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AP-42 #10

Nitrous Oxide Production throughout the Year from Fertilized and Manured Maize Fields[1]

R. L. CATES, JR. AND D. R. KEENEY[2]

ABSTRACT

Two field sites on a loam soil were established to monitor N_2O concentration in the soil atmosphere and rate of emission from the soil surface. The sites were cropped to maize (*Zea mays* L.) and managed at two high-N levels (181 or 237 kg N ha^{-1}). Both sites received 168 kg N ha^{-1} as feedlot cattle (*Bos taurus*) manure (preplant-incorporated) and 13 kg N ha^{-1} as NH_4NO_3 fertilizer in the row at planting. One site (Site B) received additional soil-incorporated N (56 kg N ha^{-1}) as urea. Fluctuations in N_2O emissions from the two sites were temporally similar, and differed only in magnitude with Site A (no additional fertilizer), emitting about 3.6 kg N_2O-N ha^{-1} yr^{-1} and Site B about 5.2 kg N_2O-N ha^{-1} yr^{-1}, or about 2% of the N applied. Most of the N_2O was emitted between mid-June and the end of July when the soil was warm and NH_4^+-N was present, and at spring thaw (late March the following year) when soils were cold and near water-saturated. High N_2O emissions during the growing season occurred following precipitation events, and hence were associated with high soil water and probably with the initiation of soil drying. Nitrous oxide production was continuous during winter months, presumably a result of denitrification. The N_2O concentration in the profile of the frozen soil increased to high levels (nearly 2000 $\mu L\ L^{-1}$ N_2O at Site B) before spring thaw. At thaw, nearly 330 d after application of the N amendments, an apparent physical release period occurred and N_2O flux was far higher (about 50 g N_2O-N ha^{-1} d^{-1}) than at most times during the growing season.

Additional index words: ***Zea mays*** **L., Nitrification, Denitrification, Cold soils, Soil atmospheres, Profile nitrous oxide, Ozone layer.**

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Nitrous oxide (N_2O) has been implicated in the destruction of stratospheric ozone (Crutzen, 1981), which protects the biosphere from harmful levels of ultraviolet radiation. The gas may also contribute to the "greenhouse" effect (Yung et al., 1976; Joyce, 1985) expected to result from increasing atmospheric CO_2 levels.

The use of N fertilizer can result in dramatic increases in N_2O emissions from soils. Annual losses of N as N_2O from fertilizer-amended soils may be as high as 40 kg ha^{-1} (Ryden and Lund, 1980a), whereas annual emissions from unfertilized soils are usually <1 to 2 kg N ha^{-1} (Colbourn and Dowdell, 1984; Sahrawat and Keeney, 1986). Losses as N_2O from anhydrous NH_3 fertilized soils can represent as much as 7% of the applied N (Bremner et al., 1981).

Production of N_2O by soils had been viewed as evidence of denitrification, but it is now accepted that N_2O is also emitted during nitrification (Bremner and Blackmer, 1978, 1981; Blackmer et al., 1980; Goodroad and Keeney, 1984b; Duxbury and McConnaughey, 1986; Sahrawat and Keeney, 1986). Although it has been assumed that most N_2O is evolved during the growing season subsequent to application of N fertilizer, there is now evidence that N_2O emissions during thaw may be as high as at any other time of the year (Bremner et al., 1980; Goodroad and Keeney, 1984c, 1985). Even though the mechanisms of production and release have not been elucidated, denitrification may be the principal source of that N_2O. The significance of high N_2O emissions at thaw in relation to time of fertilizer application is not yet established, but could be one reason for the low efficiency of fall-applied fertilizer N.

We monitored N_2O emissions for 330 d and N_2O concentration in the soil atmosphere during winter and spring in two maize (*Zea mays* L.) fields managed at two N levels (181 or 237 kg N ha^{-1}). The study was conducted to provide information relating to factors controlling temporal fluctuations in N_2O emission and production rate, and the relationship of N_2O concentration in the soil profile to N_2O emission rate.

Sites

Two sites for monitoring N_2O production were established in May 1981 on a Kidder loam soil (fine-loamy, mixed, mesic Typic Hapludalf). The field in which the sites were established had been in maize since 1978 and alfalfa (*Medicago sativa* L.) for several years prior to 1978. Some characteristics of the surface (0–15 cm) soil were: water pH 6.7; organic C 1.2 g kg^{-1}; cation exchange capacity, 13 $mmol_c\ kg^{-1}$; bulk density, 1.29 Mg m^{-3}. Feedlot cattle (*Bos taurus*) manure (ca. 33.6 Mg ha^{-1}; 750 g kg^{-1} H_2O; 168 kg N ha^{-1}) was incorporated into the top 20 cm of soil at both sites, along with residue from the previous year's maize crop, just prior to maize planting (2 May). Both sites received an additional 13 kg N ha^{-1} as NH_4NO_3 in-row at planting, but only one of the sites (Site B) received additional N fertilizer (56 kg N ha^{-1}) as urea. The fertilizer urea was broadcast and immediately incorporated in the soil on 4 May. Thus the total N added as fertilizer and manure was 181 kg N ha^{-1} or 237 kg N ha^{-1} at Sites A and B, respectively. Soil test results indicated that P and K levels were not limiting for maize growth. Broadcast herbicides Bladex (2-{[4-chloro-6-(ethylamino)-*s*-triazin1-yl]amino}-2-methylpropionitrite) and Lasso [2-chloro-2′-6′-diethyl-*N*-(methoxymethyl)-acetanilide] were applied on the soil surface at both sites on 12 May. Furadan [2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate] insecticide was surface-applied in bands at planting.

Nitrous Oxide Monitoring

Nitrous oxide flux from the soil surface was measured using a closed-chamber technique (Goodroad and Keeney, 1984a). The chambers were open, rectangular, steel frames with a 2.5-cm flange on the top to provide a sealing surface. Surface area was 100 cm^2. Chambers (three replicates per site) were pushed into the soil approximately 7.5 cm so that the height remaining above the soil surface was 2.5 cm. At each site, one of the replicates was placed in-row, the other two between-row. Chambers were left in place once established. At sampling, chambers were enclosed with 1-cm thick plywood covers that had been coated

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[2] Formerly research assistant and professor of soil science, respectively, Univ. of Wisconsin-Madison, Madison, WI 53706. Current title and address of senior author is: assistant professor, Dep. of Soils and Water, Sultan Qaboos Univ., Al Khoud, Sultanate of Oman. Reprint requests should be sent to D.R. Keeney.

with epoxy paint and fitted with high-density polyvinyl foam and a central septum. Samples of the enclosed atmosphere were withdrawn by syringe at 0, 10, and 20 min. Air samples were contained in plastic syringes until analyzed. Sampling was conducted between 1000 and 1400 h at 7-d to 30-d intervals dependent on anticipated N_2O emission activity.

Soil atmosphere samples were estimated by use of sampling probes constructed of 2.5 cm (i.d.) polyvinylchloride pipe (Goodroad and Keeney, 1985). The probes were fitted with a 20-mL diffusion chamber at the lower end. A capillary tube led from the diffusion chamber to the top of the probe to allow for withdrawal of some of the chamber atmosphere by syringe. Three replicate probes were placed at each of three depths (10, 20, and 30 cm) in-row and between-row at each site. Additionally, three replicate probes were placed at 90 cm between-row at Site B.

Soil temperature measurements were made in duplicate at 1, 10, 20, and 30 cm using soil moisture–temperature cells (Soil Test, Inc., Evanston, IL) that measure temperature directly. Precipitation data were obtained from climatological stations located in the proximity of the experimental site.

The concentration of N_2O in air samples was determined with a Perkin-Elmer Sigma 3 gas chromatograph (Perkin Elmer Corp., Norwalk, CT) equipped with a ^{63}Ni electron capture detector (Mosier and Mack, 1980; Goodroad and Keeney, 1984a) interfaced to a Perkin-Elmer Sigma 10B controller. The relationship between area of N_2O peaks and concentration (v/v) was determined by standard curves developed from appropriate dilutions of a known concentration standard. Time between sampling and analysis was never greater than 24 h.

Nitrous oxide flux was calculated by the equation:

$$F = (k/T)(V/A)(\Delta c/\Delta t)$$

where F is the N_2O flux (g N_2O–N ha^{-1} d^{-1}), k is a unit conversion factor (3.41 g N K m^2 L^{-1} ha^{-1}) for calculation of N_2O emission, T is the mean air temperature (K) corresponding to each date of sampling, V is the volume of air within the chamber (2.5 L), A is area of soil within the chamber (0.1 m^2), and $\Delta c/\Delta t$ is the rate of change in the concentration of N_2O in the air within the chamber (μL L^{-1} N_2O d^{-1}).

Coefficients of variation (CV, %) among replicate flux or depth data on a given sampling date were calculated as an indication of spatial variability at each site. Duncan's multiple range test ($P \leq 0.10$) was used to compare N_2O data from each site across sampling dates and/or depths, where applicable.

RESULTS AND DISCUSSION

May to December Nitrous Oxide Flux

One of the three chambers at each site included the soil surface area designated as in-row (the zone immediately adjacent to the maize row in which banded fertilizer was placed at time of planting); the other two were placed between-row. All data presented are averages of the three chambers; we did not distinguish N_2O flux from in-row and between-row surface areas. Between May and December, the two sites had flux patterns that were temporally similar and differed only in magnitude (Fig. 1). The higher flux of N_2O from Site B than from Site A is presumed to be due to the additional urea N (56 kg ha^{-1}) applied at Site B. Most of the N_2O that was produced at the sites was released between mid-June and the end of July (Julian Day, JD, 160 to 204) during which time surface soil temperatures were warm (within the range 17 to 26 °C at 1 cm soil depth) and the concentration of

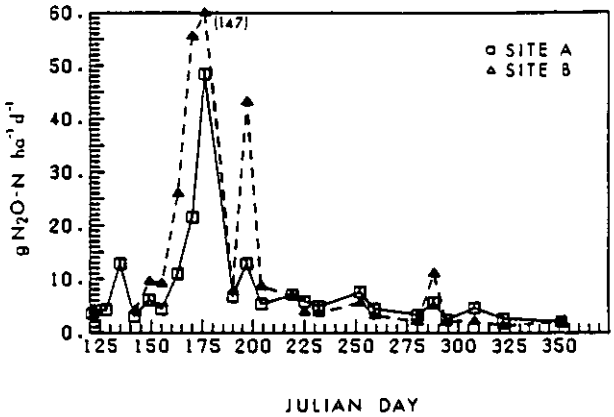

Fig. 1. Nitrous oxide flux from Sites A and B, May through December. Coefficients of variation (%) varied between 1 and 120.

soil NH_4^+-N in the top 15 cm of soil was relatively high (20 to 75 kg ha^{-1}).

The first N_2O peak (15 May, JD 135) at Site A (first sampling at Site B was 22 May, JD 142) corresponded with a dramatic increase in soil temperature. Surface soil temperature (1-cm depth) increased from 11 °C (8 May, JD 128) at 24 °C (15 May, JD 135). The soil stayed at about this temperature all summer. May was a very dry month, whereas June and August were wet (Table 1).

Broadcast herbicides (Bladex and Lasso) were applied to the maize field on 12 May (JD 132). Bremner at al. (1981) observed a small peak in N_2O emission after herbicide application. Some of the N_2O flux at Site A on 15 May may be attributed to this herbicide effect. For the remainder of the growing season, temporal fluctuations in N_2O flux over time at both sites were closely related to wetting and drying cycles. The peak emission rates during 12 June (JD 163) through 4 July (JD 185) occurred after rains (Table 1). Focht (1974) described a model for N_2O evolution that appears to fit the maximum-minimum relationship to soil water observed. The model predicts that N_2O flux would be low when the soil was saturated. Following a rain, N_2O would increase as the soil began to dry out (peak emission would occur when 12% of the pores were aerated) and then decrease. Fluctuations in N_2O production rate in response to wetting and drying have been also observed (e.g., Ryden and Lund, 1980b; Goodroad and Keeney, 1984b).

The manure applied at the sites was a major source of N for N_2O production. Duxbury et al. (1981) found that more N_2O was evolved from a maize field soil tested at

Table 1. Weekly precipitation at the sites, May through November (prior to soil freeze).

Month/day	Julian day	Precipitation
		mm
1 May–4 June	121–155	18
5 June–2 July	156–183	113
3 July–6 Aug.	184–210	132
7 Aug.–3 Sept.	219–246	167
4 Sept.–1 Oct.	247–274	59
2 Oct.–5 Nov.	275–309	61
6 Nov.–3 Dec.	310–330	34

the same N rates with manure than one that was side-dressed with liquid N fertilizer. Christiansen (1983) reported eightfold more N_2O from a manured than a fertilized grassland, and Goodroad et al. (1984) found the highest N_2O emission rates from manure-amended compared to fertilized or sludged-treated soils. Additionally, as a source of organic C, manure and residue from the 1980 maize crop would contribute to higher denitrification rates (when conditions were appropriate) and, in turn, greater N_2O production (Rolston et al., 1978; Goodroad et al., 1984; Linn and Doran, 1984).

The addition of urea to Site B resulted in a substantial increase in N_2O emissions, particularly in June. While N_2O flux from arable soils can be expected to increase with rate of fertilizer N (Bremner and Blackmer, 1978; Mosier et al., 1982; Breitenbeck and Bremner, 1986b), the form of fertilizer N can have a marked effect on the magnitude of the flux at similar N levels. Generally it has been shown that anhydrous ammonia, in particular, will result in more fertilizer-N loss as N_2O than urea (Breitenbeck et al., 1980; Bremner et al., 1981; Breitenbeck and Bremner, 1986a). Ammonium oxidizers are largely responsible for the high N_2O emission rates in arable soils (Christianson et al., 1979; Breitenbeck et al., 1980; Blackmer et al., 1980; Goodraod and Keeney, 1984b). In recent work, Duxbury and McConnaughey (1986) showed that the N flux from a urea-fertilized maize field was equally divided between dentrification and nitrification of liberated NH_4^+ over an 85-d growing period.

Average daily N_2O flux measured in our research over the 1981 sampling period (1 May to 17 December) was approximately 8 and 12 g N_2O-N ha^{-1} at Site A and Site B, respectively. In comparison, a minimum tillage maize field near Madison, WI, was sampled for N_2O emission rates over 2 years' growing seasons. This field was fertilized with 200 kg N ha^{-1} (as NH_4NO_3) both years. Average daily N_2O flux was approximately 2 g N_2O-N ha^{-1} d^{-1} in the first year and 30 g N_2O-N ha^{-1} d^{-1} in the second year (Goodroad et al., 1984). Wide yearly deviations in measured N_2O emissions appear to be related to precipitation patterns and perhaps to spacing of sampling times relative to precipitation events.

Differences in N_2O concentration with soil depth (10, 20, and 30 cm) were generally not significant ($P \leq 0.10$) due to high spatial variability. Spatial variability was usually greatest (CVs 90 to 100%) when N_2O concentrations in the soil atmosphere profile were high. This indicates localized areas of N_2O production and/or limited diffusivity of the gas due perhaps to high soil water content. Low CVs (10% or less) among replicates were often associated with low N_2O concentrations in the soil profile.

Temporal fluctuations in N_2O concentration in the soil profile were similar at both sites and for the in-row and between-row locations. Concentrations were generally highest from mid-June through the end of July (JD 165 to 204) when the soil was warm and soil NH_4^+-N was relatively high. Short-term fluctuations were related to soil wetting and drying cycles. Peak N_2O concentrations were associated with high soil water content. This observation is in agreement with findings of Goodroad and Keeney (1985). Soil N_2O sampling intensity was insufficient to establish whether maximum concentrations actually occurred at the same time as maximum soil water or after the soil began to dry. Based on the precipitation record, it would appear that most of the N_2O is produced after rainfall events and commencement of soil drying. Others have also noted that continuously wet soils where nitrification is limited and/or denitrification proceeds rapidly to N_2 emit little N_2O (Sahrawat and Keeney, 1986).

The amount of N_2O in the soil profile over the sampling period differed with site and proximity to the maize row. The highest N_2O concentrations were measured where N application rate was highest, i.e., in-row greater than between-row at each site, Site B greater than Site A. The differences were most pronounced at times of peak N_2O concentrations (JD 170, 176, 197, 252, and 288). Although only 13 kg N ha^{-1} additional N was placed in-row at planting, the effect of this N on local N_2O production was substantial. Nevertheless, given the relatively small surface area affected by the in-row treatment, the additional N_2O produced in that zone would not be expected to be a major contributor to the overall N_2O flux from the maize field. Higher N_2O concentration between-row as compared to in-row at Site A on 8 May (JD 128) could not be explained by a difference in soil water content but may be the result of an earlier initiation of nitrification of fertilizer N between-row. Differences in soil moisture in-row vs. between-row were not significant, although the in-row soil profile tended to be slightly drier in mid to late growing season (9 July, JD 190 to 28 August, JD 240), presumably due to more intensive plant uptake of available water in that zone.

Fluctuations in soil profile N_2O were closely reflected in the temporal pattern of N_2O evolution (Fig. 1) from the soil surface (high N_2O concentrations associated with high N_2O flux) with the exception of the possible herbicide-induced N_2O flux on 15 May (JD 135).

By early November (JD 305), the soil atmosphere N_2O concentration was uniformly low (ca. 1 to 3 μL N_2O L^{-1}) in the surface 30 cm at both sites. The soil profile over that depth froze later in early December and remained frozen throughout the winter.

January to March Nitrous Oxide Flux and Soil Profile Concentration

The two sites were monitored from January through initial soil thawing in late March (Table 2). Failure of the electron capture detector on the gas chromatograph forced us to terminate the experiment after 25 March. Nitrous oxide flux and concentration data and soil temperatures over this period are summarized in Table 2. There were no significant ($P = 0.10$) differences in N_2O concentration with soil depth because of the high spatial variability encountered.

The concentration of N_2O in the soil atmosphere was low in January through mid-February, but was greater than the previous November. Flux from both sites was

Table 2. Nitrous oxide flux and N_2O concentration in the soil atmosphere, late January through initial thaw in mid-March.

Sampling		Soil	N_2O flux or profile concentration†					
			Site A			Site B		
Date	Depth	temp.‡	Flux	Profile BR	Profile IR	Flux	Profile BR	Profile IR
	cm	°C	g N ha^{-1} d^{-1}	—— μL N_2O L^{-1} ——		g N ha^{-1} d^{-1}	—— μL N_2O L^{-1} ——	
26 Jan.	0	−1	7(26)b§			9(57)b		
	10	−1		8(19)b	9b		<1b	11(15)b
	20	−1		8(18)c	11(74)c		4(15)b	10(30)b
	30	−1		9(30)c	8b		7(65)b	9(22)b
	90	–					13b	
18 Feb.	0	0	13(34)b			16(75)b		
	10	0		6(72)b	11(29)b		2(76)b	15(61)b
	20	0		11(90)c	11(16)c		7(75)b	12(50)b
	30	0		1c	9(26)b		7(85)b	12(28)b
	90	–					9b	
24 Feb.	0	1	35(99)ab			15(32)b		
	10	1		83(54)b	135(48)ab		49(35)b	306(58)ab
	20	0		64(60)b	102(5)b		191(118)ab	140(92)b
	30	1		59(34)b	82(74)ab		76(83)b	94(62)a
	90	–					15b	
11 Mar.	0	0	17(32)b			29(44)b		
	10	0		156(98)b	157(6)ab		24(34)a	352(64)ab
	20	0		82(33)b	123(65)ab		163(118)b	272(32)b
	30	0		97b	118(36)a		147(27)b	147(14)a
	90	–					111(14)a	
18 Mar.	0	2	9(29)b			23(71)b		
	10	1		213(65)a	310(82)a		1900(92)a	459(84)a
	20	1		174(31)a	207(9)a		1700(138)a	1700(114)a
	30	1		177a	138(45)a		279(73)a	98(41)a
	90	–					98(19)a	
25 Mar.¶	0	4	47(12)a			49(40)a		
	10	1						
	20	1						
	30	1						

† BR, between-row; IR, in-row. Figures in parentheses are coefficients of variation in percent.
‡ Soil temperature data applicable to both sites; surface temperature (indicated as the 0-cm depth) was actually measured just below the soil surface (ca. 1 cm).
§ Flux values at a given site followed by the same letter are not significnatly different at the 10% probability level. Profile data compared at a given depth and site across sampling dates followed by the same letter are not significantly different.
¶ No profile N_2O data taken.

greater on 18 February than had been measured since the previous summer (16 July, JD 197), even though the surface soil (0 to 15 cm) was still frozen. Six days later (24 February), the profile N_2O concentration had increased considerably. The soil had partially thawed by then and the emission rate at Site A was much higher than previously observed even during the past spring-summer. This phenomenon has been observed elsewhere (Bremner et al., 1980; Goodroad and Keeney, 1984c, 1985; Goodroad et al., 1984).

The surface soil was again frozen on 11 March but the profile N_2O concentration continued to increase. By 18 March extremely high profile N_2O concentrations were measured at both sites. Concentrations of ca. 1700 to 1900 μL N_2O L^{-1} had accumulated in the surface 20 cm at Site B. The lower N_2O concentrations at 30 cm, and particularly at 90 cm at Site B between-row indicate that N_2O was probably being produced near the soil surface and then was subsequently trapped and held. Soil temperature remained above freezing after 18 March and on 25 March high N_2O emission rates were measured at both sites. Presumably soil profile N_2O concentrations declined precipitously as the release of the over-winter build-up occurred concurrent with soil thawing (Goodroad and Keeney, 1985). The N_2O flux from Site A at the end of March was as high as at any time during the previous growing season.

We cannot be certain of the mechanism(s) involved in the high N_2O production, release, or both, during the spring freeze-thaw period. Possible explanations (Goodroad and Keeney, 1984c) include: (i) rapid nitrification-denitrification at the soil surface (at low temperatures nitrous oxide reductase activity is suppressed, and almost all the gaseous N is released as N_2O; Keeney et al., 1979; Sahrawat and Keeney, 1986); (ii) nitrification, denitrification, or both below the frozen soil, leading to N_2O accumulation, with release on thawing; or (iii) N_2O production deep in the profile, including the saturated zone, with release on thawing.

It is interesting to note that there was still an effect of N applied the previous May on N_2O production during winter-early spring. Whereas flux from the two sites were comparable, higher soil profile N_2O concentrations were generally measured at Site B compared to Site A. In addition, in-row soil N_2O concentrations were higher than between-row concentrations except early in the sampling period at Site A and on 18 March at Site B. It is conceivable that emission as N_2O during thaw could represent a significant and undesirable N loss mechanism from residual fertilizer N, particularly if the N_2O is from

denitrification. This observation should be evaluated further.

Cumulative Losses of Nitrous Oxide

Cumulative annual N_2O losses from the sites monitored in this study were ca. 3.6 and 5.2 kg N_2O-N ha^{-1} at Site A and Site B, respectively. In comparison, the cumulative annual N_2O loss from an adjacent unfertilized, but grazed Kentucky bluegrass (*Poa pratensis* L.) pasture, which we monitored over the same sampling period (Cates and Keeney, 1987), was 0.34 kg N_2O-N ha^{-1}, about 15 times less than from Site B. The annual loss of N as N_2O represented 2% of the applied N at both maize sites. Mosier et al. (1986) reported a similar fraction of N from $(NH_4)_2SO_4$ lost as N_2O-N from an irrigated maize field in Colorado. The percentage of applied N lost as N_2O in other studies has varied from nil (Colbourn and Dowdell, 1984) to near 7% (Bremner et al., 1981).

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