# Broadcast Urea Reduces $N_2O$ but Increases NO Emissions Compared with Conventional and Shallow-Applied Anhydrous Ammonia in a Coarse-Textured Soil

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Despite the importance of anhydrous ammonia (AA) and urea as nitrogen (N) fertilizer sources in the United States, there have been few direct comparisons of their effects on soil nitrous oxide ($N_2O$) and nitric oxide (NO) emissions. We compared N oxide emissions, yields, and N fertilizer recovery efficiency (NFRE) in a corn (*Zea mays* L.) production system that used three different fertilizer practices: urea that was broadcast and incorporated (BU) and AA that was injected at a conventional depth (0.20 m) (AAc) and at a shallower depth (0.10 m) (AAs). Averaged over 2 yr in an irrigated loamy sand in Minnesota, growing season $N_2O$ emissions increased in the order BU < AAc < AAs. In contrast, NO emissions were greater with BU than with AAc or AAs. Emissions of $N_2O$ ranged from 0.5 to 1.4 kg N $ha^{-1}$ (50–140 g N $Mg^{-1}$ grain), while NO emissions ranged from 0.2 to 0.7 kg N $ha^{-1}$ (20–70 g N $Mg^{-1}$ grain). Emissions of total N oxides (NO + $N_2O$) increased in the order AAc < BU < AAs. Despite having the greatest emissions of $N_2O$ and total N oxides, the AAs treatment had greater NFRE compared with the AAc treatment. These results provide additional evidence that AA emits more $N_2O$, but less NO, than broadcast urea and show that practices to reduce $N_2O$ emissions do not always improve N use efficiency.

Nitrogen (N) oxide gases (i.e., nitric oxide [NO] and nitrous oxide [$N_2O$]) are important atmospheric trace gases produced in soil (Firestone and Davidson, 1989). Emissions of $N_2O$ directly from soil to the atmosphere contribute to radiative forcing, with ~300 times greater global warming potential than carbon dioxide ($CO_2$) (Forster et al., 2007). Emissions of NO can contribute to radiative forcing through indirect pathways and affect local and regional air quality (De Klein et al., 2006; Crutzen, 1979). In the United States, application of N fertilizer, together with legume cultivation, tillage, and other cropping practices, contributes approximately 70% of total national $N_2O$ emissions (USEPA, 2011). Annually, over one third of US agricultural land is used for corn production (NASS, 2011), and this portion receives more than 40% of the total N fertilizer consumed nationally (ERS, 2011). Thus, mitigation of N oxide emissions from corn production systems has the potential to significantly affect total national greenhouse gas (GHG) emissions and other measures of air quality.

Anhydrous ammonia (AA) accounted for 35% of all N fertilizer consumed in 2008 in the United States, whereas urea accounted for 24% (ERS, 2011). A recent survey of corn producers in Minnesota indicated that 46% of farmers used AA and another 45% used urea as their primary N fertilizer source in the 2009 growing season (unpublished data). Despite the importance of these two fertilizer chemical sources, there have been relatively few direct side-by-side comparisons of their relative effects on N oxide emissions. Four studies in the United States (Breitenbeck and Bremner, 1986a; Thornton et al., 1996; Venterea et al., 2005, 2010) and one in Canada (Burton et al., 2008) have compared $N_2O$ emissions from AA and urea, and two of these studies also examined NO emissions (Thornton et al., 1996; Venterea et al., 2005). Although there have been a few studies examining effects of fertilizer placement depth on $N_2O$ emissions (e.g., Hosen et al., 2002; Drury et al., 2006; Liu et al., 2006), only one study has examined depth effects with AA as the fertilizer source (Breitenbeck and Bremner, 1986b). None of these management

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**Abbreviations**: AA, anhydrous ammonia; AAc, conventional anhydrous ammonia; AAs, shallow-injected anhydrous ammonia; BU, broadcast urea; DOC, dissolved organic carbon; FIEF, fertilized-induced $N_2O$ emissions factor; GHG, greenhouse gas; NFRE, nitrogen fertilizer recovery efficiency; NUE, nitrogen use efficiency; SOM, soil organic matter; WFPS, water-filled pore space.

comparison studies has been conducted in coarse-textured or irrigated soils.

In recent analyses of fertilizer management impacts on soil N oxide emissions, there has been increased consideration of performance of the crop production system, including crop yield and N use efficiency (NUE). The general understanding of N cycling in agricultural systems suggests that management practices that improve NUE would tend to reduce soil N oxide emissions, and the results of a recent metaanalysis across cropping systems was consistent with this idea (Van Groenigen et al., 2010). However, the number of studies in corn (or other) cropping systems where yield, NUE, and N oxide emissions have been simultaneously quantified are limited (Halvorson et al., 2010; Gagnon et al., 2011; Venterea et al., 2011).

The objective of this study was to compare $N_2O$ and NO emissions, yields, and NUE in a corn production system in an irrigated loamy sand soil using three different N fertilizer management practices: (i) urea that was broadcast and then incorporated (BU), (ii) AA that was injected at conventional depth (AAc), and (iii) AA that was injected at shallower depth (AAs). The shallow-injection AA treatment used a recently developed applicator designed to decrease fuel consumption and time required for AA application.

## Materials and Methods

### Site Description and Experimental Design

The site was located at the University of Minnesota's Sand Plain Research Farm in Becker, Minnesota (45°23′ N, 93°53′ W). The site soil is an excessively well drained sandy, mixed, frigid Entic Hapludoll (Hubbard series) with loamy sand texture (82% sand and 8% clay) and pH of 4.7 to 5.0 in the upper 0.15 m. Soil organic matter (SOM) determined by loss on ignition was 2.5% (w/w) in samples from the 0- to 0.1-m depth and 1.7% (w/w) in samples from the 0.1- to 0.2 m-depth. Soil $NH_4^+$ and $NO_3^-$ concentrations averaged over the 0- to 0.6-m depth before planting were 1.2 and 0.94 μg N $g^{-1}$, respectively, in 2009 and 0.4 and 1.6 μg N $g^{-1}$, respectively, in 2010, equivalent to a total inorganic N content of 21 kg N $ha^{-1}$ in 2009 and 2010. Additional chemical properties of soil from the same site were reported by Hyatt et al. (2010). The site soil is representative of soil used for potato (*Solanum tuberosum* L.) and corn production in central Minnesota, where the typical growing season for corn is from approximately 1 May through 1 October with a 30-yr average growing season daily mean temperature of 16.0°C and precipitation of 531 mm (MCWG, 2010).

The experiment was conducted over the course of two consecutive growing seasons (2009 and 2010) using separate sections of field each year. Each section of field was planted with cereal rye (*Secale cereale* L.) for 3 yr before establishing the experiment. Rye grain was harvested in summer, followed by a rye winter cover crop. Rye residue was incorporated at the time of spring cultivation, which consisted of moldboard plowing followed by soil finishing. Experimental plots were established using a randomized complete block design with four blocks, each containing four plots, to which the following fertilizer treatments were randomly assigned: (i) BU, surface-broadcast urea that was incorporated to 0.10 m using a field cultivator on the day of application; (ii) AAc, knife-injected AA with a target depth of 0.20 m; (iii) AAs, knife-injected AA with a target depth of 0.10 m; and (iv) a control that received only starter fertilizer. Each fertilized treatment received 180 kg N $ha^{-1}$, consistent with recommended rates for this region (Rehm et al., 2008), which was added in two separate applications: 90 kg N $ha^{-1}$ applied 2 to 5 d before planting and 90 kg N $ha^{-1}$ applied 2 to 3 wk after planting. Preplant AA was applied 2 d before the preplant urea, which was followed by incorporation the same day and planting 1 to 3 d later. All treatments received starter N fertilizer at planting at the rate of 5.6 kg N $ha^{-1}$ (as 10–34–0) and additional N contained in irrigation water (described below).

Equipment used to apply AA was provided by John Deere and Company (Moline, IL). The applicator used for the AAs treatment was similar to a commercially available unit (Model 2510H) designed to allow for greater tractor speeds and more efficient fuel usage while providing sufficient soil closure after injection to minimize ammonia volatilization losses. Applicators used to apply the AA were calibrated to the desired N application rate using trial runs in nearby fields and verified by load-cell weight measurements. Tractors and applicators were operated by personnel familiar with the equipment. Urea was manually weighed with an analytical balance for each plot and applied by hand. Plots receiving AA were at least 30 m long, and BU plots were at least 7.5 m long. All plots were 6.1 m wide, which included eight rows of corn with 0.76-m row spacing. Corn was planted at a seeding rate of 79,000 seeds $ha^{-1}$ on 8 May 2009 and on 26 Apr. 2010.

Irrigation water was applied through an aluminum solid-set overhead sprinkler system. Irrigation was scheduled using the checkbook method (Wright, 2002), which estimates daily evapotranspiration and irrigation amounts to replace soil water deficit and minimize drainage. Irrigation amounts were estimated from duration of daily events and estimated irrigation water flow rates. Air temperature and daily precipitation were recorded using an on-site weather station. Irrigation water in this area generally contains nitrate concentrations in the range of 8 to 10 mg N $L^{-1}$ (Hyatt et al., 2010). Irrigation-water was sampled monthly, and total nitrite ($NO_2^-$) + $NO_3^-$ (hereafter referred to as $NO_3^-$) concentrations were measured using a flow-through colorimetric analyzer (QuickChem 8500; Lachat, Milwaukee, WI) (Wendt, 2003). These data were used together with total irrigation-water volume to estimate the amount of N applied in irrigation water, which amounted to 37 and 31 kg N $ha^{-1}$ in 2009 and 2010, respectively.

### Gas Fluxes

Soil surface fluxes of $N_2O$ were measured using static chamber methods (Venterea et al., 2005, 2010). Sampling occurred twice a week from April to August and then once a week from September to October in both growing seasons and was typically conducted between 1000 and 1300 h local time when soil temperatures were close to their daily mean values. The total number of sampling events per season was 38 in 2009 and 40 in 2010. Each year, two stainless-steel chamber bases (0.50 m long by 0.32 m wide by 0.09 m deep) were installed in each plot, adjacent to each other without overlapping. The two adjacent chambers together covered approximately 85% of the inter-row area while leaving a small distance (~0.05 m) on

either side to allow for unrestricted development of the nodal root system. Bases were inserted to be almost flush with the soil surface, and the height of each base in relation to the soil surface was measured approximately monthly at several grid positions within the base area to estimate the internal volume of each chamber. At each sampling time, insulated and vented stainless-steel chamber tops (0.5 m long by 0.3 m wide by 0.1 m high) were gently placed on the bases and secured with 60-mm binder clips. Gas samples (12 mL) were obtained initially (time 0) and then at 0.5-h intervals using a polypropylene syringe. Total measurement time was 1.0 h for the 2009 growing season (three points) and 1.5 h for the 2010 growing season (four points).

Gas samples were immediately injected into 9-mL unevacuated glass vials capped with butyl rubber septa (Alltech, Deerfield, IL), which were stored for <1 wk at room temperature before measurement of $N_2O$ using a gas chromatograph equipped with an electron capture detector (Agilent 5890; Agilent Technologies, Santa Clara, CA) (Venterea et al., 2005). After the release of positive pressure using syringe needles, vials were loaded onto a headspace auto-sampler (Teledyne Tekmar, Mason, OH) connected to the gas chromatograph/electron capture detector system, which was calibrated for each sampling date using known concentrations of standard gases that were treated identically to samples (Scott Specialty Gases, Plumsteadville, PA). Molar mixing ratios obtained from GC analyses were converted to mass per volume concentrations using air temperature at the field sampling time and the ideal gas law. Fluxes of $N_2O$ were determined from the time rate of change in concentration, chamber volume, and base area using the model of Wagner et al. (1997). In cases of chamber time series data displaying "positive curvature" (i.e., increasing concentration with second derivative >0), linear regression was used in place of the quadratic method.

Soil NO fluxes were measured weekly using a dynamic chamber method (Venterea et al., 2003, 2005) from the same chamber locations used for $N_2O$ sampling. The total number of NO flux samplings was 19 in each season, and measurements were conducted between 1000 h and 1300 h local time. Due to resource limitations, NO fluxes were not measured in the control treatment in 2010. The dynamic chamber top was identical to the static chambers but was equipped with inlet and outlet sampling ports located 0.45 m apart on the top of the chamber, with each port connected to 0.25-m sections of perforated stainless steel tubing inside the chamber that served as mixing manifolds. For each measurement, the chamber was attached to each base using binder clips, and the sampling ports were connected via flouropolymer tubing to a chemiluminescent $NO_x$ analyzer (Model LMA-3D; Unisearch Associates, Concord, Ontario, Canada). Air in the chamber was continuously recirculated through the analyzer at 0.06 $m^3$ $h^{-1}$ (1 L $min^{-1}$) for 2 min, and concentration data were manually recorded 0, 30, 60, 90, and 120 s after the chamber top was attached. Before entering the analyzer, chamber air was passed through $CrO_3$–coated porous media to convert NO to nitrogen dioxide ($NO_2$) before entering the analyzer, which detects $NO_2$. Periodic measurement without the $CrO_3$ catalyst indicated that $NO_2$ emissions from soil were negligible. After passing through the analyzer, chamber air was passed through $KMnO_4$–coated porous silica (Purafil, Doraville, GA) to remove $NO_x$. Because of the relatively short chamber deployment time (2 min), fluxes were calculated from the linear rate of change in concentration, also accounting for removal of NO in the recirculated chamber air (Venterea et al., 2003). Soil temperature at 0.05 m depth was measured during the time of gas flux measurement using manual temperature probes (Fisher Scientific, Pittsburg, PA). Soil cores (0.05 m diameter by 0.05 m deep) were collected at the same time as gas flux sampling for gravimetric determination of soil moisture content and bulk density, which were used to estimate water-filled pore space (WFPS).

## Plant and Soil Analysis

After physiological maturity, corn ears were hand harvested from a total distance of 6.1 m in the middle two rows of each plot. Grain was dried and shelled and further dried for 3 d at 65°C and weighed to obtain dry grain yields. Stover was obtained by cutting plants near the soil surface for all plants where ears were removed. Stover was weighed, and six plants were subsampled and ground, dried, and weighed to obtain dry stover yields. Grain and stover samples were further ground with a ball-mill (model 5300; Spex CertiPrep, Metuchen, NJ) and analyzed with an elemental N analyzer (VarioMax; Elementar, Germany) for total N. Yields of grain-N, stover-N, and total above-ground N (grain plus stover) were determined by multiplying grain and stover N concentrations by dry grain and dry stover yields, respectively.

After harvest, soils were sampled for determination of inorganic N content using an 18-mm-diameter soil core sampler to a depth of 0.6 m. Four cores were collected from each plot over a total depth of 0.6 m, and the entire contents of the cores from each of three depth intervals (0–0.15 m, 0.15–0.30 m, and 0.30–0.60 m) were combined within each plot to generate a single composite sample for each depth interval and plot. Subsamples (~10 g) of each composite sample were extracted with 2 mol $L^{-1}$ KCl. Extracts were stored at below −5°C until analysis for $NH_4^+$ and $NO_3^-$ concentrations using flow-through colorimetric analysis (QuickChem 8500/ASX 520; Lachat) using the methods of Hofer (2003) and Wendt (2003), respectively. Soil concentrations expressed as μg N $g^{-1}$ were converted to total kg N $ha^{-1}$ over the 0.6-m depth using bulk density values determined from total dry mass in the core samples.

## Data Analysis and Statistics

The $N_2O$ and NO fluxes for each plot and sampling date were determined as the mean of two fluxes from the two adjacent chambers, and total cumulative emissions for each growing season were calculated using trapezoidal integration. Fertilizer-induced emission factors (FIEFs) for direct $N_2O$ emissions were calculated by subtracting the cumulative $N_2O$ emissions in the control treatment from the cumulative $N_2O$ emissions in each fertilized treatment and then expressing the results as a percentage of the total amount of fertilizer N applied (180 kg N $ha^{-1}$). The FIEF for NO was not determined due to the lack of data from the control treatment in 2010. Emissions of NO were converted to indirect $N_2O$ emissions using the default emissions factor ($EF_4$) of 1% of the emitted NO for estimating the off-site (downwind) conversion of deposited NO to $N_2O$ (De Klein et al., 2006). Emissions of $N_2O$ were converted to $CO_2$

equivalents using a global warming potential of 298 (Forster et al., 2007). Nitrogen fertilizer recovery efficiency (NFRE) was calculated by subtracting aboveground N yield in the control treatment from aboveground N yield in each fertilizer treatment and dividing by the fertilizer application rate (180 kg N $ha^{-1}$). Treatment effects were analyzed using the mixed procedure (PROC MIX) in SAS version 9.1 (SAS Institute Inc., Cary, NC), with block and year as random effects and fertilizer treatment as a fixed effect. Unless otherwise indicated, means comparisons were conducted using least square means with significance criteria of $P < 0.05$. Because year was treated as a random effect, means comparisons were applied to 2-yr averages of each variable. Preliminary analysis using year as a fixed effect found no significant year-by-treatment interactions. Therefore, data for individual years are provided but were not subjected to means comparisons.

# Results

## Climate Conditions

Total growing season precipitation was 384 and 740 mm in 2009 and 2010, respectively, compared with the 30-yr average of 531 mm and range of 310 to 791 mm. Irrigation inputs in 2009 of 366 mm were 34% greater than in 2010 (274 mm) (Fig. 1a). The average daily mean air temperature was slightly lower in the 2009 growing season (16.0°C) than in 2010 (17.5°C), although air temperature rose earlier in the spring of 2009 than 2010 (Fig. 1b). Soil temperatures were similar in 2009 and 2010 and tended to be higher than air temperatures until late June, when the crop canopy covered the field (Fig. 1b). Soil WFPS was similar in 2009 and 2010 until the end of May; however, in 2010, WFPS tended to be greater than in 2009 from June to the end of the growing season (Fig. 1c). The mean soil WFPS was 25% in 2009 and 38% in 2010. Maximum WFPS values at the time of gas flux sampling each growing season were 51% (on 26 Aug. 2009) and 62% (on 20 Aug. 2010).

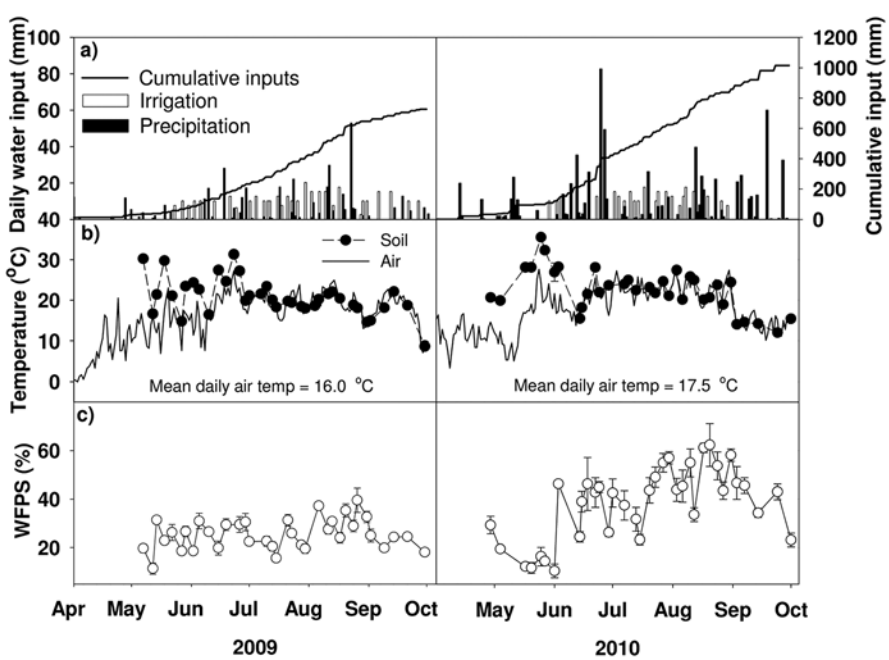


**Fig. 1. (a) Daily irrigation and precipitation and total cumulative water inputs, (b) air and soil temperature (0.05 m depth), and (c) soil water-filled pore space (WFPS) during 2009 and 2010. Values in (a) are total water inputs and in (b) are average air temperatures during 1 May through 1 Oct. Error bars indicate 1 SEM at each sampling date ($n$ = 4).**

## Agronomic Variables and Soil Inorganic Nitrogen

Grain yields, stover yields, and stover N concentrations did not differ among the three fertilizer treatments (Table 1). However, grain N concentrations, grain N yields, and total above-ground N yields were significantly greater in the AAs compared with the AAc treatment. For all agronomic variables, the broadcast urea (BU) treatment did not differ from AAs or AAc, and the control had lower values than the three fertilized treatments (Table 1). The higher grain N concentrations and N yields in the AAs treatment resulted in a NFRE of 76.5% averaged over 2 yr, which was significantly greater than the AAc treatment but not significantly different from the BU treatment (Table 2). After harvest, averaged over the two seasons, soils contained 15 to 18 kg $NH_4^+$–N $ha^{-1}$ and 13 to 15 kg $NO_3^-$–N $ha^{-1}$ over the 0- to 0.60-m depth (Table 3). Postharvest soil $NO_3^-$ content was greater in the AAc compared with the AAs treatment, and $NH_4^+$ plus $NO_3^-$ content was significantly greater in the AAc treatment than in all other treatments.

## Nitrogen Oxide Emissions

During each growing season, daily $N_2O$ fluxes increased after each of the two fertilizer applications and then gradually declined, with maximum daily $N_2O$ fluxes occurring within 10 to 40 d after each application (Fig. 2a). No fluxes greater than 21 μg N $m^{-2}$ $h^{-1}$ occurred after 1 August either year. Daily $N_2O$ fluxes were not significantly correlated with WFPS or temperature in 2009 or 2010. Trends in total cumulative growing season $N_2O$ emissions by treatment were consistent for both years, increasing in the order Control < BU < AAc < AAs (Fig. 3a). When expressed on an area basis (kg N $ha^{-1}$), growing season $N_2O$ emissions differed significantly among all four treatments. Cumulative emissions were 42% greater in the AAc treatment compared with BU and more than 100% greater in AAs compared with AAc (Fig. 3a, left). When expressed relative to corn grain yield (kg N $Mg^{-1}$ grain), growing season $N_2O$ emissions showed the same trend as the area-based emissions except that the BU treatment did not differ from the control (Fig. 3a, right). The FIEF was over two times greater with AAs (0.73%) compared with AAc (0.30%) or BU (0.10%) (Table 2). The difference in FIEF between the AAc and BU treatments was significant at $P = 0.057$.

The maximum daily NO flux occurred within 30 d after each fertilizer application, similar to the $N_2O$ daily fluxes, with the exception that no large increase occurred following the second application in 2010 (Fig. 2b). In both growing seasons, the maximum daily

**Table 1. Mean (and standard error, $n = 4$) of agronomic variables in controls plots and in plots fertilized using broadcast urea and anhydrous ammonia injected at 0.2 and 0.1 m.**

| Fertilizer treatment† | 2009 | 2010 | 2-yr mean‡ |
|---|---|---|---|
| | | **Grain yield** | |
| | | Mg ha$^{-1}$ | |
| BU | 10.6 (0.5) | 10.9 (0.2) | 10.7 (0.4)b |
| AAc | 11.2 (0.6) | 9.8 (0.5) | 10.5 (0.7)b |
| AAs | 11.2 (0.5) | 10.6 (0.8) | 10.9 (0.6)b |
| Control | 5.0 (0.3) | 4.5 (0.4) | 4.8 (0.2)a |
| | | **Stover yield** | |
| | | Mg ha$^{-1}$ | |
| BU | 10.8 (0.6) | 7.4 (0.5) | 9.1 (0.7)b |
| AAc | 11.5 (0.5) | 7.8 (0.4) | 9.6 (0.8)b |
| AAs | 11.8 (0.6) | 7.3 (0.3) | 9.6 (0.9)b |
| Control | 6.8 (0.6) | 3.2 (0.4) | 5.0 (0.8)a |
| | | **Grain N concentration** | |
| | | g N kg$^{-1}$ | |
| BU | 10.9 (0.3) | 12.9 (0.3) | 11.9 (0.4)bc |
| AAc | 11.3 (0.3) | 11.7 (0.3) | 11.5 (0.2)b |
| AAs | 11.9 (0.2) | 13.0 (0.5) | 12.5 (0.3)c |
| Control | 9.0 (0.4) | 10.4 (0.2) | 9.7 (0.3)a |
| | | **Stover N concentration** | |
| | | g N kg$^{-1}$ | |
| BU | 5.9 (0.6) | 7.3 (0.6) | 6.6 (0.5)b |
| AAc | 5.8 (0.3) | 5.9 (0.4) | 5.9 (0.2)b |
| AAs | 7.1 (0.6) | 6.5 (0.4) | 6.8 (0.4)b |
| Control | 3.0 (0.2) | 4.5 (0.5) | 3.8 (0.4)a |
| | | **Grain N yield** | |
| | | kg N ha$^{-1}$ | |
| BU | 115 (8) | 140 (5) | 127 (6)bc |
| AAc | 127 (10) | 114 (4) | 120 (6)b |
| AAs | 133 (4) | 138 (14) | 136 (7)c |
| Control | 45 (3) | 47 (5) | 46 (3)a |
| | | **Total above-ground N yield** | |
| | | kg N ha$^{-1}$ | |
| BU | 179 (13) | 194 (8) | 186 (8)bc |
| AAc | 194 (14) | 160 (6) | 177 (10)b |
| AAs | 216 (7) | 186 (12) | 201 (9)c |
| Control | 66 (5) | 61 (7) | 63 (4)a |

† BU, broadcast urea; AAc, anhydrous ammonia injected at conventional depth (0.20 m); AAs, anhydrous ammonia injected at shallower depth (0.10 m).

‡ For each variable, values having same letters are not significantly different ($P < 0.05$).

**Table 2. Mean (and standard error, $n = 4$) of apparent N fertilizer recovery efficiency and fertilizer-induced $N_2O$ emissions factor in plots fertilized using broadcast urea and anhydrous ammonia injected at 0.2 and 0.1 m.**

| Fertilizer treatment† | 2009 | 2010 | 2-yr mean‡ |
|---|---|---|---|
| | | % | |
| | | **NFRE§** | |
| BU | 62.9 (5.7) | 73.5 (6.4) | 68.2 (4.4)ab |
| AAc | 71.2 (7.9) | 54.8 (2.5) | 63.0 (4.9)a |
| AAs | 83.8 (6.4) | 69.2 (5.8) | 76.5 (4.9)b |
| | | **FIEF¶** | |
| BU | 0.12 (0.02) | 0.25(0.02) | 0.19 (0.03)a |
| AAc | 0.26 (0.04) | 0.34 (0.03) | 0.30 (0.03)a# |
| AAs | 0.65 (0.11) | 0.81 (0.06) | 0.73 (0.07)b |

† BU, broadcast urea; AAc, anhydrous ammonia injected at conventional depth (0.20 m); AAs, anhydrous ammonia injected at shallower depth (0.10 m).

‡ For each variable, values having same letters are not significantly different ($P < 0.05$).

§ NFRE, N fertilizer recovery efficiency.

¶ Fertilizer-induced $N_2O$ emissions factor.

# The FIEF in the BU and AAc treatments differed at the $P = 0.057$ level.

**Table 3. Mean (and standard error, $n = 4$) soil ammonium and nitrate content in samples collected from the 0- to 0.60-m depth after harvest in control plots and plots fertilized using broadcast urea and anhydrous ammonia injected at 0.20 and 0.10 m.**

| Fertilizer treatment† | 2009 | 2010 | 2-yr mean‡ |
|---|---|---|---|
| | | kg N ha$^{-1}$ | |
| | | **NH4$^+$** | |
| BU | 6.4 (1.7) | 24.3 (2.1) | 15.3 (1.4) |
| AAc | 9.6 (2.5) | 26.1 (5.2) | 17.6 (3.5) |
| AAs | 6.3 (0.3) | 24.5 (1.8) | 15.4 (1.0) |
| Control | 5.9 (0.9) | 27.3 (2.6) | 16.6 (1.2) |
| | | **$NO_3^-$** | |
| BU | 16.7 (2.7) | 9.2 (0.6) | 13.0 (1.5)ab |
| AAc | 19.9 (1.9) | 9.2 (1.3) | 14.7 (1.2)b |
| AAs | 18.0 (1.1) | 4.6 (0.6) | 11.6 (0.7)a |
| Control | 15.8 (2.5) | 7.1 (0.5) | 11.6 (1.5)ab |
| | | **$NH_4^+ + NO_3^-$** | |
| BU | 23.1 (3.1) | 33.5 (2.5) | 28.3 (1.2)a |
| AAc | 29.5 (3.6) | 35.3 (5.3) | 32.4 (4.3)b |
| AAs | 24.4 (1.1) | 29.2 (1.6) | 26.8 (1.2)a |
| Control | 21.7 (2.5) | 34.4 (2.8) | 28.1 (2.7)a |

† BU, broadcast urea; AAc, anhydrous ammonia injected at conventional depth (0.20 m); AAs, anhydrous ammonia injected at shallower depth (0.10 m).

‡ For each variable, values having same letters are not significantly different ($P < 0.05$).

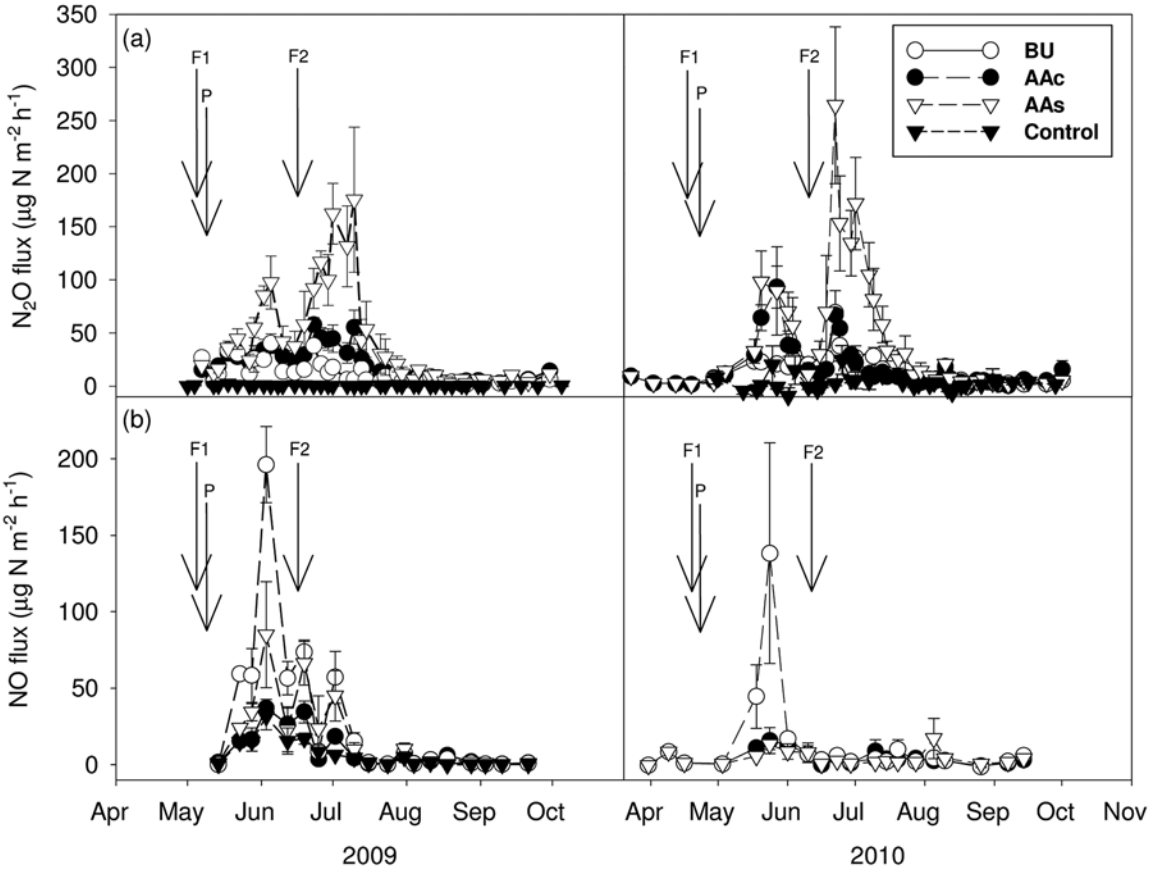


**Fig. 2. Soil-to-atmosphere fluxes of (a) $N_2O$ and (b) NO in control plots and in plots fertilized using broadcast urea (BU) and anhydrous ammonia injected at 0.2 m (AAc) and 0.1 m (AAs). Arrows indicate dates of planting (P) and pre-plant (F1) and post-plant (F2) N fertilizer applications. Error bars indicate1 SEM at each sampling date ($n = 4$).**

NO flux occurred in the BU treatment 20 d following the first urea application. No fluxes greater than 17 µg N m$^{-2}$ h$^{-1}$ occurred after 1 August either year. Daily NO flux was not significantly correlated with WFPS or temperature in 2009 or 2010. When expressed either on an area basis or relative to corn grain yield, growing season NO emissions were significantly greater in the BU treatment compared with the AAc and AAs treatments, which did not differ from each other (Fig. 3b).

Expressed in terms of total N emitted per unit area, total $N_2O$ + NO emissions averaged across the two seasons increased in the order AAc < BU < AAs (Fig. 3c, left). Expressed in terms of total N emitted per unit grain yield, emissions in the AAs treatment were significantly greater than in the AAc and BU treatments, which did not differ from each other (Fig. 3c, right). The ratios of cumulative NO to cumulative $N_2O$ emissions averaged across both seasons were 1.4, 0.3, and 0.2 in the BU, AAc, and AAs treatments, respectively. Using the IPCC default emissions factor of 1% of the emitted NO to estimate the downwind conversion of NO to $N_2O$, NO-derived indirect $N_2O$ emissions represented a relatively small contribution (<0.4% of direct $N_2O$ emissions). Total growing season direct plus indirect $N_2O$ emissions expressed as $CO_2$ eq. ranged from 0.1 to 0.7 Mg $CO_2$ eq. $ha^{-1}$ on an area basis and from 0.02 to 0.07 Mg $CO_2$ eq. $Mg^{-1}$ on a yield basis (Fig. 4).

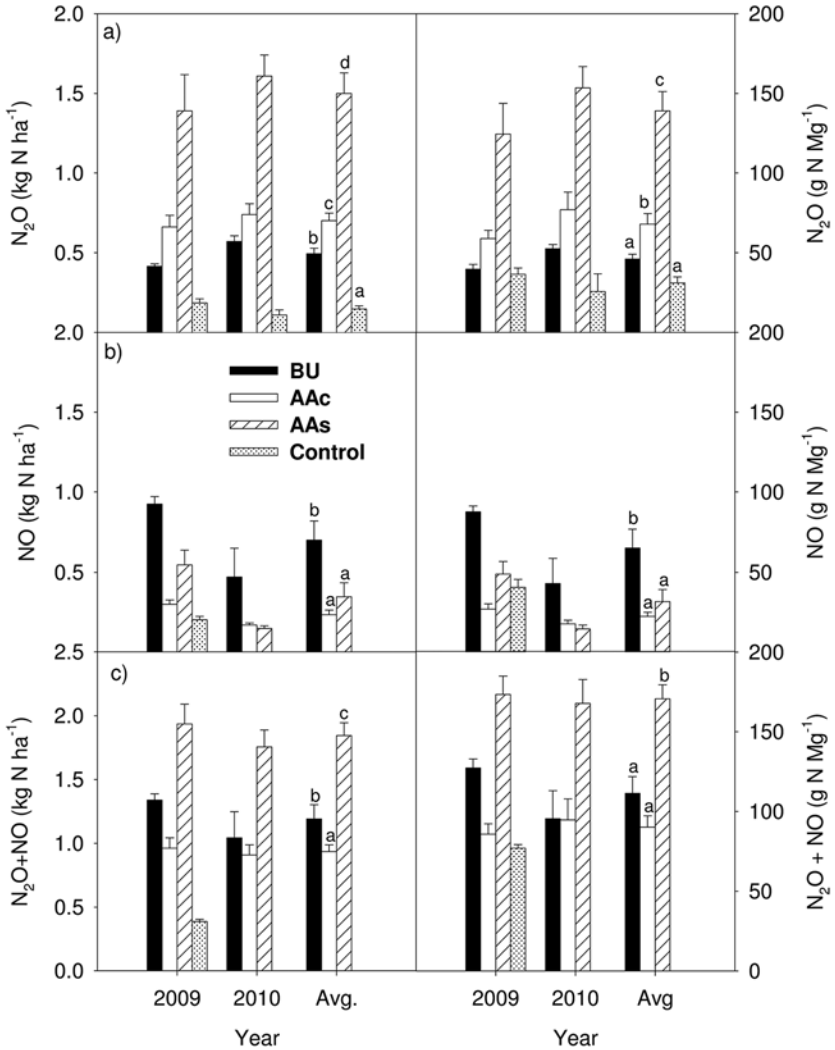


**Fig. 3. Cumulative growing season emissions of (a) $N_2O$, (b) NO, and (c) $N_2O$ + NO emissions expressed on an area scaled (left) and yield scaled basis (right) in control plots and in plots fertilized using broadcast urea (BU) and anhydrous ammonia injected at 0.2 m (AAc) and 0.1 m (AAs). Error bars indicate 1 SEM at each sampling date ($n$ = 4). For 2-yr averages, bars with the same letters are not significantly different ($P$ < 0.05). Cumulative NO emissions from control treatment was not measured in 2010; thus, the control data were excluded from 2-yr averages in (b) and (c).**

# Discussion

## Nitrous Oxide Emissions

This study provides further evidence that AA application generates greater $N_2O$ emissions than urea, at least when urea is broadcast applied. This finding is consistent with four other studies conducted on five different soil types of varying texture, organic matter content, and pH, all used for corn production in three different states (Breitenbeck and Bremner, 1986a; Thornton et al., 1996; Venterea et al., 2005, 2010). In these studies, both sources were applied at the same rates (≥120 kg N $ha^{-1}$). One study conducted in clay and clay loam soils used for wheat production in south-central Canada found no difference in $N_2O$ emissions between AA and urea when both were applied at a rate of 80 kg N $ha^{-1}$ (Burton et al., 2008).

Elevated $N_2O$ emissions with AA have been attributed to the highly concentrated zones of $NH_4^+$ and elevated pH that are generated immediately after application (Breitenbeck and Bremner, 1986a; Chalk et al., 1975; Eno and Blue, 1954). These chemical conditions combine to create high levels of free ammonia ($NH_3$), which is toxic to many organisms (Warren, 1962). Nitrite ($NO_2^-$)-oxidizing bacteria that carry out the second step of nitrification are particularly sensitive to $NH_3$ toxicity (Aleem and Alexander, 1960; Anthonisen et al., 1976). Thus, although $NO_2^-$ is commonly not present in detectable quantities in soil, AA application can result in the accumulation of $NO_2^-$ at concentrations above 25 μg N $g^{-1}$ (Nommik and Nilsson, 1963; Chalk et al., 1975; Venterea and Rolston, 2000a). Soil $NO_2^-$ is a substrate for microbiological and chemical reactions that produce $N_2O$ under highly aerobic conditions (Stevenson and Swaby, 1964; Venterea, 2007; Kool et al., 2011). In addition to promoting $NO_2^-$ accumulation and $NO_2^-$–driven $N_2O$ production, AA injection can also cause dissolution of SOM, resulting in elevated dissolved organic carbon (DOC) (Tomasiewicz and Henry, 1985; Norman et al., 1988; Venterea et al., 2010). Increased DOC can promote denitrification (e.g., Burford and Bremner, 1975) and has been positively correlated with $NO_2^-$–driven $N_2O$ production under aerobic conditions (Venterea, 2007). Thus, it is likely that AA has synergistic effects on $N_2O$ production by promoting elevated levels of $NO_2^-$ and DOC. Furthermore, $N_2O$ that is produced under aerobic conditions is not likely to be transformed in the soil, so a large proportion of the $N_2O$ produced is likely to be emitted to the atmosphere (Venterea, 2007).

Urea hydrolysis also increases soil pH and may cause $NH_3$ toxicity effects and increased soil $NO_2^-$. However, these effects have been found in cases of high (e.g., >500 kg N $ha^{-1}$) localized N addition rates, including tree fertilization (Chapman and Leibig, 1952), banded or nested urea applications (Engel et al., 2010), or using high urea/soil mixing ratios or large urea

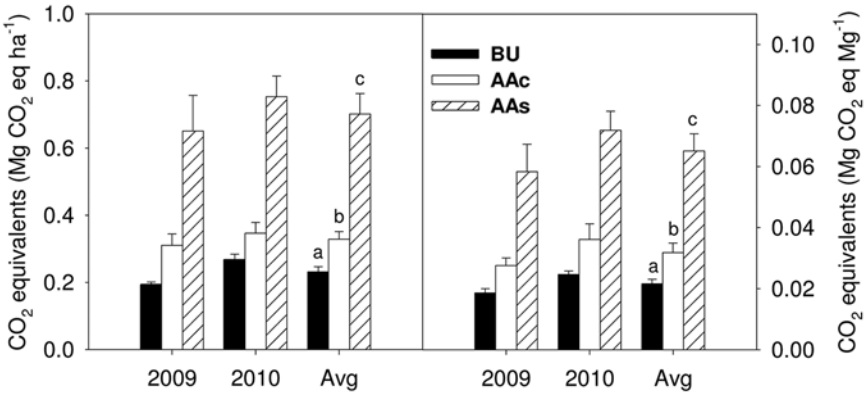


**Fig. 4. Cumulative growing season $N_2O$ emissions expressed as $CO_2$ equivalents on an area-scaled (left) and yield-scaled basis (right) in control plots and in plots fertilized using broadcast urea (BU) and anhydrous ammonia injected at 0.2 m (AAc) and 0.1 m (AAs). Error bars indicate 1 SEM at each sampling date (*n* = 4). For 2-yr averages, bars with the same letters are not significantly different (*P* < 0.05).**

granules (Hauck and Stephenson, 1965; Bezdicek et al., 1971; Tenuta and Beauchamp, 2000). With uniform broadcast urea application, the prills are distributed over approximately 10 times the area compared with banded AA application. Engel et al. (2010) and Venterea et al. (2010) could not detect $NO_2^-$ in soil after BU applications. Because the N content by weight of urea is 46%, compared with 82% for AA, banded urea applications likely do not result in localized $NH_4^+$ concentrations as high as those seen after AA application, which can exceed 1500 μg $NH_4^+$–N $g^{-1}$ (Nommik and Nilsson, 1963; Chalk et al., 1975). Also, because urea dissolution and hydrolysis is required to occur before $NH_3/NH_4^+$ is released into soil, elevated $NH_4^+$ concentrations and pH do not occur as quickly compared with AA application, where these effects occur immediately after application (Eno and Blue, 1954, 1957). Two studies have compared subsurface-injected AA with subsurface-banded urea. Thornton et al. (1996) found greater $N_2O$ emissions with AA, and Burton et al. (2008) found no differences between banded urea and AA. Thus, the evidence comparing $N_2O$ emissions after AA versus banded urea is not as strong as for AA versus broadcast urea application.

The ratio of $N_2O$ emissions with AAc versus BU averaged over two growing seasons in the current study was 1.4, compared with ratios ≥2.0 in studies by Breitenbeck and Bremner (1986a), Thornton et al. (1996), and Venterea et al. (2005, 2010). The lower ratio in the current study may have been due to the split timing of N fertilizer applications, with 50% applied before planting and 50% applied a few weeks later, whereas previous studies (cited above) used single applications, with the total N rate per application ranging from 120 to 180 kg N $ha^{-1}$ compared with 90 kg N $ha^{-1}$ in the current study. Split N applications are considered to be a best management practice on these coarse-textured irrigated soils (Rehm et al., 2008). A lower N rate per application could have resulted in less pronounced $NH_3$ toxicity effects due to lower localized $NH_4^+$ concentrations. This could also explain the findings of Burton et al. (2008), where the lower N application rate (80 kg N $ha^{-1}$, single application) may have lessened $NH_3$ toxicity, resulting in no differences between AA and banded or broadcast urea.

The role of AA in releasing SOM as described above may have been responsible for greater $N_2O$ emissions in the AAs treatment compared with the AAc treatment because the SOM content was greater in the 0- to 0.1-m depth interval (2.5%) compared with the 0.1- to 0.2-m interval (1.7%). Greater SOM at the shallower depth may have stimulated more nitrification-derived $N_2O$ production in the AAs treatment (Venterea, 2007). These results contrast with those of Breitenbeck and Bremner (1986b), who found lower $N_2O$ emissions when AA was injected at 0.1 m compared with 0.2 m in a clay loam. It is likely that denitrification was more important as a source of $N_2O$ in the Breitenbeck and Bremner (1986b) study due to the finer soil texture. Thus, decreases in oxygen availability with depth may have played a more important role in regulating denitrification-driven $N_2O$ emissions compared with the current study. In the current study, WFPS during the period of greatest $N_2O$ emissions were generally below 50%, suggesting that nitrification was most likely the dominant $N_2O$ source (Fig. 1c, 2a) (Davidson et al., 1993).

## Nitric Oxide and Total Nitrogen Oxide Emissions

The greater NO emissions found here with BU compared with AAc and AAs is consistent with previous studies by Thornton et al. (1996) and Venterea et al. (2005). The mechanisms described above involving $NH_3$ toxicity and $NO_2^-$ accumulation can also promote NO production and therefore might be expected to produce more NO with AA than urea (Venterea and Rolston, 2000b). However, because NO is highly reactive in soil under aerobic and anaerobic conditions, NO that is produced even at shallow depths is subject to substantial transformation before diffusing to the soil surface (Venterea and Rolston, 2002). The method of urea application likely resulted in more of the urea remaining closer to the soil surface compared with either of the AA treatments, as was the case for the studies of Thornton et al. (1996) and Venterea et al. (2005). Thus, the greater NO emissions with urea were likely due to less vertical distance between points of soil NO production and the soil surface, and therefore provided less opportunity for NO transformation. This effect would also be expected to result in greater NO emissions in the AAs compared with the AAc treatment. Although this trend was observed in 2009, across both years the effect was not significant ($P = 0.23$) (Fig. 3b).

Nitric oxide–derived indirect emissions were negligible compared with direct $N_2O$ emissions. The default IPCC emission factor of 1.0% used to convert NO to indirect $N_2O$ emissions is subject to high uncertainty, with a 95% confidence interval of 0.2 to 5% (De Klein et al., 2006). The quantities calculated here do not account for upstream GHG costs associated with fertilizer production and transportation, which are reported to be greater for AA than for urea (Snyder et al., 2009). A complete life-cycle analysis would need to account for these differences as well as any differences in on-farm

GHG emissions associated with urea versus AA application (e.g., fuel consumption).

## Yield-Scaled Emissions

Yield-scaled $N_2O$ emissions in the current study were in the range of 46 to 139 g N $Mg^{-1}$, similar to those reported by Halvorson et al. (2010) and Venterea et al. (2011). These values are lower than those of Gagnon et al. (2011), who found $N_2O$ emissions of 1300 to 2000 g N $Mg^{-1}$ in a clay soil using AA fertilizer in eastern Canada. We believe the current study is the first to report yield-scaled NO and $N_2O$ + NO emissions. Although there were no yield differences among the three fertilized treatments, expressing emissions on a yield-scaled basis slightly changed the pattern of treatment effects compared with area-scaled emissions. On a yield-scaled basis, $N_2O$ emissions from the BU treatment did not differ from the control (Fig. 3a, right; 4, right), and total ($N_2O$ + NO)-N emissions from the BU treatment did not differ from the AAc treatment (Fig. 3c, right).

## Nitrogen Fertilizer Recovery Efficiency

The growing season NFRE values observed here (55–84%) are greater than a mean of 37% obtained by metaanalysis for corn production in the north-central United States (Cassman et al., 2002). However, NFRE values for individual corn studies have ranged widely. In a sandy loam in central Minnesota using split N applications, NFRE ranged from 30 to 90%, depending on N rate and irrigation management. Vetsch and Randall (2004) found a NFRE of 87% for spring-applied AA in a clay loam in southern Minnesota. In the current study, the AAs treatment had greater NFRE than the AAc treatment. Greater SOM content closer to the surface could have resulted in better retention of ammonium N in the AAs treatment. Also, corn grown in coarse-textured soil tends to have greater root length density in upper 0.1-m compared with the 0.1- to 0.2-m depth (Kuchenbuch et al., 2009), and shallow-rooted crops tend to have greater N uptake with shallower N fertilizer placement (Kristensen and Thorup-Kristensen, 2007). Thus, the corn in the AAs treatment may have had better access to applied N than the AAc treatment. The greater amount of residual N in the AAc treatment after harvest is also consistent with this hypothesis. The method of differences used here to determine NFRE assumes that crop uptake of mineralized N does not vary among the fertilized and control treatments. Further study using $^{15}N$ tracer methods for measuring NFRE would be useful for confirming these effects.

## Conclusions

These results provide additional evidence that AA emits more $N_2O$, but less NO, than BU. These results also show that practices to reduce $N_2O$ emissions do not always improve NUE. That is, despite having the greatest emissions of $N_2O$ and total N oxides, the AAs treatment had greater NFRE compared with the AAc treatment. Similarly, recent studies have found greater $N_2O$ emissions with fertilizer types that produced the same or even greater NUE than other types (Halvorson et al., 2010; Gagnon and Ziadi, 2010; Gagnon et al., 2011). This decoupling of $N_2O$ emissions and NUE is not surprising because $N_2O$ losses generally represent <3% of added N and in themselves probably have negligible affects on yields or NUE in many cases. These results highlight the fact that, even if fertilizer N is applied at a time that coincides with peak crop N demand, root N uptake will still compete with soil N transformation processes for available N. Thus, the effects of particular fertilizer sources and application methods on soil N transformation processes needs to be better understood and considered in efforts to mitigate losses of $N_2O$ and other reactive N species.

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