Published May 20, 2016

Journal of Environmental Quality — TECHNICAL REPORTS

ATMOSPHERIC POLLUTANTS AND TRACE GASES

Evaluation of Intensive "4R" Strategies for Decreasing Nitrous Oxide Emissions and Nitrogen Surplus in Rainfed Corn

Rodney T. Venterea,* Jeffrey A. Coulter, and Michael S. Dolan

Abstract

The "4R" approach of using the right rate, right source, right timing, and right placement is an accepted framework for increasing crop N use efficiency. However, modifying only one 4R component does not consistently reduce nitrous oxide (N_2O) emissions. Our objective was to determine if N fertilizer applied in three split applications (Sp), by itself or combined with changes in N source and rate, could improve N recovery efficiency (NRE) and N surplus (NS) and decrease N_2O emissions. Over two corn (*Zea mays* L.) growing seasons in Minnesota, N_2O emissions ranged from 0.6 to 0.9 kg N ha^{-1}. None of the treatment combinations affected grain yield. Compared with urea applied in a single application at the recommended N rate, Sp by itself did not improve NRE or NS and did not decrease N_2O. Combining Sp with urease and nitrification inhibitors and/or a 15% reduction in N rate increased NRE from 57 to >73% and decreased NS by >20 kg N ha^{-1}. The only treatment that decreased N_2O (by 20–53%) was Sp combined with inhibitors and reduced N rate. Emissions of N_2O were more strongly correlated with NS calculated from grain N uptake (R^2 = 0.61) compared with whole-plant N uptake (r^2 = 0.39), possibly because most N losses occurred before grain filling. Optimizing both application timing and N source can allow for a moderate reduction in N rate that does not affect grain yield but decreases N_2O. Grain-based NS may be a more useful indicator of N_2O emissions than whole-plant-based NS.

Core Ideas

- Split application by itself did not decrease N_2O compared with single application.
- Microbial inhibitors did not decrease N_2O unless combined with reduced N rate.
- Some treatments increased N recovery efficiency but did not reduce N_2O.
- N_2O was more strongly related to N surplus on a grain- compared with whole-plant basis.
- Strategies that modify more than one 4R component may be needed to reduce direct N_2O.

OPTIMIZING the four basic aspects of N fertilizer management—the "4R" approach of using the right rate, right source, right timing, and right placement—is often recommended for increasing crop N use efficiency and decreasing soil N_2O emissions (Snyder et al., 2009). However, modifying one of the 4R components by itself may not be reliable in reducing N_2O emissions, particularly in rainfed cropping systems (Decock, 2014). For example, the use of delayed application and/or split application (Sp) while maintaining N rate, source, and placement (Phillips et al., 2009; Zebarth et al., 2008, 2012) or the use of specialized N fertilizer sources (e.g., urea containing microbial inhibitors [UI]) while maintaining N rate, timing, and placement (Parkin and Hatfield, 2014; Sistani et al., 2011) have been inconsistent in reducing N_2O emissions.

The inconsistency of single-modification strategies is likely due to interactions of crop, soil, and weather factors. Recent studies in Minnesota corn systems using broadcast urea (U) showed no effectiveness of inhibitors alone over 5 site-years (Maharjan and Venterea, 2013; Venterea et al., 2011a) or timing alone over 2 site-years (Venterea and Coulter, 2015). Few studies have attempted to optimize combinations of timing, source, and rate to maintain corn yield and decrease N_2O. Burzaco et al. (2013, 2014) measured crop response and N_2O emissions after application of urea–ammonium nitrate, with and without a nitrification inhibitor, using two application timings and three N rates. As far as we know, studies examining multiple combinations of timing, source, and rate have not been conducted with U, which is widely used for corn production in the US Corn Belt (Bierman et al., 2012). One objective of this study was to determine if Sp, alone or in combination with inhibitors and/or reduced N rate, could decrease N_2O compared with the common practice of a single, early-season U application over 2 site-years using a "management systems" experimental approach for corn production.

A basic principle underlying any N conservation management strategy is that practices that enhance crop N uptake will reduce reactive N losses, including leaching or runoff of

J. Environ. Qual.
doi:10.2134/jeq2016.01.0024

Received 19 Jan. 2016.
Accepted 28 Mar. 2016.
*Corresponding author (Venterea@umn.edu).

R.T. Venterea, USDA–ARS, Soil and Water Management Unit, 1991 Upper Buford Circle, St. Paul, MN 55108 and Dep. Soil, Water, and Climate, Univ. of Minnesota, St. Paul, MN 55108; J.A. Coulter, Dep. Agronomy and Plant Genetics, Univ. of Minnesota, St. Paul, MN 55108; M.S. Dolan, USDA–ARS, Soil and Water Management Unit, 1991 Upper Buford Circle, St. Paul, MN 55108. Assigned to Associate Editor Stephen Del Grosso.

Abbreviations: EF, fertilizer-induced N_2O emission factor; aN_2O, cumulative area-scaled N_2O emissions; yN_2O, cumulative yield-scaled N_2O emissions; dN_2O, daily N_2O flux; NRE, nitrogen recovery efficiency; NS, nitrogen surplus; RN, recommended N rate; Sp, split application; U, urea; UI, urea containing microbial inhibitors.

nitrate (NO_3) and atmospheric emissions of ammonia (NH_3), nitric oxide (NO), and N_2O. However, improvements in N recovery efficiency (NRE) do not necessarily reduce losses of each reactive N species to the same extent. For example, N management practices that result in increased NRE can have the same, or even greater, N_2O emissions compared with less efficient treatments (Fujinuma et al., 2011). Such counterintuitive findings may result from the much larger proportion of the total N budget represented by NH_3 and NO_3 losses, which can account for 10 to 30% (or more) of applied N, compared with N_2O losses, which are usually <3% of applied N (Venterea et al., 2012). Thus, a second, parallel objective of the current study was to explore relationships between NRE and N_2O emissions across a range of N management systems that were expected to range widely in both variables. In addition to NRE, we quantified N surplus (NS), which has been used as an indicator of reactive N losses to the environment (van Beek et al., 2003; Zhang et al., 2015) as well as a predictive metric of N_2O emissions (Van Groenigen et al., 2010), although few site-specific relationships between NS and N_2O emissions have been reported.

Materials and Methods

Site Description and Experimental Design

The experiment was conducted at the University of Minnesota Research Station in St. Paul (44.99° N, 93.17° W), where the soil is a Waukegan silt loam (fine-silty over sandy or sandy-skeletal, mixed, superactive, mesic Typic Hapludolls) with 25.4% sand and 14.9% clay in the upper 0.15 m with pH (in H_2O) of 7.1, total C of 25.1 g kg^{-1}, and C/N ratio of 11.9. The 30-yr (1981–2010) average precipitation during April through October is 542 mm (Minnesota Department of Natural Resources, 2016). A 2-yr experiment (2014 and 2015) was conducted using a randomized complete block design with four blocks, each containing six 5.3 by 5 m plots. Treatments were applied to the same plot areas both years and consisted of a nonfertilized control plus five N management systems: U-S100, single U application at 100% of the recommended N rate (RN) (146 kg N ha^{-1}); U-Sp100, split U application at 100% of the RN; U-Sp85, split U application at 85% of the RN (124 kg N ha^{-1}); UI-Sp100, split application of UI at 100% of the RN; and UI-Sp85, split UI application at 85% of the RN. For the UI treatments, SuperU (Koch Agronomic Services) was used, which contains the urease inhibitor *N*-(n-Butyl)-thiophosphoric triamide and the nitrification inhibitor dicyandiamide. The RN according to University of Minnesota guidelines (Kaiser et al., 2012) and application timing and placement were the standard N management practices in production fields adjacent to the research plots. The selected N rate was similar to the rate (155 kg N ha^{-1}) that achieved maximum yield in a study with the same soil type and climate regime (Venterea and Coulter, 2015). All fertilizers were hand applied and broadcast uniformly. Separate applications were made to soil within the flux chamber measurement areas to ensure the prescribed N rates.

Corn was planted on 19 May 2014 (Pioneer 36V51) and 27 Apr. 2015 (Mycogen F2F379) at 79,100 seeds ha^{-1} in 0.76-m rows in a field with a cropping history in corn for at least the previous 10 yr. Corn residue remaining after grain harvest was managed by stalk chopping. Tillage involved rotary plowing to a depth of 0.2 m in the fall after stalk chopping and in spring before planting. The single U application was applied 10 to 11 d after planting on 29 May 2014 and 8 May 2015. The Sp treatments received one third of the N rate on the same dates as the single application, another one third at the V6 corn stage on 27 June 2014 and 19 June 2015, and the final one third at the V14 corn stage on 18 July 2014 and 13 July 2015 (Abendroth et al., 2011). The first application was incorporated into the soil using metal rakes with 100-mm tines. The V6 and V14 applications were not incorporated. Application dates for the V6 and V14 applications were selected to precede forecasted precipitation. Rainfall of 24 and 11 mm was recorded within 24 h of the V6 application in 2014 and 2015, respectively, but no substantial rainfall occurred within 24 h of the V14 applications either year.

N_2O Emissions

Soil-to-atmosphere N_2O fluxes were measured using non–steady-state chambers (Parkin and Venterea, 2010) constructed of acrylic (Rochette and Bertrand, 2008). One chamber anchor (0.69 by 0.34 m) was installed in each plot to a depth of 0.10 m centered between rows. Sampling was conducted once weekly beginning in mid-April through planting and then twice weekly after planting through mid-September, with 34 sampling dates each year totaling 816 individual measurements. Insulated and vented chamber tops (0.13 m high) were secured to anchors using binder clips, and gas samples were collected 0, 0.5, 1.0, and 1.5 h after chamber placement using a polypropylene syringe. Samples were transferred to glass vials sealed with butyl rubber septa (Alltech) and analyzed within 1 wk using a headspace autosampler (Teledyne Tekmar) connected to a gas chromatograph (model 5890, Agilent/Hewlett-Packard) equipped with an electron capture detector. Fluxes of N_2O were calculated from the rate of change of N_2O concentration using methods designed to account for suppression of the surface–atmosphere concentration gradient (Venterea, 2010). Daily N_2O fluxes (dN_2O) were used to calculate cumulative growing season area-scaled N_2O emissions (aN_2O) by trapezoidal integration (Parkin and Venterea, 2010). Fertilizer-induced aN_2O was calculated by subtracting aN_2O in the nonfertilized control from aN_2O in each N-amended treatment. The fertilizer-induced N_2O emission factor (EF) was calculated by dividing fertilizer-induced aN_2O by the N rate. Cumulative yield-scaled N_2O emissions (yN_2O) were calculated as the ratio of aN_2O to grain yield.

Weather and Soil Measurements

A weather station 1 km away recorded air temperature and precipitation. Soil temperature and moisture content were measured during each N_2O sampling period. Soil temperature was measured using a probe (Fisher) inserted to the 0.05-m depth within 1 m of the chambers. Gravimetric water content was determined by collecting 0.05-m-diameter by 0.05-m-long cores collected within 1 h of each flux measurement and drying overnight at 105°C. Additional soil samples were collected weekly for analysis of extractable soil N concentrations. Two cores from each plot were collected to a depth of 0.30 m using a 20-mm-diameter sampler. Cores were divided into 0- to 0.15-m and 0.15- to 0.30-m depth intervals and combined into two samples (one per depth interval) per plot. Cores from the 0.15- to 0.30-m depth interval were not collected after 23 July 2014 and 29 July 2015 due to dry soil conditions. Samples were homogenized before removing two separate 10-g subsamples, which were extracted using separate 2 mol L^{-1} KCl solutions (Maharjan and Venterea, 2013). One subsample was extracted for nitrite (NO_2) plus nitrate (NO_3) using the Greiss–Ilosvay method with cadmium reduction (Mulvaney, 1996), and the other subsample was extracted for analysis of ammonium (NH_4) using the sodium salicylate-nitroprusside method (Mulvaney, 1996), both using a flow-through injection analyzer (Lachat). Henceforth "nitrate" (NO_3) refers to the sum of NO_2 plus NO_3. We also calculated soil N intensity by trapezoidal integration of weekly soil NO_3 and NH_4 concentrations (mg N kg^{-1}) versus time (day), resulting in units of mg N kg^{-1} d^{-1}. Other studies (e.g., Burton et al., 2008; Maharjan and Venterea, 2013; Venterea et al., 2015) have reported soil N intensity calculated in this manner as a time-integrated index of soil N availability. Intensities were determined separately for the two sampling depths and summed to represent the 0- to 0.30-m depth interval for each of the NO_3 and NH_4 species.

After crop harvest, additional soil samples were collected to the 0.60-m depth using a hydraulic sampler (37 mm in diameter) (Giddings). Each core sample was segregated into 0- to 0.15-m, 0.15- to 0.30-m, and 0.30- to 0.60-m depth intervals and analyzed as described above. Postharvest (residual) mineral soil N content was calculated using soil bulk density measured for each depth interval.

Grain Yield and Aboveground N Uptake

Crop sampling was done in the middle two rows of each plot, which were avoided during gas-flux and soil sampling. After crops reached physiological maturity, plants were manually harvested from the midsection of the plot, which represented 58% of the total plot area. Ears were picked, and corn stover was sampled after cutting at 0.10 m above the soil. Stover was weighed and subsampled (six plants per plot). Ears were air dried and shelled. Grain, stover, and cobs were further dried for 3 d at 65°C and weighed to obtain dry matter yields. Dried materials were ground with a ball mill and analyzed for N content with an elemental analyzer (VarioMax, Elementar). Total N uptake in aboveground biomass was calculated from the sum of N masses harvested in grain, stover, and cob. Crop NRE was calculated from the difference in aboveground N uptake between the nonfertilized control and each fertilizer treatment divided by the amount of fertilizer N applied. Nitrogen surplus was calculated on both a whole-plant and a grain basis, from the fertilizer N rate minus the N recovered in aboveground plant material, or in grain alone, respectively.

Data Analysis

Data were analyzed at $P \leq 0.05$ using the MIXED procedure of SAS (SAS Institute, 2011). Year and N management system were considered fixed effects, and block and interactions with block were considered random effects. Residuals were evaluated for homogeneity of variance and normality using scatterplots of residuals versus predicted values (Kutner et al., 2004) and the UNIVARIATE procedure of SAS; these requirements were met for all dependent variables. Mean comparisons were made at $P \leq$ 0.05 with independent pairwise *t* tests using the PDIFF option of the MIXED procedure of SAS. When the main effect of N management system was significant at $P \leq 0.05$, linear contrasts were made using the MIXED procedure of SAS to compare (i) UI versus U across N rates and years and (ii) 100 versus 85% of the RN across N sources and years. Linear and nonlinear regression analyses were conducted using Statistix 9 (Analytical Software) and SigmaPlot 12.5 (Systat), respectively.

Results

Weather

Total precipitation during April through September was greater in 2014 (711 mm) than in 2015 (602 mm) and compared with the 30-yr mean of 599 mm (Fig. 1a). In 2014, 70% of growing season precipitation occurred in April, May, and June (combined), compared with 46% in 2015, which was identical to the 30-yr mean. In 2014, a dry period occurred from 13 July through 9 August, during which 17 mm of rainfall was recorded and soil moisture content in the upper 50 mm decreased to 10% (Fig. 1b). In 2015, a dry period occurred from 29 July through 6 August, during which 6 mm of rainfall was recorded and soil moisture content decreased to 14%. Averaged across the growing season, soil moisture content (21.3% both years) and temperature (19.8 and 19.7°C in 2014 and 2015, respectively) at the time of gas-flux sampling were similar for both years.

Crop Response

Corn grain yield, whole-plant yield, and aboveground N uptake were greater in 2015 than in 2014 by 9 to 16% (Table 1). There were no differences in grain or whole-plant yield among treatments receiving N fertilizer. Whole-plant N uptake was greater in the UI-Sp100 treatment compared with U-S100 and UI-Sp85. Both estimates of NS were reduced (more negative) in 2015 than 2014 by >30 kg N ha^{-1}. On a whole-plant basis, NS was decreased in U-Sp85, UI-Sp100, and UI-Sp85 compared with U-S100 and was decreased in U-Sp85 compared with U-Sp100. On a grain basis, NS was reduced in U-Sp85 and UI-Sp85 compared with the other fertilized treatments. Nitrogen recovery efficiency did not vary by year but was greater in U-Sp85 and UI-Sp100 compared with U-S100 and greater in U-Sp85 than in U-Sp100.

N_2O Response

Daily mean N_2O fluxes ranged from <1 to >140 μg N m^{-2} h^{-1}, with episodic increases observed after each fertilization event (Fig. 1c). Fluxes diminished and remained <25 μg N m^{-2} h^{-1} during August and September. Year and N management system affected both aN_2O and yN_2O, which were more than twice as great in 2014 than in 2015 (Table 2). All treatments receiving N fertilizer had greater aN_2O than the nonfertilized control. The UI-Sp85 treatment had decreased aN_2O (by 20–28%), fertilizer-induced aN_2O (by 42–53%), yN_2O (by 20–30%), and EF (by 32–53%) compared with all other fertilized treatments. The EF for the UI-Sp100 treatment also was decreased compared with U-Sp85. Across the four treatments with Sp, all measures of N_2O emissions were greater with U compared with UI ($P \leq 0.002$). Both aN_2O and yN_2O were positively correlated

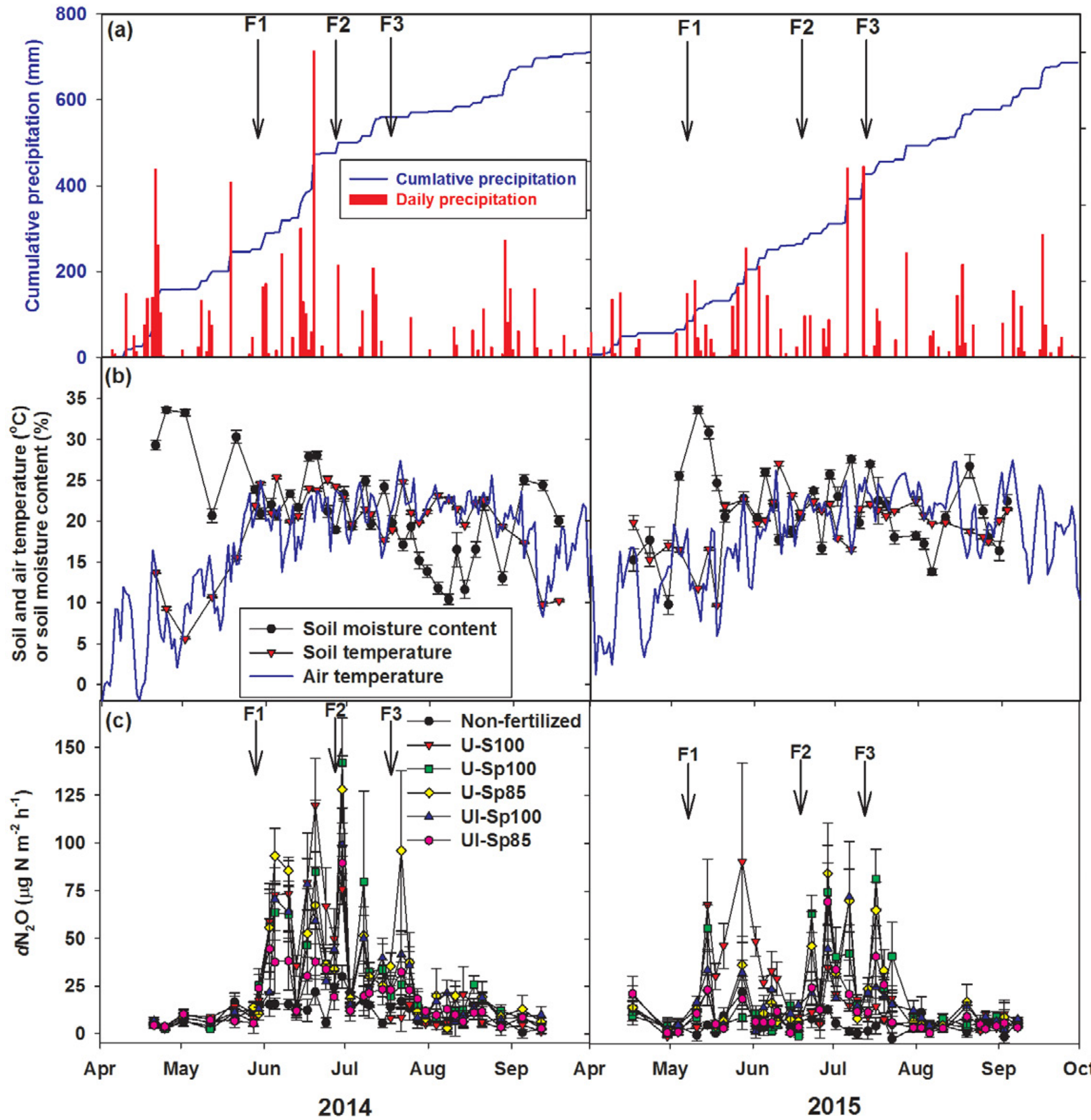

Fig. 1. (a) Precipitation, (b) air and soil temperature and soil moisture, and (c) daily N_2O fluxes during 2014 and 2015. S, single application; Sp, split application; U, urea; UI, urea with microbial inhibitors; 85 and 100 refer to percentages of recommended rate. Arrows indicate dates of N fertilizer application. The S treatment received all fertilizer at F1, and the Sp treatments received three equal applications at F1, F2, and F3.

with NS calculated on a whole-plant and grain basis ($P < 0.001$) (Fig. 2). For grain-based NS, exponential models were a better fit ($R^2 = 0.61$ and 0.47 for aN_2O and yN_2O, respectively) than linear relationships ($r^2 = 0.57$ and 0.39, respectively). For whole-plant–based NS, exponential models did not provide a better fit than linear models. There was no correlation between NRE and aN_2O ($P = 0.36$) or yN_2O ($P = 0.65$). Grain-based NS was positively but weakly correlated with fertilizer-induced aN_2O ($P = 0.040$; $r^2 = 0.11$).

Soil N Response

Soil NH_4 and NO_3 concentrations displayed episodic increases above baseline levels over the course of the growing season (Fig. 3). Mean weekly NH_4 ranged from 0.1 to 36 μg N g^{-1} at 0 to 0.15 m and from 0.2 to 13 μg N g^{-1} at 0.15 to 0.30 m. Mean weekly NO_3 ranged from 0.5 to 47 μg N g^{-1} at 0 to 0.15 m and from 0.2 to 18 μg N g^{-1} at 0.15 to 0.30 m. Soil N intensity was greater in 2014 than in 2015 for both NH_4 and NO_3 (Table 3). Soil N intensity was decreased in the nonfertilized control compared with the fertilized treatments, with the exception that NH_4 intensity did not differ between the control and the U-Sp85 treatment, which also had less soil NH_4 intensity than the U-S100 and UI-Sp85 treatments. Soil NO_3 intensity in both treatments receiving 85% of the RN was less than in the 100% of the RN treatments. Across the four treatments with Sp, NH_4 intensity was greater with UI than U ($P = 0.036$), and NO_3 intensity was greater with 100 compared with 85% RN ($P = 0.018$). Soil NO_3 and NH_4 intensity were positively correlated with aN_2O and yN_2O ($P < 0.001$) and explained 44 and 21% of the overall variance in aN_2O and yN_2O, respectively. Post-harvest residual NH_4 was greater in 2015 and did not differ by N management (Table 3). Residual NO_3 was greater in 2014 and was greater in the UI-Sp100 treatment than all other treatments except U-Sp100 and UI-Sp85. The UI-Sp85 treatment had greater residual NO_3 than the nonfertilized control and U-S100. Across the four treatments with Sp, residual NO_3 was greater with UI than U ($P = 0.015$).

Table 1. Means of agronomic response variables and significance of *F* values for fixed sources of variation.

	Grain yield	Whole plant yield	Aboveground N uptake	N surplus		N recovery efficiency
				Whole plant	Grain	
	Mg DM† ha^{-1}		kg N ha^{-1}			%
By year‡						
2014	9.04	17.6	183	−69.1	−1.7	69.2
2015	10.01	19.2	213	−99.6	−35.4	65.2
P > *F*	**0.031§**	**0.042**	**0.014**	**0.014**	**0.003**	0.428
By N management system¶						
Nonfertilized	7.12b#	14.1b	122c	−122.1d	−81.1c	–
U-S100	9.79a	18.5a	205b	−59.8a	4.59a	57.2c
U-Sp100	10.36a	19.8a	210ab	−64.7ab	−0.84a	60.6bc
U-Sp85	9.94a	19.5a	215ab	−92.2c	−15.8b	75.7a
UI-Sp100	9.95a	19.5a	229a	−83.1bc	−1.06a	73.2ab
UI-Sp85	9.97a	18.8a	207b	−84.1bc	−17.0b	69.2abc
P > *F*	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**0.050**
By N source††						
U	10.15	18.4	207	−72.8	−8.33	66.9
UI	9.96	18.0	212	−78.0	−9.02	70.0
P > *F*	0.546	0.422	0.472	0.472	0.867	0.525
By N rate						
85	9.95	17.9	206	−84.4	−16.40	71.2
100	10.16	18.4	214	−66.3	−0.95	65.7
P > *F*	0.521	0.396	0.272	0.054	**0.002**	0.267

† Dry matter.

‡ The year-by-N management system interaction was not significant for any variable ($P \geq 0.291$).

§ Significant differences ($P \leq 0.05$) are shown in bold type.

¶ S, single application; Sp, split application; U, urea; UI, urea with microbial inhibitors; 85 and 100 refer to percentages of recommended rate.

Within a column, N management system means followed by the same lowercase letter are not significantly different at $P \leq 0.05$.

†† Linear contrasts were used to determine N source and rate effects using data from the treatments with split application (U-Sp100, U-Sp85, UI-Sp100, and UI-Sp85).

Table 2. Means of N_2O response variables and significance of *F* values for fixed sources of variation.

	Area-scaled N_2O	Fertilizer-induced N_2O	Yield-scaled N_2O	Emission factor
	kg N ha^{-1}		g N Mg^{-1} DM†	%
By year‡				
2014	1.05	0.432	116.3	0.317
2015	0.47	0.351	47.2	0.256
P > *F*	**<0.001§**	0.136	**<0.001**	0.145
By N management system¶				
Nonfertilized	0.436c#	–	66.5b	–
U-S100	0.867a	0.432a	92.6a	0.300ab
U-Sp100	0.876a	0.441a	87.1a	0.303ab
U-Sp85	0.911a	0.476a	94.6a	0.386a
UI-Sp100	0.823a	0.387a	83.3a	0.266b
UI-Sp85	0.659b	0.223b	66.4b	0.181c
P > *F*	**<0.001**	**0.005**	**<0.001**	**0.003**
By N source††				
U	0.894	0.458	90.8	0.344
UI	0.740	0.305	74.9	0.223
P > *F*	**<0.001**	**0.002**	**0.002**	**<0.001**
By N rate				
85	0.785	0.349	80.5	0.284
100	0.849	0.414	85.2	0.285
P > *F*	0.128	0.161	0.331	0.985

† Dry matter.

‡ The year-by-N management system interaction was not significant for any variable ($P \geq 0.347$).

§ Significant differences ($P \leq 0.05$) are shown in bold type.

¶ S, single application; Sp, split application; U, urea; UI, urea with microbial inhibitors; 85 and 100 refer to percentages of recommended rate.

Within a column, N management system means followed by the same lowercase letter are not significantly different at $P \leq 0.05$.

†† Linear contrasts were used to determine N source and rate effects using data from the treatments with split application (U-Sp100, U-Sp85, UI-Sp100, and UI-Sp85).

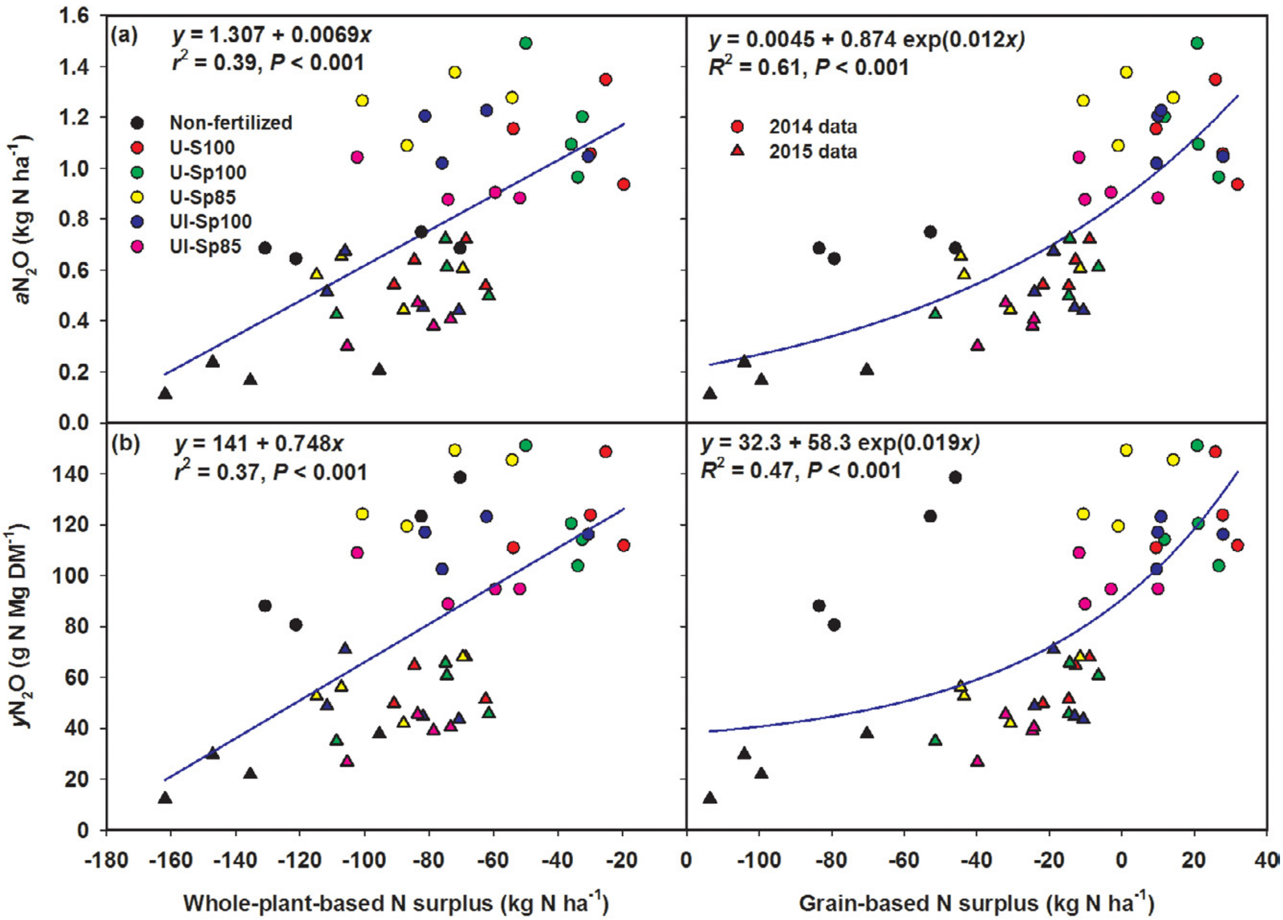

Fig. 2. Relationships between whole-plant and grain-based N surplus and (a) area-scaled (*a*N_2O) and (b) yield-scaled (*y*N_2O) N_2O emissions. Symbol colors indicate N management system treatments; circles are 2014 data, and triangles are 2015 data. S, single application; Sp, split application; U, urea; UI, urea with microbial inhibitors; 85 and 100 refer to percentages of recommended rate.

Discussion

Crop Response

Conditions during this study were favorable for corn production. Averaged across treatments, grain yield in 2014 and 2015 was 7 and 18% greater than the average of 253 treatment means from field experiments across the United States during 2006 to 2012 (Ciampitti and Vyn, 2014), respectively. Decreased grain and whole-plant yields in 2014 than 2015 were likely related to later planting, greater precipitation during the early-vegetative stages, and an extended dry period encompassing the late-vegetative and early-reproductive stages. Greater precipitation during June (231 and 95 mm in 2014 and 2015, respectively) likely enhanced losses of fertilizer N applied near planting and may have restricted root development in 2014 compared with 2015, thereby limiting crop N uptake, particularly during the longer midseason dry period; reduced crop N uptake also was likely responsible for greater soil N intensities in 2014. The lack of difference in grain and whole-plant yields among treatments receiving N fertilizer may have been partially due to a relatively high amount of N supplied from soil N mineralization. This is indicated by the grain yield of the nonfertilized control, which was 14% greater than that of the nonfertilized control from a similar study in 2012 and 2013 on the same soil type (Venterea and Coulter, 2015). The findings that Sp by itself compared with single application timing, or UI by itself compared with U, did not improve any measure of crop performance corroborate previous results in rainfed corn systems (Jaynes and Colvin, 2006; Randall et al., 1997; Sistani et al., 2014). The current results demonstrate that a moderate (i.e., 15%) reduction in N rate, when combined with modification of application timing and/or N source, can maintain grain yield and improve NS and NRE.

N_2O and Soil N Responses

The N_2O emissions observed here are in the same range (0.7–0.9 kg N ha^{-1}) as those observed in previous studies where broadcast urea was applied to corn in similar soil and climate conditions (Venterea et al., 2010, 2011a). Greater N_2O emissions in 2014 compared with 2015 were likely due to greater rainfall during April through June combined with the aforementioned factors, which may have limited crop N uptake in 2014. The finding that Sp, by itself, did not reduce N_2O emissions is consistent with other studies (e.g., Burton et al., 2008; Venterea and Coulter, 2015; Zebarth et al., 2012). If crop N demand were the only factor affecting N_2O flux, a larger pulse of N_2O would be expected after the single application compared with after the split applications. However, as observed in previous studies, N fertilizer applied later in the season preceded increases in N_2O flux that were equivalent to or greater in magnitude than responses after the single N application. This was likely due to the rapid rates of U hydrolysis and nitrification relative to transport of soil N to roots. Depending on the proximity of a given U granule

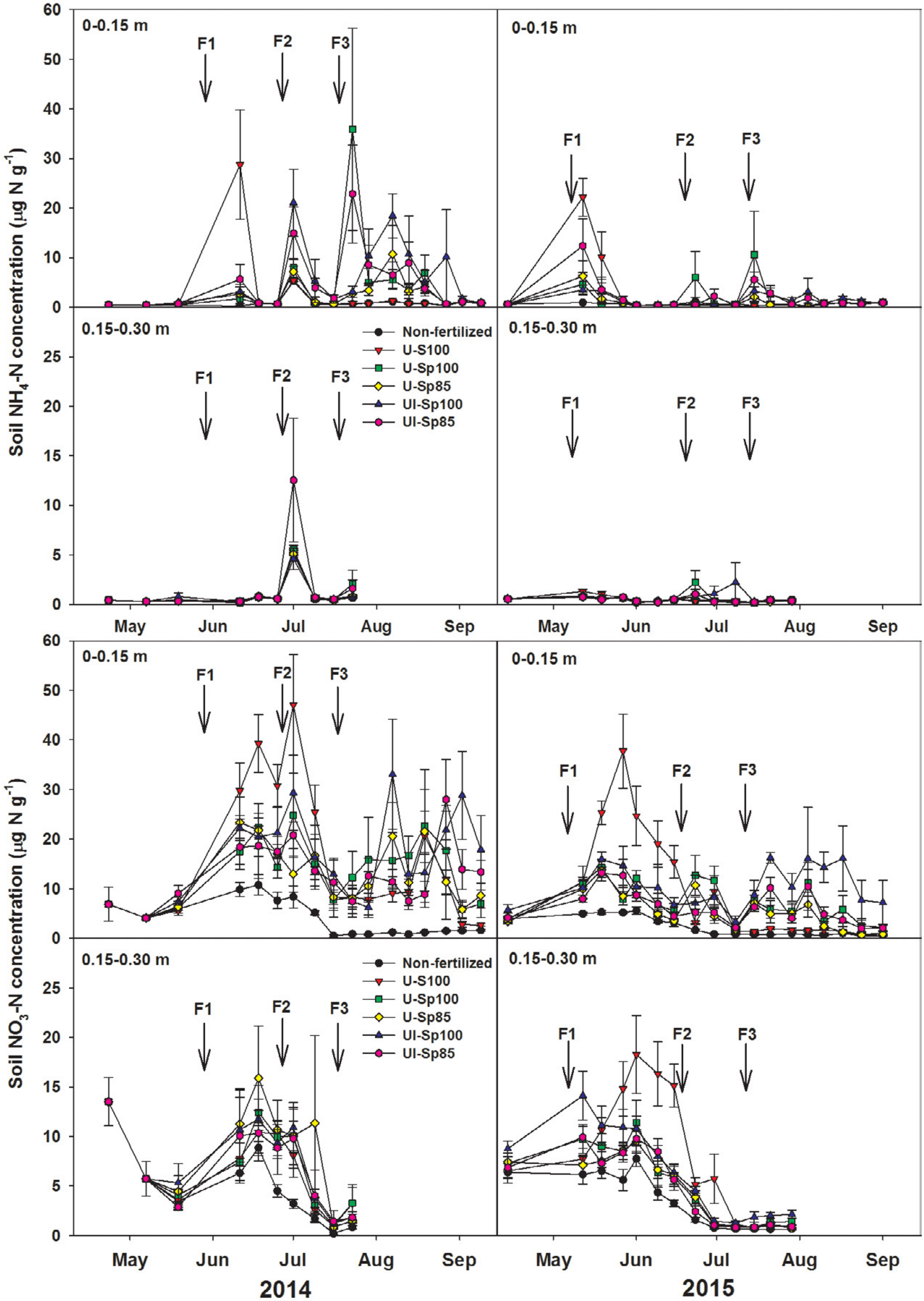

Fig. 3. Concentrations of soil ammonium (NH_4) (upper four plates) and nitrate (NO_3) (lower four plates) in the 0- to 0.15-m and the 0.15- to 0.30-m depth intervals under varying N management in 2014 and 2015. S, single application; Sp, split application; U, urea; UI, urea with microbial inhibitors; 85 and 100 refer to percentages of recommended rate. The S treatment received all fertilizer at F1, and the Sp treatments received three equal applications at F1, F2, and F3.

to a plant root, NH_4 released during U hydrolysis may not be readily accessible for root uptake due to the interaction of NH_4 with soil-surface and diffusion limitations. Under these conditions, factors affecting N_2O production, such as soil moisture content, temperature, and C availability, may be more important in regulating N_2O flux than crop stage. Another factor may be related to the effects of U hydrolysis on soil pH. The larger single application treatment would be expected to cause greater temporary increases in soil pH compared with Sp (Mulvaney et al., 1997). Greater pH increases the potential for NH_3 volatilization and increases the likelihood of nitrite accumulation and NO production (Venterea and Rolston, 2000; Venterea et al., 2015). Greater gaseous NH_3 and NO losses in the single application treatment could have decreased the availability of soil N substrates to participate in N_2O-producing processes compared with Sp. This hypothesis is supported by the decreased NRE and increased NS in the single application treatment, which may reflect greater NH_3 and/or NO losses. Few studies have simultaneously measured the dynamics of N_2O, NH_3, NO, soil N, and pH, which could help elucidate these processes. For example, it is not known how N rate and/or pH affect NH_3/N_2O and NO/N_2O ratios after U application.

Urea amended with microbial inhibitors applied at 100% RN did not decrease N_2O, as found in other studies using the same UI product used here (e.g., Parkin and Hatfield, 2014; Sistani et al., 2011; Venterea et al., 2011a). As discussed by Parkin and Hatfield (2014), even though UI may be effective in delaying U hydrolysis and nitrification, the resulting timing of soil N availability may coincide with precipitation events and/or with increased root-derived soil C, both of which tend to promote N_2O production.

Soil N intensities were greater in 2014 than in 2015, which again may have resulted from reduced crop N uptake in 2014. Soil NH_4 intensity was significantly greater with UI than with U. This is consistent with (i) inhibition of U hydrolysis by the urease inhibitor, which also would slow the rate of pH elevation and NH_3 volatilization, and (ii) inhibition of nitrification, which would slow the conversion of NH_4 to NO_3. However, NO_3 intensity was not reduced with UI and was actually 25% greater in UI-Sp100 compared with U-Sp100. This could have resulted from reduced NH_3 losses with UI, which would allow for greater availability of NH_4 that could eventually be nitrified to NO_3. Both of the treatments with reduced N rate (UI-Sp85 and U-Sp85) decreased soil NO_3 intensity by 21% compared with treatments receiving the full N rate. However, only the UI-Sp85 treatment decreased N_2O. Thus, a decrease in cumulative NO_3 availability by itself was not sufficient for reducing N_2O. This may have resulted from denitrification not being limited by NO_3 even at soil concentrations as low as 5 μg N g^{-1} (Parkin and Hatfield, 2014). Also, the correlation between N_2O and NO_3 ($r^2 = 0.44$) does not necessarily indicate that denitrification was the most important source of N_2O. Because NO_3 is the end product of nitrification, this correlation may also reflect nitrification-derived N_2O (Wrage et al., 2001).

The lack of a decrease in N_2O in the U-Sp85 treatment compared with either U-S100 or U-Sp100 is not consistent with the

Table 3. Means of soil N response variables and significance of *F* values for fixed sources of variation.

	Soil N intensity (0–0.3 m)		Residual soil N (0–0.6 m)	
	NH_4	NO_3	NH_4	NO_3
	mg N kg^{-1} d^{-1}		kg N ha^{-1}	
		By year†		
2014	0.541	2.13	3.58	31.2
2015	0.339	1.60	8.25	19.4
P > *F*	**0.050‡**	**0.020**	**0.015**	**0.024**
		By N management system§		
Nonfertilized	0.157c¶	0.829d	5.58	13.9d
U-S100	0.603a	2.33ab	5.76	20.6cd
U-Sp100	0.453ab	1.95bc	5.83	23.1bcd
U-Sp85	0.316bc	1.83c	5.91	26.8abc
UI-Sp100	0.524ab	2.43a	5.93	36.2a
UI-Sp85	0.586a	1.83c	6.49	31.2ab
P > *F*	**0.002**	**<0.001**	0.633	**0.001**
		By N source#		
U	0.384	1.89	5.87	24.9
UI	0.555	2.13	6.21	33.7
P > *F*	**0.036**	0.105	0.368	**0.015**
		By N rate		
85	0.451	1.83	6.20	29.0
100	0.488	2.19	5.88	29.6
P > *F*	0.632	**0.018**	0.391	0.853

† The year-by-N management system interaction was not significant for any variable ($P \geq 0.275$ except for residual NH_4 where $P = 0.063$).

‡ Significant differences ($P \leq 0.05$) are shown in bold type.

§ S, single application; Sp, split application; U, urea; UI, urea with microbial inhibitors; 85 and 100 refer to percentages of recommended rate.

¶ Within a column, N management system means followed by the same lowercase letter are not significantly different at $P \leq 0.05$.

Linear contrasts were used to determine N source and rate effects using data from the treatments with Sp (U-Sp100, U-Sp85, UI-Sp100, and UI-Sp85).

general principle that decreasing N rate reduces N_2O. Most, if not all, N rate versus N_2O studies have compared treatments with greater differences in N rate than the 15% difference compared here. In this study, the relatively small difference in N rate by itself was likely not sufficient to decrease N_2O emissions to an extent that could be resolved from the inherent variability resulting from spatial variation in soil properties that affect N_2O production (e.g., moisture content, C availability, and bulk density). However, the moderate N rate reduction examined here is likely to be more realistic in terms of farmer adoption.

Some treatments that improved NRE compared with the standard practice did not reduce N_2O, as found previously in rainfed (Gagnon et al., 2011; Gagnon and Ziadi, 2010) and irrigated (Fujinuma et al., 2011) corn. Halvorson et al. (2010) found that irrigated corn fertilized with U had greater grain N uptake, but also greater aN_2O and yN_2O, over 2 yr than corn fertilized with the same UI product used in this study. These results may not be surprising given the relatively low contribution of N_2O to the N budget (EF <0.4% in the current study) and suggest that increased NRE resulted from decreased losses of reactive N species other than N_2O. This also implies that so-called "indirect" N_2O emissions that result from the transformation of NH_3, NO, and/or NO_3 to N_2O in downwind or downstream ecosystems would be reduced in these management systems. Additionally, residual postharvest soil NO_3 was greater with UI. An unintended consequence of controlled release fertilizer products is the potential to increase postseason N losses (Venterea et al., 2011b; Zvomuya et al., 2003), which also could contribute to indirect N_2O emissions. Turner et al. (2015) estimated that indirect N_2O emissions in streams and rivers for a region encompassing the current study were nine times greater than IPCC EF-based estimates. More research is needed to assess the full impact of N management systems on total direct + indirect N_2O emissions.

The "management systems" approach used here allowed us to examine practical combinations of N rate, timing, and source more efficiently than a full factorial experimental design. We did not evaluate reduced N rate combined with UI using a single application, although our previous studies in the same soil and cropping system have shown that single broadcast applications of UI without N rate reductions have not been effective for reducing N_2O (Maharjan and Venterea, 2013; Venterea et al., 2011a). The limited duration of microbial inhibitors in the soil could limit their effectiveness with single application (Engel et al., 2015; Weiske et al., 2001). If effective, single application practices would have obvious practical advantages to Sp and need to be evaluated in future studies. More adaptive management approaches (e.g., variation of N rate and/or timing based on real-time evaluation of crop status and/or extended weather forecasts) are also worthy of future study. Another consideration is that the energy consumption associated with multiple split applications could offset greenhouse gas benefits of Sp management if conventional fossil fuels are used to power farm equipment. For example, based on fertilizer spreading data from Lal (2004), each urea application requires fuel equivalent to 0.04 to 0.08 kg N_2O–N ha^{-1}, amounts that could be substantial relative to the differences in N_2O emissions by treatment observed here (Table 2). It should also be noted that we did not measure N_2O fluxes during the spring thaw period, which can be substantial in some cases (e.g., Johnson et al., 2010); thus, these results represent growing-season (not annual) N_2O emissions that could be affected by differences in residual soil N from the previous growing season.

The exponential model used here to describe the relationships between grain-based NS and N_2O is the same model used by Van Groenigen et al. (2010) in a meta-analysis and by Venterea et al. (2011a) in a site-specific study, although the regression parameters obtained here differ from previous results. Previous relationships used NS calculated from whole-plant N uptake. The stronger relationship found here with grain-based compared with whole-plant NS may be related to the timing of N accumulation in grain versus whole plant and the timing of N losses. Nitrogen accumulation in nongrain (stover and cob) portions of the plant occurs earlier in the growing season (Abendroth et al., 2011), whereas grain N uptake in this climate generally occurs during late July and all of August. In this study, elevated N_2O fluxes occurred before the expected grain-filling period. Although other losses such as NH_3 volatilization and NO emissions were not measured here, these losses tend to occur within a similar time frame after N fertilizer application (Martins et al., 2015; Venterea and Rolston, 2000). Treatments having greater N losses before the grain-filling period would have less N available for grain uptake, and this limitation on grain N uptake would likely affect grain-based NS to a greater extent than whole-plant–based NS. The stronger relationship obtained using grain-based NS may have a practical advantage for modeling because it can be obtained without the need for measurement or estimation of whole-plant N uptake. Grassini and Cassman (2012) used the Van Groenigen et al. (2010) relationship to model N_2O emissions based on estimation of whole-plant N uptake. Grain-based NS could be estimated more directly from grain yield, if data for grain N content were not available, using literature values (e.g., Zhang et al., 2015).

Conclusions

Intensive strategies that modify more than one 4R component may be needed to reduce direct N_2O in rainfed systems. Optimizing both application timing and N source can allow for a moderate reduction in N rate that does not affect yield but decreases N_2O emissions and NS. This is the first study to report a stronger relationship of N_2O emissions with grain-based NS compared with whole-plant–based NS. Collection of further NS data across sites and years is needed to evaluate the usefulness of NS versus N_2O relationships for purposes of modeling at the site or larger scales. The finding that increasing NRE did not necessarily reduce direct N_2O emissions highlights the need for improved quantification of total N losses (i.e., NH_3, NO, NO_3, and N_2O) and indirect N_2O emissions to improve assessments of the full greenhouse-gas impact of management practices.

Acknowledgments

The authors thank Ms. Libby Mills and Mr. Paxer Vang for assistance with field and lab work and Dr. Greg Schwab and Koch Agronomic Services for providing the SuperU product. This work was supported in part by a grant from the Minnesota Corn Research and Promotion Council. Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the USDA or the University of Minnesota.

References

Abendroth, L.J., R.W. Elmore, M.J. Boyer, and S.K. Marlay. 2011. Corn growth and development. PMR 1009. Iowa State Univ. Extension, Ames.

Bierman, P., C.J. Rosen, R.T. Venterea, and J. Lamb. 2012. Survey of nitrogen fertilizer use on corn in Minnesota. Agric. Syst. 109:43–52. doi:10.1016/j.agsy.2012.02.004

Burton, D.L., B.J. Zebarth, K.M. Gillam, and J.A. MacLeod. 2008. Effect of split application of fertilizer nitrogen on N_2O emissions from potatoes. Can. J. Soil Sci. 88:229–239. doi:10.4141/CJSS06007

Burzaco, J., I.A. Ciampitti, and T.J. Vyn. 2014. Nitrapyrin impacts on maize yield and nitrogen use efficiency with spring-applied nitrogen: Field studies vs. meta-analysis comparison. Agron. J. 106:753–760. doi:10.2134/agronj2013.0043

Burzaco, J., D.R. Smith, and T.J. Vyn. 2013. Nitrous oxide emissions in Midwest U.S. maize production vary widely with band-injected N fertilizer rates, timing and nitrapyrin presence. Environ. Res. Lett. 8:035031. doi:10.1088/1748-9326/8/3/035031

Ciampitti, I.A., and T.J. Vyn. 2014. Understanding global and historical nutrient use efficiencies for closing maize yield gaps. Agron. J. 106:2107–2117. doi:10.2134/agronj14.0025

Decock, C. 2014. Mitigating nitrous oxide emissions from corn cropping systems in the midwestern U.S.: Potential and data gaps. Environ. Sci. Technol. 48:4247–4256. doi:10.1021/es4055324

Engel, R.E., B.D. Towey, and E. Gravens. 2015. Degradation of the urease inhibitor NBPT as affected by soil pH. Soil Sci. Soc. Am. J. 79:1674–1683. doi:10.2136/sssaj2015.05.0169

Fujinuma, R., R.T. Venterea, and C. Rosen. 2011. Broadcast urea reduces N_2O emissions but increases NO emissions compared with conventional and shallow-applied anhydrous ammonia in a coarse-textured soil. J. Environ. Qual. 40:1806–1815. doi:10.2134/jeq2011.0240

Gagnon, B., and N. Ziadi. 2010. Grain corn and soil nitrogen responses to sidedress nitrogen sources and applications. Agron. J. 102:1014–1022. doi:10.2134/agronj2010.0011

Gagnon, B., N. Ziadi, P. Rochette, M.H. Chantigny, and D.A. Angers. 2011. Fertilizer source influenced nitrous oxide emissions from a clay soil under corn. Soil Sci. Soc. Am. J. 75:595–604. doi:10.2136/sssaj2010.0212

Grassini, P., and K.G. Cassman. 2012. High-yield maize with large net energy yield and small global warming intensity. Proc. Natl. Acad. Sci. USA 109:1074–1079. doi:10.1073/pnas.1116364109

Halvorson, A.D., S.J. Del Grosso, and F. Alluvione. 2010. Nitrogen source effects on nitrous oxide emissions from irrigated no-till corn. J. Environ. Qual. 39:1554–1562. doi:10.2134/jeq2010.0041

Jaynes, D.B., and T.S. Colvin. 2006. Corn yield and nitrate loss in subsurface drainage from midseason nitrogen fertilizer application. Agron. J. 98:1479–1487. doi:10.2134/agronj2006.0046

Johnson, J.M., D. Archer, and N. Barbour. 2010. Greenhouse gas emission from contrasting management scenarios in the northern Corn Belt. Soil Sci. Soc. Am. J. 74:396–406. doi:10.2136/sssaj2009.0008

Kaiser, D.E., J.A. Lamb, and R. Eliason. 2012. Fertilizer guidelines for agronomic crops in Minnesota. BU-06240-S. Univ. of Minnesota Ext., St. Paul. www.extension.umn.edu/agriculture/nutrient-management/nutrient-lime-guidelines/fertilizer-recommendations-for-agronomic-crops-in-minnesota/docs/BU-6240S-PUB.pdf (accessed 19 Jan. 2016).

Kutner, M.H., C.J. Nachtsheim, and J. Neter. 2004. Applied linear regression models. 4th ed. McGraw-Hill, New York.

Lal, R. 2004. Carbon emission from farm operations. Environ. Int. 30:981–990. doi:10.1016/j.envint.2004.03.005

Maharjan, B., and R.T. Venterea. 2013. Nitrite intensity explains N management effects on N_2O emissions in maize. Soil Biol. Biochem. 66:229–238. doi:10.1016/j.soilbio.2013.07.015

Martins, M.R., C.P. Jantalia, J.C. Polidoro, J.N. Batista, B.J.R. Alves, R.M. Boddey, and S. Urquiaga. 2015. Nitrous oxide and ammonia emissions from N fertilization of maize crop under no-till in a Cerrado soil. Soil Tillage Res. 151:75–81. doi:10.1016/j.still.2015.03.004

Minnesota Department of Natural Resources. 2016. Past climate data for Minnesota. Minnesota Dep. of Nat. Resources, St. Paul. www.dnr.state.mn.us/climate/historical/index.html (accessed 19 Jan. 2016).

Mulvaney, R.L. 1996. Nitrogen-inorganic forms. In: D.L. Sparks, editor, Methods of soil analysis. Part 3. ASA, Madison, WI. p. 1123–1184.

Mulvaney, R.L., S.A. Khan, and C.S. Mulvaney. 1997. Nitrogen fertilizers promote denitrification. Biol. Fertil. Soils 24:211–220. doi:10.1007/s003740050233

Parkin, T.B., and J.L. Hatfield. 2014. Enhanced efficiency fertilizers: Effect on nitrous oxide emissions in Iowa. Agron. J. 106:694–702. doi:10.2134/agronj2013.0219

Parkin, T.B., and R.T. Venterea. 2010. Chamber-based trace gas flux measurements. In: R.F. Follett, editor, USDA–ARS GRACEnet Project protocols/sampling protocols. USDA–ARS, Beltsville, MD. www.ars.usda.gov/SP2UserFiles/Program/212/Chapter%203.%20GRACEnet%20Trace%20Gas%20Sampling%20Protocols.pdf (accessed 19 Jan. 2016).

Phillips, R.L., D.L. Tanaka, D.W. Archer, and J.D. Hanson. 2009. Fertilizer application timing influences greenhouse gas fluxes over a growing season. J. Environ. Qual. 38:1569–1579. doi:10.2134/jeq2008.0483

Randall, G.W., T.K. Irgavarapu, and B.R. Bock. 1997. Nitrogen application methods and timing for corn after soybean in a ridge-tillage system. J. Prod. Agric. 10:300–307. doi:10.2134/jpa1997.0300

Rochette, P., and N. Bertrand. 2008. Soil-surface gas emissions. In: M.R. Carter and E.G. Gregorich, editors, Soil sampling and methods of analysis. CRC Press, Boca Raton, FL. p. 851–861.

SAS Institute. 2011. The SAS system for Windows. Version 9.3. SAS Inst., Cary, NC.

Sistani, K.R., M. Jn-Baptiste, N. Lovanh, and K.L. Cook. 2011. Atmospheric emissions of nitrous oxide, methane, and carbon dioxide from different nitrogen fertilizers. J. Environ. Qual. 40:1797–1805. doi:10.2134/jeq2011.0197

Sistani, K.R., M. Jn-Baptiste, and J.R. Simmons. 2014. Corn response to enhanced-efficiency nitrogen fertilizers and poultry litter. Agron. J. 106:761–770 \. doi:10.2134/agronj2013.0087

Snyder, C.S., T.W. Bruulsema, T.L. Jensen, and P.E. Fixen. 2009. Review of greenhouse gas emissions from crop production systems and fertilizer management effects. Agric. Ecosyst. Environ. 133:247–266. doi:10.1016/j.agee.2009.04.021

Turner, P.A., T.J. Griffis, X. Lee, J.M. Baker, R.T. Venterea, and J.D. Wood. 2015. Indirect nitrous oxide emissions from streams within the US Corn Belt scale with stream order. Proc. Natl. Acad. Sci. USA 112:9839–9843. doi:10.1073/pnas.1503598112

van Beek, C.L., L. Brouwer, and O. Oenema. 2003. The use of farmgate balances and soil surface balances as estimator for nitrogen leaching to surface water. Nutr. Cycling Agroecosyst. 67:233–244. doi:10.1023/B:FRES.0000003619.50198.55

Van Groenigen, J.W., G.L. Velthof, O. Oenema, K.J. Van Groenigen, and C. Van Kessel. 2010. Towards an agronomic assessment of N_2O emissions: A case study of arable crops. Eur. J. Soil Sci. 61:903–913. doi:10.1111/j.1365-2389.2009.01217.x

Venterea, R.T. 2010. Simplified method for quantifying theoretical underestimation of chamber-based trace gas fluxes. J. Environ. Qual. 39:126–135. doi:10.2134/jeq2009.0231

Venterea, R.T., T.J. Clough, J.A. Coulter, F. Breuillin-Sessoms, P. Wang, and M.J. Sadowsky. 2015. Ammonium sorption and ammonia inhibition of nitrite-oxidizing bacteria explain contrasting soil N_2O production. Sci. Rep. 5:12153. doi:10.1038/srep12153

Venterea, R.T., and J.A. Coulter. 2015. Split application of urea does not decrease and may increase nitrous oxide emissions in rainfed corn. Agron. J. 107:337–348. doi:10.2134/agronj14.0411

Venterea, R.T., M.S. Dolan, and T.E. Ochsner. 2010. Urea decreases N_2O emissions compared with anhydrous ammonia in a Minnesota corn cropping system. Soil Sci. Soc. Am. J. 74:407–418. doi:10.2136/sssaj2009.0078

Venterea, R.T., A.D. Halvorson, N.R. Kitchen, M.A. Liebig, M.A. Cavigelli, S.J. Del Grosso, et al. 2012. Challenges and opportunities for mitigating nitrous oxide emissions from fertilized cropping systems. Front. Ecol. Environ 10:562–570. doi:10.1890/120062

Venterea, R.T., C.R. Hyatt, and C.J. Rosen. 2011b. Fertilizer management effects on nitrate leaching and indirect nitrous oxide emissions in irrigated potato production. J. Environ. Qual. 40:1103–1112 \. doi:10.2134/jeq2010.0540

Venterea, R.T., B. Maharjan, and M.S. Dolan. 2011a. Fertilizer source and tillage effects on yield-scaled nitrous oxide emissions in a corn cropping system. J. Environ. Qual. 40:1521–1531. doi:10.2134/jeq2011.0039

Venterea, R.T., and D.E. Rolston. 2000. Nitric and nitrous oxide emissions following fertilizer application to agricultural soil: Biotic and abiotic mechanisms and kinetics. J. Geophys. Res. Atmos. 105:15117–15129. doi:10.1029/2000JD900025

Wrage, N., G.L. Velthof, M.L. van Beusichem, and O. Oenema. 2001. Role of nitrifier denitrification in the production of nitrous oxide. Soil Biol. Biochem. 33:1723–1732. doi:10.1016/S0038-0717(01)00096-7

Weiske, A., G. Benckiser, T. Herbert, and J.C.G. Ottow. 2001. Influence of the nitrification inhibitor 3,4-dimethylpyrazole phosphate (DMPP) in comparison to dicyandiamide (DCD) on nitrous oxide emissions, carbon dioxide fluxes and methane oxidation during 3 years of repeated application in field experiments. Biol. Fertil. Soils 34:109–117. doi:10.1007/s003740100386

Zebarth, B.J., P. Rochette, D.L. Burton, and M. Price. 2008. Effect of fertilizer nitrogen management on N_2O emissions in commercial corn fields. Can. J. Soil Sci. 88:189–195. doi:10.4141/CJSS06010

Zebarth, B.J., E. Snowdon, D.L. Burton, C. Goyer, and R. Dowbenko. 2012. Controlled release fertilizer product effects on potato crop response and nitrous oxide emissions under rain-fed production on a medium-textured soil. Can. J. Soil Sci. 92:759–769. doi:10.4141/cjss2012-008

Zhang, X., E.A. Davidson, D.L. Mauzerall, T.D. Searchinger, P. Dumas, and Y. Shen. 2015. Managing nitrogen for sustainable development. Nature 528:51–59. doi:10.1038/nature15743

Zvomuya, F., C.J. Rosen, M.P. Russelle, and S.C. Gupta. 2003. Nitrate leaching and nitrogen recovery following application of polyolefin-coated urea to potato. J. Environ. Qual. 32:480–489. doi:10.2134/jeq2003.4800