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NITROUS OXIDE EVOLUTION RATES FROM FERTILIZED SOIL: EFFECTS OF APPLIED NITROGEN

D. J. McKENNEY[1], K. F. SHUTTLEWORTH[1], and W. I. FINDLAY[2]

[1]Department of Chemistry, University of Windsor, Windsor, Ontario N9B 3P4 and [2]Research Station, Agriculture Canada, Harrow, Ont. N0R 1G0.

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Nitrous oxide emission from agricultural soil has been measured in two relatively long-term studies over two different soil types, Brookston clay and Fox sandy loam, located at Woodslee and Harrow Ontario, respectively. The clay plots treated with various amounts (0–366 kg N·ha^{-1}) of ammonium nitrate, potassium nitrate, or urea were routinely monitored for periods up to 1 yr. Extreme variability in rates within the range 10^{8}–10^{13} molecules·cm^{-2}·s^{-1} was observed (1×10^{9} molecules·cm^{-2}·s^{-1} = 4.02 = 10^{-4} kg N·ha^{-1}·day^{-1} = 1.68 μg N·m^{-2}·h^{-1}). Over sandy loam, rates which were lower and more uniform (10^{8}–10^{11} molecules·cm^{-2}·s^{-1}) showed a strong correlation with amount of NH_4NO_3 applied. About 0.25% of applied fertilizer was released as N_2O within 80 days following treatment.

Total

On a mesuré l'émission d'azote nitreux dans le cadre de deux études de longue haleine portant sur deux types de sols agricoles, soit l'argile Brookston et le loam sableux Fox, situés à Woodslee et Harrow (Ontario) respectivement. Les parcelles d'argile diversement fumées (0–336 kg de N/ha) au nitrate d'ammonium, au nitrate de potassium ou à l'urée ont été régulièrement étudiées pendant certaines périodes allant jusqu'à 1 an. On observe une extrême variabilité des taux d'émission dans l'écart de 10^{9}–10^{13} molécules/s/cm. Sur loam sableaux, les taux d'émission, plus faibles et plus uniformes (10^{8}–10^{11} molécules/s/cm) révèlent une forte corrélation avec les apports de NH_4NO_3. Environ 0.25% de l'engrais appliqué se dégage sous forme de N_2O dans les 80 jours suivant le traitement.

We have recently published reports (McKenney and Findlay 1978; McKenney et al. 1978) of our study showing a strong correlation between nitrous oxide (N_2O) production and extent of nitrogen fertilizer application on Fox sandy loam. In this paper an extension of the investigation involving two relatively long-term studies is presented.

Some incentives for interest in this problem are: Nitrous oxide is a product of denitrification and other processes in soils. These constitute a major source of atmospheric N_2O (Hahn and Junge 1977) which in turn is considered to be the dominant source of stratospheric nitric oxide, NO (Crutzen 1971). Since subsequent chemical reaction of NO and NO_2 can catalytically destroy O_3 in the stratosphere there is concern over anthropogenic activities that might alter global N_2O levels. In particular, the effect on atmospheric N_2O levels resulting from the rapidly increasing agricultural use of industrially produced N-fertilizer has been the subject of a number of reports (Crutzen 1974; McElroy 1976; McElroy et al. 1976; Crutzen and Ehhalt 1977; Liu et al. 1976, 1977; Sze and Rice 1976). Estimates of the extent of O_3 depletion, however, show considerable disagreement, largely because major gaps exist in our understanding of the nitrogen cycle. Without precise quantitative knowledge of global sources and sinks of

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atmospheric N_2O, no confidence can be placed in any predictions. Essential information includes knowledge of the fraction of applied N-fertilizer that is returned to the atmosphere as N_2O in a relatively short period of time, and whether there is a long-term effect on N_2O evolution rates from agricultural soils or associated lakes and river systems which are major receptacles for large quantities of nitrogenous wastes. This work is addressed primarily to the former (short-term) problem.

In addition, more efficient use of nitrogen fertilizer depends on an adequate knowledge of potential losses of soil nitrogen. Dentrification and other processes of nitrogen removal have not been fully evaluated, partly because of difficulties in measuring flux of N_2O and N_2 under natural field conditions.

MATERIALS AND METHODS

Sites

HARROW. The sample sites were located on Fox sandy loam, a well-drained soil described by Richards et al. (1949) and currently classified as a Gray Brown Luvisol. The plots were planted to corn (*Zea mays* L.) and treated with different rates of NH_4NO_3 in the range 0–336 kg N·ha^{-1}. The fertilizer was broadcast (17 May 1978 and 10 May 1979) and incorporated into the soil. Planting took place on 19 May 1978 and 10 May 1979. The sample chambers were placed mid-row. These plots were part of a longer-term study where the treatments had been repeated on the same plots annually since 1970. Consequently the rate information must include consideration of any residual effects from previous years.

WOODSLEE. In this case the sites were located on Brookston clay (Orthic Humic Gleysol) with poor natural drainage (Richards et al. 1949). A 10-m^2 plot was cultivated and divided into five 2-m^2 sites. Four of these sites were treated with different rates of fertilizer: KNO_3 and urea each at 168 and 336 kg N·ha^{-1}, respectively. KNO_3 was applied on 19 Oct. 1977 and urea was applied on 11 Apr. 1978. One site was left untreated as a control plot. Four chambers were installed in each for replicate measurements. During the period 14 May–13 June 1979, sites of the same soil type treated with NH_4NO_3 at rates of 0, 112, 224, 336 kg N·ha^{-1} and planted to corn were studied. In this case, fertilization and planting was done on 16 May 1979.

Field Chambers

The chambers or canopies were open-ended aluminum cylinders, ~15 cm diam by ~25 cm length. The cylinders had a sharpened cutting edge on the bottom and were carefully driven about 5–10 cm into the soil by even pressure applied to a heavy metal plate placed on top of the cylinder. Care was taken to minimize disturbing the soil. The cylinders were left in place throughout the entire study, open to the atmosphere except during the actual sampling period. Immediately prior to sampling, a plexiglass lid, fitted with a compression-sealing neoprene 0-ring, was applied. Air samples were drawn into the evacuated tubes through a hypodermic needle inserted through a septum port in the cover. The needle was left in the chamber cover throughout the sampling period in order to minimize pressure fluctuations between the inside and the outside of the chamber. Losses of N_2O due to diffusion through the needle were calculated to be insignificant. A paddle-wheel fitted through the lid was gently rotated several times before each sampling. Air and soil temperatures could be measured inside and outside the chamber.

Sampling

Gas samples were collected as described previously (Findlay and McKenney 1979) using small (~20 cm^3) evacuated Pyrex tubes fitted with rubber septums.

For the long-term studies it was considered advantageous to monitor as many as 12 chambers over three different plots (four replicates) within a reasonably convenient time interval. In most cases, therefore, it was necessary to sample only three times per chamber at 30-min intervals

Analytical

Analyses for N_2O were carried out in the laboratory using a Perkin-Elmer 3920 B gas chromatograph equipped with a ^{63}Ni electron capture detector and a Porapak Q stainless steel column, 3 m × 0.3 cm (10 ft × 1/8 in.). Operating temperatures of the detector, interface between column and detector (ECD), and column were 350, 150 and 50°C, respectively (Rasmussen et al. 1976). The carrier gas (95% argon

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methane) flow rate was 30 cm^3·min^{-1}. The standing current was 3.0 × 10^{-9}A. Precise injection to the G.C. was accomplished through a hypodermic needle into an evacuated 1-cm^3 loop of a gas sampling valve. Precision of 1% or better was possible using peak height measurements.

Soil moisture was determined gravimetrically.

Calibration

The G.C. was routinely calibrated (usually daily) against 20–100 ppm mixtures of N_2O in air (Liquid Carbonic Analyzed Calibration mixtures). Calibrations were made using aliquots chosen to span the range of N_2O levels normally measured, ~10 ppb to >10^4 ppb. We have found no evidence of instability of the primary reference standards over durations of more than 1 yr.

Holding times, Denmead.

Calibration drift resulting from variations in laboratory temperature (Pierotti et al. 1978) was taken into account. Possible error caused by variations of moisture level (relative humidity) in samples (Goldan et al. 1978) was investigated using standards containing known added amounts of water vapor. The ECD sensitivity for N_2O was apparently unaffected by the relatively small quantities of water vapor in field samples.

Ambient N_2O levels were measured routinely and were similar to those reported by others (Pierotti et al. 1978; Goldan et al. 1978; Pierotti and Rasmussen 1977). For the period July 1977–July 1979, ambient levels averaged 335.7 ± 15.8 ppb (± δ). This value is higher than the value we reported earlier (303 ± 10 ppb, Findlay and McKenney 1979) when a different calibration standard was used.

Several papers (Pierotti et al. 1978; Goldan et al. 1978; Pierotti and Rasmussen 1977) have stressed the need for interlaboratory comparisons of calibration standards where absolute accuracy is to be estimated. Whereas this is required for determining absolute tropospheric concentrations of N_2O and possibly for identifying long-term trends, it should perhaps be emphasized that rate measurements reported here require only relative concentration measurements. Thus rates can, in principle at least, be measured quite accurately. Although good precision can be obtained in practice, it is extremely difficult to determine the level of accuracy because of experimental and environmental factors (Denmead 1979; Mathias et al. 1979). The scatter observed in yield-time plots (5 or more points) corresponded to a resolution of ~8 × 10^8 molecules·cm^{-2}·s^{-1}; i.e. about ± 5% uncertainty for rates greater than 15 × 10^9 molecules cm^{-2}·s^{-1} (Findlay and McKenney 1979).

Reproducibility of measurements on a field sample taken from a Pyrex sample tube was better than 1% and the reproducibility of successive measurements of ambient air drawn in from inside or outside the laboratory over a period ~2 h was typically 0.7%. Reproducibility of successive measurements of standard mixtures was similar or better.

Calculation of Rates

Rates of N_2O emission from soils in the field were calculated from the slopes (least squares) of linear N_2O yield versus time plots. As reported previously (McKenney et al. 1978; Findlay and McKenney 1979), ordinarily samples would be taken at 15-min intervals over a period of 60–75 min. The linear plots obtained indicated no obvious effect of increasing concentration of N_2O in the chamber on the measured rate of N_2O evolution. Obviously the N_2O concentration will increase within the closed chamber to a limit. It is therefore expected that yield-time curves should be non-linear. Initially, however, even for relatively high rates of production, approximate linearity was observed. No great advantage was obtained by using curvilinear analysis to calculate initial rates (Findlay and McKenney 1979).

RESULTS AND DISCUSSION

Harrow Site (Fox Sandy Loam)

Nitrous oxide emission rates were measured in the range ~10^8 to 6 × 10^{10} molecules N_2O cm^{-2}·s^{-1}, which were comparable to rates measured on the same site during the summer of 1977 (McKenney et al. 1978). Table 1 shows the calculated rates measured for the periods 9 June–16 Nov. 1978 and 9–16 May 1979. It should be noted that over much of the early time period (9 June–20 July 1978), despite considerable variability, there was clearly a strong correlation between N_2O flux and rate of nitrogen fertilizer (NH_4NO_3) treatment. The data can be represented by a simple regression equation (Table 2) during the month or two following fertilization.

These observations confirm our earlier 1977 study (McKenney et al. 1978) where a similar correlation was obtained for this type of soil. In that case, $\log_{10}$ [Flux (molecules

Table 1. Mean N_2O emission rates ± σ (three replicates) measured over Fox sandy loam, Harrow, for the period June 9-16 Nov. 1978 and 9-16 May 1979

	Molecules $N_2O \times 10^{9} \cdot cm^{-2} \cdot s^{-1}$			
	NH_4NO_3 treatment (kg N · ha^{-1})			
Date	0	112	224	336
06-09-78	1.43±1.13	3.04±1.94	14.3±2.84	24.8±11.5
06-12-78	1.84±1.01	3.67±1.76	23.5±19.2	41.4±25.4
06-15-78	1.82±1.42	5.39±1.82	31.4±29.3	41.8±24.2
07-06-78	3.26±1.89	2.73±1.23	18.6±20.4	23.4±18.4
07-13-78	1.03±0.20	1.42±0.84	1.43±0.33	4.35±4.10
07-20-78	0.53±0.09	0.70±0.54	3.16±3.12	4.08±0.80
07-27-78	0.28±0.27	0.65±0.71	2.66±1.80	2.30±0.58
08-03-78	1.03±1.20	0.30±0.28	7.92±6.02	2.80±1.12
08-17-78	0.64±0.56	0.85±0.52	2.35±2.90	3.86±3.20
08-24-78	0.41±0.70	6.52±10.6	1.63±2.01	0.82±0.96
09-07-78	0.81±0.36	0.85±0.79	1.22±0.63	2.21±1.65
09-19-78	1.65±0.24	1.52±0.42	2.61±2.18	5.69±4.19
09-28-78	0.52±0.60	0.58±0.49	1.69±0.39	4.17±1.02
10-04-78	1.19±0.56	3.55±4.27	2.08±1.43	3.14±1.16
10-19-78	1.05±0.59	0.01±0.01	0.83±0.76	3.86±4.77
10-30-78	0.53±0.49	1.26±1.08	1.15±0.10	3.21±4.19
11-16-78	1.32±1.01	0.37±0.41	1.63±1.49	4.70±5.03
05-09-79	0.16±0.14	0.41±0.12	0.53±0.33	0.71±0.30
05-11-79	0.27±0.10	0.47±0.31	0.37±0.16	0.65±0.18
05-16-79	0.24±0.10	0.32±0.25	0.53±0.22	1.00±0.53

$N_2O\ cm^{-2}s^{-1})] = 0.00232\ [NH_4NO_3\ (kg\ N \cdot ha^{-1})] + 9.39$ over the period 20–24 June 1977. It appears, therefore, that loss of fertilizer nitrogen as N_2O occurs soon after application and may persist for several months before emission rates are reduced to "background." Weather conditions will have an influence. For example, increased moisture levels will increase rates of N_2O evolution (Hahn and Junge 1977; Freney et al. 1978; Hutchinson and Mosier 1979).

Figure 1 shows a rate versus time graph for the plot treated with 336 kg N · ha^{-1}. The data plotted are those measured in the chamber which showed the largest emission rates, along with the data from the control site for comparison.

Graphical integration of the curve obtained for the most heavily fertilized site over the first 80 days indicates a total loss of 0.846 kg N · ha^{-1}. This amounts to only 0.25% of the applied NH_4NO_3. Losses measured on the other sites were smaller. It should be emphasized, however, that the soil here is coarse-textured and was considered to be well-aerated with a moisture level well below field capacity (13%, McKenney et al. 1978) over most of the period (Table 2). The variability observed (Table 1) may be the result of changing oxygen levels at microscopic sites in the soil (Hutchinson and Mosier 1979; Smith et al. 1978) where denitrification processes are assumed to occur (Russell 1973; Alexander 1977). There is laboratory evidence, however, to show that significant production of N_2O can be obtained by autotrophic nitrification (Bremner and Blackmer 1978). Our earlier field measurements (McKenney et al. 1978) and those reported here from over well-aerated sandy loam lend some support to the suggestion (Hutchinson and Mosier 1979

Table 2. Regression analysis $Y = a + bX$, where $Y = \text{Log}_{10}$ [N_2O flux (molecules $cm^{-2} \cdot s^{-1}$)] and $X = NH_4NO_3$, kg $N \cdot ha^{-1}$, applied N fertilizer, Field 52, Fox sandy loam, Research Station, Harrow

Date†	*a*	*b*	*r*‡	*F*	Soil moisture (%)
06-09-78	9.00	.00432	0.87	31.90**	11.4
06-12-78	9.17	.00421	0.87	32.44**	8.2
06-15-78	9.14	.00464	0.84	24.11**	8.5
07-06-78	9.34	.00281	0.75	13.13**	8.1
07-13-78	8.96	.00137	0.61	6.00*	5.4
07-20-78	8.61	.00293	0.78	15.76**	-
07-27-78	8.42	.00283	0.55	4.40	2.2
08-03-78	8.95	.00181	0.48	3.08	3.6
08-17-78	8.86	.00144	0.46	2.73	5.6
08-24-78	9.38	.0005	−0.14	<1	3.0
09-10-78	8.90	.0009	0.46	2.63	2.8
09-19-78	9.09	.00119	0.34	1.35	11.9
09-28-78	8.66	.00253	0.78	15.63**	8.1
10-04-78	9.05	.00153	0.48	3.04	10.6
10-19-78	8.20	.00167	0.25	<1	11.8
10-30-78	8.87	.00100	0.38	1.70	10.1
11-16-78	9.08	.00090	0.27	<1	-
05-09-79	9.18	.00238	0.60	6.75*	-
05-11-79	9.50	.00090	0.53	3.98	-
05-16-79	9.35	.00191	0.69	9.21*	-

*, ** = Significant at a probability of 0.05 and 0.01, respectively.

†Sample collection dates, fertilized with 0, 112, 224 and 336 kg $N \cdot ha^{-1}$ on 17 May 1978 and 10 May 1979.

‡*r* = correlation coefficient; *F* = ratio, regression mean square/residual mean square.

that nitrification processes can contribute substantial amounts of N_2O to the atmosphere.

Woodslee Site (Brookston Clay)

Nitrous oxide emission rates measured over Brookston clay generally tended to be one or two orders of magnitude greater than those over sandy loam. Fluxes ranging from 7×10^8 to 1.5×10^{13} molecules $N_2O \cdot cm^{-2} \cdot s^{-1}$ were measured over the period 3 Oct. 1977–Nov. 1978 on the control, KNO_3 and urea sites, and for the period 14 May–13 June 1979 on the NH_4NO_3 site. Rate data are shown in Fig. 2 and 3 and Table 3. It is evident that the degree of variability is much more pronounced over this type of soil than over sandy loam. Variations in rate from day to day and site to site were often as much as two or more orders of magnitude over clay. On sandy loam, variability of about one order of magnitude was the maximum observed. Figure 2 shows rates measured on the KNO_3 site for the period 3 Oct. 1977–20 Dec. 1978, and illustrates the typical variability observed from chamber to chamber within one 2-m² area sampled only minutes apart. Figure 2 and 3, and Table 3 clearly show that there is no apparent correlation between N_2O emission and KNO_3 application rate. N_2O flux is more pronounced during the fall and spring periods where high moisture levels limit aeration.

The urea plots (not shown) also showed similar variability from site to site and from day to day. Again no obvious correlation was seen between N_2O flux and fertilizer treatment.

Results obtained from the plots treated with NH_4NO_3 are shown in Table 3. The extreme variability observed can also be seen in Table 4 which shows a regression analysis for data obtained over the NH_4NO_3

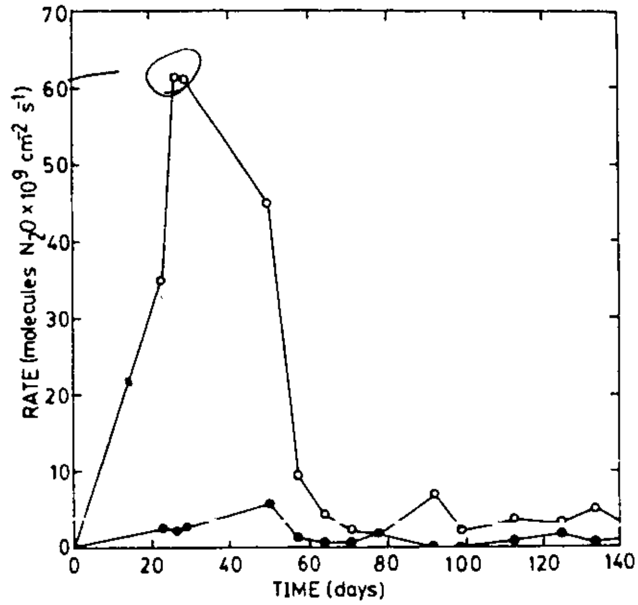

Fig. 1. N_2O emission rates for 140 days following NH_4NO_3 fertilization 17 May 1978 on Fox sandy loam, Harrow. Results shown are from the chamber giving highest rates over the site treated with 336 kg N · ha^{-1} (○). Control site data (●) are shown for comparison.

sites. Comparison of Tables 2 and 4 shows the marked contrast between results obtained from Fox sandy loam and from Brookston clay where the same fertilizer was used. The precise reason for the difference is not clear. The soils are different with respect to texture, organic matter and drainage. In addition the sandy soil had been fertilized since 1970 at the rates indicated so that the control plots were undoubtedly lower in N than their clay counterparts. In any case there was no apparent correlation of N_2O rate with the substantial amounts of fertilizer nitrogen added to the clay soil.

CONCLUSIONS

The data presented here are not sufficient to distinguish between the possible mechanisms of N_2O production. The results do not disagree with the well-known hypotheses

Table 3. Mean N_2O emission rates ± σ (3 replicates) measured over Brookston clay, Woodslee for the period 14 May–13 June 1979

	Molecules $N_2O \times 10^9 \cdot$ cm$^{-2} \cdot$ s^{-1}			
	NH_4NO_3 treatment (kg N · ha^{-1})			
Date	0	112	224	336
05-14-79	15.5±5.20	2.65±1.16	34.5±39.6	8.74±10.6
05-17-79	17.0±13.0	5.35±1.18	13.4±16.9	19.5±9.16
05-22-79	14.7±189	20.3±14.4	16.8±15.8	43.4±41.8
06-04-79	580±690	1190±1060	641±460	2180±1370
06-13-79	16.1±12.8	5.63±5.70	43.0±56.3	32.2±42.9

5/16 fert

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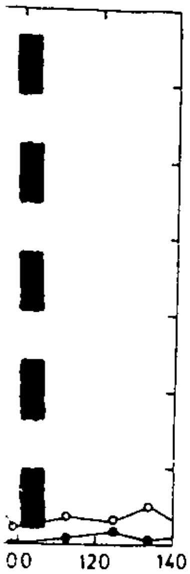

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cm⁻²·s⁻¹	
N · ha⁻¹)	
224	336
34.5±39.6	8.74±10.6
4±16.9	19.5±9.16
8±15.8	43.4±41.8
1±460	2180±1370
43.0±56.3	32.2±42.0

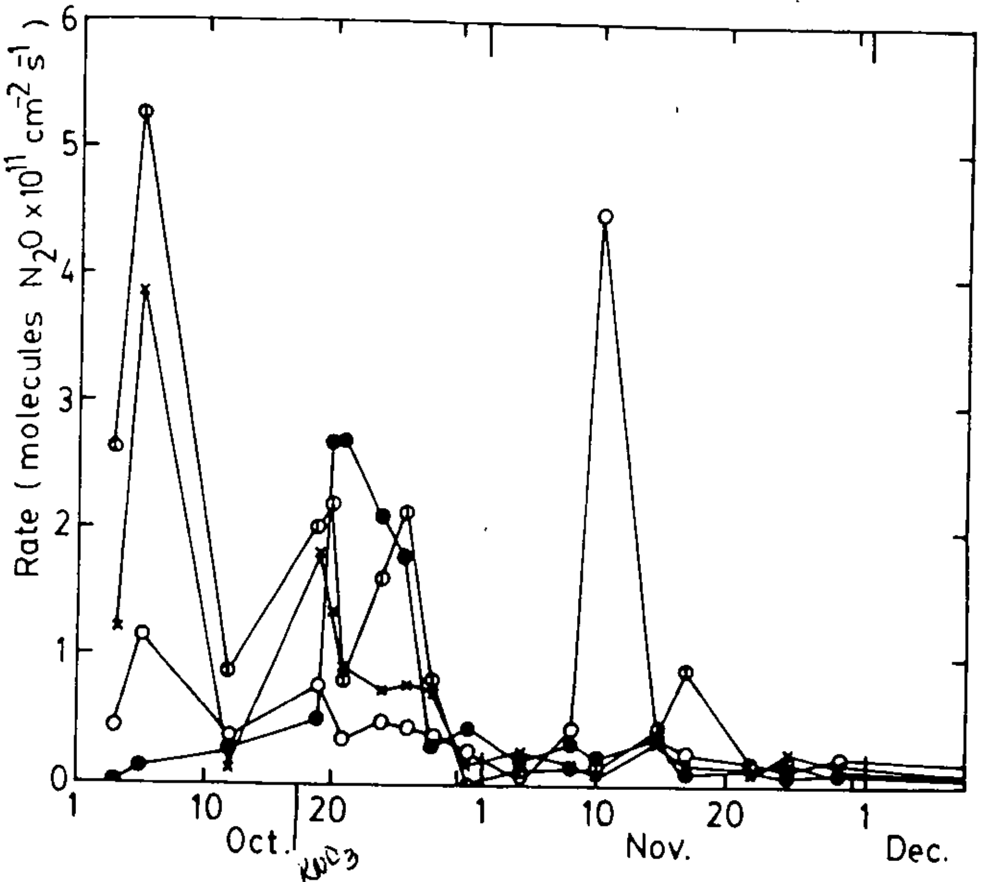


Fig. 2. N_2O emission rates for Woodslee Brookston clay, October–December 1977 illustrating typical variability for this soil. Results shown were obtained from the four chambers situated on the site treated with KNO_3 at 336 kg N · ha⁻¹.

Table 4. Regression analysis $Y = a + bX$, where $Y = \text{Log}_{10}$ [N_2O flux (molecules · cm⁻² · s⁻¹)] and $X = NH_4NO_3$, kg N · ha⁻¹, applied N-fertilizer, Brookston clay, Woodslee

Date†	a	b	Correlation coefficient r	F-value F
05-14-79	9.86	−0.00167	−0.17	<1
05-17-79	9.86	0.00069	0.22	<1
05-22-79	10.57	−0.00092	−0.24	<1
06-04-79	11.37	0.00227	0.43	2.32
06-13-79	9.69	−0.00113	−0.09	<0.09

†Sample collection dates, fertilized with 0, 112, 224 and 336 kg N · ha⁻¹ on 16 May 1979.

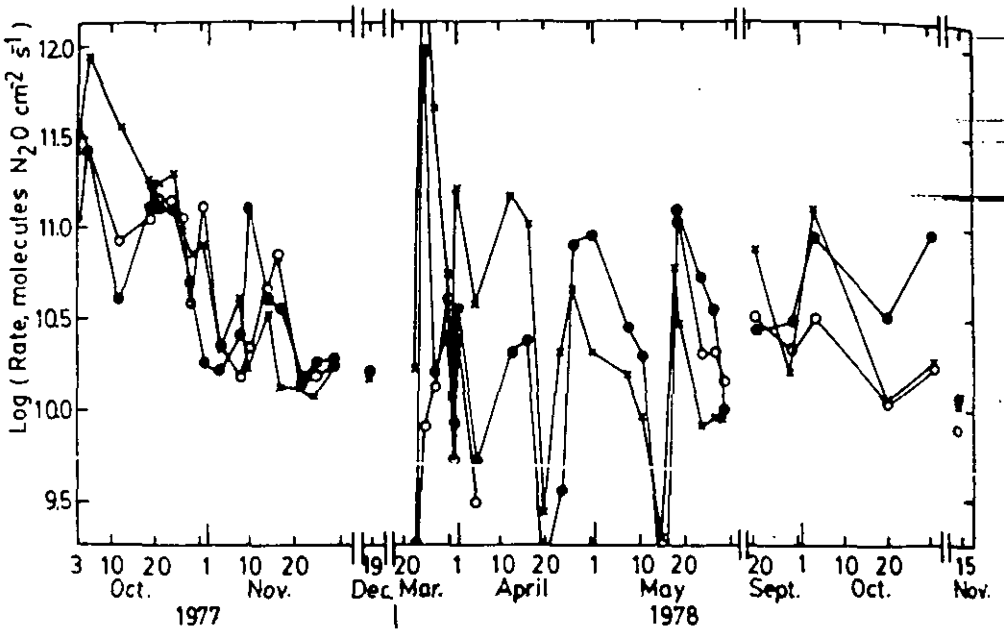
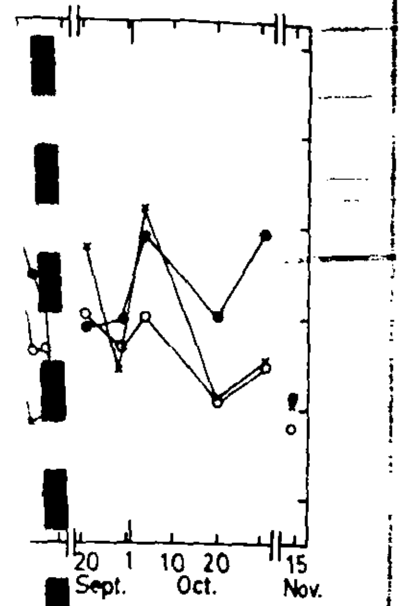


Fig. 3. Log average N_2O emission rates over Brookston clay, Woodslee, for the period 3 Oct. 1977–15 Nov. 1978. KNO_3 treatment: ●, 336; ○, 168; ×, 0 kg N · ha^{-1}.

that denitrification may occur in anaerobic microsites in a generally aerobic soil mass (Russell 1973; Alexander 1977). If so, these data show that N_2O evolution from such microsites must be quite intense and persistent over a relatively long period of time. The data also suggest that the number of such microsites is much greater in clay soil where aeration may be more restricted. According to Smith et al. (1978), denitrification rates in some soils are apparently not increased by either NO_3^- or NO_2^- additions. It is possible that the N_2O produced, especially in the well-aerated sandy loam, may be from nitrification processes as indicated earlier (Hutchinson and Mosier 1979).

The relatively large variability in rates of N_2O evolution, particularly from clay soil, illustrates the difficulty involved in assessing net global production rates required for calculation of effects on the ozone layer. Rates integrated over relatively long durations and under many soil situations are required if long-term effects of applied fertilizer on N_2O evolution are to be observed. Our results for sandy loam show that it is possible to obtain reasonable estimates of fertilizer-derived nitrogen returned to the atmosphere as N_2O for periods of several months following application, information which is required to assess the impact on stratospheric ozone levels. Our data which show relatively small losses of fertilizer nitrogen as N_2O during the few months following fertilization agree with those reported by Hutchinson and Mosier (1979). The control site on sandy loam had not been fertilized with nitrogen since 1969, a period of 9 yr. Consequently, soil nitrogen levels on this site were considerably below those required for adequate plant growth, yet N_2O emission rates remained measureable at $\sim 10^9$ molecules · cm^{-2} · s^{-1}. Within about 80 days following fertilization, "background" rates of N_2O evolution were obtained on all sites. It would appear



odslee, for the period 3 Oct.

-term effects of applied O evolution are to be s for sandy loam show le to obtain reasonable rtilizer-derived nitrogen a osphere as N_2O for m ths following applica- hich is required to assess a spheric ozone levels. relatively small losses s N_2O during the few fertilization agree with H tchinson and Mosier e on sandy loam had n nitrogen since 1969. nsequently, soil nitrogen considerably below uate plant growth, yet remained measureable at $m^{-2} \cdot s^{-1}$. Within about ing fertilization. N_2O evolution were tes. It would appear.

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therefore, that short-term (decade or less) effects on tropospheric N_2O levels from applied fertilizer may be less serious than that suggested by McElroy et al. (1977).

The apparent lack of correlation between N_2O flux and fertilizer treatment on Brookston clay in natural field conditions also suggests that short-term effects on N_2O emission are unlikely to be very large.

Our data can be used to roughly estimate total N_2O production from land surfaces. Using a rate of 3×10^{10} molecules $\cdot$ $cm^{-2} \cdot s^{-1}$, which may be considered typical for Brookston clay, and multiplication by the reported (CAST 1976) estimates of harvested and non-harvested land areas, we obtain 13×10^9 kg N $\cdot$ yr^{-1} in reasonable agreement with the estimate, 20×10^9 kg N $\cdot$ yr^{-1} made by Hutchinson and Mosier (1979), but considerably less than the global estimate of 120×10^9 kg N $\cdot$ yr^{-1} (McElroy et al. 1977). The implication of this lower value in view of the known burden of atmospheric N_2O has been discussed by Hutchinson and Mosier (1979). We concur with their conclusion that either the atmospheric lifetime is considerably greater than 10 yr as estimated by Junge (1974), thus implying smaller global emissions, and/or that the oceans, fresh water media or some unknown source constitute a substantial net source of N_2O.

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