J. Environ. Qual. Accepted Paper, posted 04/06/2016. doi:10.2134/jeq2016.01.0024

# Evaluation of intensive '4R' strategies for decreasing $N_2O$ emissions and N surplus in rainfed corn

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**ACKNOWLEDGMENTS**

The authors thank Ms. Libby Mills and Mr. Paxer Vang for assistance with field and lab work. This work was supported in part by a grant from the Minnesota Corn Research and Promotion Council.

*Abbreviations*: EF, fertilizer-induced $N_2O$ emission factor; *a*$N_2O$, cumulative area-scaled $N_2O$ emissions; *y*$N_2O$, cumulative yield-scaled $N_2O$ emissions; *d*$N_2O$, 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.

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## Abstract

The '4R' approach of using the 'right' rate, source, timing and 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 to urea (U) 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 to whole-plant N uptake ($r^2$ = 0.39), possibly because most N losses occurred prior to grain filling. Optimizing both application timing and N source can allow for a moderate reduction in N rate that does not impact grain yield but decreases $N_2O$. Grain-based NS may be a more useful indicator of $N_2O$ emissions than whole-plant-based NS.

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## Introduction

Optimizing the four basic aspects of N fertilizer management, i.e., the ‘4R’ approach of using the ‘right’ rate, source, timing and placement, is often recommended for increasing crop N use efficiency and decreasing soil $N_2O$ emissions (Snyder et al., 2014). However, modifying one of the ‘4Rs’ by itself may not be reliable in reducing $N_2O$ emissions, particularly in rainfed cropping systems (Decock, 2014). For example, the use of delayed and/or Sp while maintaining N rate, source and placement (Zebarth et al. 2008; Phillips et al. 2009; Zebarth et al. 2012), or the use of specialized N fertilizer sources [e.g., U containing microbial inhibitors (UI)] while maintaining N rate, timing, and placement (Sistani et al., 2011; Parkin and Hatfield, 2014) 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 U showed no effectiveness of inhibitors alone over five site-years (Venterea et al., 2011a; Maharjan and Venterea, 2013) or timing alone over two site-years (Venterea and Coulter, 2015). There are few studies that attempt 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 following 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 U.S. 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 to the common practice of a single, early-season U application over two site-years using a ‘management systems’ experimental approach for corn production.

A basic principle underlying any N conservation management strategy is that practices which enhance crop N uptake will reduce reactive N losses, including leaching or runoff of nitrate ($NO_3$) and atmospheric emissions of ammonia ($NH_3$), nitric oxide (NO) and $N_2O$. However, improvements in 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 to less efficient treatments (Fujinuma et al., 2011). Such counter-intuitive 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 to $N_2O$ 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 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 Dep. of Nat. Resources, 2016). A 2-yr experiment (2014 and 2015) was conducted using a randomized

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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 non-fertilized 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, Wichita, KS) was used, which contains the urease inhibitor *N*-(n-Butyl)-thiophosphoric triamide (NBPT) and the nitrification inhibitor dicyandiamide (DCD). 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 prior to 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 hr of the V14 applications either year.

*Nitrous Oxide Emissions*

Soil-to-atmosphere $N_2O$ fluxes were measured using non-steady-state chambers (Parkin and Venterea, 2010) constructed of acrylic (Rochette and Betrand, 2007). 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, Deerfield, IL) and analyzed within 1 wk using a headspace autosampler (Teledyne Tekmar, Mason, OH) connected to a gas chromatograph (model 5890 Agilent/Hewlett-Packard, Santa Clara, CA) 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 non-fertilized control from $aN_2O$ in each N-amended treatment. The fertilizer-induced $N_2O$ emission factor (EF) was calculated by dividing

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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, Hampton, NH) 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-long cores collected within 1 h of each flux measurement and drying overnight at 105ºC. 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- 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 M 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 for analysis of ammonium ($NH_4$) using the sodium salicylate-nitroprusside method (Mulvaney, 1996), both using a flow-through injection analyzer (Lachat, Loveland, CO). 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 $kg^{-1}$) vs. time (day), resulting in units of mg N $kg^{-1}$ day. Other studies (e.g., Burton et al., 2008; Maharjan et al., 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 then summed to represent the 0- to 0.30-m depth interval for each of the $NO_3$ and $NH_4$ species.

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

*Grain Yield and Above-ground Nitrogen 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 mid-section 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$^{o}$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, Hanau, Germany). Total N uptake in above-ground biomass was calculated from the sum of N masses harvested in grain, stover and cob. Crop NRE was calculated from the difference in above-ground N uptake between the non-fertilized 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 above-ground plant material, or in grain alone, respectively.

*Data Analysis*

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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 vs. 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 vs. U, across N rates and years and (ii) 100% vs. 85% of the RN, across N sources and years. Linear and non-linear regression analyses were conducted using Statistix 9 (Analytical Software, Tallahassee, FL) and SigmaPlot 12.5 (Systat, San Jose, CA), respectively.

## Results

### *Weather*

Total precipitation during April through September was greater in 2014 (711 mm) than 2015 (602 mm) and compared to the 30-yr mean of 599 mm (Fig. 1a). In 2014, 70% of growing season precipitation occurred in April, May and June (combined) compared to 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 19.7ºC in 2014 and 2015, respectively) at the time of gas-flux sampling were similar both years.

*Crop Response*

Corn grain yield, whole-plant yield and above-ground N uptake were greater in 2015 than 2014 by 9 to 16%, respectively (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 to 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 to U-S100, and decreased in U-Sp85 compared to U-Sp100. On a grain basis, NS was reduced in U-Sp85 and UI-Sp85 compared to the other fertilized treatments. Nitrogen recovery efficiency did not vary by year, but was greater in U-Sp85 and UI-Sp100 compared to U-S100, and greater in U-Sp85 than in U-Sp100.

*Nitrous Oxide Response*

Daily mean $N_2O$ fluxes ranged from <1 to >140 μg N $m^{-2}$ $h^{-1}$ with episodic increases observed following 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 both affected $aN_2O$ and $yN_2O$, which were more than twice as great in 2014 than 2015 (Table 2). All treatments receiving N fertilizer had greater $aN_2O$ than the non-fertilized 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 to all other fertilized treatments. The EF for the UI-Sp100 treatment also was decreased compared to U-Sp85. Across the four treatments with Sp, all measures of $N_2O$ emissions were greater with U compared to UI ($P \leq 0.002$). Both $aN_2O$ and $yN_2O$ were positively correlated 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-

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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 Nitrogen 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 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 0.2 to 18 µg N $g^{-1}$ at 0.15 to 0.30 m. Soil N intensity was greater in 2014 than 2015 for both $NH_4$ and $NO_3$ (Table 3). Soil N intensity was decreased in the non-fertilized control compared to 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 to 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 treatments except U-Sp100 and UI-Sp85. The UI-Sp85 treatment had greater residual $NO_3$ than the non-fertilized control and U-S100. Across the four treatments with Sp, residual $NO_3$ was greater with UI than U ($P = 0.015$).

## 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 U.S. during 2006 to 2012 (Ciampitti et al., 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 to 2015, thereby limiting crop N uptake, particularly during the longer mid-season 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 non-fertilized control, which was 14% greater than that of the non-fertilized 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 to single application timing, or UI by itself compared to U, did not improve any measure of crop performance corroborate previous results in rainfed corn systems (Randall et al., 1997; Jaynes and Colvin, 2006; 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.

*Nitrous Oxide and Soil Nitrogen 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

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(Venterea et al., 2010, 2011a). Greater $N_2O$ emissions in 2014 compared to 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; Zebarth et al., 2012; Venterea and Coulter, 2015). If crop N demand were the only factor affecting $N_2O$ flux, a larger pulse of $N_2O$ would be expected following the single application compared to following 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 following 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 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-surfaces 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 to 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 et al., 2000, 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 to 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 the ratios of $NH_3$:$N_2O$ and NO:$N_2O$ following 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., Sistani et al., 2011; Venterea et al., 2011a; Parkin and Hatfield, 2014). 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 2015 which again may have resulted from reduced crop N uptake in 2014. Soil $NH_4$ intensity was significantly greater with UI than 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 to 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 to 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 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).

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The lack of a decrease in $N_2O$ in the U-Sp85 treatment compared to either U-S100 or U-Sp100 is not consistent with the general principle that decreasing N rate reduces $N_2O$. Most if not all N rate vs. $N_2O$ 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 which improved NRE compared to the standard practice did not reduce $N_2O$, as found previously in rainfed (Gagnon and Ziadi, 2010; Gagnon et al., 2011) 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 two years 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 suggests 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 post-harvest soil $NO_3$ was greater with UI. An unintended consequence of controlled release fertilizer products is the potential to increase post-season N losses (Zvomuya et al., 2003; Venterea et al., 2011b), 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 $N_2O$ (Venterea et al., 2011a; Maharjan and Venterea, 2013). The limited duration of microbial inhibitors in the soil could limit their effectiveness with single application (Weiske et al., 2001; Engel et al., 2015). 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 and not annual $N_2O$ emissions which could be affected by differences in residual soil N from the previous growing season.

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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 to whole-plant NS may be related to the timing of N accumulation in grain vs. whole-plant and the timing of N losses. Nitrogen accumulation in non-grain (stover and cob) portions of the plant occurs earlier in the growing season (Abendroth et al., 2011) while grain N uptake in this climate generally occurs during late July and all of August. In this study, elevated $N_2O$ fluxes occurred prior to the expected grain-filling period. While other losses such as $NH_3$ volatilization and NO emissions were not measured here, these losses tend to occur within a similar time-frame following N fertilizer application (Venterea and Rolston, 2005; Martins et al., 2015). Treatments having greater N losses prior to 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 which 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 impact 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 to whole-plant-based NS. Collection of further NS data across sites and years is needed to evaluate the usefulness of NS vs. $N_2O$ 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 in order to improve assessments of the full greenhouse-gas impact of management practices.

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

| | Grain yield | Whole-plant yield | Above-ground 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 | | | | | | |
| Non-fertilized | 7.12 b‡ | 14.1 b | 122 c | -122.1 d | -81.1 c | - |
| U-S100§ | 9.79 a | 18.5 a | 205 b | -59.8 a | 4.59 a | 57.2 c |
| U-Sp100 | 10.36 a | 19.8 a | 210 ab | -64.7 ab | -0.84 a | 60.6 bc |
| U-Sp85 | 9.94 a | 19.5 a | 215 ab | -92.2 c | -15.8 b | 75.7 a |
| UI-Sp100 | 9.95 a | 19.5 a | 229 a | -83.1 bc | -1.06 a | 73.2 ab |
| UI-Sp85 | 9.97 a | 18.8 a | 207 b | -84.1 bc | -17.0 b | 69.2 abc |
| *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 |

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

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

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

¶ 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).

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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 DM$^{-1}$ | % |
| 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 | | | | |
| Non-fertilized | 0.436 c‡ | - | 66.5 b | - |
| U-S100 § | 0.867 a | 0.432 a | 92.6 a | 0.300 ab |
| U-Sp100 | 0.876 a | 0.441 a | 87.1 a | 0.303 ab |
| U-Sp85 | 0.911 a | 0.476 a | 94.6 a | 0.386 a |
| UI-Sp100 | 0.823 a | 0.387 a | 83.3 a | 0.266 b |
| UI-Sp85 | 0.659 b | 0.223 b | 66.4 b | 0.181 c |
| *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 |

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

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

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

¶ 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).

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

| | Soil N intensity (0 to 0.3 m) | | Residual soil N (0 to 0.6 m) | |
|---|---|---|---|---|
| | $NH_4$ | $NO_3$ | $NH_4$ | $NO_3$ |
| | mg N kg$^{-1}$ day | | 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 | | | | |
| Non-fertilized | 0.157 c | 0.829 d | 5.58 | 13.9 d |
| U-S100 § | 0.603 a | 2.33 ab | 5.76 | 20.6 cd |
| U-Sp100 | 0.453 ab | 1.95 bc | 5.83 | 23.1 bcd |
| U-Sp85 | 0.316 bc | 1.83 c | 5.91 | 26.8 abc |
| UI-Sp100 | 0.524 ab | 2.43 a | 5.93 | 36.2 a |
| UI-Sp85 | 0.586 a | 1.83 c | 6.49 | 31.2 ab |
| *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 $P = 0.063$).

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

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

¶ 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).

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## Figure Captions

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.

Fig. 2. Relationships between whole-plant and grain-based N surplus and (a) area-scaled ($aN_2O$) and (b) yield-scaled ($yN_2O$) $N_2O$ 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.

Fig. 3. Concentrations of soil ammonium ($NH_4$) (upper four plates) and nitrate ($NO_3$) (lower four plates) in the 0- to 0.15- and 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.

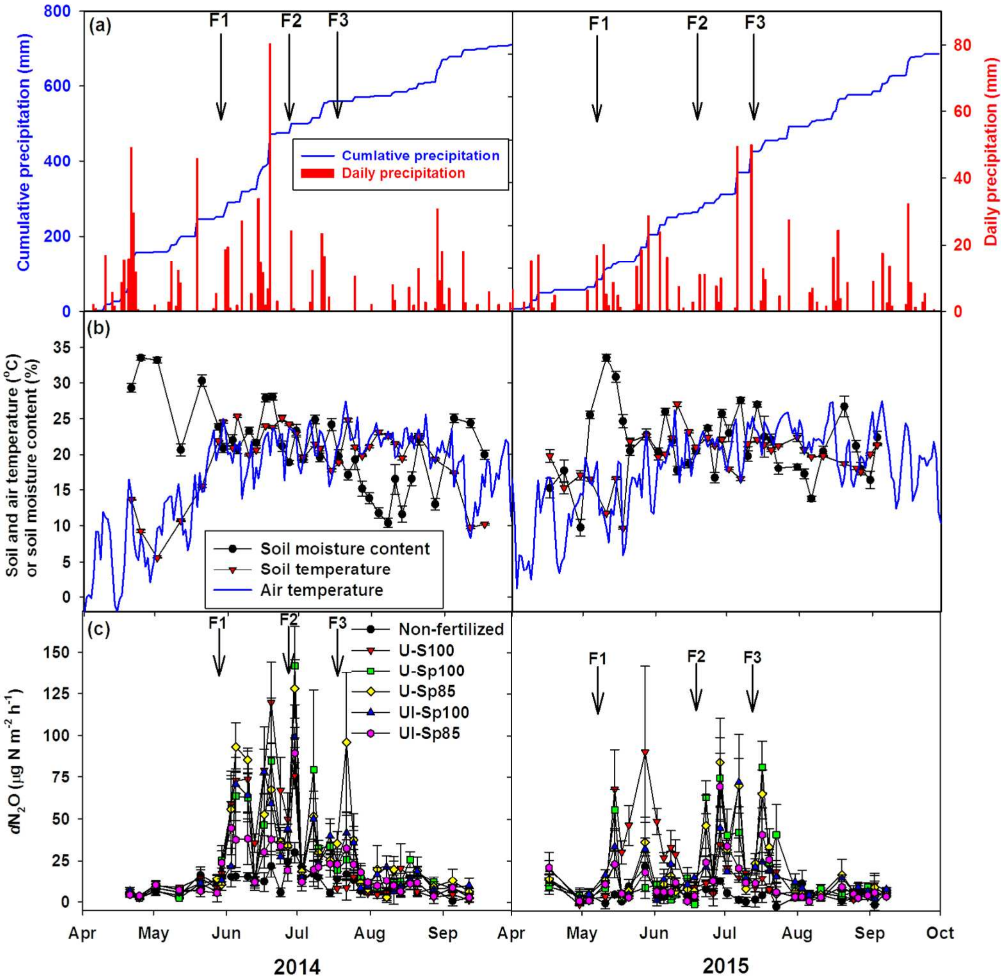


Fig. 1. (a) Precipitation, (b) air and soil temperature and soil moisture, and (c) daily N2O fluxes during 2014 and 2015. S, single application; Sp, split application; U, urea; UI, urea with microbial inhibitors; 85 and 100 refer to percentages of recommended rate. Arrows indicate dates of N fertilizer application. The S treatment received all fertilizer at F1 and the Sp treatments received three equal applications at F1, F2 and F3.

295x303mm (150 x 150 DPI)

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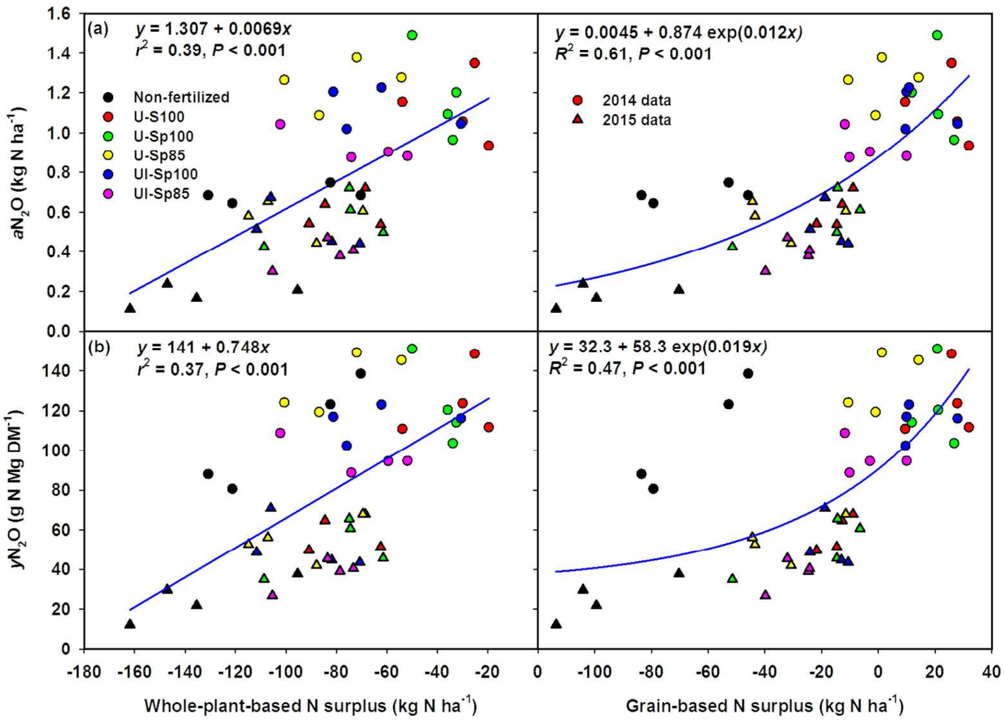


Fig. 2. Relationships between whole-plant and grain-based N surplus and (a) area-scaled (aN2O) and (b) yield-scaled (yN2O) N2O emissions. Symbol colors indicate N management system treatments; circles are 2014 data and triangles are 2015 data. S, single application; Sp, split application; U, urea; UI, urea with microbial inhibitors; 85 and 100 refer to percentages of recommended rate.
279x279mm (150 x 150 DPI)

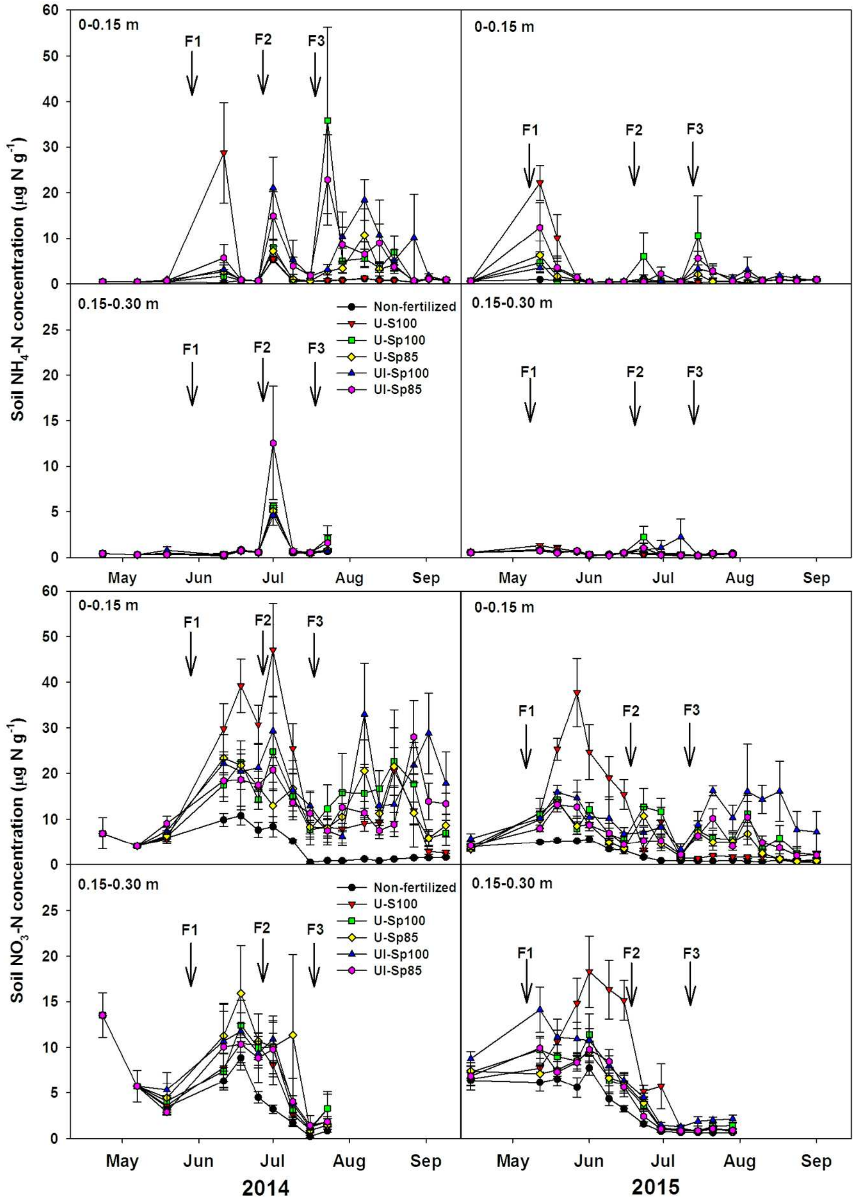


Fig. 3. Concentrations of soil ammonium (NH4)-N (upper four plates) and nitrate (NO3)-N (lower four plates) in the 0- to 0.15- and 0.15- to 0.30-m depth intervals under varying N management in 2014 and 2015. S, single application; Sp, split application; U, urea; UI, urea with microbial inhibitors; 85 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.
275x389mm (150 x 150 DPI)