

Comparative Analysis of Nitrous Oxide Fluxes in Dryland Cropping Systems

D.R. Huggins and S.S. Higgins

Introduction

Agricultural activities influence atmospheric concentrations of greenhouse gasses (GHG), e.g. carbon dioxide (CO₂), methane (CH₄) and nitrous oxide, (N₂O), and contribute about 20% of the world's global radiative forcing (Lal et al., 1999). On the other hand, agricultural management can mitigate global radiative forcing by increasing storage of soil organic carbon (SOC), increasing oxidation of CH₄ in soil, or by reducing N₂O emissions (Mosier et al., 2003). However, crop recovery of N can often be low and single season nitrogen removal in harvested grain is estimated worldwide at only 33% of applied N (Raun and Johnson, 1999). Poor N recovery is a function of a portion of N cycled to competing pathways such as leaching, gaseous losses (e.g. N₂O) and biological immobilization (Legg and Meisinger, 1982; Ladd and Amoto, 1986; Haynes, 1997) and inefficiencies in crop physiological processes that affect the acquisition of available N (Moll et al., 1982; Huggins and Pan, 1993). Losses of N in agroecosystems commonly range from 1 to 35% of available N supplies (Kumar and Goh, 2000). Globally, reactive N (e.g. NH₄⁺, NO₃⁻) cycling in the environment, resulting from increased fertilization, has more than doubled since the 1940s, with 86% originating from agricultural activities. Agriculture is also a major contributor to atmospheric N₂O which has 298 times the global warming potential of CO₂ (IPCC, 2007). Therefore, cropping systems with inefficient N use are under increased scrutiny as N movement beyond agroecosystem boundaries results in degradation of air (Mosier et al., 1996) and water (Huggins et al., 2001) at watershed and global scales (Tilman et al., 2001). Improving nitrogen use efficiency (NUE) has been identified as a national goal (CAST, 2004), a goal shared by producers who seek greater NUE to reduce farm costs.

Agriculture was identified as a source of the greenhouse gas, N₂O, over 30 years ago (Crutzen, 1974; Crutzen and Ehhalt, 1977; Liu et al., 1977). In the 1980s, numerous studies were done to identify factors regulating agricultural emissions of N₂O (e.g., McKenney et al., 1980; Burford et al., 1981; Cochran et al., 1981; Blackmer et al., 1982; Conrad et al., 1983; Linn and Doran, 1984). More recent research has focused on quantifying and characterizing agriculture's contribution to greenhouse gas production and global climate change (Williams et al., 1992; Matson et al., 1998; Mosier, 1998; Smil, 1999; Robertson et al., 2000).

Six et al. (2004) reported that during the first decade after the transition to no till (NT), N₂O fluxes are higher in NT than under conventional tillage (CT) management, but would eventually decrease below CT in humid climates. Dalal et al. (2003) also presented an example of higher N₂O emissions under NT than CT in a wet region where fertilizer rates are high and soluble carbon is readily available. Such conditions are conducive to denitrification. Given the difficulty in measuring N₂O in

the field, they suggest that agroecosystem modeling would be a necessary tool for researchers to draw meaningful conclusions regarding the long-term effects of management on N₂O emissions, and they caution that the models will need to be parameterized and validated using local data.

We are applying the cropping systems simulation model, CropSyst (Stöckle et al., 2003), to evaluate the long-term effects of various farm management strategies on carbon sequestration and N₂O emissions. As noted above, an important component of modeling efforts is an accounting of N₂O production. To ensure accurate simulations, measurements of the largest potential N₂O fluxes in various management systems of interest are required. That is, modelers need to know the range of N₂O fluxes that could reasonably be expected in the systems being simulated. We conducted a series of experiments to achieve the following objectives: 1) Determine the maximum and minimum N₂O fluxes that could be expected in contrasting dryland management systems. 2) Assess the role of various environmental factors as they affect N₂O emissions. 3) Estimate the seasonal pattern of N₂O flux.

Methods and Materials

Three distinct agricultural management systems were sampled at the Palouse Conservation Field Station near Pullman, WA. The first management system was a continuous NT system established in 1996 which since 2002 has been in a crop rotation of winter wheat (*Triticum aestivum* L.) – spring barley (*Hordeum vulgare* L.) – spring wheat. Our first sampling of N₂O fluxes from the NT rotation was in October of 2005 after the harvest of spring barley. Spring wheat was seeded into this rotation in the spring of 2006, three days prior to sampling of N₂O flux. At seeding, 107 kg N ha⁻¹ was applied as urea ammonium nitrate (solution 32) where one half of the N is derived from urea, one quarter is nitrate-N and one quarter is ammonium-N. The second management system consisted of native perennial grasses (NP) seeded in 2002 to bluebunch wheatgrass (*Pseudoroegneria spicata* (Pursh) Á. Löve) and Idaho fescue (*Festuca idahoensis* Elmer) at rates of 6.5 kg ha⁻¹. In June, 2006, coverage of these two species in sample areas was 40% and 37%, respectively. Other species present in 2006 were annual grasses and forbs consisting of raitail fescue (*Vulpia myuros* (L.) D. D. Gmel), downy brome (*Bromus tectorum* L.) and catchweed bedstraw (*Galium aparine* L.), with coverages of 11%, 9% and 7%, respectively. The NP received no fertilizers, and was sprayed with herbicides as needed. The third management system was an organic pasture (ORG) seeded on 17 May 2006 to a grass/clover mix. The grasses seeded were orchardgrass (*Dactylis glomerata* L.), perennial rye (*Lolium perenne* L.) and meadow brome (*Bromus riparius* Rehm), at 4.5, 6.7 and 7.9 kg ha⁻¹, respectively. Clovers seeded were ladino clover (*Trifolium repens* L.) and red clover (*Trifolium pratense* L.), at 1.1 and 3.4 kg ha⁻¹, respectively. Prior to seeding the pasture mix in 2006, the ORG site had been, since 2002, in a legume forage – spring wheat – buckwheat (*Fagopyrum sagittatum* Gilib)/legume rotation under management practices consistent with certified organic production.

We sampled N₂O flux at four times over the course of the cropping season, which times were representative of different seasonal conditions that we hypothesized would differentially influence N₂O flux. At each of the four sampling times, we established three treatments within each of the three management systems. The first treatment was an untreated control (C), the second consisted of irrigated plots (W) and the third consisted of plots that were irrigated with a potassium nitrate solution that provided 89 kg ha⁻¹ N. This treatment was designated WF. The W and WF plots were irrigated with enough water to bring the top 20 cm of soil to a target of 80% water filled pore space (WFPS). Water filled pore space was determined as described by Elliott et al. (1999).

Approximately one week prior to the application of treatments, 12 circular, 0.61 m diameter plots were established within a 4 m by 3.7 m area located within each of the management systems. All treatments had four replicate plots within each management system. In the center of each plot, a cylindrical chamber base was installed. The chamber bases were constructed of polyvinyl chloride pipe with an inside diameter of 0.31 m. They were driven into the soil to a minimum depth of 5 cm. Just prior to sampling N₂O flux the W and WF treatments were applied. Immediately after irrigation was completed N₂O flux measurements were initiated. Sampling protocols and chamber design followed GRACEnet (2003) guidelines. Vented chamber lids were placed on the chamber bases. The lids were sealed in place with rubber gaskets.

Chamber lids were fitted with a septum through which a 30 mL headspace gas sample was obtained with a 35 mL plastic syringe (Monoject). The 30 mL headspace sample was injected into a 12 mL screw-top vial (Labco International, Houston TX) that had been previously evacuated. The vials were evacuated by first securing a lid with septum on the vial, then inserting the needle of a 60 mL syringe, and withdrawing the plunger of the syringe to the 40 mL mark. The plunger was held under tension at this position long enough to equilibrate tension between the syringe and vial, then the needle was withdrawn from the septum. This vial evacuation process was completed within 15 minutes of filling the vials with gas samples from the chamber headspace. Four headspace gas samples were used to determine N₂O flux. These samples were collected at 15-minute intervals. Application of treatments and gas sampling were done simultaneously in all three management systems.

Flux measurements were taken at 0, 3, 6, 24 and 27 hours after the irrigation treatments had been applied. This sampling schedule was designed to capture the peak N₂O fluxes which are known to occur after application of water (Rolston et al., 1982; Mulvaney and Kurtz, 1984; Sexstone et al., 1985).

At each time N₂O flux was sampled, calibration standards were prepared in the field. A series of vials was evacuated as described above. A 30 mL aliquot of calibration gas (Alltech, Deerfield, IL) was then injected into an evacuated vial. Three standard concentrations were used, 0.1, 1 and 2 ppm N₂O in N₂ and four vials of each concentration were prepared. These vials were stored under the same conditions as

the headspace samples collected. The field standards were used to generate the calibration curves from which N₂O gas concentrations were determined for all headspace samples collected at the respective sampling time.

Concurrent with N₂O flux samples, we collected soil samples that were assayed for nitrate, ammonium, soluble carbon and gravimetric water content (GWC). These soil samples were collected from the treated portion of each plot at the periphery of the chamber base. Soil samples collected at 0, 3 and 27 hours after application of the treatments. Soil samples were collected to 20 cm depth with a 1.9 cm diameter probe. At each plot at each time, four soil cores were taken and composited. A portion of the composited sample was used for gravimetric water content (GWC) determination. The remainder of the sample was stored at 4°C until processed for nitrate, ammonium and soluble organic carbon.

Soil surface temperature was measured in the shade of three chambers with a thermocouple thermometer (Omega Supermeter, model HHM290, Stamford, CT) at the end of each sampling session in each of the three management treatments. The average of these temperature measurements was taken as the soil surface temperature during the 45 min sampling period.

Nitrous oxide concentration in all samples was determined within one week of collection using a gas chromatograph (Shimadzu GC-8A, Kyoto, Japan) with an electron-capture detector. The column was a Porapak Q 80/100. Column temperature was 80 °C and the detector temperature was 340 °C. The carrier gas was nitrogen with a minimum purity of 99.998%. Nitrous oxide fluxes determined from chamber samples were calculated according to GRACenet (2003) and are reported as g N₂O-N ha⁻¹ h⁻¹. Total N₂O-N emission during a given 27 h sampling time was determined for each plot by geometric determination of the area under the curve of N₂O flux over time. These integrated values of N₂O-N lost are reported as N₂O-N ha⁻¹ in a 27 h period.

Nitrate and ammonium concentrations were determined on a QuickChem FIA+ 800 (Lachat, Milwaukee, WI) after extraction in 2M KCL as described by Keeney and Nelson (1982). Soluble organic carbon in soil samples was determined by infra-red gas analysis of carbon dioxide after combustion in a TOC-V_{CSH} total organic carbon analyzer (Shimadzu, Kyoto, Japan).

We were unable logistically to include in our experimental design repetitions of the three management systems, NT, NP and ORG. Therefore, in deference to concerns about pseudoreplication (Hurlbert, 1984) all analyses of variance were done separately within a given management system. Furthermore, to reduce the potential for unequal variances, analyses of variance for the four sampling times were performed separately; no direct statistical comparisons among the management systems were attempted. As noted above, 12 plots were established in each management system. The three treatments (4 replicates of each) were assigned at random to the plots for a completely randomized design. Two factors were analyzed; treatment with 3 levels (C, W and WF) and time with 4 levels for N₂O

flux (0, 3, 6, 24 and 27 hours) and with 3 levels for soil responses (0, 3 and 27 hours) with repeated measures over time. All repeated measures data were analyzed with the MIXED procedure of SAS (Littell et al., 1996). For each separate analysis of variance, five models of covariance structure were compared and the most appropriate model was used for that particular analysis (Littell et al., 1996). Additionally, residual plots were examined, and transformations were applied as needed to equilibrate error variances (Kuehl, 1994). Analysis of total N_2O -N lost during the sampling period used the GLM procedure of SAS (1988) after appropriate transformation to stabilize variances (Kuehl, 1994). The correlation between the independent variables, soil temperature, WFPS, soil ammonium concentration, soil nitrate concentration and soil soluble carbon concentration, and the dependent variables, maximum N_2O flux and total N_2O -N lost, was evaluated by obtaining the Pearson Correlation Coefficients (r) using the CORR procedure of SAS. Values of r were generated at each level of the treatment effects, e.g., for all the data obtained in August, or for the combination of ORG management in October.

Results

Selected N_2O -N flux results are presented in Figure 15.1. In May the addition of nitrate and water caused an increase in N_2O -N flux over control plots. The peak flux occurred about 6 hours after the application of water, but fluxes did not return to the control level for the remainder of the sampling period. The N_2O -N flux from NT control plots sampled in May was somewhat higher than that from ORG control plots sampled in August (Figure 15.1). But in August, the addition of water with nitrate fertilizer caused a large increase in N_2O flux, although the increase was transient.

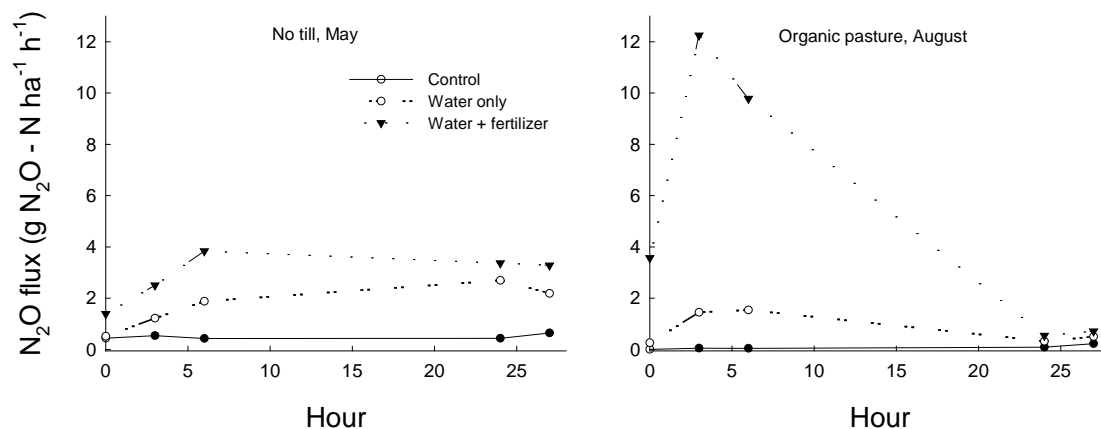


Figure 15.1. Nitrous oxide fluxes near Pullman, WA, measured in May and August, 2006 over a 27 hour period in no-till, winter wheat – spring barley – spring wheat rotation and a recently seeded organic pasture, respectively.

The total amount of N_2O-N emitted during the May sampling period (27 h) is presented in Figure 15.2. Management system (NP, ORG or NT) and treatments with water (water only or water + fertilizer) affected the amount of N_2O-N lost as compared to the control (no water or fertilizer added). NP and ORG emitted similar quantities of N_2O-N in control and water only plots, while the emission of N_2O-N from NT was higher in the treatments with added water and water plus fertilizer. This larger loss from NT was probably due to N fertilization of the NT plots that occurred during planting. The addition of nitrate with water increased the amount of N_2O-N emitted for all management systems although the increase was not significant in the NP system (Figure 15.2).

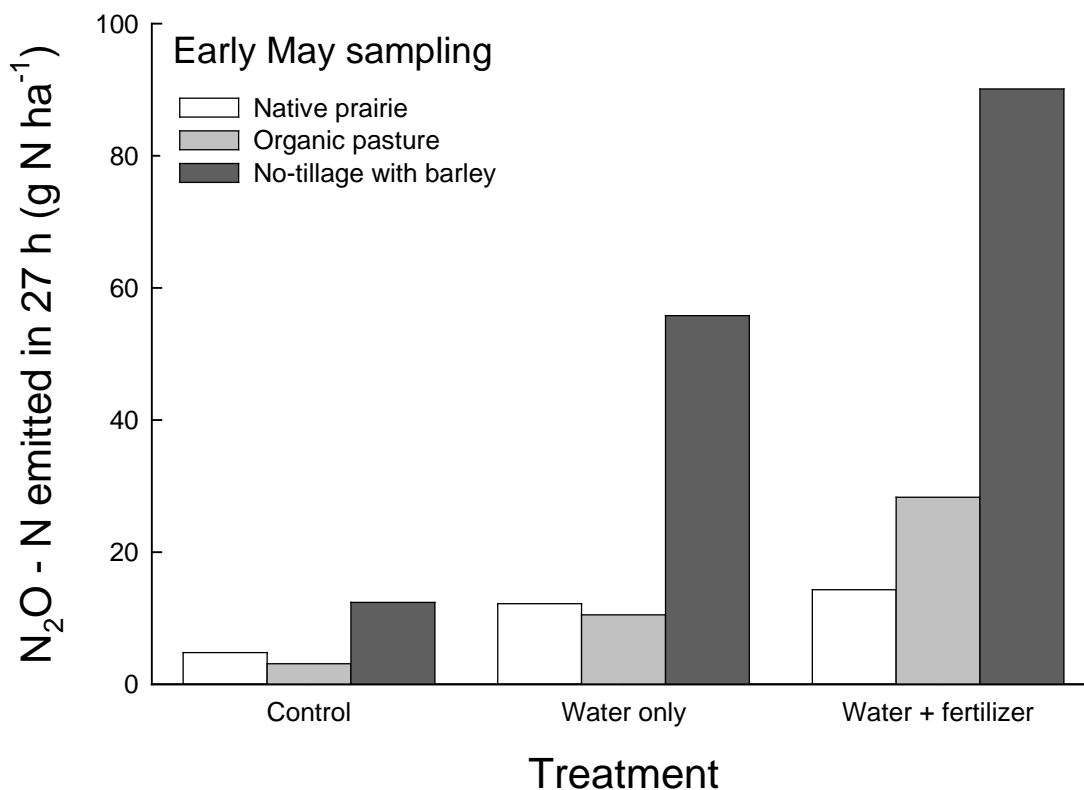


Figure 15.2. Nitrous oxide – N emitted to the atmosphere near Pullman, WA, in early May during a 27 hour sampling period from either native prairie, recently seeded organic pasture or a no-till, winter wheat – spring barley – spring wheat rotation. Sampling began immediately after the application of water only or water + fertilizer treatments.

Discussion

The maximum measured N_2O flux for any given replicate in this series of experiments was 18.7 g N_2O-N ha⁻¹ h⁻¹, a value that occurred in two of four replicates within 6 h of the application of water + fertilizer. These fluxes occurred in the ORG

management, under WF treatment in August when WFPS was about 73%. The maximum average N_2O -N flux for this treatment was $12.3 \text{ g N}_2\text{O-N ha}^{-1} \text{ h}^{-1}$ (Figure 15.1). Taking the area under the curve that includes this flux reveals that $151 \text{ g N}_2\text{O-N ha}^{-1}$ were lost from this treatment in 27 h. For comparison, Cochran et al., (1981) reported maximum emission in a 24 h period of about $15 \text{ g N}_2\text{O-N ha}^{-1}$ on similar but fallow soils in the same region in mid June. The Chocran et al. (1981) measurements were made shortly after rainfall, but 28 days after fertilizer had been applied. Although our N_2O emissions were comparatively high, not all studies are designed, as ours was, to capture the peak flux under ideal conditions for denitrification. So it is not surprising that we should have measured high N_2O losses. Also, although our maximum flux was high, it was transient, returning to un-watered control levels within 27 hours (Figure 15.1, August measurements).

Our lowest average N_2O flux was $-0.1 \text{ g N}_2\text{O-N ha}^{-1} \text{ h}^{-1}$, which represented flux of N_2O into the soil. This negative flux occurred in the NP control plots in June (data not shown). We also measured a negative flux in August in NT control plots. Although we measured fluxes of N_2O into the soil of control plots, ordinarily the fluxes were positive but near zero except in the spring when the soil was moist, leading to larger emissions of N_2O .

When we calculated the quantity of N_2O -N emitted during each 27 h experimental period, the result was always positive regardless of the occasional negative fluxes. Several of our treatments (Figure 15.2) provided N_2O -N losses comparable to the maximum value reported by Cochran et al. (1981). Although irrigation tended to enhance N_2O emissions, the addition of nitrate in the irrigation water generally resulted in substantial increases in N_2O emissions.

Conclusions

From the brief results summarized here, it is apparent that seasonal climatic conditions, soil moisture and nitrate availability all influence N_2O fluxes, as expected. Under control conditions, N_2O fluxes are generally constant and low, regardless of management regime, but rainfall and fertilizer applications can elevate N_2O fluxes to quite high values, particularly during summer. Fortunately, high N_2O fluxes are generally transient. The values reported herein can be used to guide modeling efforts designed to predict N_2O emissions from soils in the region.

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