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DISTINGUISHING NITRIFICATION AND DENITRIFICATION SOURCES OF N_2O IN A MEXICAN WHEAT SYSTEM USING ^{15}N

J. A. PANEK,[1,4] P. A. MATSON,[2] I. ORTÍZ-MONASTERIO,[3] AND P. BROOKS[1]

[1]*Environmental Science, Policy, and Management, 151 Hilgard Hall, University of California, Berkeley, California 94720 USA*
[2]*Department of Geological and Environmental Sciences, Stanford University, Stanford California 94305 USA*
[3]*Centro Internacional de Mejoramiento de Maiz y Trigo, Dr. Norman E. Borlaug Km. 12, Apdo. Postal 140, 85000 Ciudad Obregón, Sonora Mexico*

Abstract. Irrigated wheat systems in the Yaqui Valley of Sonora, Mexico, receive high nitrogen inputs and large discrete inputs of irrigation water, with extended drying periods between irrigation events. We used this system to determine the contribution of the separate processes of nitrification and denitrification to the total N_2O flux from the soil and to link each process with important driving variables. At the beginning of the wheat cycle, in an experimental wheat field, we established and maintained replicated, paired soil plots labeled with 25% atom excess (a.e.) $K^{15}NO_3$ and $(^{15}NH_4)_2SO_4$ at a rate of 7% of the existing pool of NO_3^- and NH_4^+, respectively, and measured the evolution of $^{15}N_2O$ in each over the course of an irrigation/fertilization cycle. Denitrification losses of N_2O predominated over nitrification in the two days following irrigation, and continued for six days. The duration of denitrification was corroborated by measures of $^{15}N_2$ flux. Nitrification became increasingly important as soils drained. Each process contributed equally to total N_2O losses over the 4-wk period after the wheat cycle began.

Key words: denitrification; dinitrogen flux; Mexican wheat system; nitrification; nitrous oxide flux; soil microbial processes; trace gas loss; wheat cycle, N_2O emissions.

INTRODUCTION

Nitrous oxide (N_2O) is an important and highly effective greenhouse gas as well as a reactant in the destruction of stratospheric ozone (Cicerone 1987, Houghton et al. 1992); its atmospheric concentration is increasing at ~0.25% per yr (Kim and Craig 1993). Despite the importance of its buildup to human and environmental health, estimates of global emissions of N_2O are highly uncertain and the global budget remains unconstrained. Soils are a dominant source of N_2O, and uncertainty in emissions from soils is a significant cause of uncertainty in the global budget.

In soils, N_2O is primarily produced by two microbial processes: denitrification and nitrification. These processes, as well as the physical transport of the gas through the soils, are regulated by a number of environmental and edaphic factors, many of which are highly variable over space and time. At coarse scales, these factors include soil type and climate (Matson and Vitousek 1990), and at local scales, soil moisture and temperature, soil organic matter and nitrogen availability, pH, topographic position, and agricultural management practices (Firestone and Davidson 1989, Robertson 1989, Bouwman 1990, Robertson 1993). Until the late 1970's, denitrification was believed to be the principal source of microbially derived N_2O, but laboratory and field studies since then have demonstrated that N_2O is also a product of nitrification (for a review see Bremner 1997). Few studies, however, have attempted to partition N_2O flux by process under field conditions.

Differentiating nitrification and denitrification sources, and understanding how gas emissions are influenced by changes in environmental factors, is important for the accurate estimation and prediction of soil gas fluxes (Matson et al. 1989, Matson 1997). Despite substantial progress, this understanding has been limited by constraints imposed by the techniques used to separate the processes of nitrification and denitrification under field conditions (Bremner 1997). In this study, we used nitrogen isotope tracers to attribute N_2O to sources to nitrification vs. denitrification in undisturbed soils in the field.

Cultivated ecosystems are the single most important anthropogenic source of N_2O (Intergovernmental Panel on Climate Change 1996), and some of the highest fluxes of N_2O to the atmosphere to date have been measured in irrigated and fertilized systems (e.g., Matson et al. 1998). In these systems, the factors regulating soil processes and gas emissions are largely under the control of management, and thus are relatively easy to anticipate and track. We used an irrigated and fertilized agricultural system to ask two questions. How much N_2O is derived from the microbial process of denitrification and how much from nitrification? And what are the environmental factors that control whether the source of N_2O is one or the other process? We established an in situ ^{15}N tracer study to attribute N_2O fluxes

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[4] E-mail: jpanek@nature.berkeley.edu

to either nitrification or denitrification. We also used ^{15}N to measure N_2 emissions during denitrification. We expected N_2 and N_2O fluxes to be highest and to be derived primarily from denitrification, an anaerobic process, during peak soil moisture periods, and at lower soil moistures, we expected nitrification, an aerobic process, to be the major source of N_2O (Robertson 1989, Davidson 1991, Davidson et al. 1993).

Methods

Study site

The study site was located in a furrow-irrigated wheat field in the Yaqui Valley of Sonora Mexico (26°45′–27°33′ N, 109°30′–110°37′ W; 40 m above sea level); the valley encompasses 225,000 ha of cultivated and irrigated land. Mean annual precipitation is 29.2 cm, and falls predominantly in the late summer, with a smaller set of rain events in December (García 1981). Before being brought into cultivation, the natural vegetation of the valley was a thorn scrub forest type. Soils are coarse sandy clay mixed with montmorillonitic clay (classified typic calciorthid in the U.S. system). Average pH of the upper soil horizon is 7.7 and average percent organic matter for the valley's agricultural soils is an extremely low 0.8% (Meisner et al. 1992).

The main crops in the valley are presently wheat (both durum and bread wheats [*Triticum* spp.]) during the winter and maize (*Zea mays* L.) in the summer, grown for grain production. These crops are frequently grown sequentially in the same fields in the same year when there is sufficient water available for irrigation. In low water years only wheat is grown. For our experiment, we planted spring bread wheat (*Triticum aestivum* L.) cultivar Rayon F89, which is the most widely grown bread wheat in Yaqui Valley. In the typical management practice, farmers burn aboveground residues in October left over from the previous maize cycle. In early November, they apply 75% of the total 250 kg N/ha fertilizer as urea or anhydrous ammonium, and form furrows (trenches) and beds (raised mounds of soil). Within a week, fields are furrow-irrigated, then allowed to dry for three to four weeks before planting on residual moisture. Six weeks following planting, the remaining 25% of the N fertilizer is applied as anhydrous ammonia bubbled into irrigation water. Harvest is in late March or early April.

In earlier work at these sites, we simulated the typical farmers' practice and a number of alternatives in the experimental fields at the CIMMYT (Centro Internacional de Mejoramiento de Maiz y Trigo) Field Station (Matson et al. 1998). Soil inorganic N pools and nitrogen trace-gas fluxes changed dramatically during the month prior to planting. Immediately following irrigation, urea was rapidly hydrolyzed to ammonium and then nitrified to nitrate. Extremely high fluxes of N_2O (up to 650 $ng \cdot cm^{-2} \cdot h^{-1}$) peaked within seven days, followed by high nitric oxide (NO) fluxes (up to 300 $ng \cdot cm^{-2} \cdot h^{-1}$); despite the fact that high concentrations of nitrate remained in the soil, emissions of both gases dropped to near zero by planting (Matson et al. 1998).

Field experiments

We carried out two ^{15}N tracer studies in the 1995–1996 wheat cycle, using the farmers' practice treatment plots (250 kg/ha N as urea, 75% applied one month prior to planting, 25% applied one month after planting) and control plots (no fertilizer, but irrigated and shaped in the same manner as the treatment plots) that had been established as part of our larger study to measure nitrogen trace-gas loss (Matson et al. 1998). Experimental plots were 22 × 27.5 m. One of the ^{15}N studies was designed to evaluate the role of denitrification vs. nitrification as the source for N_2O; the other was used to estimate N_2 emissions from denitrification. Both studies were carried out during the 14-d period following initial fertilization and irrigation, when N_2O losses were expected to be highest and when soil moisture and inorganic N pools changed dramatically. Both studies measured fluxes in bed positions, because earlier measurements indicated that most of the fertilizer nitrogen and nitrogen gas fluxes occurred there (Matson et al. 1998).

N trace gas measurements.—In four replicate plots of the simulated farmer's practice, one 25 cm diameter polyvinyl chloride (PVC) ring was placed in the soil in both bed and furrow positions and remained in the same location for the entire growing cycle. N_2O was measured midday, daily at the beginning of the cycle when fluxes were high and at less frequent intervals later in the season. After placing a 9-L plastic chamber over the ring, gas samples were removed from the headspace at 0, 10, 20, and 30 min with nylon syringes for the analysis of N_2O flux (Matson et al. 1996). NO emissions were measured using the same PVC rings within 1 h before or after sampling for N_2O, with a Scintrex LMA-3 chemoluminescence detector modified for field measurements (Davidson et al. 1991, Matson et al. 1996). Standard curves (with dilution of a 0.1 μL/L standard) were run in the field before and after sets of 10–20 gas measurements. Minimum detectable flux was ~ 0.05 $ng \cdot cm^{-2} \cdot h^{-1}$.

$^{15}N_2O$ measurements.—In three of the four replicate plots of the simulated farmer's practice, three rings were located ~20 cm apart in bed positions. After 16 h, the soil in one of the rings was labeled with 100 mL of an aqueous solution of 25% atom excess (a.e.) $K^{15}NO_3$ and a second received 25% a.e. $(^{15}NH_4)_2SO_4$ to bring the mix of native soil N and labeled solution N to approximately 2% a.e. N additions were 7% of the soil NO_3-N and NH_4-N pools and ranged from 1.5 to 18 μg N/g dry soil. The solution was injected to 10 cm depth in 20 5-mL aliquots distributed across the ring using a standardized grid. Injections were made continuously as the needle was retracted to distribute the solution throughout the profile. The final ring was

unamended and served as a control. At 2 h and 24 h after labeling N_2O, measurements were made using the method described above. After the 30 min sample, a 60-mL air sample was removed from the chamber headspace and stored in a pre-evacuated 50-mL glass vial for $^{15}N_2O$ analysis. Air temperature and soil temperature at 2 cm depth were recorded. After the 24-h gas samples were taken, three 10 cm deep soil cores were removed from the center of the 25 cm diameter ring, handsieved to remove rocks and organic matter, and subsampled for gravimetric water content and KCl extractable NH_4^+, $^{15}NH_4^+$, NO_2^-, NO_3^-, and $^{15}(NO_3^- + NO_2^-)$ as described below. The entire protocol (labeling, 2 h and 24 h gas sampling, and soil sampling) was repeated at five new ring locations sequentially over a period of two weeks immediately following the initial fertilization and irrigation event.

$^{15}N_2$ measurements.—N_2 flux was measured during the two weeks following irrigation by labeling the soil NO_3^- pool with a ^{15}N tracer and collecting evolved $^{15}N_2$. This experiment had three replicates, one replicate each in three of the four 22 × 27.5 m control plots from the larger study. A major difficulty in measuring the emission of N_2 is the high concentration of N_2 in the air (78%). This necessitates a strong label and a small headspace to concentrate the labeled, evolved N_2 within the huge amount of natural abundance N_2. Using unfertilized control plots allowed us to label the entire NO_3^- pool and follow the label into N_2. In each plot, one 25-cm PVC ring similar to the ones used for the N_2O plots was located in a bed. The soil within the ring was amended to 10 cm depth with an aqueous solution of 80% a.e. $K^{15}NO_3$ in 20 5-mL aliquots at a rate designed to simulate the amount of NO_3^- in the adjacent farmer's practice treatment plots. The application rate was determined using inorganic N concentration data from the previous year. The accuracy of these estimates was later checked by comparing inorganic N concentrations measured after the ^{15}N was added vs. concentrations measured in the farmer's practice treatment at the same time. Additions were within the variation found in the farmer's practice (±1 SD) at the time of application, except for the first two additions when soil concentrations were extremely low (4.5 and 35.6 μg/g, respectively). These soils were overamended by 20 μg/g each, which may have led to overestimates of early fluxes. At 24 and 48 h after labeling, the ring was fit with a 5-L plastic chamber and a 60-mL sample of air was taken from the headspace after the chamber had been in place 2 h and stored in a pre-evacuated 50-mL glass vial. Air temperature and soil temperature at 2 cm depth were recorded. The measurement protocol (installation of three rings, labeling, 24 h and 48 h gas sampling, and soil sampling) was repeated at five new locations in each replicate sequentially over the two-week postirrigation period.

Soil water and N concentration measurements.—Soil samples were collected from beds after each flux was measured. Unlabeled soil was sampled from a bed adjacent to the permanent N_2O flux ring sites. Soils labeled with NH_4^+, soils labeled with NO_3^- for the $^{15}N_2O$ experiment, and soils labeled with NO_3^- for the $^{15}N_2$ experiment were taken from within the ring after the final flux measurement. Soil was extracted to 15 cm depth, sieved, and mixed. Samples were weighed fresh, then dried at 105°C for 2 d and reweighed to determine water content. Water-filled pore space was calculated from gravimetric water content and soil bulk density. A 10-g subsample was placed in 100 mL of 2mol/L KCl, shaken for one minute, and allowed to equilibrate for 18–24 h. Supernatant was removed and stored at 4°C until analysis. Soils from isotopically labeled treatments were further filtered using KCl-extracted Number 1 Whatman filter paper.

Laboratory analyses

Gas analyses.—N_2O gas samples were analyzed within 24 h of sampling using a Shimadzu 14A gas chromatograph model 2 (Shimadzu Scientific Instruments, Columbia, Maryland) configured with an electron capture detector. Standards (0.1, 0.5, and 1.0 ppm, Scott Research Laboratory, Incorporated, Plumsteadville, Pennsylvania USA) bracketed every 12–20 samples. Coefficients of variation of the standards were <1%. Fluxes were calculated as in Matson et. al. (1996). In short, a regression line was fit to the four sequential headspace N_2O concentrations. The slope of this line, the change in N_2O concentration over time per unit ground area, is the flux.

$^{15}N_2O$ and $^{15}N_2$ samples were stored at room temperature until they were transported to the University of California (UC) Berkeley and analyzed on a Europa Scientific 20/20 magnetic sector continuous flow GC mass spectrometer with trace gas analyzer (Europa Scientific, Crewe, Cheshire, UK), using a method similar to that described by Atkins et al. (1992). In brief, a subsample of each gas sample was transferred to an evacuated 13-mL Hungate tube and placed on an autosampler. This sample was purged onto a gas chromatograph column and the N_2/O_2 separated from the N_2O, and then O_2 was removed in a Cu reduction furnace. The N_2 was then carried to the inlet split of the mass spectrometer and analyzed for $^{15}N_2$. The N_2O was concentrated on a molecular sieve at room temperature and then baked off at 250°C into the mass spectrometer. The ion source was automatically shifted between masses 28, 29, and 30 for N_2, and 44, 45, and 46 for N_2O.

Soil analyses.—All KCl extracts were stored at 4°C, transported to UC Berkeley on ice, and analyzed on a Lachat QuikChem AE automated ion analyzer (Lachat Instruments, Milwaukee, Wisconsin) for soil NH_4^+, NO_2^-, and NO_3^-. Isotopically labeled extracts were diffused to isolate soil $^{15}NH_4^-$ and $^{15}(NO_3^- + NO_2^-)$ using the method of Brooks et al. (1989), as follows. To

isolate $^{15}NH_4^+$ from soil extracts, H_2SO_4-acidified disks were suspended on wires above the KCl solution. MgO was added to the solution to increase the pH and the container quickly capped. Containers were stirred, then left untouched for 7 d. The high pH drives NH_4^+ out of solution as NH_3 into the headspace of the container, where it is trapped on the acidified disk as NH_4^+. After 7 d, the disks were removed and dried overnight in a NH_4-free desiccator, then wrapped in tin and analyzed on a Europa Scientific Tracermass mass spectrometer (Europa Scientific, Crewe, Cheshire, UK). The remaining solution was treated with Devarda's alloy, which reduces NO_3^- and NO_2 to NH_4^+, and the process repeated to isolate $NO_3^- + NO_2^-$ ^{15}N.

Separating nitrification and denitrification sources of N_2O

The contribution of either nitrification or denitrification to the overall N_2O flux was estimated from measurements of $^{15}N_2O$ and soil ^{15}N pools (see the Appendix for equations). For each of the paired plots labeled with $^{15}NO_3^-$ or $^{15}NH_4^+$, the number of moles of N_2O evolved from the labeled source was calculated from the ^{15}N of the headspace N_2O and the ^{15}N of the soil solution using a standard mixing equation. The headspace N_2O was assumed to be at natural abundance and the N_2O evolved from the soil was assumed to be the same as the soil N pool. Fractionation during either denitrification or nitrification has negligible effect on the isotopic composition of the evolved gas when using such highly enriched isotopic tracers. For the 2-h sample, the soil ^{15}N abundance was assumed to be 2% a.e. since this value could not be measured without disturbing the experiment. For the 24-h sample the soil ^{15}N abundance was measured directly. The proportion of N_2O derived from denitrification was calculated from the moles of $^{15}N_2O$ measured in the flux from the plot labeled with $K^{15}NO_3$. The proportion of N_2O coming from nitrification was calculated from the number of moles of $^{15}N_2O$ generated in the plot labeled with $(^{15}NH_4)_2SO_4$ minus the number of moles generated in the adjacent KNO_3-labeled plot, weighted by the amount of $^{15}NH_4$ label that had moved into the soil water nitrate pool and could potentially be denitrified to N_2O. For the 2-h sampling time, we assumed that no label had moved. For the 24-h sampling time, the amount of labeled NO_3^- in the soil was measured directly. The proportions of N_2O coming from denitrification or nitrification were then applied to the fluxes of N_2O generated from the unamended rings to quantify the actual N_2O losses from either process. The method relies on similarity of the triplet rings in each plot. We tested this assumption by comparing the N_2O fluxes evolved from each pair and found that the difference between pairs was within the variation found in N_2O fluxes between replicates of the larger study.

For estimates of N_2 evolved from the sites, N_2 flux was calculated using the modified Hauck technique and equations for a triple-collector mass spectrometer (Hauck et al. 1958, 1994, Mulvaney 1984, Mulvaney and Boast 1986, Arah 1992, Mosier and Schimel 1993, Mosier and Klemedtsson 1994). These equations take advantage of the fact that $^{15}N_2$ evolved from the soil does not equilibrate with the N_2 in the chamber. The gas evolved from the labeled source has a predictable distribution of masses. Once mixed with the headspace air, the flux can be backcalculated. The calculations use the 29/28 and 30/28 ratios of the sample and of a reference (in this case air), as well as chamber volume, duration of sample, and soil temperature, which were recorded separately for each measurement, to determine N_2 flux. This method relies on a uniform labeling of the soil N pool, which we tried to achieve by (1) injecting the enriched solution in 20 separate aliquots uniformly distributed across the ring, (2) continuously injecting while pulling the needle through the 10-cm soil profile, and (3) repositioning the ring in unlabeled soil before each new experiment. A nonuniform labeling of the soil N pool would result in an overestimate of the N_2 flux.

Results and Discussion

Soil water and inorganic nitrogen

The patterns of soil water, soil nitrogen, and trace-gas flux observed over the one-month routine sampling were the same as those found the previous year (Matson et al. 1998). Water-filled pore space (WFPS) and soil inorganic N changed dramatically during the preplanting period. WFPS in the beds between flooded furrows peaked at 82% the day following irrigation (Fig. 1a), remained high for 3 d, then gradually diminished to 52% over the next two weeks. Soil and air temperatures were high during the period, but remained relatively constant (Fig. 1b). The concentration of available NH_4^+ peaked 2 d after irrigation as urea-N was hydrolyzed to NH_4 (Fig. 2a). As NH_4^+ gradually declined over the next two weeks, soil NO_3^- concentration rose and peaked 10 d postirrigation, then remained very high throughout the sampling period (Fig. 2a). N_2O fluxes (Fig. 2b) rose quickly following irrigation, dropping as the soils dried out. The peak of NO following that of N_2O (Fig. 2b) indicated that soil conditions were more conducive to nitrification than denitrification by that time.

Sources of N_2O

The pattern of $^{15}N_2O$ evolved from the labeled plots showed a general temporal transition from the dominance of a denitrification source to a nitrification source of N_2O. On the first day following irrigation, the ^{15}N abundance of the N_2O evolved from the NO_3-amended plots equaled that of the NH_4-amended plots (Fig. 3a), and both nitrification and denitrification contributed equally to the N_2O flux (Fig. 3b) as the beds became progressively more water saturated. By the second day,

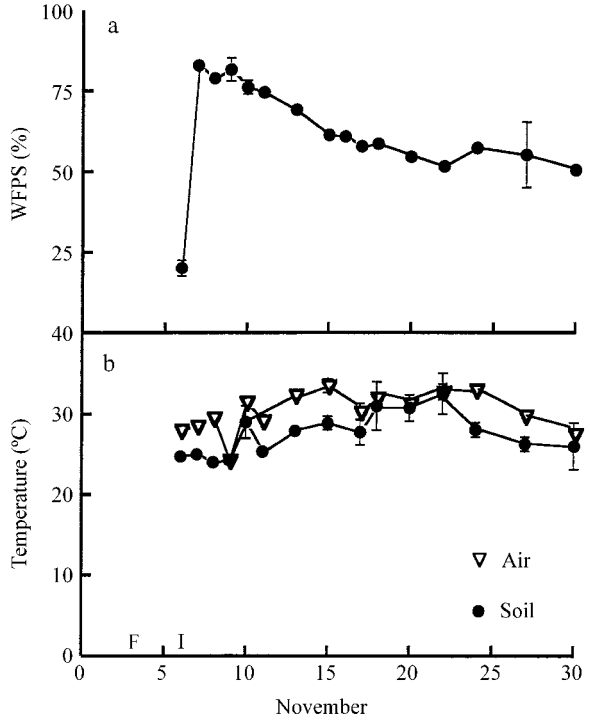

FIG. 1. (a) Water-filled pore space (WFPS) and (b) temperature for the 0–15 cm horizon during the first month of the 1995/1996 wheat cycle. Fertilization (urea at 187.5 kg/ha), indicated by ''F,'' occurred 3 November. Irrigation, indicated by ''I,'' occurred 6 November. Error bars represent ±1 SE of four replicate plots.

soils had become fully water saturated and denitrification losses of N_2O dominated. By the fourth day after irrigation, denitrification and nitrification were again contributing roughly equally to the N_2O flux as bed soils drained. By 6 d postirrigation, denitrification, at least in these upper layers, had apparently stopped and nitrification was the primary source of N_2O. N_2O fluxes dropped to near zero 18 d after irrigation (Fig. 2b).

The proportion of N_2O fluxes from either denitrification or nitrification over time was multiplied by total N_2O fluxes to determine the N_2O-N coming from each (Fig. 4). After converting to daily flux measurements (as described in Matson et al. 1998) and integrating over the time period, we estimate that approximately 50% of N_2O losses integrated over the entire preplant period came from each process.

N_2 emissions

Peak emissions of N_2 during denitrification were more than an order of magnitude greater than peak N_2O fluxes. Peak N_2 fluxes occurred 2 d following irrigation and declined to zero within 7 d (Fig. 5). The maximum N_2 flux was 4.8 $\mu g \cdot cm^{-2} \cdot h^{-1}$ with high variability across replicates. These rates compare well with measurements of ≤4.6 $\mu g \cdot m^{-2} \cdot h^{-1}$ for perennial ryegrass (Rolston et al. 1982), but are higher than uncropped soils of 0.8 $\mu g \cdot cm^{-2} \cdot h^{-1}$ (Rolston et al. 1978). After one week, denitrification apparently was no longer going to completion, based on a comparison of N_2 results with denitrification N_2O results.

Patterns of N gases over time

The dynamics in soil water content and forms of available nitrogen following fertilization and irrigation appeared to cause systematic responses from soil microbial processes, resulting in changes in the magnitude and species of nitrogen gas losses (Fig. 4). The activity of denitrifiers or nitrifiers prior to irrigation was probably limited by dry soil. Within 2 d following irrigation, when the combination of wet soil and residual soil NO_3^- pools created an environment conducive to denitrification, nearly the entire N_2O flux came from denitrifiers. The largest measured hourly flux of N_2O for the cycle occurred from denitrification (86.5 ng $cm^{-2} \cdot h^{-1}$), but relatively small soil NO_3^- pools probably limited the magnitude of the fluxes. As the soils drained, air spaces again developed in the soil sufficient to drive nitrification. Denitrification-controlled N_2O fluxes continued longer than N_2 emissions, indicating that as soils dried out denitrifiers did not reduce N_2O to N_2, perhaps due to the increasing availability of oxygen (Firestone and Davidson 1989). Nitrification losses of N_2O continued until soil NH_4^+ pools were depleted.

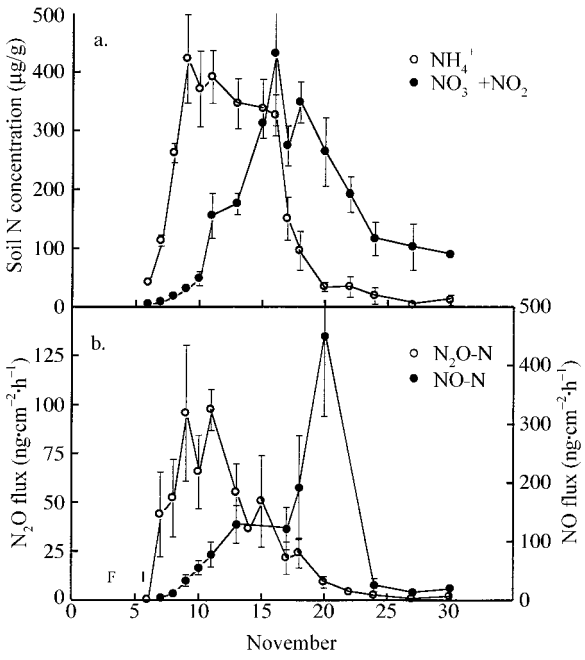

FIG. 2. Nitrogen dynamics over time in beds in the farmer's practice treatment during the first month of the wheat cycle: (a) inorganic nitrogen pools in the top 15 cm of soil in beds; (b) nitrogen trace-gas flux from the beds. Error bars represent ±1 SE of four replicate plots.

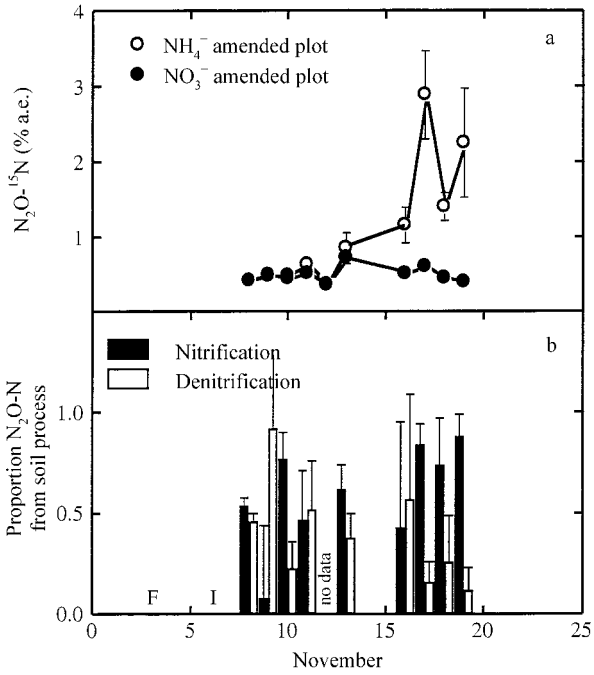

FIG. 3. (a) Nitrogen isotope (a.e = atom excess) abundance in N_2O evolved from treatments labeled with either $^{15}NH_4^+$ or $^{15}NO_3^-$. Plots were sampled at 2 h and 24 h after labeling (first and second points in sequence of five repeated experiments) and then relocated on the beds. Error bars represent ± 1 SE of three replicate plots. (b) Proportion of N_2O evolved from either nitrification or denitrification, calculated from ^{15}N-N_2O abundance, soil ^{15}N abundance, and N_2O flux as described in text. Error bars represent +1 SE of three replicate plots.

The pattern of trace gas emission that accompanied changes in soil water (Fig. 6) generally fits the conceptual model of gas flux presented by Davidson (1991). In accordance with the Davidson model, production of NO via nitrification dominated in dry soils.

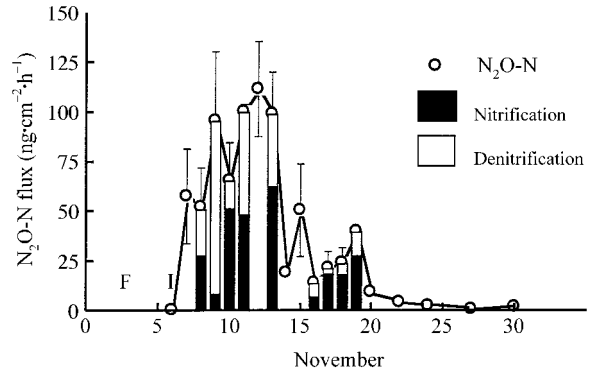

FIG. 4. Temporal trends in denitrification and nitrification losses of N_2O from the farmer's practice treatment during the first month of the 1995/1996 wheat cycle. Circles indicate measured fluxes in bed positions as reported by Matson et al. (1998). Bars represent proportions attributable to either denitrification or nitrification. Error bars represent +1 SE of four replicate plots of N_2O flux measurements.

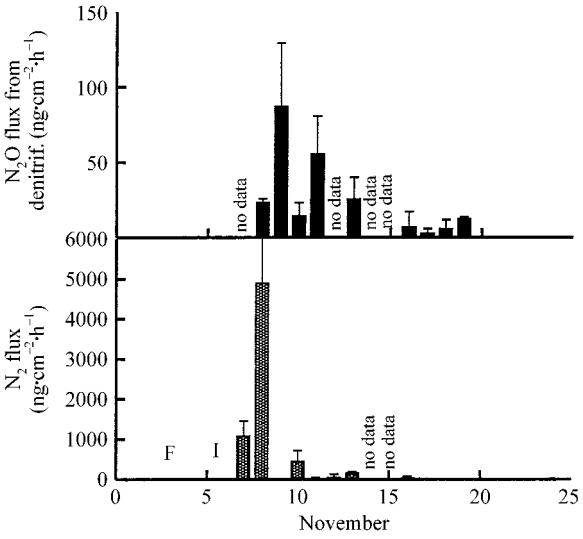

FIG. 5. N_2O flux attributable to denitrification from the farmer's treatment compared with N_2 flux determined concurrently in an adjacent experiment using isotope tracers and the modified Hauck technique. Error bars represent +1 SE of three replicate plots.

At intermediate soil moistures, both NO and N_2O were produced and emitted as a net flux from the soil. Davidson posits that under moderately high soil moisture, more of the NO produced is consumed before escaping the soil, which fits the pattern we see (Fig. 6b). At high soil moisture N_2 became the major end product. Fluxes of N_2, while highly variable when present, dominated the gas fluxes and were 5–40× higher than N_2O fluxes

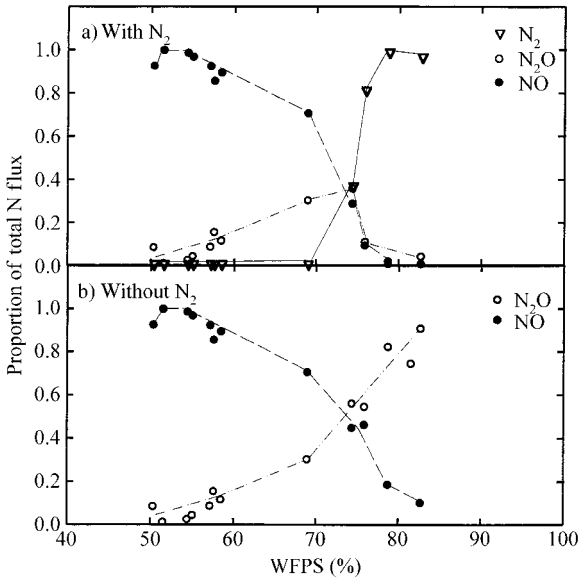

FIG. 6. (a) The relationship between water-filled pore space (WFPS) and relative proportions of nitrogen gas fluxes N_2, N_2O, and NO. (b) The relationship between N_2O and NO above 75% WFPS is more easily seen without the contribution of N_2. Lines are drawn to illustrate general trends.

(Fig. 6a). In contrast to the Davidson model, N_2O never dominated N gas emission in our study. The critical threshold that determined whether soil emissions were dominated by denitrification or nitrification processes occurred at 75% WFPS, a ''triple-point'' for the three N gas species. Gas losses from nitrification were dominated by NO and denitrification gas losses were dominated by N_2.

The consequences of water and fertilizer management are clear from these results. When soils were saturated early in the cycle, denitrification was likely NO_3^- limited. Had fertilizers been applied in the form of NO_3^-, much more significant N_2O gas losses probably would have occurred. By three weeks after irrigation, NO_3^- pools sufficient to drive high rates of denitrification remained in the soil, yet N_2O fluxes had stopped. During this period, denitrification apparently was limited by aerobic soils, while nitrification was limited by low NH_4 concentrations in the soil. Rainfall or irrigation events during this time could have led to substantial denitrification N_2O gas losses.

The Mexican agricultural system in which this study was conducted is representative of developing world irrigated areas with very low rainfall (Mega-environment 1). Roughly 32 million hectares of wheat (42.7% of the total) are grown in this environment worldwide (Meisner et al. 1992). Under the pressure of an increasing global demand for food, such agricultural systems are expected to experience intensification of management, including increases in fertilizer inputs (Matson et al. 1998). This study demonstrated that the soil microbial communities in these systems are very sensitive to the management of nitrogen and water. N gas loss is strongly dependent on the timing and species of nitrogen inputs relative to the water content of the soil. While intensive field-scale studies can elucidate the interactions between soil water content, soil N species, and soil N levels, process simulation models may be the only way to capture that variability and to scale it to regions or the global scale. Field-based measurements such as those reported here are useful for developing and testing such models (Li et al. 1992, Parton et al. 1996, Potter et al. 1996, Riley and Matson 1999).

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APPENDIX

Calculations for N_2O Source Study

1) Chamber volume was calculated from height measurements.
2) N_2O-N in chamber atmosphere before flux (μmol N) was calculated as follows:

$$0.01267\left(\frac{\mu\text{mol } N_2O}{\text{L air}}\right) \times 2\left(\frac{\mu\text{mol N}}{\mu\text{mol } N_2O}\right)\left(\frac{\text{chamber volume (cm}^3)}{1000\ \text{cm}^3 \cdot \text{L}^{-1}}\right).$$

3) N_2O-N in flux (μmol) was calculated as:

$$\frac{\text{measured flux (ng} \cdot \text{cm}^{-2} \cdot \text{h}^{-1})}{1000\ (\text{ng}/\mu\text{g})} \times 14\ (\text{g } N_2O\text{-N/mol}(N_2O\text{-N}) \times 508.6\ (\text{cm}^2 \text{ in chamber area}) \times 0.5\ (\text{h}).$$

4) Corrected ^{15}N of flux $^{15}N_2O$ was calculated using a mixing equation of the general form:

$$\%^{15}\text{N of mix} = \frac{(\text{N conc}_1)(\%^{15}\text{N}_1) + (\text{N conc}_2)(\%^{15}\text{N}_2)}{\text{N conc}_1 + \text{N conc}_2}$$

rearranged to solve for $\%^{15}N$ of flux from the known measured $\%^{15}N$ of mix, with natural abundance assumed to be 0.3663%. Corrected ^{15}N of flux $^{15}N_2O$ was calculated as follows:

$$\frac{(\%^{15}\text{N of flux})[\text{chamber } N_2O\ (\mu\text{mol N})] + \text{flux } N_2O\ (\mu\text{mol N}) - [\text{chamber } N_2O\ (\mu\text{mol N}) \times 0.3663]}{\text{flux } N_2O\ (\mu\text{mol N})}.$$

5) N_2O-N flux (μmol) from either the treatment amended with NH_4 or the treatment amended with NO_3^- was calculated as follows:

(a) For 2-h sample, assume soil ^{15}N pool of 2% after adding label:

$$N_2O\text{-N flux } (\mu\text{mol}) = \frac{(\text{corrected } \%^{15}\text{N of flux})[N_2O\ (\mu\text{mol N})] - (0.3663 \times \text{flux } N_2O)}{2\% - 0.3663\%}.$$

(b) For 24 h sample, calculate soil N pool using mixing equation with native concentration and natural-abundance ^{15}N and with known concentration and ^{15}N abundance of added label:

$$\%^{15}\text{N of soil mix} = \frac{[\text{native soil N amount } (\mu\text{g per plot}) \times 0.3663] + [\text{label N amount } (\mu\text{g added per plot}) \times 25]}{\text{native soil N amount } (\mu\text{g per plot}) + \text{label N amount } (\mu\text{g added per plot})}$$

$$N_2O\text{-N flux } (\mu\text{mol}) = \frac{(\text{corrected } \%^{15}\text{N of flux})[\text{flux } N_2O\ (\mu\text{mol N})]}{\text{calculated } \%^{15}\text{N of soil mix} - 0.3663}.$$

6) We calculated μmol N_2O-N from nitrification or denitrification:

$$\text{denitrification } N_2O\text{-N } (\mu\text{mol}) = N_2O\text{-N from } (NO_3^-)\text{-amended plot}$$

$$\text{nitrification } N_2O\text{-N} = [\mu\text{mol } N_2O\text{-N from } (NH_4^+)\text{-amended plot}] - \{[\mu\text{mol } N_2O\text{-N from } (NO_3^-)\text{-amended plot}] \times [\text{ratio of } {}^{15}NO_3^- \text{ in } (NH_4^+)\text{-amended plot to } {}^{15}NO_3^- \text{ in } (NO_3^-)\text{-amended plot}]\}.$$

7) Proportion from nitrification or denitrification is obtained as follows:

$$\text{nitrification } (\mu\text{mol})/[\text{nitrification} + \text{denitrification } (\mu\text{mol})]$$

$$\text{denitrification } (\mu\text{mol})/[\text{nitrification} + \text{denitrification } (\mu\text{mol})].$$

8) Flux N_2O-N from nitrification or denitrification is then calculated as follows:

$$(\text{proportion from nitrification})(N_2O\text{-N flux measured in control plots})$$

$$(\text{proportion from denitrification})(N_2O\text{-N flux measured in control plots}).$$