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NITROUS OXIDE FLUXES FROM A CLAYPAN SOIL OVERLYING NITRATE-ENRICHED GLACIAL DRIFT

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*The closed chamber method was used to assess nitrous oxide (N_2O) fluxes from corn (*Zea mays*, L.) fields during the 1995 growing season. The study area was characterized by a claypan soil overlying a nitrate (NO_3^{1-})-enriched glacial-drift aquifer. Denitrification produced N_2O fluxes of 0.2-6.9 $g\ ha^{-1}\ hr^{-1}$ early in the growing season. Fluxes increased with increasing soil temperature, soil water potential, and soil saturation. However, greatly diminished N_2O fluxes (0.001-0.09 $g\ ha^{-1}\ hr^{-1}$) occurred when soil saturation increased to 94 percent. Losses of N_2O increased linearly during the day and decreased at night, probably because of declining soil temperatures. Declines in soil saturation (less than 80 percent) and soil moisture potential (less than -10 kPa) produced late season N_2O fluxes (0.03-0.8 $g\ ha^{-1}\ hr^{-1}$) attributable to nitrification. Results indicate that denitrification would not significantly reduce claypan soil NO_3^{1-} concentrations.*

INTRODUCTION

Claypan soils cover about 41,000 km² of Illinois, Indiana, Kansas, Missouri, Ohio, and Oklahoma (Figure 1). These soils are characterized by the development of a clay layer between 18 and 46 cm deep that generally restricts the movement of air and water and slows the development of roots (Jamison et al., 1968). Ground water¹ in the region is especially vulnerable to nitrate (NO₃¹⁻) contamination (Kellogg et al., 1994; Puckett, 1996) because intensive row-crop farming and heavy reliance on inorganic fertilizers are common place (Mueller et al., 1995), and because preferential flowpaths often develop in claypan soils that allow nitrate (NO₃¹⁻) fertilizer to leach from the soil to ground water (Blevins et al., 1996).

Soil and ground water NO₃¹⁻ can be lost during denitrification when microorganisms, restricted to anoxic environments, use NO₃¹⁻ as a terminal electron acceptor in metabolic processes (Korom, 1992). Denitrification proceeds in a series of steps that terminate with the production of nitrogen gas (N₂), which escapes to the atmosphere. Nitrous oxide (N₂O) is a reactive intermediate by-product of denitrification and a green house gas. It contributes to global warming (Dickinson and Cicerone, 1986) and catalyzes the stratospheric depletion of ozone (Cicerone, 1987). Nitrification, in which aerobic microorganisms convert ammonium (NH₄⁺) to NO₃¹⁻, can also release N₂O to the atmosphere (Haynes, 1986). Globally, N₂O fluxes from agricultural soils amount to 2-3 Tg nitrogen (N) annually and account for 20 to 30 percent of the N₂O emitted from the earth's surface (Mosier, 1994).

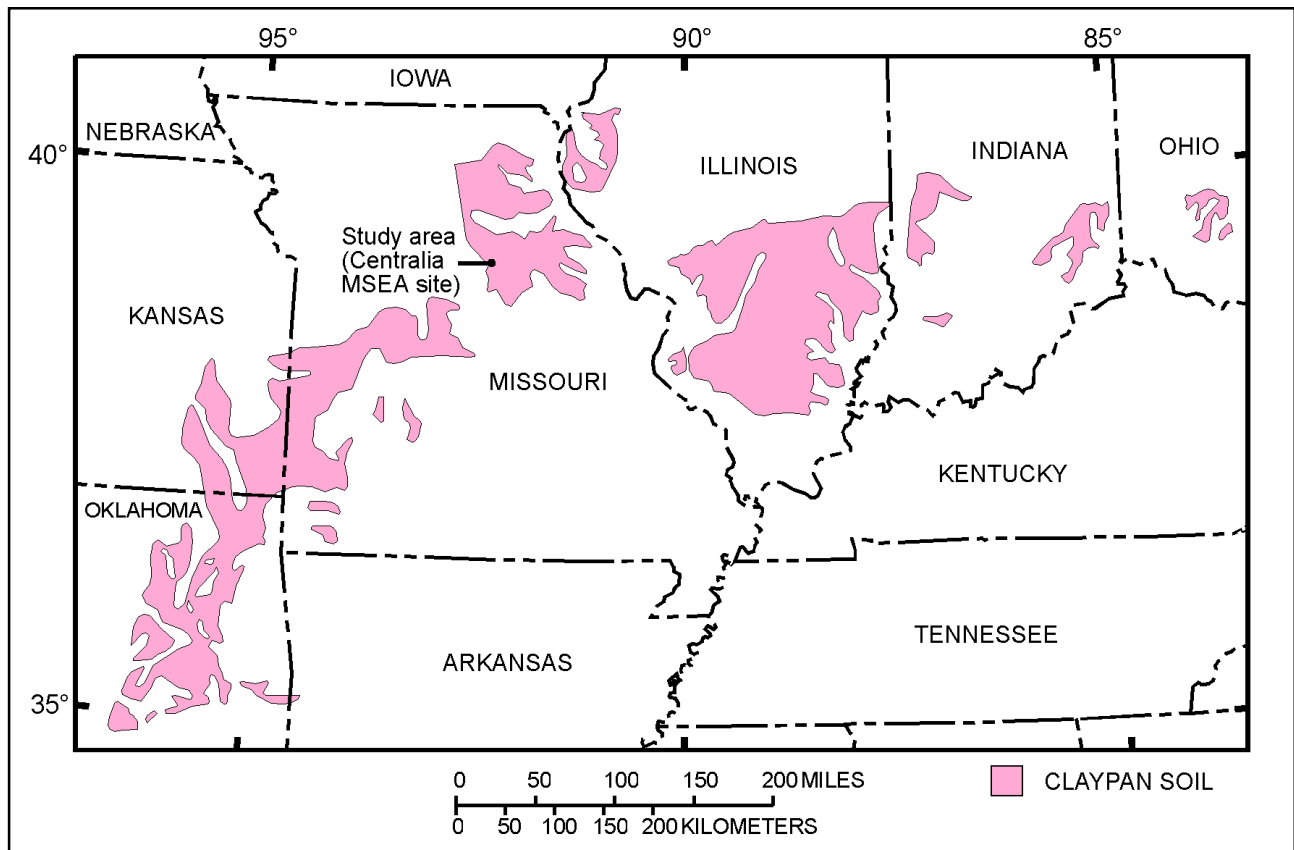


Figure 1. Location of study area and distribution of claypan soils in Illinois, Indiana, Kansas, Missouri, Ohio, and Oklahoma (MSEA, Management Systems Evaluation Area; modified from Smith et al., 1979, p. 3).

¹ The U.S. Geological Survey spells ground water as two words.

Data concerning N_2O losses for different soil types and agricultural uses are important to understand the variables and to predict gas emissions over time and to evaluate the potential for natural NO_3^- attenuation. Field estimates of fluxes generally fix N_2O through acetylene blockage (Ryden et al., 1979; Duxbury and McConnaughey, 1986; Bronson et al., 1992; Hilton et al., 1994), although some problems with the method have been reported (Haider et al., 1983; Adkins and Knowles, 1984; Mosier et al., 1986; Klemetsson et al., 1988). Nitrogen balance methods that utilize labeled ^{15}N can provide estimates of gaseous N losses but often do not distinguish between denitrification losses and ammonia (NH_3) volatilization (Parker et al., 1985; Mosier et al., 1986; Wilkison et al., 1996). Denmead and Raupach (1993) describe several promising, but currently cost prohibitive, micrometeorological techniques for N_2O estimating fluxes. Gas collection chambers, although not without limitations (Mosier, 1989; Healy et al., 1996) combine portability and economy in flux estimations. This study used closed chamber samplers to evaluate N_2O fluxes, and processes controlling those fluxes, at a claypan soil site under corn (*Zea mays* L.) cultivation.

MATERIALS AND METHODS

Test plots and instrumentation

The field site used for the study was located at the Missouri Management Systems Evaluation Area (MSEA) site near Centralia, Missouri (Figure 1). The claypan soil (fine, montmorillonitic, mesic Udollic Ochrapqualf) at the site contains preferential flowpaths developed from desiccation cracks, root channels, and burrows (Baer et al., 1995; Tindall and Vencill, 1993). Ground-water samples collected from monitoring wells installed in the loess and glacial drift underlying the site have yielded ground water with concentrations of NO_3^- larger than the drinking water standard of 10 mg L^{-1} as N (Wilkison et al., 1994).

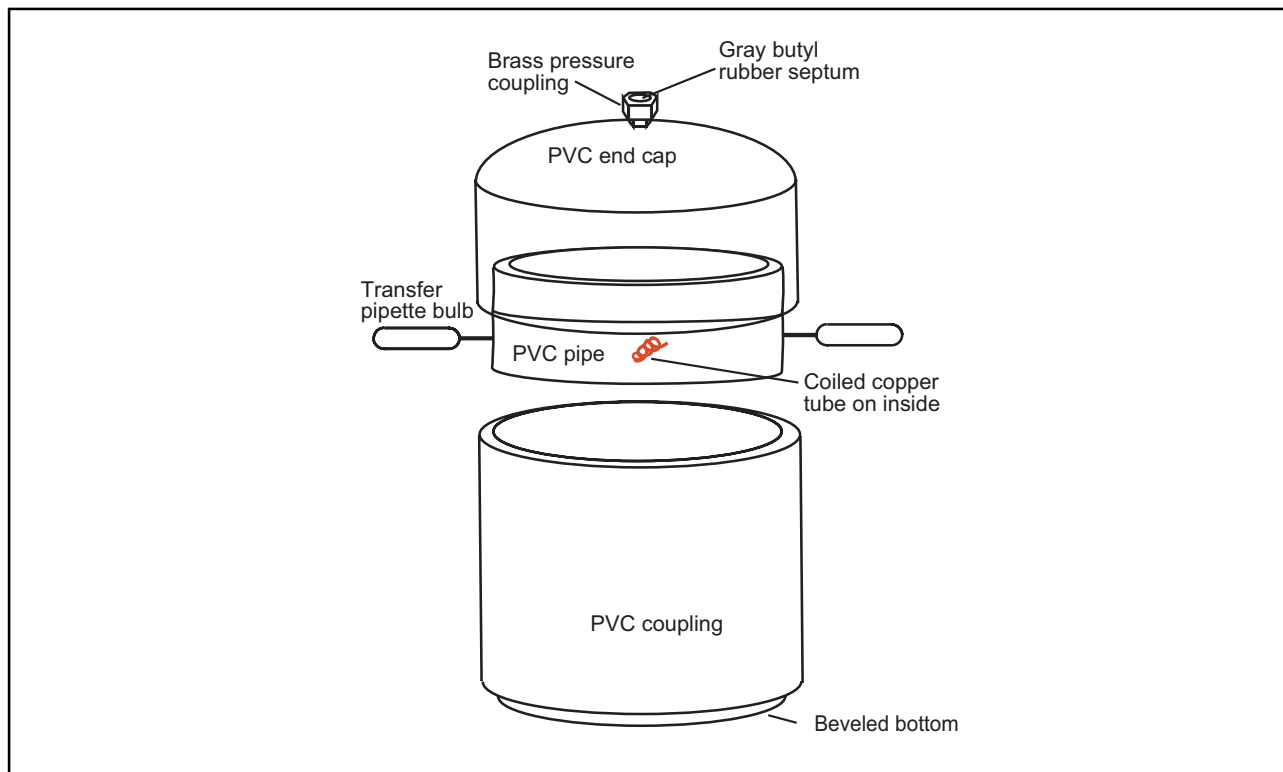


Figure 2. Sample chamber for collection of N_2O soil gas. The coiled copper tube placed inside the chamber is for pressure equilibration.

Two test plots (46.5 m²) were established within a larger field (0.1 ha) and seeded to corn on 13 June 1995. Prior to planting, the plots were fertilized at rates of 134 kg N ha⁻¹ (urea) and 168 kg N ha⁻¹ (urea and liquid NO₃⁻) using conventional tillage methods. The fertilizer was incorporated into the upper 10 cm of the soil.

Fluxes of N₂O were sampled from three closed chambers placed on each test plot. The chambers consisted of two parts (Figure 2): a schedule 40, 0.15-m diameter PVC coupling pounded into the soil to a depth of 0.1 m and a removable, 15-cm diameter end cap with a 10-cm segment of pipe cemented inside. Holes were drilled into the end cap for the addition of a brass reducing union that held a gray butyl rubber septum (Wheaton Science Products², Millville, NJ) and into the pipe for the addition of a coiled copper tube (0.05 cm diameter) and 13-mL capacity transfer pipettes. Capped chambers had 0.23 m of headspace height above the land surface.

The use of permanently buried couplings avoided any soil disturbance that could affect N₂O measurements (Mosier and Heinemeyer, 1985) and inserting the coupling 10 cm into the soil helped decrease radial diffusion (Healy et al., 1996) and allowed N₂O fluxes inside the chamber to more closely resemble natural atmospheric diffusion. The coiled copper tube served as a vent to equilibrate pressure fluctuations. The transfer pipettes were used to mix chamber air. This mitigated distorted concentration gradients, allowing chambers to be capped for extended periods of time.

Soil moisture was determined weekly by neutron probe at 0.15-m depth increments using methods described in Gardner (1986). Percent soil saturation was calculated by dividing the measured soil moisture by the porosity at that particular depth. The soil moisture value at 100 percent saturation was assumed to equal the porosity. Hourly measurements of precipitation, soil water potential, and soil temperature at a depth of 0.10 m (Alberts et al., 1993) were recorded at an automated weather station located 100 m northeast of the plots.

Sample Collection

Air samples for N₂O determination were collected every two weeks during the growing season. Sample collection procedures were modified from Dick and Jacinthe (1993) and Jacinthe (1995). To ensure an air tight chamber seal, contacting surfaces were cleaned and coated with water prior to assembly. Both pipette bulbs were squeezed 10 times to circulate air inside the chamber. Headspace samples (10-mL) were then withdrawn with a gas-tight glass syringe and injected into pre-evacuated 10-mL (Wheaton Science Products) amber-glass serum vials, crimp-capped with gray butyl rubber septa. Time-series samples were collected from two chambers to establish the linearity of changes in N₂O concentration with time. Samples were collected immediately after the chambers were capped, again after 1 minute, and then at increasingly longer time intervals until approximately 20 hr had passed since the chambers were capped. Samples from the remaining chambers were removed at times ranging from 1 to 10 hr. The precision of the collection technique, as determined by field replicates, was ± 5.2 percent. The coefficient of variance within plots was ± 2.9 percent, indicating that soil heterogeneities within each plot were minimal. Although not rigorously tested, leakage of N₂O from the sample chamber or through the coiled copper tube was not a concern because of the low percentage of error.

Atmospheric N₂O concentrations were determined from 10-mL atmospheric air samples injected into pre-evacuated vials. Ambient N₂O concentrations, as measured in samples withdrawn from the

² The use of trade and company names is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

sample chambers immediately after assembly, were not significantly different from those measured in atmospheric samples (matched pair t-tests; $p > 0.05$).

N₂O Analysis

Nitrous oxide gas samples were analyzed at the U.S. Geological Survey laboratory (Lakewood, CO) using an HP-5890 gas chromatograph (GC) equipped with an ⁶³Ni electron capture detector and a 1.8 m x 0.32 cm stainless steel column packed with 80/100 Porapak Q (Supelco, Bellefonte, PA). The inlet temperature was 75 °C, the oven temperature was 60 °C, and the detector temperature was 300 °C. The carrier gas, 5 percent methane and 95 percent Ar, flowed at a rate of 30 mL min⁻¹. Gas samples were injected directly into the GC. The response of the detector to N₂O was calibrated, and the retention time of N₂O was confirmed using certified gas standards. The detection limit was 9 ng L⁻¹. The precision of the analyses, based on the analysis of laboratory duplicates, was ± 2.7 percent. The accuracy, as determined by matrix spikes, was ± 4.4 percent.

Data Analysis

The initial N₂O concentration was subtracted from the final concentration to give the change in N₂O concentration between sampling intervals. Nitrous oxide fluxes were calculated using an equation adapted from Jacinthe (1995):

$$F = \left(\frac{dC}{dt} \right) \left(\frac{V}{A} \right), \quad (1)$$

where F is the N₂O flux, in grams per square meter per hour; dC is the change in concentration of N₂O, in grams per cubic meter of air; dt is the elapsed time, in hours; V is the inside volume of chamber above ground surface, in cubic meters; and A is area of ground surface circumscribed by the coupling, in square meters.

Least squares analysis of time-series data yielded slopes (m) which corresponded to the (dC/dt) term of Equation 1. Multiplication of these slopes by the V/A term of Equation 1 yielded N₂O fluxes in grams per square meter per hour, and these subsequently were converted to daytime (12 h) N₂O fluxes of grams per hectare. Least squares analysis of plots of the natural logarithms of daily N₂O fluxes and time after planting yielded an equation in the form of

$$F = e^{mt+b}, \quad (2)$$

where F is the N₂O flux, in grams or kilograms per hectare; m is the slope determined during least squares analysis; t is time, in days after planting; and b is the intercept determined during least squares analysis.

Two methods were used to calculate the mass of N₂O lost from the study plots. In the first method, the mass was determined by integrating Equation 2 using N₂O concentrations derived from daytime time-series sample collections over a 120-d growing season. This provided daytime losses. Nighttime N₂O losses were evaluated by entering the difference in N₂O concentrations between morning and the last evening sample collection into Equation 1, determining 12-h fluxes, then integrating the line equation of the natural logarithms of the fluxes and time after planting. The second method involved the conversion of hourly N₂O fluxes obtained with Equation 1 to 12-h N₂O fluxes. The mass of N₂O lost from the plots was then determined by integration of the line equation of the natural logarithms of the 12-h N₂O fluxes and time after planting.

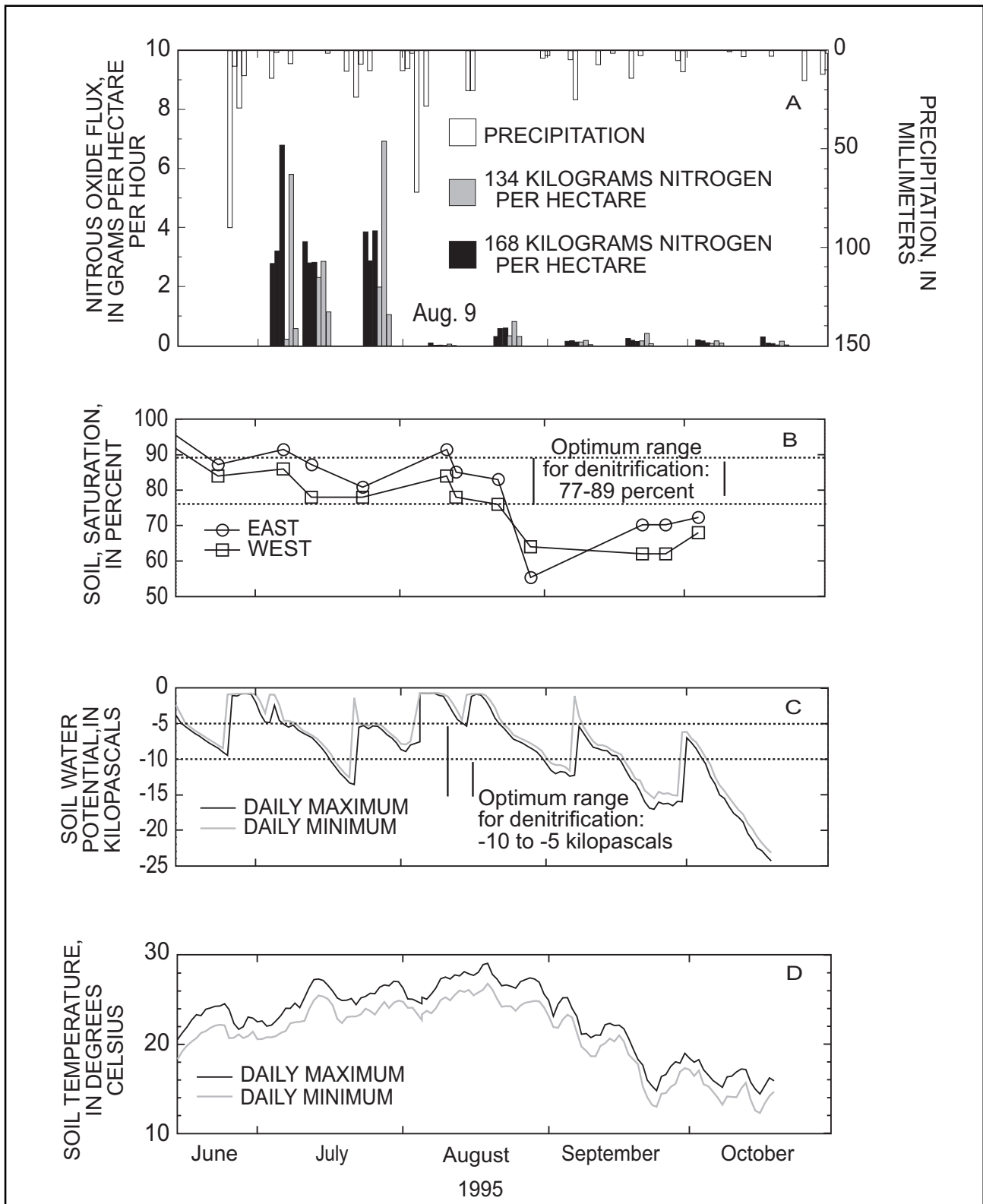


Figure 3. Values of constituents measured during the 1995 growing season: A. N₂O flux from six sample chambers installed in plots under two fertilizer treatments (134 and 168 kg N ha⁻¹) and daily precipitation; B. Soil saturation at a depth of 0.15 m from two neutron probe access tubes (east and west); C. Daily maximum and minimum soil water potential; and D. Daily maximum and minimum soil temperature measured at a depth of 0.10 m. Conditions favorable for denitrification illustrated on plot (soil saturation of 77 to 89 percent and soil water potential between - 10 and -5 kPa).

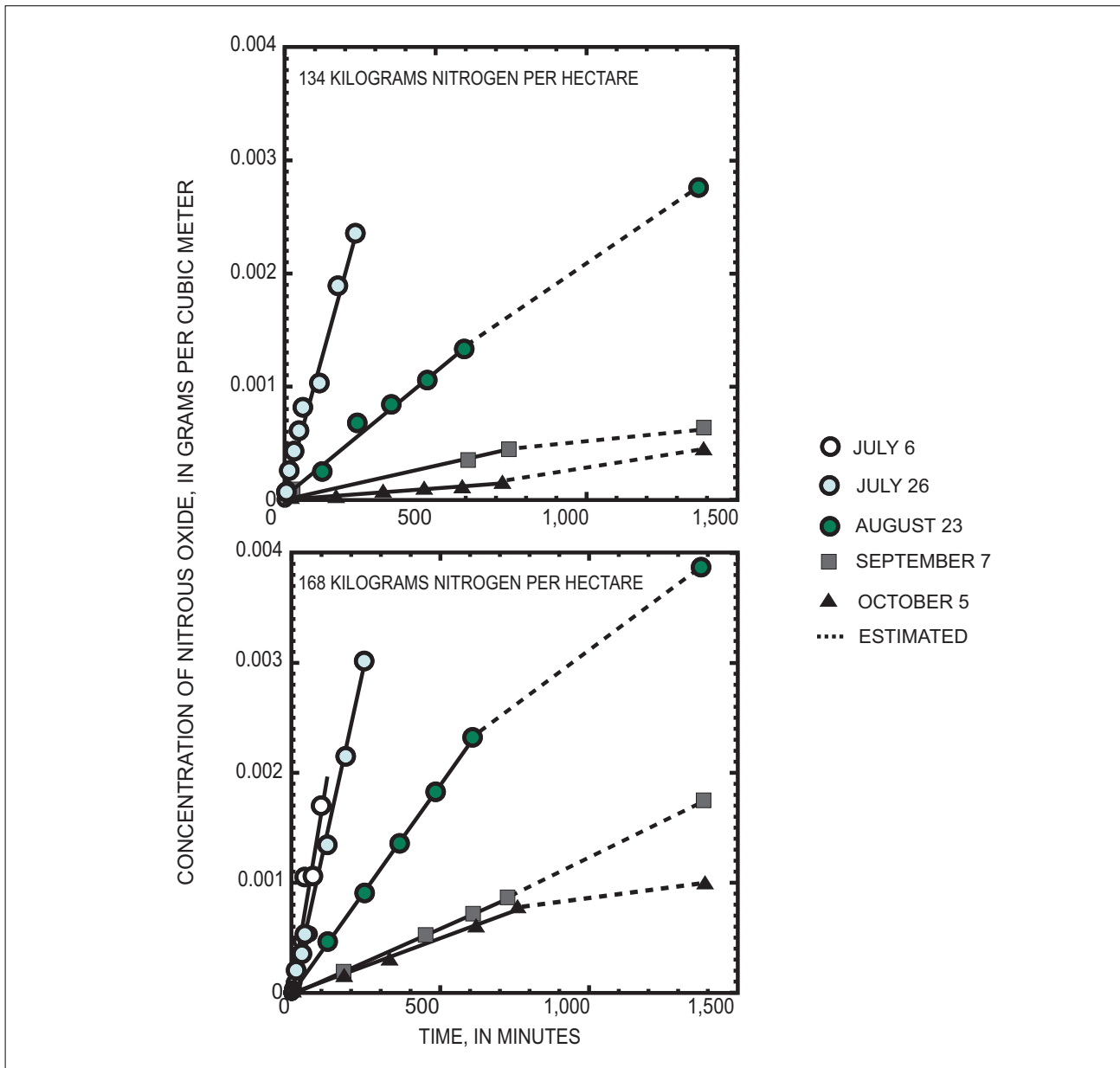


Figure 4. N₂O concentrations inside sample chambers installed on 134 and 168 kg N ha⁻¹ plots as a function of time of sample collection between July 6 and October 5, 1995. Least squares curve (solid) for times less than 12 h (daytime). Dotted lines show changes in slopes for times greater than 12 h (evening/nighttime).

The Kruskal-Wallis and test matched pair t-tests (Helsel and Hirsch, 1992) were used to compare N₂O concentrations and fluxes between fertilizer treatments. Statistical relations between hourly N₂O fluxes and time after planting, soil saturation, soil water potential, and soil temperature were determined from least squares analysis.

RESULTS AND DISCUSSION

N₂O fluxes and denitrification

Fluxes of N₂O were highest (0.2-6.9 g ha⁻¹ hr⁻¹) early in the growing season and then declined. The early season was characterized by frequent precipitation (Figure 3A), soil saturation near or above 80 percent (Figure 3B), soil water potentials between -7.0 and -4.5 kPa (Figure 3C), and soil

Table 1. Calculation of Seasonal N₂O Losses from Study Plots Using Hourly or Time-Series Flux Data.

N ₂ O flux calculation and time	Seasonal N ₂ loss (kg ha ⁻¹)	Predicted seasonal N ₂ loss (kg ha ⁻¹)	Total predicted seasonal N loss (kg ha ⁻¹)
Hourly fluxes (day)	1.94	0.23-0.99	2.17-2.93
Time series (day)	1.88	0.23-0.96	2.11-2.84
Hourly fluxes (night)	1.76	0.21-0.90	1.97-2.66
Total (night and day)	3.64-3.70	0.44-1.89	4.08-5.59

Note: Hourly fluxes were calculated from Equation 1 then converted to 12-h N₂O fluxes. Times of sample collection indicated as day or night. Range of N₂/N₂O ratios (0.12 to 0.51) used to predict N₂ losses from Fillery (1983). The total predicted seasonal N losses represent 2.49 to 4.17 percent of the 134 and 168 kg N ha⁻¹ fertilizer applications used on the study plots.

temperatures at 0.10-m depth between 18.4 and 27.4 °C (Figure 3D). Daytime N₂O emission rates were constant (r^2 ranged from 0.934 to 1.00) and rates slowed during the evening and nighttime (Figure 4).

Because the effect of fertilizer treatment was not statistically significant between plots (Kruskal-Wallis test; $p > 0.05$), data from both study plots was combined for N₂O calculations. The daytime 120-d N₂O loss calculated using time-series data was 1.88 kg ha⁻¹ compared to 1.94 kg ha⁻¹ calculated from hourly flux data (Table 1). Flux estimates by the two methods agreed within 3 percent. The similarity of the results indicates the validity of both approaches, even though a smaller number of time-series data ($n=10$) existed than hourly flux data ($n=48$). Nighttime 120-d N₂O loss was 1.76 kg ha⁻¹. Diurnal fluctuations are probably related to cooler nighttime soil temperatures (Blackmer et al., 1984; and Ruz-Jerez et al., 1994). Combined daytime and nighttime 120-d N₂O losses ranged from 3.64 to 3.70 kg ha⁻¹ (Table 1). Calculation procedures for N₂O losses often assume constant flux rates over 24 h (Jacinthe, 1995). However, neglecting diurnal flux variations would have overestimated plot losses by 10 percent even though little difference ($p < 0.05$) existed between the daytime and nighttime curves.

Denitrification losses determined from N₂O fluxes are generally measured with the acetylene block technique that prevents the reduction of N₂O to N₂ by microorganisms in the soil (Yoshinari et al., 1977; Ryden et al., 1979). Because previous site work (Tindall et al., 1995) had shown that soil macropores and fractures allowed the leakage of acetylene from the soil and prevented the development of inhibitory concentrations, this method could not be used. A surrogate method was utilized based on measured N₂O fluxes and the relative portions of N₂ and N₂O released during denitrification. Several factors, including soil pH, temperature, and moisture potential, affect the N₂/N₂O ratio. Fillery (1983) reported that acidic soils favored release of N₂O relative to N₂ during denitrification and produced N₂/N₂O ratios in the range of 0.12 to 0.51. Soil pH at the study plots ranged from 4.6 to 5.9 (Blevins et al., 1996). Soil temperature at the site averaged 23.9° C during the study and N₂/N₂O ratios of 0.34 were reported for similar (25° C) soil temperatures (Keeney et al., 1979). At soil moisture potentials between -20 and -5 kPa, N₂O production exceeded that of N₂

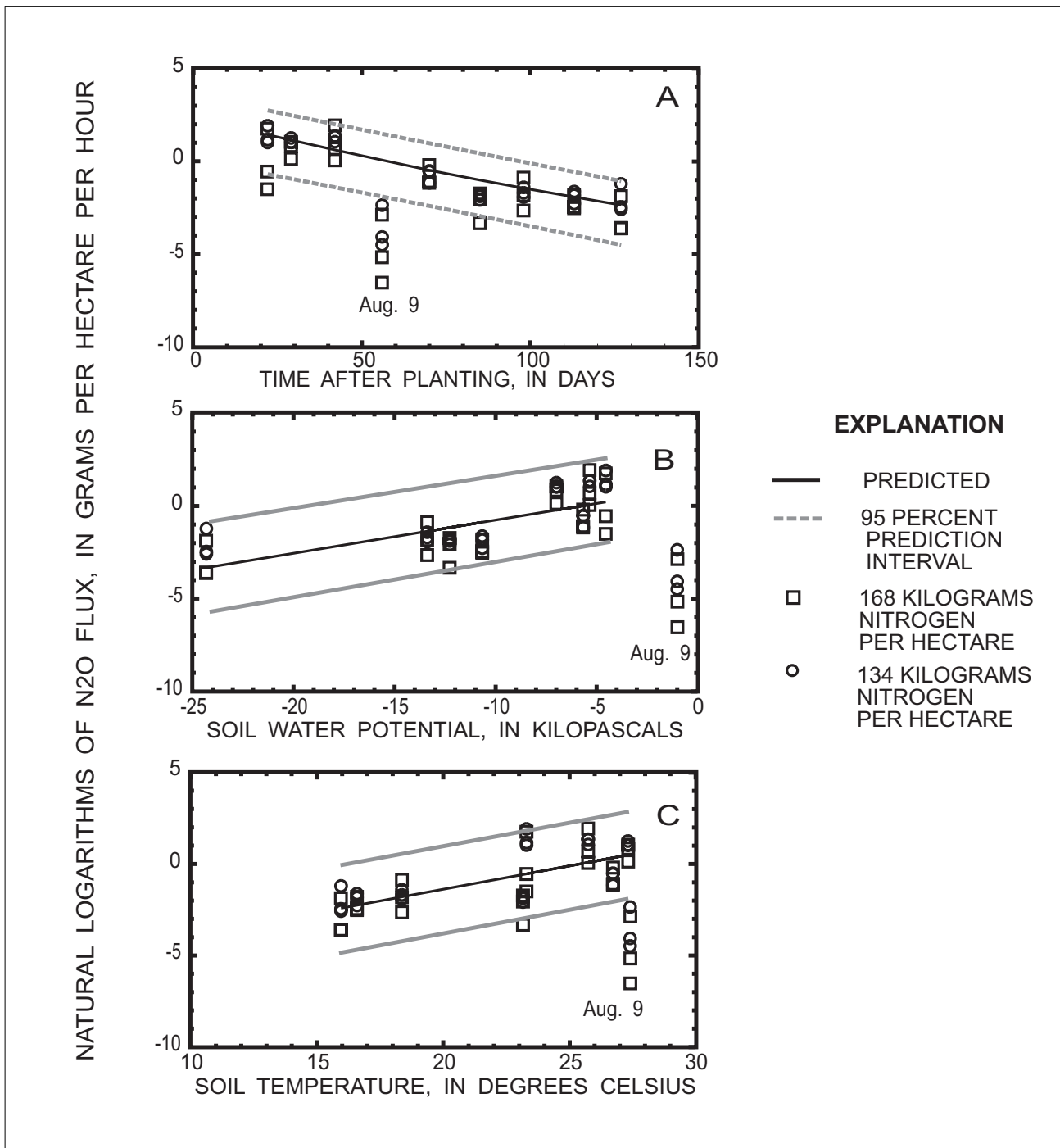


Figure 5. Plots of natural logarithms of hourly N_2O flux and A. Time after planting; B. Soil water potential; and C. Soil temperature. Plots show curves for predicted N_2O flux and 95 percent prediction intervals. Data from August 9, 1995, plot below lower 95 percent prediction interval.

(Fillery, 1983) and plot soil water potentials averaged -8 kPa. Thus, denitrification N_2/N_2O ratios at the plots would have been expected to fall in the range of 0.12 to 0.51. These ratios, in addition to the measured N_2O fluxes, were used to provide estimates of total N losses.

However, the approach needs qualification. First, N_2/N_2O ratios vary temporally dependent on soil conditions. Saturated conditions on 9 August 1995 dramatically decreased the N_2O flux at the plot and probably increased the N_2 flux. Ratios of N_2/N_2O can differ among fields undergoing

different treatments. Mosier et al. (1986) reported a N_2/N_2O ratio of 0.43 in a clay loam soil under corn cultivation while the ratio in an adjacent fallow field was 0.50. Finally, total N losses from the study plots probably resulted from a combination of denitrification early in the growing season and, to a lesser extent, nitrification later in the growing season. With these qualifications, estimated total N losses ranged from 4.1 to 5.6 kg ha⁻¹ (Table 1) and accounted for 2.4 to 4.3 percent of the fertilizer applied to the study plots. Even under favorable soil conditions, denitrification proceeded at low rates at the study site. The inference of low denitrification rates in this study supports earlier MSEA research. Tindall et al. (1995) found that over a 6-wk period, N_2O fluxes from soil cores accounted for only 0.1 to 0.6 percent of applied fertilizer N.

Factors controlling N_2O fluxes

Least squares analysis was performed on the natural logarithms of hourly N_2O fluxes and time after planting, soil saturation, soil water potential, and soil temperature to determine the effect of the variables on soil N_2O production. Because of highly saturated conditions on Aug. 9, 1995, the N_2O fluxes for that date plotted below the lower 95 percent prediction interval on plots of flux and time after planting (Figure 5A), soil water potential (Figure 5B), and soil temperature (Figure 5C) and were not used to compute linear regressions. Excluding these data, least squares analysis yielded highly significant relations ($p < 0.01$) and coefficients of determination (r^2) greater or equal to 0.5 for the four variables under consideration. Overall, N_2O fluxes decreased with time after planting and increased with increasing soil saturation, soil water potential, and soil temperature.

Fluxes of N_2O were highest early in the growing season; however, this period was characterized by frequent precipitation with some events exceeding 20 mm (Figure 3A). A highly significant positive relation ($r^2 = 0.60$) existed between N_2O fluxes and soil saturation at the study plots, and it is likely that soil moisture conditions were greater limiting factors on N_2O flux than time after application. Dick and Jacinthe (1993) reported N_2O flux rates were highest following a 29-mm precipitation event that occurred 4 d after anhydrous ammonia application and Goulding et al., (1993) reported peak N_2O loss after the first substantial rainfall following fertilizer application. Most N_2O flux from the study plots occurred at soil saturations of 77-89 percent. A previous study (Tindall et al., 1995), conducted on soil cores from the site, found minimal denitrification activity at saturations below 80 percent. Work at other sites identified optimum identification soil saturation ranges of 67 to 80 percent (Ruz-Jerez et al., 1994) and 55 to 87 percent (Parsons et al., 1994).

However, when soils were very near saturation (>90 percent), N_2O fluxes greatly diminished. Between Aug. 4 and 6, 1995 (Figure 3A), 100 mm of precipitation fell resulting in 94 percent soil saturation (estimated from soil water potential of -0.7 kPa; Figure 3B) on the 9 August collection date. Low N_2O fluxes (0.001-0.09 g ha⁻¹ hr⁻¹) occurred on that date. Tindall et al. (1995) suggested that when soils are saturated, soluble N_2O may move into soil pore water and reduce N_2O fluxes. Alternately, saturation may produce anoxic soil conditions that favor N_2 production over N_2O (Firestone et al., 1979; Rolston, 1981).

Because soil water potential increased as soil saturation increased, it also showed a positive relation ($r^2 = 0.50$, $p < 0.01$) to N_2O flux. Flux was greatest at soil water potentials from -7.0 to -4.5 kPa (Figure 5B).

Much of the N_2O flux from the study plots occurred at soil temperatures from 23.3-27.4 °C (Figure 5B). Hilton et al. (1994) reported substantially increased denitrification (50-230 percent) when soil temperature increased from 21 to 28 °C. Soil temperatures did not limit N_2O flux, because

the upper temperature limit on denitrification is 75 °C (Keeney et al., 1979), which was not approached in the study plots.

Of the variables considered earlier, soil saturation and soil water potential control which process, denitrification or nitrification, produces N₂O. As soil water content increases, air is displaced from soil pores and anaerobic microsites, necessary for denitrification, develop (Parsons et al., 1994; Ruz-Jerez et al., 1994). Claypan soil denitrification occurs when soil saturation exceeds 80 percent (Tindall et al., 1995). Furthermore, -10 to -5 kPa soil water potentials constitute the optimum denitrification range (Firestone, 1982). Early in the growing season, soil saturation at the plots often exceeded 80 percent and soil water potential ranged from -7.0 to -4.5 kPa. Therefore, observed N₂O fluxes probably were the result of soil denitrification, although denitrification rates were not large enough to consume much fertilizer. Rates are low because O₂ is abundant in soil gas (Blevins et al., 1996).

Maximum nitrification occurs at soil water potentials between -33 to -10 kPa (Haynes, 1986). Late in the growing season, when soil saturation declined below 80 percent and the soil water potential declined from -11 to -24 kPa, N₂O fluxes probably resulted from nitrification. However, the small magnitude of N₂O fluxes during these times, indicates nitrification also proceeded at low rates.

CONCLUSIONS AND IMPLICATIONS

Nitrous oxide flux from corn fields was evaluated at two test plots. Fluxes of N₂O, produced by denitrification, generally exceeded 2.0 g ha⁻¹ hr⁻¹ within 40 d after planting when soil saturation exceeded 80 percent and soil water potential ranged from -7.0 to -4.5 kPa. Flux of N₂O decreased with time after planting and increased with increasing soil saturation, soil water potential, and soil temperature. However, greatly diminished N₂O fluxes (0.001-0.09 g ha⁻¹ hr⁻¹) occurred when soil saturation increased to 94 percent and soil water potential increased to -0.7 kPa, possibly due to anoxic conditions or the dissolution of N₂O in soil pore water. Late season N₂O fluxes (0.03-0.8 g ha⁻¹ hr⁻¹) attributable to nitrification, occurred when soil saturation declined to less than 80 percent and soil water potential declined to less than -11 kPa.

Both denitrification and nitrification proceeded at low rates in the claypan soil of the study site. Seasonal denitrification N losses (4.1 to 5.6 kg ha⁻¹) accounted for only 2.4-4.2 percent of the applied fertilizer. With limited denitrification, excess soil NO₃¹⁻ is available to leach to ground water rather than being consumed in the soil. Experimental work with ¹⁵N labeled NO₃¹⁻ confirmed that large amounts of excess fertilizer (>30 percent) can quickly move into ground water at the site.

Concentrations of N₂O increased at constant rates during the daytime and N₂O production decreased at night, probably as a consequence of declining soil temperatures. Although the difference between daytime and nighttime losses was not statistically significant, not accounting for diurnal variation overestimated N₂O losses by about 10 percent

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