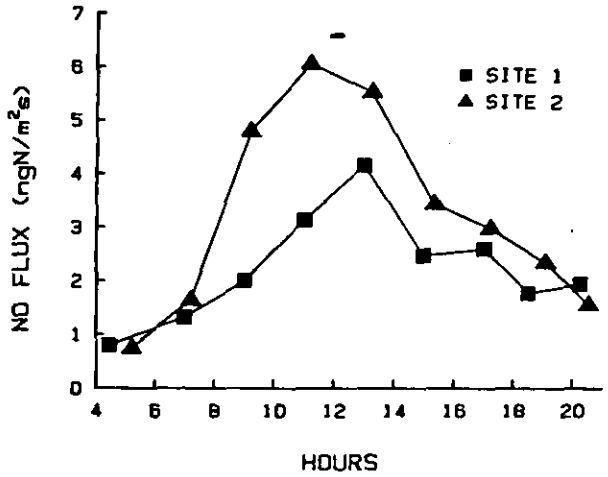

Fig. 6a. Diurnal study—Colorado. NO fluxes were measured at a wheat field site in Bennett, Colorado, between 0400 and 2000 LT. Site 1 was vegetated; site 2 was not. Soil moisture was 11%.

vegetated and unvegetated plots in a meaningful way, since several soil parameters, including moisture, temperature, and available nitrate, were considerably different. Considering those differences, fluxes from vegetated plots in Colorado were only slightly less than fluxes from unvegetated plots, perhaps because of depressed microbiological activity in the dry soil.

Although NO was not emitted from water-saturated soil, N_2O emissions increased dramatically as soil moisture approached or exceeded field capacity, implying that N_2O was produced primarily by denitrification. As suggested by *Anderson and Levine* [1986] and demonstrated by *Poth and Focht* [1985], denitrification can be performed by either nitrifying or denitrifying bacteria as conditions become anaerobic. We did not attempt to calculate an annual flux for N_2O, since the fluxes measured were extremely variable and dependent upon percent soil moisture. Many other workers have similarly reported high spatial [*Folorunso and Rolston*, 1985, 1984; *Goodroad et al.*, 1984] and temporal [*Blackmer et al.*, 1982; *Slemr et al.*, 1984; *Terry et al.*, 1981; *Goodroad and Keeney*, 1984; *Conrad et al.*, 1983] variability. Because of the high spatial variability, *Folorunso and Rolston* [1984] have determined that no less than 350 N_2O flux measurements on a 3- by 36-m plot are required in order to estimate the "true" mean flux to within ±10% of the estimated mean. We did, however, estimate the loss of nitrogen as N_2O from fertilizer. We observed high N_2O fluxes from site 1 in Virginia during June and July after fertilization and while percent soil moisture was high. Fertilizer loss was 1.2% as $N_2O(N)$, very similar to the 1.3% loss of fertilizer (N) from a cornfield reported by *Mosier and Hutchinson* [1981].

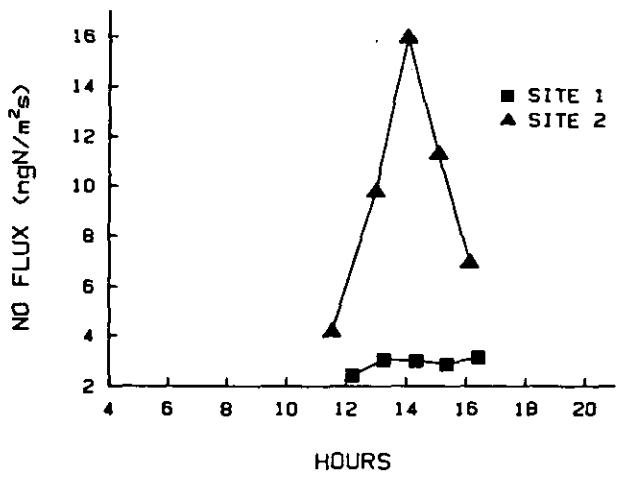

Fig. 6b. Effect of rewetting dry soil. Site 2 was irrigated with water (2.54 cm) one day after performing the above diurnal study (Figure 6a). Soil moisture was 11% at site 1 and 25% at site 2 after irrigation. Field capacity was approximately 32%.

We conclude from our results that it is not valid to assume that fluxes measured in temperate climates, such as those reported in this paper, are representative of globally averaged land emissions. More must be understood about the relationships between biogenic NO and N_2O emissions from soil, temperature, moisture, and available substrates before meaningful annual global extrapolations can be made.

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