

**CORN PRODUCTION AND ENVIRONMENTAL IMPLICATIONS
UNDER VARYING NITROGEN AND MANAGEMENT PRACTICES**

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Dedication

This thesis is dedicated to my parents Mr. Dhan Bahadur Maharjan and Mrs. Narayani Maharjan, my beloved wife Dr. Erandi S Gunapala, and my spiritual master, His Holiness Gopal Krishna Goswami Srila Bhagavatapada.

Abstract

Economic and environmental issues combined have increased the need for better understanding of the fate of nitrogen (N) applied to crop production systems. The objectives of this dissertation were to evaluate the effects of different N sources including conventional urea (CU), polymer-coated urea (PCU), stabilized urea with chemical inhibitors (IU), and anhydrous ammonia (AA) on N losses and yield. Besides N sources, their interaction with placement (deep- versus shallow-banded; broadcast/incorporation versus subsurface banding), tillage management (conventional tillage versus no tillage) and irrigation management (irrigated versus rain fed) were also studied.

In the first experiment, split-applied CU increased yield and N uptake compared with preplant applied PCU or IU and decreased nitrate (NO_3^-) leaching compared with PCU in a sandy loam soil. Direct soil-to-atmosphere nitrous oxide (N_2O) emissions were significantly less with IU or split-U than with PCU and there was a trend for greater emissions with split-U than with IU ($P = 0.08$). Irrigation significantly increased NO_3^- leaching during the growing season, but had no effect on direct N_2O emissions in the same experiment. Indirect emissions due to NO_3^- leaching were estimated to be 79–117% of direct emissions using the default value of EF_5 , thus signifying the potential importance of indirect emissions in evaluating management effects on N_2O emissions.

In the second experiment, no-till significantly increased N_2O emissions in fertilized treatments in a dry year and decreased crop yield in the control treatment in a

silt loam soil. There were no significant differences in N_2O emissions, grain yield or NO_3^- leaching potential with AA placement depth.

In the third experiment, mid-row banding (MRB) significantly increased N_2O emissions compared to broadcast/incorporation (BI) for PCU and CU in silt loam soils. Nitrous oxide emissions were correlated to a greater extent with soil nitrite (NO_2^-) intensity than with nitrate (NO_3^-) intensity; N intensity being a measure of integrated N concentrations over time. Compared to BI, MRB reduced NH_3 volatilization loss and the CU treatment had greater NH_3 loss than PCU or IU had. All these experiments highlighted the significant roles that N and other management practices can play in mitigating N losses.

Table of Contents

Acknowledgements.....	i
Dedication.....	ii
Abstract.....	iii
Table of Contents.....	v
List of Tables.....	vii
List of Figures.....	ix
Introduction.....	1
Chapter 1 – Fertilizer and Irrigation Management Effects on Nitrous Oxide Emissions and Nitrate Leaching.....	6
Introduction.....	7
Materials and Methods.....	9
Results.....	18
Discussion.....	22
Conclusions.....	30
References.....	30
Chapter 2 – Nitrous oxide emissions and nitrate leaching potential under shallow and deep application of anhydrous ammonia in different tillage systems.....	48
Introduction.....	49
Materials and Methods.....	51
Results.....	57
Discussion.....	60
Conclusions.....	67
References.....	68

Chapter 3 – Soil Inorganic Nitrogen Dynamics and Nitrous Oxide Emissions: Broadcast versus Band application of Conventional Urea and Controlled–release Fertilizers	83
Introduction.....	84
Materials and Methods.....	86
Results.....	93
Discussion.....	98
Conclusions.....	103
References.....	104
Conclusions.....	122
Bibliography	125

List of Tables

Table 1-1: Date, source and amount of fertilizer application.	39
Table 1-2: Results of statistical analyses with mean (standard error) for different dependent variables as affected by year, irrigation and N sources.	40
Table 1-3: Means (standard error) for variables where significant 3–way interaction effect of year, irrigation and N source were found.	41
Table 1-4: Results of statistical analyses with mean (standard error) for post–harvest residual soil inorganic N and NO ₃ ⁻ concentration in water	42
Table 2-1: Results of statistical analyses for different dependent variables as affected by year, N source and tillage, and their interactions.....	76
Table 2-2: Mean (standard error) of soil and soil-water N intensities during the season.	76
Table 2-3: Results of linear regression analysis for cumulative N ₂ O emissions versus soil N intensities of nitrite and nitrate (NO ₃ I) and ammonium (NH ₄ I)	77
Table 3-1: Results of statistical analyses for different dependent variables as affected by year, N source and placement, and their interactions.	112
Table 3-2: Results of statistical analyses for different dependent variables as affected by N source in MRB treatments in 2012.	113

Table 3-3: Results of statistical analyses for soil N (NO_2^- -N, NO_3^- - N and NH_4^+ - N) intensity at center and off-center locations. 114

Table 3-4: Means (SE) for soil NO_2^- -N intensity where significant year-by-N source-by-placement treatment interaction effects were found. 115

Table 3-5: Correlation coefficient (r^2) (and P values) for linear regression analyses of cumulative N_2O emissions versus different soil N intensity metrics..... 116

Table 3-6: Means (SE) for cumulative area-based NH_3 volatilization in BI treatments where year-by-N source treatment interaction effects were found..... 117

List of Figures

Figure 1-1: Daily irrigation and cumulative water input and drainage in IRG and DRY plots during 2009 and 2010.....	43
Figure 1-2: (a) Air temperature and mean (standard error) soil temperature, and (b) mean (standard error) water-filled pore space (WFPS) at the 0.05-m depth at the time of N ₂ O sampling in IRG and DRY plots during 2009 and 2010.....	44
Figure 1-3: Mean (standard error) N ₂ O emissions in IRG and DRY plots under different N sources;.....	45
Figure 1-4: Daily mean (standard error) NO ₃ ⁻ concentrations in lysimeter water samples in IRG and DRY plots under different N sources;.....	46
Figure 1-5: Mean total (direct plus indirect) N ₂ O emissions estimated using different default IPCC published emission factors	47
Figure 2-1: (a) Daily precipitation and air temperature, and (b) mean (with standard error) soil temperature and water-filled pore space (WFPS) at time of N ₂ O sampling.	78
Figure 2-2: Mean (with standard error) growing season N ₂ O emissions in plots under conventional tillage (CT) and no-till (NT) systems.....	79
Figure 2-3: Mean (with standard error) (a) growing season N ₂ O emissions, (b) soil nitrite plus nitrate intensity (NO ₂ 3I), (c) soil ammonium intensity (NH ₄ I),	80
Figure 2-4: Mean (and standard error) soil nitrate (NO ₃ ⁻) concentrations in the upper 0-0.3 m depth in plots under conventional tillage (CT) and no-till (NT).....	81

Figure 2-5: Cumulative N ₂ O emissions following anhydrous ammonia application at different depths in three different soil types;	82
Figure 3-1: Daily precipitation, mean daily air temperature and mean (SE) soil temperature, and mean (SE) water-filled pore space (WFPS)	118
Figure 3-2: Mean (SE) N ₂ O emissions in (a) broadcast incorporation (BI) and (b) mid-row band (MRB) application of fertilizers and (c) mean (SE) NH ₃ emissions	119
Figure 3-3: Mean (SE) cumulative N ₂ O emissions (a) expressed per unit of area, (b) per grain yield and (c) fertilizer-induced emissions factors (FIEF).	120
Figure 3-4: Mean (SE) soil concentrations of (a) nitrite (NO ₂ ⁻), (b) nitrate (NO ₃ ⁻) and (c) ammonium (NH ₄ ⁺) and (d) pH during 2011.	121
Figure 3-5: Mean (SE) soil concentrations of (a) nitrite (NO ₂ ⁻), (b) nitrate (NO ₃ ⁻) and (c) ammonium (NH ₄ ⁺) and (d) pH during 2012.	122

Introduction

Economic and environmental issues combined have increased the need for better understanding the fate of nitrogen (N) applied to crop production systems. On one hand, there is a need of growing world population for food, fiber, and energy that drives demand for N fertilizers in agriculture. On the other hand, there are environmental consequences associated with increasing use of N. The greatest shift of the global N cycle brought about by human activities such as agriculture is the change associated with the huge increase in reactive N (Millar et al., 2010). Nonreactive N is dinitrogen N compound (N_2) and reactive N includes any biologically, photochemically, and radiatively active N compounds in the Earth's atmosphere and biosphere (Galloway et al., 2003). Inorganic reduced forms of N such as ammonia (NH_3) and inorganic oxidized forms such as nitrous oxide (N_2O) and nitrate (NO_3^-) are some major reactive N forms of great concerns.

Nitrous oxide is a major greenhouse gas (GHG) and also the single most important ozone-depleting emission (Ravishankara et al., 2009). Agricultural activities are responsible for 10-12% of total anthropogenic GHG emissions and more than half of agricultural GHG emissions are derived from N_2O emissions (Smith et al., 2007). Increasing N_2O emissions from agriculture are linked to soil management and application of N fertilizers. Ammonia volatilization from fertilized agricultural land also has adverse environmental quality impacts (Zaman et al, 2009). Upon deposition to the ground, NH_3 can cause soil acidification (van der Eerden et al., 1998), become a secondary source of N_2O emission, or promote eutrophication of surface water bodies (Sutton et al., 2008).

Considerable amounts of N in fertilized agricultural land can also reach groundwater or surface water through leaching of NO_3^- , which is a groundwater contaminant. Nitrogen lost from fertilized fields through NO_3^- leaching can also contribute to N_2O emissions by conversion of NO_3^- to N_2O in a receiving aquatic ecosystem.

Global N fertilizer consumption has increased from ~10 Tg in late 1950s to ~100 Tg N in 2008 (Robertson and Vitousek 2009), with the global N input into agricultural systems from fertilizer increasing more than 40 fold since 1930 (Mosier et al. 1999). Currently, the US is one of the largest global producers and consumers of fertilizer N [8.3 and 11.5 Gg of N, respectively (FAO 2010)]. About 46% of all N fertilizers used in the US in 2010 were applied to corn (ERS, 2012). Hence, N management in corn production can potentially play a role in mitigating reactive N release (N loss, henceforth) from agriculture. Management practices such as tillage, irrigation, and N source, rate, placement, and timing can also affect N losses.

In this dissertation, the effects of different N sources such as conventional urea (CU), polymer-coated urea (PCU), stabilized urea with chemical inhibitors (IU), and anhydrous ammonia (AA) on N losses and yield were evaluated. Besides N sources, their interaction with placement (deep- versus shallow-banded; broadcast/incorporation versus subsurface banding), tillage management (conventional tillage versus no tillage) and irrigation management (irrigated versus rain fed) were also studied.

Chapter 1 – Fertilizer and irrigation management effects on nitrous oxide emissions and nitrate leaching (Agronomy Journal, 2013)

The main objective of this study was to compare area- and yield-based direct N₂O emissions, NO₃⁻ leaching, and N use efficiency (NUE) in fully irrigated, non water-stressed and minimally irrigated, water-stressed corn plots each of which received split applications of CU (split-U) and single pre-plant applications of either PCU or IU over two consecutive growing seasons. Split-U is considered a best management practice in sandy soils in the region (Rehm et al., 2008) and thus, the objective of the study was to compare alternative best management practices. We also estimated direct plus indirect N₂O emissions by adding direct soil-to-atmosphere emissions to indirect N₂O emissions due to NO₃⁻ leaching estimated using published emission factors (De Klein et al., 2006).

Chapter 2 – Nitrous oxide emissions and nitrate leaching potential under shallow and deep application of anhydrous ammonia in different tillage systems

The objective of this study was to examine the effects of long-term (~20 yr) tillage treatments and AA placement depths on area- and yield-based N₂O emissions and agronomic indices (grain yield, N uptake, NUE) over two growing seasons. Soil-water NO₃⁻ concentration was also measured to compare NO₃⁻ leaching potential in these treatments.

Chapter 3–Soil inorganic nitrogen dynamics and nitrous oxide emissions: Broadcast versus band application of conventional urea and controlled-release fertilizers

(Soil Biology and Biochemistry, 2013 in revised form)

The main objective of this study was to compare area- and yield-based N₂O emissions, NH₃ volatilization, grain yield, and NUE in corn plots each of which received

either broadcast/incorporated (BI) or mid-row banding (MRB) post-emergence application of one of three fertilizer sources (CU, PCU or IU) over two consecutive growing seasons. The study also investigated temporal soil inorganic N dynamics during the season and the relationship of soil N (NO_2^- -N, NO_3^- -N and NH_4^+ -N) accumulation to N_2O emissions.

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Chapter 1 – Fertilizer and Irrigation Management Effects on Nitrous Oxide Emissions and Nitrate Leaching

Irrigation and nitrogen (N) fertilizer management are important factors affecting crop yield, N fertilizer recovery efficiency (NFRE), and N losses as nitrous oxide (N_2O) and nitrate (NO_3^-). Split-application of conventional urea (split-U) and/or one-time application of products designed to perform as enhanced-efficiency N fertilizers (EENF) may mitigate N losses. The objective of this study was to compare the effects of controlled-release polymer-coated urea (PCU), stabilized urea with urease and nitrification inhibitors (IU) and split-U on direct soil-to-atmosphere N_2O emissions, NO_3^- leaching, and yield for irrigated and minimum-irrigated corn in loamy sand. Indirect N_2O emissions due to NO_3^- leaching were estimated using published emission factors (EF_5). Split-U increased yield and N uptake compared with preplant applied PCU or IU and decreased NO_3^- leaching compared with PCU. Direct N_2O emissions were significantly less with IU or split-U than with PCU and there was a trend for greater emissions with split-U than with IU ($P = 0.08$). Irrigation significantly increased NO_3^- leaching during the growing season but had no significant effect on direct N_2O emissions. However, after accounting for significantly increased yields with irrigation, N losses expressed on a yield basis did not differ and in some cases decreased with irrigation. Post-harvest soil N and soil-water NO_3^- in spring showed potential for greater N leaching in minimum-irrigated plots than in irrigated. Indirect emissions due to NO_3^- leaching were estimated to be 79–117% of direct emissions using the default value of EF_5 , thus signifying the potential importance of indirect emissions in evaluating management effects on N_2O emissions.

Abbreviations: EENF, enhanced–efficiency N fertilizers; PCU, polymer–coated urea; IU, stabilized urea containing urease and nitrification inhibitors; split–U, split–application of conventional urea; FIEF, fertilizer–induced emission factor; FILF, fertilizer–induced leaching factor; DI, direct N₂O emissions plus indirect emissions due to NO₃[–] leaching; EF₅, emission factor to estimate amount of leached NO₃[–] that would convert to N₂O downstream; NUE, nitrogen use efficiency; NFRE, nitrogen fertilizer recovery efficiency; IRG, irrigated system; DRY, minimum–irrigated system.

Introduction

Nitrous oxide is a major greenhouse gas and also the single most important ozone–depleting emission (Ravishankara et al., 2009). Its exponential buildup in the atmosphere during the past 300 years is of increasing concern and agricultural land is its primary anthropogenic source (Denman et al., 2007). Increasing N₂O emissions from agriculture are linked to soil management and application of N fertilizers. About 46% of all N fertilizers used in the US in 2010 were applied to corn (ERS, 2012). Hence, management of corn production can potentially play a role in N₂O mitigation efforts.

Use of PCU or IU has the potential to mitigate N₂O emissions. These products are designed to release N more gradually over the course of the season compared with conventional urea in order to minimize N loss and improve synchrony between soil N availability and crop N demand. Some field studies have shown the effectiveness of these products in improving plant N use efficiency (NUE) (Shoji et al., 2001; Freney et al., 1992) and reducing N₂O emissions (Halvorson et al., 2010; 2011; 2013; Hyatt et al.,

2010; Bronson et al., 1992) while others have shown limited or no effectiveness (Sistani et al., 2011; Venterea et al., 2011; Parkin and Hatfield., 2010). These products, if effective, may also eliminate the need for multiple split applications of N, which are recommended to reduce NO_3^- leaching (Rosen and Bierman, 2008) especially in irrigated sandy soils.

In 2008, 16% of total corn acres in US were under irrigation (USDA, NASS, 2008). Irrigation is a major factor that influences leaching of NO_3^- , which is a groundwater contaminant. Nitrogen lost from fertilized fields through NO_3^- leaching can also contribute to so-called “indirect” N_2O emissions by conversion of NO_3^- to N_2O in a receiving aquatic ecosystem. Apart from direct soil-to-atmosphere N_2O emissions occurring in-field, indirect emission of N_2O downstream may be significant, especially in sandy soils under irrigation. There are few studies, to our knowledge, that compares effects of irrigation versus no irrigation on direct N_2O emissions (Horvath et al., 2010) and there have been no studies as far as we know that report direct N_2O emissions and indirect N_2O emissions due to NO_3^- leaching simultaneously for corn production.

In evaluating management impacts on N_2O emissions, altered crop yield resulting from a shift in N and irrigation management also needs to be considered (Venterea et al., 2011; Van Groenigen et al., 2010). Corn is very sensitive to water stress (El-Hendawy, et al., 2010; NeSmith and Ritchie, 1992) and timely water input by irrigation has been shown to increase yield (Stone et al., 2010). However, loss of N through leaching, which can be significant in some irrigated systems, can negatively affect NUE (Errebhi et al., 1998) and yield. Irrigation can also increase direct N_2O emissions compared with water-stressed systems (Horvath et al., 2010). Split application of N can increase grain yield

compared to single application (Sitthaphanit et al., 2009). Hence, expressing N₂O emissions per unit yield can be a useful metric to compare impacts of different fertilizer and irrigation management practices on N₂O emissions.

The main objective of this study was to compare area- and yield-based direct N₂O emissions, NO₃⁻ leaching, and NFRE in fully irrigated, non water-stressed (IRG) and minimally irrigated, water-stressed (DRY) corn plots each of which received split applications of urea and a onetime application of urea-ammonium nitrate for the IRG plots to simulate fertigation (split-U) and single pre-plant applications of either PCU or IU over two consecutive growing seasons. Split-U is considered a best management practice in sandy soils in the region (Rehm et al., 2008) and thus, the objective of the study was to compare alternative best management practices. We also estimated direct plus indirect N₂O (DI) emissions by adding direct soil-to-atmosphere emissions to indirect N₂O emissions due to NO₃⁻ leaching estimated using published emission factors (De Klein et al., 2006).

Materials and Methods

Site Description and Experimental Design

The site is located at the University of Minnesota's Sand Plain Research Farm in Becker, MN (45°23'N, 93°53'W), where the soil is a Hubbard loamy sand (sandy, mixed, frigid Entic Hapludoll) containing 820 g kg⁻¹ sand, 100 g kg⁻¹ silt, and 80 g kg⁻¹ clay in the upper 0.15 m. Soil organic matter (SOM) determined by loss on ignition was 25 g kg⁻¹ in samples from the 0 to 0.1 m depth and 17 g kg⁻¹ in samples from the 0.1- to 0.2-

m depth. The 30-year average precipitation and daily temperature during Apr through Oct are 531 mm and 16.0°C, respectively (MCWG, 2011).

The experiment was conducted over the course of two consecutive growing seasons (2009 and 2010) using adjacent sections of the farm each year. The fields were planted to non-irrigated, non-fertilized rye (*Secale cereal L.*) for 3 years prior to the experiment. Rye grain was harvested in summer followed by a rye winter cover crop each year. In spring, rye residue was incorporated using chisel plowing followed by shallow disking. An experiment was then established using a randomized complete block design with irrigation as the main treatment in each of four main plots and N fertilizer as a subplot. In this region of the state and on this soil type, corn is grown under both irrigated and rain-fed conditions. However, a preliminary experiment conducted at the site in 2008 found that completely non-irrigated corn had a significant loss in yield (32 – 84%) compared to irrigated corn. Therefore, experiments in subsequent years compared standard irrigation to minimal irrigation applied only to prevent extreme water stress. Irrigation treatments were designated as (i) IRG, where main plots were irrigated based on the checkbook method for determining frequency and amount of water inputs as described in Wright (2002), and (ii) DRY, where main plots were not irrigated except in mid-season (Jul and early Aug) when soil matric potential at 0.3 m depth was close to or below –50 KPa for 2 to 4 consecutive days and coincided with matric potential of less than –100 KPa at 1.2 m depth (amounts of irrigation applied to DRY plots are given in results section). Irrigation in all cases was applied using an aluminum solid-set overhead sprinkler system.

Each of four main IRG and DRY plots was subdivided into four 5-m by 5-m subplots, which were assigned randomly to N fertilizer treatments consisting of: (i) split-U (46-0-0) applied in two and three separate applications in DRY and IRG plots, respectively, (ii) PCU (44-0-0) (ESN; Agrium Advanced Technologies, Loveland, CO) applied in a single pre-plant application, (iii) IU (46-0-0) containing the urease inhibitor N-(n-Butyl)-thiophosphoric triamide and the nitrification inhibitor dicyandiamide, (Super U; Agrotain International, St. Louis, MO) also applied in a single pre-plant application, and (iv) an unfertilized control. All N treatments, including the control, received liquid starter N fertilizer at planting at the rate of 5.6 kg N ha⁻¹ as 10-34-0. Corn was planted at a seeding rate of 79,000 seeds ha⁻¹ on May 8 2009 and on Apr 26 2010. Each fertilized treatment received a total of 180 kg N ha⁻¹ (excluding starter) which is the recommended rate for this region (Rehm et al., 2008). The third application of split-U in the IRG plots was applied as urea-ammonium nitrate to simulate a fertigation event, which is a recommended practice with irrigation but would not be advisable under dryland production (Rehm et al., 2008). A separate N rate study at the same site showed that an N rate of 180 kg N ha⁻¹ was towards lower end of a range of economic optimum N rate for irrigated corn and towards higher end of that for water-stressed corn (unpublished data). Fertilizers were surface-broadcast and incorporated using a cultivator except for the third split-U application in IRG plots, which was irrigated immediately following surface application using 13 and 15 mm water respectively in 2009 and 2010. During application, the N₂O flux chamber measurement areas (described below) were initially covered. After the initial application, separately weighed portions of fertilizers were applied within the chamber measurement areas to

ensure accurate application rates. Table 1-1 provides details of date, source and amount of fertilizers application for both years. An on-site weather station was used to measure air temperature, wind speed, relative humidity, precipitation and net solar radiation at 10-min intervals. Irrigation- and precipitation-water was periodically sampled and was analyzed for the sum of nitrite (NO_2^-) plus nitrate (NO_3^-) (hereafter, referred as NO_3^-) using flow-through colorimetric analyzer (QuickChem 8500 with ASX 520 Series autosampler, Lachat Instruments, Milwaukee, WI).

Nitrous Oxide Emissions

Soil-to-atmosphere N_2O fluxes were measured using static chamber methods (Venterea et al., 2005; 2010; Rochette et al, 2000). In 2009, fluxes were measured twice a week from May to Oct; in 2010, fluxes were measured once a week in Apr, Sept and Oct and twice a week from May to Aug, for a total of 41 sampling dates each year. Sampling was generally made during 1000 h to 1200 h local time when soil temperature in the upper 0.10 m was close to its daily mean value. In 50% of irrigation events in 2010 and 70% in 2009, N_2O flux samplings were carried out within 24 hrs after irrigation. One stainless steel chamber anchor (0.50 m \times 0.29 m \times 0.086 m deep) was installed in each subplot, centered between corn rows with the short side parallel to the corn row encompassing 70% of the inter-row width. Since fertilizers were uniformly applied, it was assumed that gas fluxes in the uncovered areas did not differ from the covered areas. On each sampling day, insulated and vented chamber tops (0.50 m \times 0.29 m \times 0.102 m high) were secured to anchors with binder clips and samples were collected at 0, 0.5, 1 h using a 12-mL polypropylene syringe. In 2010, a fourth sample was also collected after

1.5 h. Samples were immediately transferred to glass vials sealed with butyl rubber septa (Alltech, Deerfield, IL) and analyzed within 2 wk using a headspace autosampler (Teledyne Tekmar, Mason, OH) connected to a gas chromatograph (GC) (model 5890, Agilent /Hewlett–Packard, Santa Clara, CA) equipped with an electron capture detector. The equipment was calibrated with analytical grade standards (Scott Specialty Gases, MI) each day when samples were analyzed. Gas concentrations in molar mixing ratios determined by the GC were converted to mass per volume concentrations using ideal gas law and air temperatures at the sampling time. Gas fluxes were calculated from the rate of change of gas concentration, chamber volume, and base area using quadratic regression (QR) as the default calculation scheme (Wagner et al., 1997) and using correction factors to account for suppression of the surface–atmosphere concentration gradient (Venterea, 2010). Linear regression was used in place of QR when time series gas concentration data had completely linear or positive curvature, i.e., when second derivative of QR results was ≥ 0 (Venterea, 2013; Venterea et al., 2009). The QR method was evaluated using the LINEST function in Excel (v. 2010, Microsoft).

Soil Water Nitrate Concentrations

Nitrate concentrations in soil water were determined using suction cup lysimeters installed to a depth of 1.2 m as described by Venterea et al. (2011). Each lysimeter was constructed of a 1.3-m long polyvinylchloride (PVC) pipe (48-mm internal diameter, I.D.) with one end fitted with epoxy to a round-bottom, 100-kPa high-flow porous ceramic cup (Soilmoisture Equipment Corp., Santa Barbara, CA) and the other end to a rubber stopper. Two sections of 5.35-mm (I.D.) polyethylene tubing were inserted

through the rubber stopper: one tube (vent tube) was short and extended inside the lysimeter only to 0.1 m below the stopper, while the other (sample tube) extended to 2 mm above the ceramic cup. The vent and sample tubes were connected to 6-mm (I.D.) Tygon® laboratory tubing equipped with polypropylene ratcheting clamps (Halkey–Roberts Corp., St. Petersburg, FL). Lysimeters under vacuum were submerged in water to fill them with water before installing them.

Each year within a wk of planting, one lysimeter was installed in each sub-plot in a corn-planted row. A 1.3-m-deep borehole was made using an 83-mm diam. soil auger. Silica flour slurry was added to a depth of 0.1 m before installing lysimeters. Soil was poured back into gap between lysimeter and sides of the hole in reverse order of its removal from the borehole. At a depth of 0.15 m, a 10-mm-thick layer of powdered bentonite was evenly applied around the lysimeter to prevent preferential water flow. On the following day, water was evacuated from each lysimeter by applying pressure through the vent tube while allowing water to exit the sample tube. Lysimeters were then prepared for subsequent water sampling by leaving them under vacuum of 40 KPa for 1 wk. Water samples were collected once per wk during the growing season in 50-mL polypropylene vials and stored at -5°C before being analyzed for NO_3^- using a flow-through colorimetric analyzer (QuickChem 8500 with ASX 520 Series autosampler, Lachat Instruments, Milwaukee, WI). Upon freeze up in the fall, vacuum was removed from lysimeters, which were left in field through winter. Once soil thawed in early spring, the vacuum was restored to collect water samples as explained above. Depending on conditions of lysimeters in soil, water samples were collected once a week for 6 weeks

in spring 2011 following 2010 corn and could be collected only one time in spring 2010 following 2009 corn.

Drainage and Nitrate Leaching

The amount of water draining below the root zone was estimated using a water mass balance equation as used in previous studies at this and other sites with excessively well-drained soils (Venterea et al., 2011; Wilson et al., 2010; Waddell et al., 2000).

Water balance and drainage rates were determined from

$$D = (P + I - ET) - \Delta S \quad [1]$$

where D is drainage (mm d^{-1}), P is precipitation (mm d^{-1}), I is irrigation water applied (mm d^{-1}), ET is evapotranspiration (mm d^{-1}), and ΔS is the daily change in soil water storage in the soil profile (mm d^{-1}). P was determined using a National Weather Service catch can and gauge stick, and I was calculated based on irrigation flow rate and duration of application. ET values were calculated as a product of a crop coefficient given in Stegman et al. (1977) based on stage of corn growth and potential ET estimated using the Penman–Monteith equation (Allen et al., 1998) with daily weather data recorded at the site. S on any given day was assumed not to exceed field capacity (FC) which was measured to be 140 mm to a depth of 1.2 m (Gremy et al., 1993). Water content in a soil profile of 0 – 1.2 m was measured during the growing season in total of 5 times each year to confirm that it did not exceed FC. To determine D , Eq. [1] was expanded as follows:

$$D_n = (P_n + I_n - ET_n) + S_{n-1} - S_n \quad [2]$$

where the subscripts n and $n-1$ denote the current and previous day respectively. The initial amount of water (S) in the soil profile at the start of the growing season was assumed equal to FC. Daily rates of NO_3^- leaching ($\text{mg NO}_3^- \text{-N d}^{-1}$) during the growing season were determined as the product of D and daily NO_3^- concentrations, which were estimated using linear interpolation of weekly NO_3^- concentrations measured in lysimeter water samples as described above.

Yield and Plant Nitrogen Content

After physiological maturity, corn ears were harvested from a distance of 1.5 m in the middle two rows of each sub-plot. Ears were dried, shelled, and further dried for 3 d at 65°C and weighed to obtain dry grain and cob yield. Stover was collected by cutting six plants just above their crowns where corn ears were harvested. Stover was weighed, and the six plants from each sub-plot were subsampled and ground, weighed and then dried for moisture content determination. Grain and stover samples were further ground with a grinding mill and analyzed with an elemental N combustion analyzer (VarioEL; Elementar, Hanau, Germany) for total above-ground N.

Soil Physical and Chemical Properties

Soil temperature was measured on each N_2O flux measurement day using temperature probes (Fisher, Hampton, NH) inserted to the 0.05-m depth within 1 m of the chambers. Soil water content and bulk density were determined on samples collected from control and split-U plots in both IRG and DRY treatments to the 0.05-m depth within 1 hr of each flux measurement period by drying at 105°C. Bulk density values

were used together with gravimetric water content to estimate water-filled pore space (WFPS). Soil moisture sensors (6450WD, Spectrum Technologies, Inc.) were installed at depths of 0.3 m and 1.2 m in one sub-plot of IRG and DRY plots. Probes were connected to a datalogger (3345WD, Spectrum Technologies, Inc.) from which high frequency (every 10 min) data were collected and daily averages were calculated. These data are not presented, but were used in determining when DRY plots should be irrigated to prevent extreme water stress and crop failure.

Additional soil samples to a depth of 0.6 m were collected at the end of the season (post-harvest) for analysis of extractable inorganic N. Two cores from each subplot were pooled, homogenized, and refrigerated before analysis. Subsamples of ~ 10 g were extracted in 2 M KCl, filtered (Whatman no. 42), and analyzed for ammonium (NH_4^+) and NO_3^- using a flow-through injection colorimetric analyzer (Lachat, Loveland, CO).

Data Analysis and Statistics

Nitrous oxide fluxes measured on each sampling date for each subplot were used to estimate cumulative area-based direct N_2O emissions (hereafter, N_2O emissions refer to direct soil-to-atmosphere emissions, unless mentioned otherwise) using trapezoidal integration of flux versus time. The fertilizer-induced emissions factor (FIEF) (%) was calculated by subtracting cumulative area-based N_2O emissions in the control treatment from that in each N treatment and then expressing the result as a percentage of the total amount of fertilizer N applied (180 kg N ha^{-1}). Yield-based N_2O emissions (g N Mg^{-1} yield) were calculated by dividing cumulative area-based N_2O emissions by grain yield. Nitrogen fertilizer recovery efficiency was calculated by subtracting the total

aboveground N uptake in the control treatment from that in each N treatment and expressing the result as a percentage of the total fertilizer N applied.

Cumulative NO_3^- leaching ($\text{kg NO}_3^- \text{-N ha}^{-1}$) was estimated by summing daily rates of NO_3^- leaching. A fertilizer-induced leaching factor (FILF) (%) was calculated by subtracting cumulative NO_3^- leaching in the control treatment from that in each N treatment and by expressing the result as a percentage of the total fertilizer N applied. Yield-based NO_3^- leaching was calculated by dividing cumulative NO_3^- leaching by grain yield. Indirect N_2O emissions due to NO_3^- leaching were estimated by multiplying the cumulative NO_3^- leaching by emission factors ($\text{EF}_5 = 0.05, 0.75$ and 2.5%) which represent the lower limit of the 95% confidence interval (CI), the best estimate, and the upper limit of the 95% CI, respectively, based on the Intergovernmental Panel on Climate Change (IPCC) Guidelines for Greenhouse Gas Inventories (De Klein et al., 2006). The EF_5 value represents the percentage of leached NO_3^- that subsequently converts to N_2O in groundwater, surface drainage, rivers and estuaries. Indirect N_2O emissions were added to direct N_2O emissions from the same subplots to estimate DI N_2O emissions.

Effects of year, irrigation, and N source treatments were determined using Proc Mixed in SAS with block, block-by-year, and block-by-year-by-irrigation treated as random effects and fertilizer, irrigation and year as fixed effects (Littell et al., 2006; SAS, 2003). When the main effect was significant, means comparisons were conducted using contrasts in SAS with significance criteria of $P < 0.05$, unless otherwise mentioned.

Results

Climate, Soil Moisture and Drainage

Total precipitation amounts during 1 Apr through 31 Oct in 2009 and 2010 were 532 mm and 732 mm, respectively, with the latter being greater than the 30-yr average (531 mm) by 38% (Figure 1-1). Monthly rainfall patterns also varied between years. In 2009, precipitation from 1 Apr until 1 Jul was 208 mm whereas in 2010 it was 458 mm. Irrigation was the equivalent of 41% of total water inputs in IRG plots in 2009, compared with 27% in 2010. Irrigation was the equivalent of 6 and 2% of total water inputs in the DRY plots in 2009 and 2010 respectively. Irrigation was applied to DRY plots on 13 Jul (13 mm), 15 Jul (8 mm) and 3 Aug (15 mm) in 2009, and 15 Jul (18 mm) in 2010. Total seasonal drainage in IRG and DRY plots was the equivalent of 46% and 14% of respective total water inputs in the growing season in 2009 and 64% and 54% in 2010 (Figure 1-1a, b). Mean daily temperature in 2010 was 17.4°C compared with 15.8°C in 2009 (Figure 1-2a). Soil WFPS at the time of N₂O flux sampling was below 70% throughout the seasons in both years (Figure 1-2b). Mean soil WFPS was 30 and 40% in IRG plots in 2009 and 2010, respectively, compared to 22 and 30% in DRY plots.

Agronomic Responses

Averaged across N sources, grain yield was greater in 2009 than in 2010 and in IRG than in DRY treatment (Table 1-2). Averaged across years and irrigation treatments, yield was greater with all three N sources than the control, and was significantly greater with split-U than with PCU or IU (Table 1-2).

The 3-way interaction effect of year, irrigation and N source was significant for above-ground N uptake and NFRE (Table 1-2). Above-ground N uptake was greater in IRG plots than in DRY in 2010 for all the N sources, including the control whereas in

2009, it held true only for the split-U (Table 1-3). Above-ground N uptake was always greater in split-U than in any other N treatments in both IRG and DRY plots each year. In 2010, NFRE did not differ by irrigation for any of N sources and split-U had greater NFRE than PCU or IU in both IRG and DRY treatments. In 2009, NFRE was greater in DRY than in IRG treatment for PCU and IU but the reverse was true for split-U.

Direct Nitrous Oxide Emissions

During each growing season, fluxes greater than $20 \mu\text{g N m}^{-2} \text{h}^{-1}$ were observed in the months of May, Jun, and Jul (Figure 1-3). There was no significant difference in area-based N_2O emissions by year or irrigation (Table 1-2). Cumulative area-based N_2O emissions were greater in all fertilized treatments than in the control. Among fertilized treatments, area-based N_2O emissions were significantly greater with PCU than with IU or split-U (Table 1-2). There was also a trend ($P = 0.08$) for greater emissions with split-U than with IU.

When N_2O emissions were expressed per unit of grain yield, there was a significant 3-way interaction effect of year, irrigation and N source (Table 1-2). Yield-based direct emissions were greater in DRY treatment than in IRG in 2010 for the control and PCU treatments. This trend was not observed in 2009 (Table 1-3). The control treatment in IRG plots in 2010 had greater yield-based N_2O emissions than any other N sources in both irrigation systems (Table 1-3). The FIEF did not differ by year or irrigation (Table 1-2). Among N sources, the FIEF with PCU was significantly greater than with IU or split-U. There was a trend ($P = 0.09$) for greater FIEF with split-U than with IU.

Nitrate Leaching

Soil–water NO_3^- concentrations varied over the season from <1 to 63 mg N L^{-1} , and all fertilized treatments had their maximum soil–water NO_3^- concentrations in the IRG plots in 2009 (Figure 1-4). In each season, NO_3^- concentrations seemed to level to baseline at the beginning of Sept, except for PCU, which had NO_3^- concentrations as high as 29 mg N L^{-1} in DRY plots in Sept – Oct 2010. The Jun–Aug period accounted for 60 – 98% of total amount of NO_3^- leached during the season each year, except for DRY plots in 2009 where cumulative leaching during the season was about only 2 kg N ha^{-1} . Averaged across N sources, cumulative NO_3^- leaching varied significantly by year (2010 $>$ 2009) and irrigation (IRG $>$ DRY) (Table 1-2). The PCU and IU treatments had greater cumulative NO_3^- leaching than the control while among fertilized treatments PCU had greater cumulative NO_3^- leaching than split–U (Table 1-2).

When NO_3^- leaching was expressed per grain yield, there was a 3–way interaction effect of year, irrigation and N source (Table 1-2). Yield–based NO_3^- leaching was greater in DRY treatments than in IRG in 2010 for the control and PCU treatments. This trend was not observed in 2009 (Table 1-3). The FILF was significantly different by year (2010 $>$ 2009) at $P = 0.07$ and by irrigation (IRG $>$ DRY) at $P = 0.08$ (Table 1-2). The FILF was not affected by N sources at $P = 0.05$, but there was a trend for greater FILF with PCU compared with split–U ($P = 0.10$) and greater FILF with IU compared with split–U ($P = 0.12$).

Direct plus Indirect Nitrous Oxide Emissions

Figure 1-5 shows DI N₂O emissions in three different scenarios of indirect emissions estimated using EF₅ of 0.05% (lower limit), 0.75% (default value) and 2.5% (upper limit). At EF₅ of 0.05%, indirect emissions accounted only for 5–8% of DI emissions while at EF₅ of 0.75% and 2.5%, indirect emissions accounted for 44–54% and 73–80% of DI emissions respectively. Averaged across years and irrigation treatments, fertilized treatments always had greater DI emissions than the control at all EF₅ values. At EF₅ of 0.05% and 0.75%, PCU had significantly greater DI emissions than IU or split-U whereas fertilized treatments did not differ in DI emissions at EF₅ of 2.5%. At EF₅ of 0.05%, DI emissions did not differ by year or irrigation. At EF₅ of 0.75% and 2.5%, DI emissions were greater in 2010 than in 2009 and in IRG treatment than in DRY.

Post-harvest Soil N and Soil-Water NO₃⁻ in the spring

Soil profile of 0–0.6 m had greater residual NO₃⁻ and less residual NH₄⁺ (post-harvest) in 2009 than in 2010. Total residual soil N (NO₃⁻ + NH₄⁺) did not differ by year but was greater in DRY than in IRG treatment. There was no significant N source effect on residual soil N, individually or together. Mean NO₃⁻ concentration in soil water sampled in early spring the year following corn harvest differed by year (2009 > 2010) and by irrigation (DRY > IRG). There was no difference in NO₃⁻ concentration in spring soil water among fertilized treatments.

Discussion

Direct Nitrous Oxide Emissions

Averaged across all N sources and both years, there was no significant irrigation effect on area-based N₂O emissions. To our knowledge, there is only one study that compared N₂O emissions in irrigated and non-irrigated systems. Horvath et al. (2010) reported that area-based N₂O emissions from irrigated plots were 70% greater than from non-irrigated plots in a loess soil in a drier than normal year with WFPS in irrigated plots almost twice that in non-irrigated plots (87 vs. 47%). In a normal year, Horvath et al. (2010) observed mean WFPS in irrigated and non-irrigated plots differed by only 5% (61 vs. 56%) with no irrigation effect on N₂O emissions. In the current study, the difference in mean WFPS under regular and minimal irrigation was within 10%. This small difference in WFPS may have been the reason why the effect of irrigation on area-based emissions was not significant.

Averaged over years and irrigation, IU or PCU did not reduce area-based N₂O emissions compared to split-U, instead, PCU had greater emissions than with split-U. However, it is important to note that unlike PCU or IU, which was applied pre-plant and all in one application, split-U was applied two times in the DRY plots and three times in the IRG plots. When all N sources were applied in the same manner (one-time application and at same time), many studies have shown that compared to urea, PCU and/or IU reduced N₂O emissions (Halvorson et al., 2010; 2013; Jumadi et al., 2008; Delgado and Mosier, 1996). Limited or no effectiveness of these products has been reported in other studies (Sistani et al., 2011; Venterea et al., 2011). Different N management practices such as timing of N application (post-emergence application in case of Venterea et al., 2011), or application method itself (surface broadcast without incorporation as in Sistani et al., 2011) may limit the effectiveness of PCU or IU in

mitigating N₂O emissions. Site specific conditions and climate conditions may also explain some differences observed in their effectiveness in mitigating emissions. These products are designed to release N more gradually over the course of the season compared with urea in order to minimize N susceptibility to loss and improve synchrony between soil N availability and crop N demand. Soluble urea, when split-applied, also serves the same purpose and as was observed in the current study, performed better than PCU in relation to mitigating N₂O emissions. However, there was still a trend ($P=0.08$) for greater emission in split-U than with IU. This result signifies that even though split-U reduced emissions compared to PCU, onetime pre-plant application of IU can be an alternative to labor-intensive and time-consuming split-U in terms of mitigating N₂O emissions.

The IU treatment significantly reduced N₂O emissions compared to PCU. Similar results were reported by Venterea et al (2011) in a rain-fed corn and Halvorson et al (2011; 2010) in irrigated corn. These observations suggest that the chemical inhibition of urea hydrolysis and nitrification in the IU treatment is more effective than physical inhibition of N release in the PCU treatment in reducing N₂O emissions.

The FIEF was in the range of 0.04 – 0.11 % which is lower than that reported in other studies, which is close to 1% (Stehfest and Bouwman, 2006; Akiyama et al., 2006). Default emission factor published in IPCC guidelines for national greenhouse gas inventories to estimate N₂O emissions from managed soils is also 1% but has a wide variability (95% CI = 0.3 – 3 %). The mean growing season area-based N₂O emissions in the current study were only 0.30 and 0.31 kg N ha⁻¹ for IRG and DRY treatments respectively. Linn and Doran (1984) noted linear relationship for N₂O production with WFPS at values between 30% and 70%, and WFPS values in the current study were

towards the lower end of the range (30 – 70%) most of the season. Accumulation of nitrite (NO_2^-), a precursor to N_2O emissions, is decreased in a low pH soil, as is the case in the current study (pH ~ 5.7 in 1:1 soil and water mixture) and also, when PCU or IU is applied or urea is split-applied (Van Cleemput and Samatar, 1996). The acidic and sandy nature of soil combined with low WFPS and subsequently possible low NO_2^- accumulation might explain low emissions that were observed in the current study. Burton et al (2008) also attributed less N_2O emission (0.5 kg N ha^{-1}) in clay loam soil versus clay (1.8 kg N ha^{-1}) to differences in soil texture and moisture. The composition, abundance and spatial distribution of different functional groups of soil microorganisms may vary by soil types and that can also affect emissions (Inselsbacher et al, 2010). Compared with PCU, IU had a significantly smaller FIEF. This was evident with greater N_2O emissions with the PCU treatment than with the IU.

Nitrate Leaching

Abundant irrigation and/or precipitation can greatly increase NO_3^- leaching especially on sandy soils (Petrovic, 2004; Morton et al., 1988). Timing and intensity of precipitation and irrigation could also be vital and induce greater N loss through NO_3^- leaching. In a rainfall simulation experiment, NO_3^- leaching was shown to be greater after a larger rainfall (pulse of 15 mm on a day) compared with smaller ones (3 pulses of 5 mm each in three consecutive days) (Yahdjian and Sala, 2010). In the current study, there were 12 rainfall events in 2010 that were greater than 20 mm d^{-1} compared with only 6 such rainfall events in 2009. In 2010 when precipitation and total water inputs

were greater than in 2009 by 26% and 5% respectively, NO_3^- leaching correspondingly was significantly greater.

Irrigation had a significant effect on NO_3^- leaching when expressed per unit area. When NO_3^- leaching was expressed per unit yield, there was no effect of irrigation except for the PCU and control treatments in 2010 where DRY treatment had greater yield-based NO_3^- leaching than in IRG (Table 1-3). This, combined with increase in yield with irrigation, indicates that if irrigation is minimized or avoided in fertilized agriculture in sandy soils to reduce N loss through leaching, which is important from the perspective of groundwater contamination, then minimum-irrigated system may generate more NO_3^- leaching in order to grow the same amount of crops as in an irrigated system. In addition to this, post-harvest residual soil N and NO_3^- concentration in water collected in the spring showed that there was greater residual N in soil and subsequently greater potential for post-seasonal NO_3^- leaching in DRY treatments than in IRG. These findings support the conclusion that similar grain yields would eventually result in greater N loss through leaching in DRY treatment than in IRG.

Venterea and Hyatt (2011) reported no difference in NO_3^- leaching under split-U and PCU (with two different polymer formulations) in irrigated potato production in the same research station where the current study was conducted. However, one type of PCU still had greater residual soil N and greater soil-water NO_3^- concentration in the following spring, which suggested possible greater total (seasonal plus post-season) NO_3^- leaching in that PCU treatment compared to split-U. Total N applied was also higher than in the current study (270 kg N ha^{-1} versus 180 kg N ha^{-1}) and thus, the advantages of split-U compared to PCU that were observed in the current study could

have been minimized in their study. In a field experiment on a permanent pasture, Zaman et al (2008) found urea with only urease inhibitor or with both urease and nitrification inhibitors (as in IU in the current study) reduced NO_3^- leaching compared to urea alone. Diez et al (2010) also reported significantly lower NO_3^- leaching with the use of DCD with a traditional N source. In the current study, greater NO_3^- leaching with PCU than with split-U and the trend for greater NO_3^- leaching with IU compared with split-U, were most likely due to better synchrony of N application with crop demand with split-U.

Direct plus Indirect Nitrous Oxide Emissions

At EF_5 of 0.05% and 0.75%, estimated DI N_2O emissions were significantly greater with PCU than with IU or split-U. The same fertilizer effect was observed for direct N_2O emissions. Indirect N_2O emissions due to NO_3^- leaching accounted for > 50% of DI emissions at EF_5 2.5%. Therefore, the irrigation effect on NO_3^- leaching was carried over to DI emissions. These estimates show how indirect emissions due to NO_3^- leaching can be significant in N_2O inventory and cannot be ignored. However, there is a wide range of uncertainty in currently available emission factors for estimating indirect emissions and there is a great need of improvement.

In addition to NO_3^- leaching, other possible sources of indirect N_2O emissions include NH_3 volatilization and NO_x flux which were not measured here (IPCC, 2006). Incorporation of urea mechanically or with water (rain or irrigation) is recommended to reduce NH_3 volatilization (Dawar et al., 2011; Rochette et al., 2001). Field studies have reported the effectiveness of PCU and IU in reducing NH_3 volatilization loss (Connel et

al., 2011; Rochette et al., 2009). The default IPCC emission factor of 1% to estimate indirect N₂O emission due to NH₃ volatilization loss plus NO_x flux also has a high uncertainty (0.2 – 5%) (De Klein et al., 2006). Hence, more robust studies are needed that include all N losses and estimate what fraction of those N losses convert into N₂O within the receiving ecosystems.

Agronomic Responses

Grain yields were significantly greater in 2009 than in 2010. More precipitation and more frequent big pulses of precipitation and subsequently, greater NO₃⁻ leaching in 2010 than in previous year, apparently affected yield. Similar results were reported by Errebhi et al. (1998) for irrigated potato. Grain yields were significantly greater in IRG plots compared to DRY plots as reported in other studies (Simsek et al., 2011; Yi et al., 2011; Follett et al., 1978). Since irrigation was well-timed as per crop need according to the checkbook method, it ensured water availability based on crop need during the season and had a positive effect on agronomic responses. Yields were significantly greater with split-U compared with PCU or IU. Our study plots also had sub-plots where urea was also applied as a single pre-plant application and had significantly lower grain yields (8.6 Mg ha⁻¹ and 5.8 Mg ha⁻¹ in IRG and DRY treatments respectively) than with pre-plant PCU or IU (unpublished data). Therefore, split applications of N fertilizer appear to be an effective practice for increasing agronomic responses (Rosen and Bierman, 2008; Abdin et al., 1996).

Plant N uptake is generally considered to be a function of soil water status (Djaman et al., 2013) and in the current study, IRG treatment had greater above-ground

N uptake than in DRY in 2010 and for split-U in 2009. However, there was no irrigation effect on N uptake in 2009 for the control, PCU, and IU treatments. Buljovic and Engels (2001) reported that N uptake by maize was not affected at moderate levels of soil drought (10% w/w water content). Plant N uptake can sometimes be more dependent on applied N than water supply (Pandey et al., 2000). In this study, no irrigation effect on N uptake in the control, PCU, and IU treatments in 2009 was observed due to greater N concentration in grain in DRY treatments than in IRG. Hons et al (1986) also noted that a sorghum cultivar that produced less biomass had higher nutrient concentrations and vice-versa. In the current study, irrigation increased grain yield but decreased N concentrations in grain. A positive irrigation effect on N uptake was observed for all N treatments in 2010 and for split-U in 2009 because of the significant increase in biomass yields (26 – 49 %) rather than N concentrations in biomass. In 2009, since biomass yields for the control, PCU, and IU treatments in IRG treatments were greater than in DRY by < 14 % (compared to 26–49% above-mentioned), and N concentration in grain was greater in DRY than in IRG treatments, there was no irrigation effect on N uptake.

In 2010, NFRE did not differ by irrigation while in 2009, NFRE were greater in DRY treatment than in IRG for the PCU and IU treatments and the reverse was observed for split-U. Nitrogen fertilizer recovery efficiency was calculated based on differences in above-ground N uptake in fertilized plots and that in the control. That would make it possible that NFRE was greater in DRY treatments than in IRG in some cases as above-ground N uptake for the control treatment in DRY treatment was almost half of that in IRG.

Conclusions

In the current study, urea was split applied whereas PCU and IU were applied as a single pre-plant application. Thus, the greater N_2O and NO_3^- losses observed with PCU and the lower NFRE observed with both PCU and IU compared with split-U need to be interpreted with this in mind. Another important finding of this study was that irrigation did not increase and in some cases decreased N_2O and NO_3^- losses when emissions were expressed on a yield-basis. This result points out the limitations of reporting environmental impacts of agricultural practices only on an area-scaled basis. Depending on the value of EF_5 assumed to account for off-site conversion of NO_3^- to N_2O , estimated indirect N_2O emissions due to NO_3^- leaching accounted for 5 to 80% of total (direct plus indirect) N_2O emissions. The wide range and high upper limit of these estimates point out the need for improved methods of quantifying indirect N_2O emissions in evaluating management effects on total greenhouse gas budgets.

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Table 1-1: Date, source and amount of fertilizer application.

Date	Year	Irrigation treatment †	N source ‡	N applied (kg N ha ⁻¹)
May 1	2009	IRG, DRY	PCU, IU	180
May 8	2009	IRG, DRY	Starter	6
May 28	2009	IRG, DRY	split-U	90
Jun 17	2009	DRY	split-U	90
Jun 17	2009	IRG	split-U	56
Jul 13	2009	IRG	split-U	34
Apr 23	2010	IRG, DRY	PCU, IU	180
Apr 26	2010	IRG, DRY	Starter	6
May 26	2010	IRG, DRY	split-U	90
Jun 9	2010	DRY	split-U	90
Jun 9	2010	IRG	split-U	56
Jul 8	2010	IRG	split-U	34

† Irrigation treatment included irrigated (IRG) and minimum-irrigated (DRY)

‡ N source included Starter as (10-34-0), PCU (Polymer-coated urea), IU (stabilized urea with chemical inhibitors), and split-U (split-applied urea); the third application of the split-U in the IRG plots was applied as urea ammonium nitrate to simulate a fertigation.

Table 1-2: Results of statistical analyses with mean (standard error) for different dependent variables as affected by year, irrigation and N sources.

Source of Effects	Grain Yield (Mg ha ⁻¹)	Above-ground N Uptake (kg N ha ⁻¹)	NFRE † (%)	N ₂ O emissions (kg N ha ⁻¹)	Yield-scaled N ₂ O emissions (g N Mg ⁻¹ grain)	FIEF † (%)	NO ₃ leaching (kg N ha ⁻¹)	Yield-scaled NO ₃ leaching (kg N Mg ⁻¹ grain)	FILF † (%)
Year (Y)									
2009	9.8 (0.5) a	143.9 (9.6) a	64.2 (2.7) a	0.33 (0.02)	30.3 (1.6)	0.08 (0.01)	15.8 (2.8) b	1.6 (0.3) b	4.5 (1.3)
2010	7.7 (0.6) b	114.5 (8.6) b	50.0 (3.1) b	0.28 (0.02)	47.4 (6.7)	0.07 (0.01)	30.3 (2.8) a	5.0 (0.7) a	8.5 (2.0)
<i>Significance</i>	**	**	*	NS	<i>P</i> = 0.07	NS	*	**	<i>P</i> = 0.07
Irrigation † (I)									
IRG	10.2 (0.5) a	139.5 (8.8) a	55.2 (3.3)	0.30 (0.02)	30.3 (1.6) b	0.08 (0.01)	30.6 (2.1) a	3.1 (0.2)	8.4 (1.4)
DRY	7.4 (0.6) b	118.9 (9.9) b	59.0 (3.2)	0.31 (0.02)	52.5 (6.4) a	0.07 (0.01)	15.5 (3.3) b	3.4 (0.9)	4.6 (2.0)
<i>Significance</i>	***	**	NS	NS	**	NS	**	NS	<i>P</i> = 0.08
N sources ‡ (N)									
Control	4.4 (0.4) c	52.1 (4.7) c	–	0.20 (0.01) c	61.5 (11.8) a	–	14.6 (2.3) c	5.0 (1.4) a	–
PCU	9.9 (0.5) b	147.2 (7.0) b	52.8 (3.9) b	0.41 (0.03) a	42.5 (4.3) b	0.11 (0.02) a	29.7 (5.7) a	3.3 (0.8) b	8.7 (2.9)
IU	9.8 (0.6) b	146.6 (8.7) b	52.5 (4.2) b	0.28 (0.02) b	30.0 (2.8) c	0.04 (0.01) b	26.8 (4.8) ab	2.8 (0.5) b	6.9 (1.9)
Split-U	11.0 (0.6) a	170.9 (6.8) a	66.0 (3.0) a	0.34 (0.03) b	31.6 (2.4) bc	0.07 (0.01) ab	21.0 (3.3) bc	2.0 (0.4) b	3.9 (1.0)
<i>Significance</i>	***	***	***	***	***	**	**	**	NS
Interaction									
N × Y	NS	***	**	NS	*	NS	NS	*	NS
N × I	NS	**	**	NS	**	NS	NS	NS	NS
N × Y × I	NS	**	**	NS	*	NS	NS	*	NS

† Irrigation treatment included irrigated (IRG) and minimal-irrigated (DRY)

‡ N source included Starter as (10–34–0), PCU (Polymer-coated urea), IU (urea with inhibitors), and split-U (split-applied urea)

*** Significant at *P* < 0.001, ** at *P* < 0.01, * at *P* < 0.05 and NS – not significant

† NFRE – Nitrogen fertilizer recovery efficiency, FIEF – Fertilizer-induced emission factor, FILF – Fertilizer-induced leaching factor

Table 1-3: Means (standard error) for variables where significant 3-way interaction effect of year, irrigation and N source were found.

N sources	2009		2010	
	IRG	DRY	IRG	DRY
Above-ground N uptake (kg N ha⁻¹)				
Control	65.2 (8.2) f	49.5 (12.8) fg	64.9 (14.3) f	29.0 (11.7) g
PCU	160.8 (8.3) bc	179.0 (9.6) ab	136.3 (25.2) d	112.6 (6.7) e
IU	162.1 (8.4) bc	181.7 (3.0) ab	145.8 (25.2) cd	97.0 (12.5) e
split-U	199.4 (28.0) a	154.0 (22.0) cd	181.7 (3.1) ab	148.6 (13.1) cd
NFRE † (%)				
Control	–	–	–	–
PCU	43.7 (6.6) cdef	72.0 (6.1) ab	39.7 (15.0) ef	46.4 (7.3) def
IU	53.1 (6.3) cde	73.5 (8.7) ab	44.9 (13.1) def	37.8 (13.0) f
split-U	74.5 (16.0) a	58.1 (12.9) bcd	64.9 (9.5) abc	66.4 (5.3) abc
Yield-scaled direct N₂O emissions (g N kg⁻¹)				
Control	35.9 (1.8) bcd	52.3 (16.8) bc	31.9 (11.4) cd	126.1 (55.2) a
PCU	37.7 (7.8) bcd	39.4 (6.8) bcd	32.9 (6.40) cd	60.2 (27.7) b
IU	27.5 (9.8) cd	24.3 (7.7) d	25.9 (9.2) d	42.2 (9.7) bcd
split-U	29.4 (11.0) cd	36.7 (4.6) bcd	21.3 (4.0) d	39.1 (7.1) bcd
Yield-scaled NO₃ leaching (g N Mg⁻¹)				
Control	3.2 (0.7) cdef	0.4 (0.1) def	4.0 (0.6) bc	12.3 (3.4) a
PCU	3.0 (0.4) cdef	0.2 (0.1) ef	3.3 (0.5) cde	6.8 (2.2) b
IU	3.0 (0.7) cdef	0.4 (0.1) def	4.3 (0.7) bc	3.7 (0.9) bc
split-U	2.1 (0.2) cdef	0.1 (0.1) f	2.3 (0.2) cdef	3.5 (0.7) cd

† Irrigation treatment included irrigated (IRG) and minimal-irrigated (DRY)

‡ N source included PCU (Polymer-coated urea), IU (stabilized urea with chemical inhibitors), and split-U (split-applied urea)

‡ NFRE – Nitrogen fertilizer recovery efficiency

For each variable, means followed by the same letter are not significantly different ($P < 0.05$).

Table 1-4: Results of statistical analyses with mean (standard error) for post-harvest residual soil inorganic N and NO₃⁻ concentration in water sampled in early spring following corn harvest

Source of Effects	Post-harvest soil inorganic N			Water sampled in spring
	NO ₃ ⁻ (kg N ha ⁻¹)	NH ₄ ⁺ (kg N ha ⁻¹)	Total N (kg N ha ⁻¹)	NO ₃ ⁻ concentration (mgNL ⁻¹)
Year				
2009	12.6 (0.7) a	10.8 (0.9) b	23.4 (1.3)	10.5 (0.7) a
2010	7.6 (0.3) b	25.2 (1.4) a	32.8 (1.4)	5.3 (0.4) b
<i>Significance</i>	*	*	<i>P</i> = 0.06	*
Irrigation†				
IRG	9.7 (0.7)	16.7 (1.6)	26.4 (1.4)	7.1 (0.5)
DRY	10.4 (0.7)	19.3 (1.9)	29.8 (1.7)	8.7 (0.9)
<i>Significance</i>	NS	NS	<i>P</i> = 0.06	<i>P</i> = 0.07
N sources‡				
Control	9.5 (1.2)	18.3 (2.3)	27.7 (2.2)	6.4 (0.8)
PCU	11.1 (1.2)	17.4 (2.0)	28.5 (1.6)	8.4 (1.5)
IU	9.8 (0.7)	17.2 (2.5)	27.1 (2.0)	8.5 (1.0)
Split-U	9.9 (0.8)	19.1 (3.1)	29.0 (3.1)	8.2 (0.6)
<i>Significance</i>	NS	NS	NS	NS

† Irrigation treatment included irrigated (IRG) and minimal-irrigated (DRY)

‡ N source included Starter as (10-34-0), PCU (Polymer-coated urea), IU (stabilized urea with chemical inhibitors), and split-U (split-applied urea)

‡ For each variable, means followed by the same letter are not significantly different (*P* < 0.05).

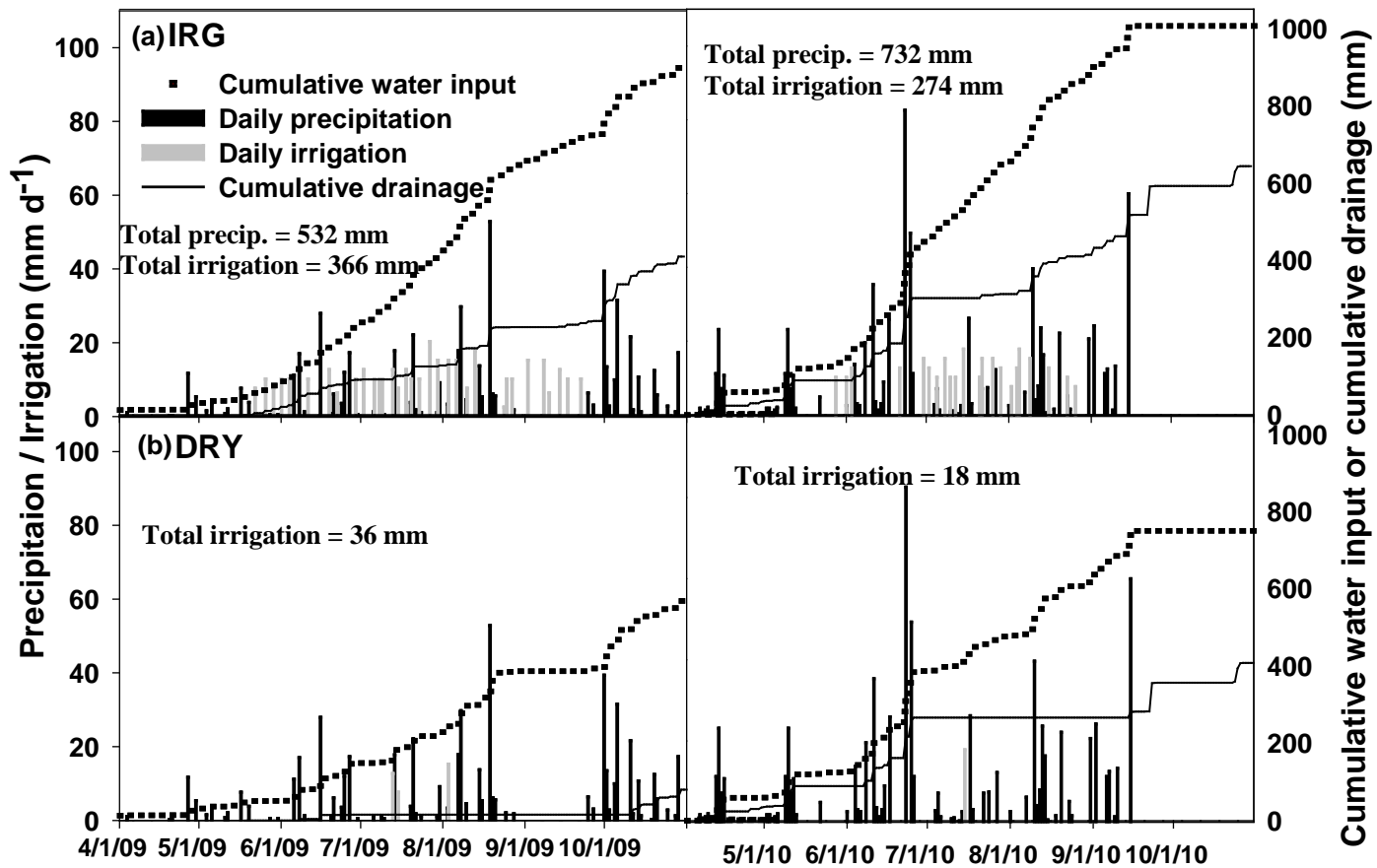


Figure 1-1: Daily irrigation and cumulative water input and drainage in IRG and DRY plots during 2009 and 2010.

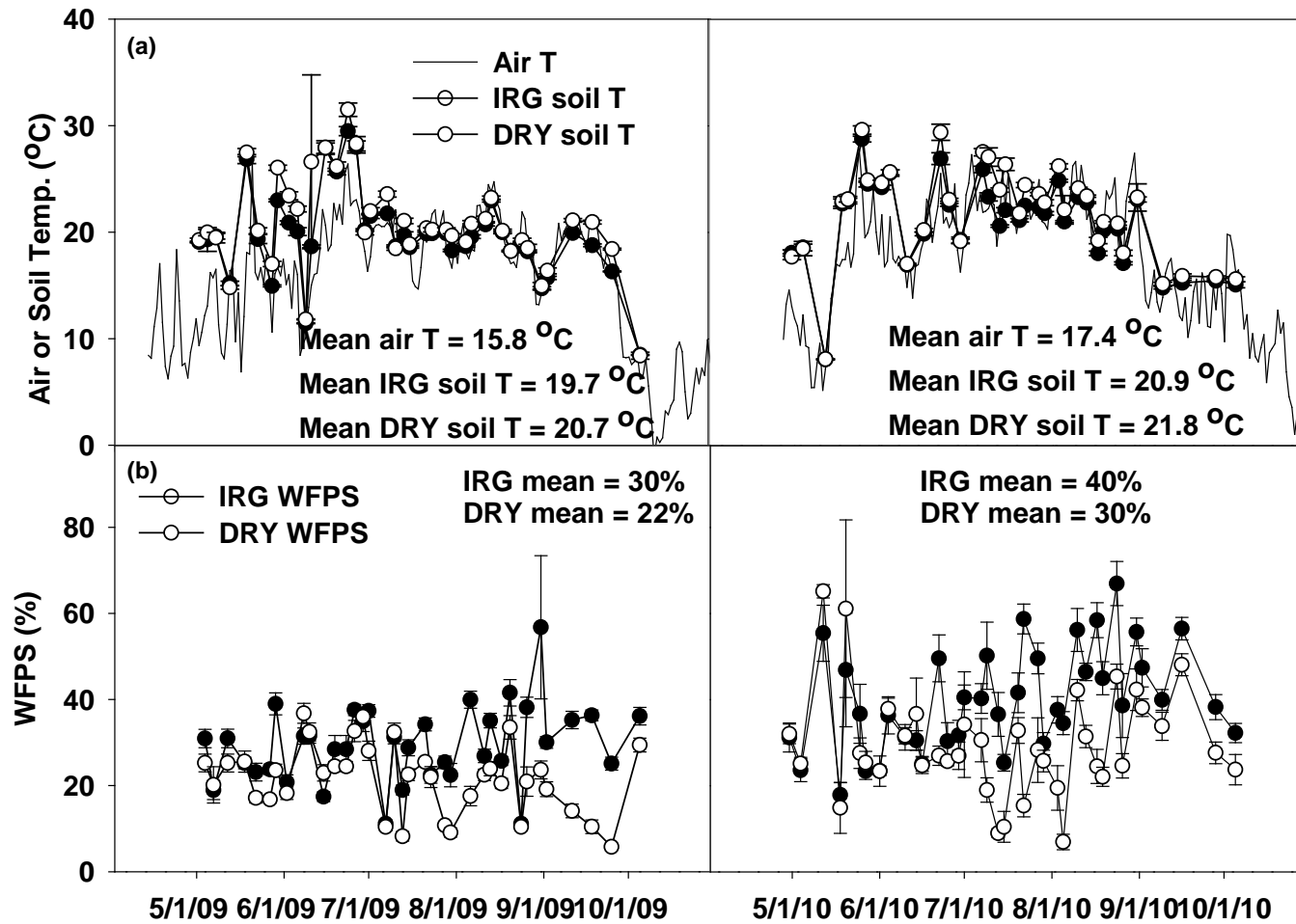


Figure 1-2: (a) Air temperature and mean (standard error) soil temperature, and (b) mean (standard error) water-filled pore space (WFPS) at the 0.05-m depth at the time of N₂O sampling in IRG and DRY plots during 2009 and 2010.

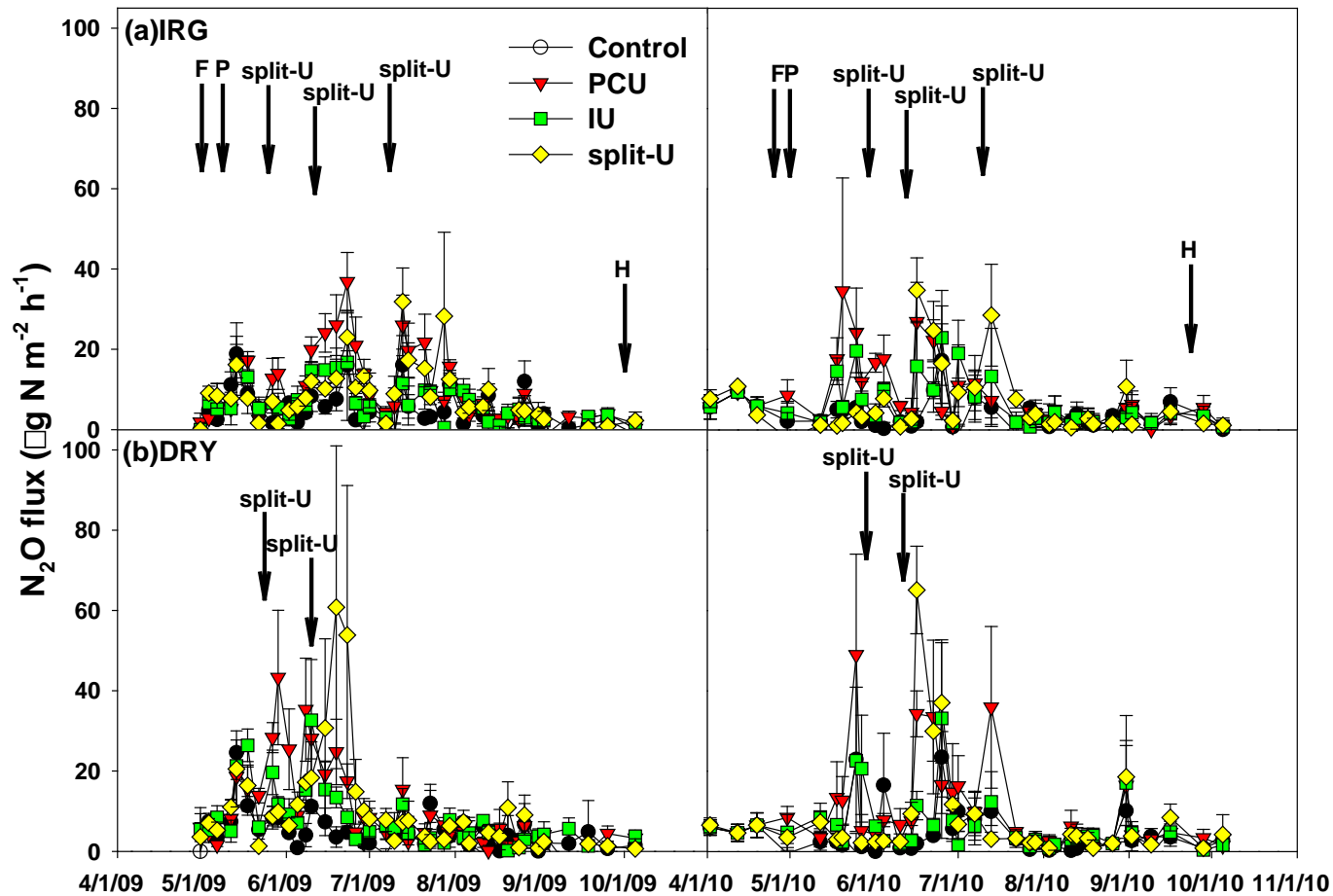


Figure 1-3: Mean (standard error) N_2O emissions in IRG and DRY plots under different N sources; no N (control), polymer-coated urea (PCU), stabilized urea with inhibitors (IU) and split conventional urea (split-U) during (a) 2009 and (b) 2010. Downward-pointing arrows indicate dates of Planting (P), split-U application (split-U) and PCU/IU fertilizer application (F) and harvest (H).

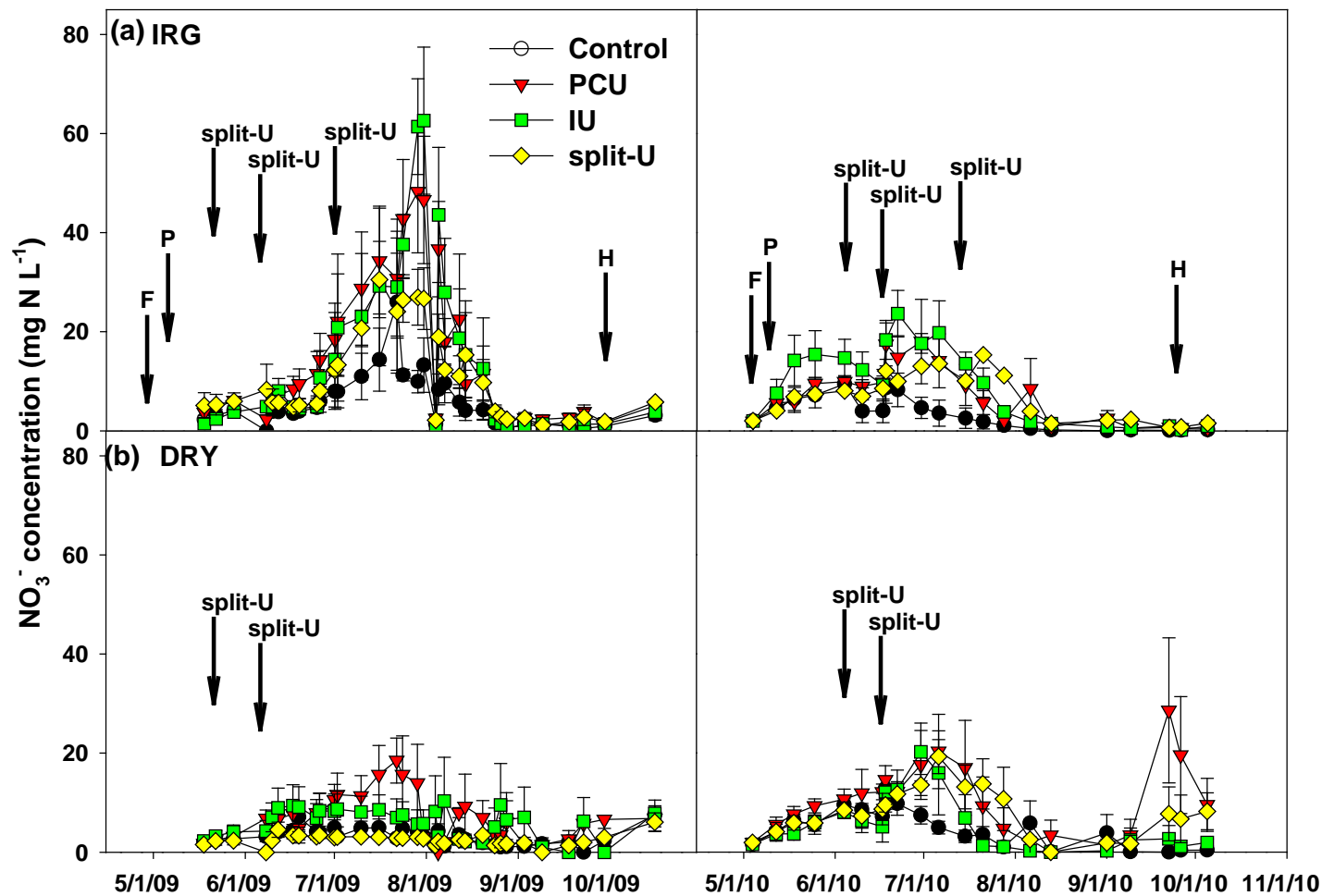


Figure 1-4: Daily mean (standard error) NO_3^- concentrations in lysimeter water samples in IRG and DRY plots under different N sources; no N (control), polymer-coated urea (PCU), stabilized urea with inhibitors (IU) and split conventional urea (split-U) during (a) 2009 and (b) 2010. Downward-pointing arrows indicate dates of Planting (P), split-U application (split-U) and fertilizer application other than split-U (F) and harvest (H).

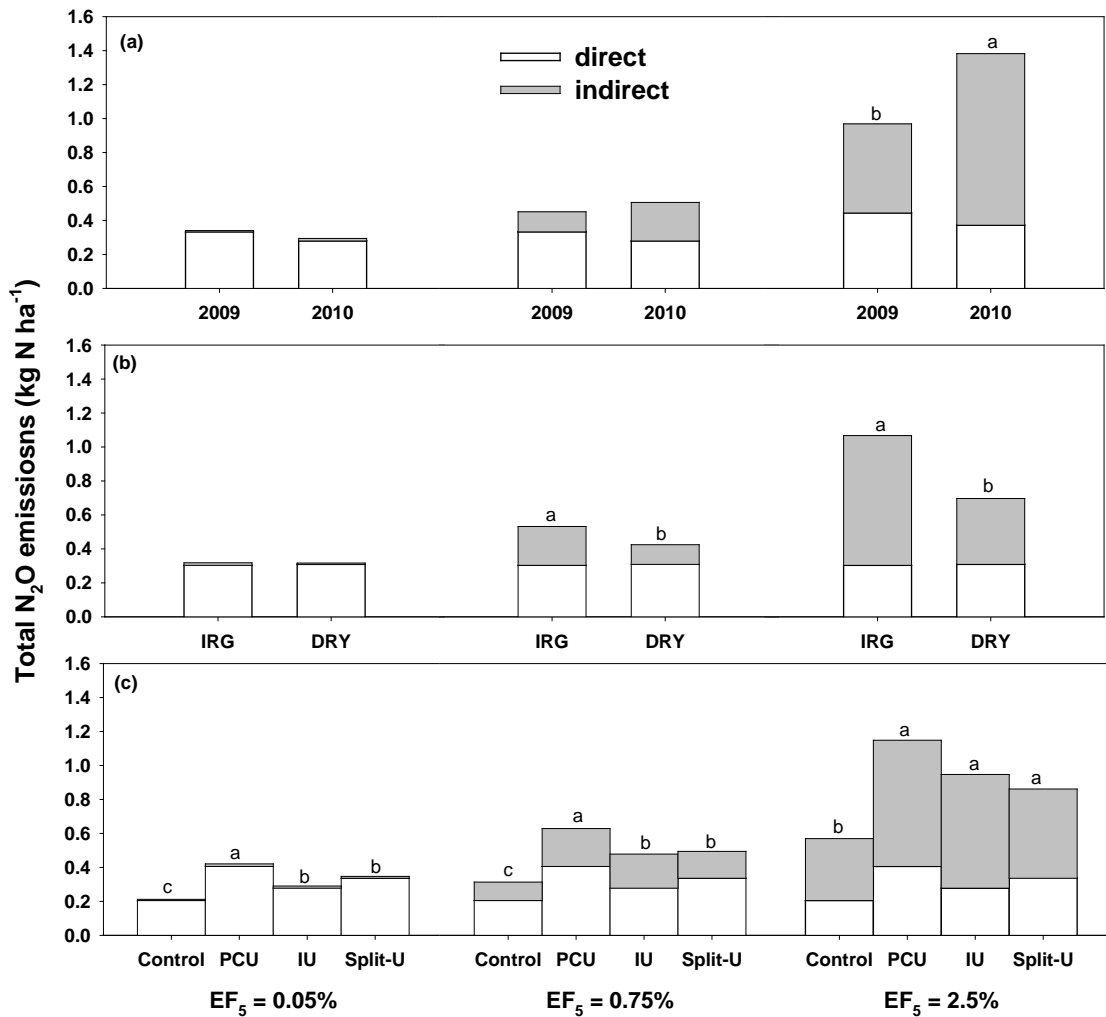


Figure 1-5: Mean total (direct plus indirect) N_2O emissions estimated using different default IPCC published emission factors (EF_5) of 0.05%, 0.75 % and 2.5% by (a) year, (b) irrigation, and (c) N sources; no N (control), polymer-coated urea (PCU), stabilized urea with inhibitors (IU) and split conventional urea (split-U) during 2009 and 2010 by. For each EF_5 values, bars having the same letter are not significantly different ($P < 0.05$).

Chapter 2 – Nitrous oxide emissions and nitrate leaching potential under shallow and deep application of anhydrous ammonia in different tillage systems

Anhydrous ammonia (AA) is a major N source in agriculture and the understanding of its management effect on agronomic production and nitrous oxide (N₂O) emissions can be important in greenhouse gas (GHG) mitigation efforts. Nitrous oxide is not only a potent GHG but also a major stratospheric ozone depleter, and constitutes more than half of total GHG emissions from agriculture. A 2-yr field study was conducted to compare effects of AA placement depths on N₂O emissions, nitrate (NO₃⁻) leaching potential and grain yield in conventional tillage (CT) and no-till (NT) systems. Nitrogen concentrations (nitrite; NO₂⁻ plus nitrate; NO₃⁻) in monthly soil and weekly soil-water samples were measured to estimate time-weighted soil and soil-water nitrite plus nitrate intensity (NO₂₃I). Nitrous oxide emissions were significantly correlated to soil NO₂₃I ($r^2=0.42$, $P<0.001$). There was an interacting effect of tillage and year on N₂O emissions following AA placement at different depths. No-till significantly increased N₂O emissions in fertilized treatments in a dry year and decreased crop yield in the control treatment only. No significant difference was observed in N₂O emissions, grain yield or NO₃⁻ leaching potential by AA placement depth. However, shift in placement depth affects speed of AA application, tractor-fuel consumption and soil disturbance which can have associated economic and environmental implications. Therefore, a full life-cycle analysis would be required to determine effects of AA placement depth in mitigating GHG emissions.

Abbreviations: AA, anhydrous ammonia; FIEF, fertilizer-induced emission factor; NUE, nitrogen use efficiency; NFRE, nitrogen fertilizer recovery efficiency; CT, conventional tillage; NT, no-tillage; NO₂I, nitrite plus nitrate intensity; NH₄I, ammonium intensity.

Introduction

Nitrous oxide (N₂O) is a major greenhouse gas and also the single most important ozone-depleting emission (Ravishankara et al., 2009). Agricultural activities are responsible for 10-12% of total anthropogenic greenhouse gas emissions (GHG) and more than half of agricultural GHG emissions are derived from N₂O emissions (Smith et al., 2007). Increasing N₂O emissions from agriculture are linked to soil management and application of nitrogen (N) fertilizers. About 46% of all N fertilizers used in US in 2010 were applied to corn (ERS, 2012), and anhydrous ammonia (AA), which contains ~ 82% N, is a major N source in much of the US Corn Belt. In the US, AA accounted for 27% of all N applied in agriculture in 2010 (ERS, 2012). In Minnesota, AA accounts for about 50% of the N applied to corn (Bierman et al., 2012). Hence, management of AA in corn production can potentially play a significant role in total GHG mitigation efforts.

Anhydrous ammonia applicators knife-inject AA in the soil and provide soil closure after injection to hold in AA and minimize soil disturbance. There have been many studies examining timing and optimal depth of application and soil conditions to reduce ammonia (NH₃) volatilization loss during and after AA application (Baker et al., 1959; Stanley and Smith, 1956; Jackson and Change, 1947). A few studies have compared N₂O emissions following AA application and other N sources (Fujinuma et al., 2011; Venterea et al., 2005; Thornton et al., 1996). However, there are just two studies,

so far we know that compared N₂O emissions by AA placement depths (Fujinuma et al., 2011; Breitenbeck and Bremner, 1986) and they have contrasting results.

It is, however, important to consider that N₂O emissions from fertilized treatments can be affected by many other factors, such as soil type, climatic conditions and soil management practices. Conservation tillage or no-till (NT) is a common practice in North America (Vetsch and Randall, 2004) and has shown a number of agronomic benefits (Holland, 2004). However, there is little consensus on how tillage affects N₂O emissions in fertilized treatments. There are studies reporting greater N₂O emissions under reduced tillage or NT compared to conventional tillage (CT) (Liu et al., 2006; Goodroad et al., 1984) and vice-versa (Kessavalou et al., 1998; Jacinthe and Dick, 1997). However, effects of tillage regime on N₂O emissions depend on many other factors, such as climatic conditions, and duration of tillage practices (Six et al., 2004). In a meta-analysis, van Kessel et al (2013) reported that when averaged across all comparisons (239), NT did not alter N₂O emissions compared to CT. In their meta-analysis, van Kessel et al (2013) reported that NT had a lower N₂O emissions compared to CT in humid climates when fertilizers were placed at a depth ≥ 5 cm, but stated a need for further evaluation of N fertilizers such as AA, which are injected in concentrated bands during their deep placement.

Conventional tillage disrupts soil structures and destroys macropores in the tilled layer. In NT moisture is assumed to move more quickly through the soil profile. There have been reports on increased drainage and greater NO₃⁻ concentration in NT leachate (Kanwar et al., 1988; Tyler and Thomas, 1977) and greater NO₃⁻ leaching in NT in a wet year (Byre et al., 2000).

The objective of this study was to examine the effects of long-term (~20 yr) tillage treatments and AA placement depths on area- and yield-based N₂O emissions and agronomic indices (grain yield, N uptake, N fertilizer recovery efficiency [NFRE]) over two growing seasons. Soil-water NO₃⁻ concentration was also measured to compare NO₃⁻ leaching potential in these treatments.

Materials and Methods

Site Description and Experimental Design

The site is located at the University of Minnesota's Outreach, Research, and Education Park in Rosemount, MN (44°45' N, 93°04' W), where the soil is a naturally drained Waukegan silt loam containing 220 g kg⁻¹ sand, 550 g kg⁻¹ silt, and 230 g kg⁻¹ clay in the upper 0.2 m. The 30-year mean annual precipitation and temperature are 834 mm and 7.3°C, respectively (MCWG, 2013).

A 2-yr study (2010 and 2011) was conducted in a long-term study site (since 1990) with a randomized complete block design having crop rotation and tillage intensity as the main treatments. The current experiment studied the corn phase of the corn/soybean rotation at two levels of tillage in 3 reps each. The plots used in 2009 were planted to soybean in 2010 and conversely, the plots used in 2010 were previously planted to soybean. Tillage treatments included (i) conventional tillage (CT), which used fall chisel plowing, or disk-ripping following soybean, with spring pre-plant cultivation before corn and soybean, and (ii) no-till (NT).

Each of three main CT and NT plots was subdivided into three 5-m by 5-m subplots which were assigned randomly to N fertilizers consisting of: (i) AA-d, knife-

injected AA with a target depth of 0.20 m, (ii) AA-s, knife-injected AA with a target depth of 0.10 m, and (iii) a control. Fertilizers were applied at rate of 146 kg N ha⁻¹ (excluding starter) on 3 May in 2010 and 6 May in 2011. Equipment provided by John Deere (Moline, IL) to apply AA was similar to a commercially available AA applicator (Model 2501H, John Deere, Moline, IL) and designed to provide sufficient soil closure after AA injection to minimize NH₃ volatilization loss. Applicators were calibrated to the desired N application rate using trial runs on separate area and verified by load-cell weight measurements. Shallow application was conducted at a faster rate (7-8 mph) compared to deep placement (4 mph). Tractors and applicators were operated by personnel familiar with the equipment.

Corn was planted at a seeding rate of 79,000 seeds ha⁻¹ on 6 May 2010 and on 17 May 2011 using a John Deere model 7100 MaxEmerge planter. A GPS device was used to off-set seed rows away from AA band rows such that AA band rows would be in the middle of two seed rows. Row cleaning coulters were used in the NT treatments to produce a seed bed. Liquid starter fertilizer was applied within 5 cm of the seed row at planting at 4.5, 9.0, and 4.5 kg ha⁻¹ of N, P, and K, respectively.

Nitrous Oxide Emissions

Soil-to-atmosphere N₂O fluxes were measured using static chamber methods (Venterea et al., 2010). In 2010, fluxes were measured starting Apr 1 through Oct 4 and from Apr 7 through Sept 21 in 2011. In both years, fluxes were measured twice a week after fertilizer application until the end of Aug and once a week at other times, for a total of 44 sampling dates in 2010 and 40 in 2011. In 2010, 48% of N₂O flux samplings were

carried out within 24 hrs after precipitation events and 44% in 2011. One stainless steel (SS) chamber anchor (0.50 m × 0.29 m × 0.086 m deep) was installed in each control subplot, centered between corn rows with the short side parallel to the corn row encompassing 70% of the inter-row width. In each fertilized subplot, two SS chamber anchors were installed, adjacent to each other without overlapping. The two chambers together covered ~ 85 % of the inter-row width, which left ~ 0.05 m on either side of corn rows for unrestricted development of the nodal root system. On each sampling day, insulated and vented chamber tops (0.50 m × 0.29 m × 0.102 m high) were secured to anchors with binder clips and samples were collected at 0, 0.5, 1 and 1.5 h using a 12-mL polypropylene syringe. Samples were immediately transferred to glass vials sealed with butyl rubber septa (Alltech, Deerfield, IL) and analyzed within 2 wk using a headspace autosampler (Teledyne Tekmar, Mason, OH) connected to a gas chromatograph (GC) (model 5890, Agilent /Hewlett-Packard, Santa Clara, CA) equipped with an electron capture detector. The equipment was calibrated with analytical grade standards (Scott Specialty Gases, MI) each day when samples were analyzed. Gas concentrations in molar mixing ratios determined by the GC were converted to mass per volume concentrations using ideal gas law and air temperatures at the sampling time. Fluxes of N₂O were calculated from the rate of change of chamber N₂O concentration using methods designed to account for suppression of the surface-atmosphere concentration gradient (Venterea, 2010; 2013).

Soil-water Nitrate Concentrations

Nitrate concentrations in soil-water were determined using suction cup lysimeters installed to a depth of 0.6 m as described by Maharjan et al. (2013). Each lysimeter was constructed of a 0.3-m long polyvinylchloride (PVC) pipe (48-mm internal diameter, I.D.) with one end fitted with epoxy to a round-bottom, 100-kPa high-flow porous ceramic cup (Soilmoisture Equipment Corp., Santa Barbara, CA) and the other end to a rubber stopper. Two sections of 5.35-mm (I.D.) polyethylene tubing were inserted through the rubber stopper: one tube (vent tube) was short and extended inside the lysimeter only to 0.1 m below the stopper, while the other (sample tube) extended to 2 mm above the ceramic cup. The vent and sample tubes were connected to 6-mm (I.D.) Tygon® laboratory tubing equipped with polypropylene ratcheting clamps (Halkey-Roberts Corp., St. Petersburg, FL). Lysimeters under vacuum were submerged in water to fill them with water before installing them.

Each year within a wk of planting, one lysimeter was installed in each control subplot in a corn-planted row and two lysimeters were installed in each fertilized subplot one each in a corn-planted row and in the middle of the inter-row region. A 0.6-m-deep borehole was made using an 83-mm diam. soil auger. Silica flour slurry was added to a depth of 0.1 m before installing lysimeters. Soil was poured back into gap between the lysimeter and sides of the hole in reverse order of its removal from the borehole. At a depth of 0.10 m from lysimeter's upper-end, a 10-mm-thick layer of powdered bentonite was evenly applied around the lysimeter to prevent preferential water flow. Sample and vent tubes were carefully stuck out of soil surface after completely filling in soil over lysimeter. On the following day, water was evacuated from each lysimeter by applying pressure through the vent tube while allowing water to exit the sample tube. Lysimeters

were then prepared for subsequent water sampling by leaving them under vacuum of 40 KPa for 1 wk. Water samples were collected once per wk during the growing season in 50-mL polypropylene vials and stored at -5°C before being analyzed for nitrite (NO_2^-) plus NO_3^- (hereafter referred as nitrate, NO_3^-) using the Greiss-Ilosvay method with cadmium reduction of NO_3^- to NO_2^- (Mulvaney, 1986) modified for use with flow-through injection analysis (FIA) (Lachat, Loveland, CO).

Yield and Plant Nitrogen Content

After physiological maturity, corn ears were harvested from a distance of 1.5 m in the middle two rows of each subplot. Ears were dried, shelled, and further dried for 3 d at 65°C and weighed to obtain dry grain and cob yield. Stover was collected by cutting six plants just above their crowns where corn ears were harvested. Stover was weighed, and the six plants from each subplot were subsampled and ground, weighed and then dried for moisture content determination. Grain, cob, and stover sub-samples were further ground with a grinding mill and analyzed with an elemental N combustion analyzer (VarioMax; Elementar, Hanau, Germany) for N content. Total N content in above-ground biomass was calculated from the sum of N harvested in grain, cob, and stover from each subplot.

Soil Physical and Chemical Properties

Soil temperature was measured on each N_2O flux measurement day using temperature probes (Fisher, Hampton, NH) inserted to the 0.05-m depth within 1 m of the chambers. Soil water content and bulk density were determined on samples collected one

from each of CT and NT plots to the 0.05-m depth within 1 hr of each flux measurement period by drying at 105°C. Bulk density values were used together with gravimetric water content to estimate water-filled pore space (WFPS). Two cores of soil samples (one from mid-row position and the other from position between mid-row and corn-row) to a depth of 0.3 m were collected from each subplot once every month during the season. Each core was divided into two depths (0 - 0.15 m and 0.15 - 0.30 m) for analysis of extractable inorganic N. Soil samples from each subplot for each depth were pooled, homogenized, and refrigerated before analysis. Subsamples of ~ 10 g were extracted in 2 M KCl, filtered (Whatman no. 42), and analyzed for ammonium (NH_4^+) and NO_2^- plus nitrate (hereafter referred as nitrate, NO_3^-) using the sodium salicylate-nitroprusside method and Greiss-Ilosvay method with cadmium reduction of NO_3^- to NO_2^- respectively (Mulvaney, 1986) modified for use with FIA (Lachat, Loveland, CO).

Data Analysis and Statistics

Nitrous oxide fluxes (averaged over two adjacent chambers in the case of fertilized subplots) measured on each sampling date for each subplot were used to estimate cumulative area-based N_2O emissions using trapezoidal integration of flux versus time. The fertilizer-induced emissions factor (FIEF) (%) was calculated by subtracting cumulative area-based N_2O emissions in the control treatment from that in each fertilized treatment within the same block and then expressing the result as a percentage of the total amount of fertilizer N applied (146 kg N ha^{-1}). Yield-based N_2O emissions (g N Mg^{-1} yield) were calculated by dividing cumulative area-based N_2O emissions by grain yield. Nitrogen fertilizer recovery efficiency was calculated by

subtracting the total aboveground N uptake in the control treatment from that in each fertilized treatment and expressing the result as a percentage of the total fertilizer N applied. Nitrite plus nitrate intensity (NO₂3I) in soil-water was determined from each subplot by linear interpolation of the soil-water NO₃⁻ concentrations (averaged over two lysimeters in case of fertilized subplots) between successive sampling dates over the measurement period (Engel et al., 2010) and was used as a measure for NO₃⁻ leaching potential from that subplot. Soil NO₂3I and ammonium intensity (NH₄I) were calculated from each subplot by linear interpolation of the soil NO₃⁻ and NH₄⁺ concentrations respectively between successive sampling dates over the measurement period, separately for the 0-0.15 m and 0-0.30 m depths, the latter using the mass-weighted mean of corresponding soil N concentrations at both depths. Soil NO₂3I expresses the magnitude of soil NO₃⁻ present in the soil with the duration to provide an integrated measure of NO₃⁻ availability.

Effects of year, tillage, and N fertilizer were determined using Proc Mixed in SAS with block, block-by-year, and block-by-year-by-tillage treated as random effects and fertilizer, tillage and year as fixed effects (Littell et al., 2006; SAS, 2003). When the main effect was significant, means comparisons were conducted using contrasts in SAS with significance criteria of $P < 0.05$, unless otherwise mentioned. Regression analysis was conducted in SAS (SAS, 2003).

Results

Climate and Soil Properties

Mean daily air temperatures during the growing seasons were 17.6°C and 18.6°C in 2010 and 2011 respectively (Figure 2-1a). The 2011 growing season was drier than normal (a 30-yr average), as total precipitation for the period of May 01 through Sept 30 was recorded to be 437 mm in 2011 compared to 630 mm in 2010. As a result, mean soil WFPS at the upper 0.05 m was lower in 2011 than in 2010 by about 14% in both tillage systems. Mean soil WFPS was respectively 52% and 55% in CT and NT treatments in 2010 and 38% and 41% in CT and NT treatments in 2011 (Figure 2-1b). Mean soil temperatures in the upper 0.05 m at the time of gas flux measurement was 20°C in both CT and NT treatments each year.

Agronomic Responses

There were no significant two- or three-way interaction effects of year, N fertilizer, and tillage on agronomic responses (grain yield, above-ground N uptake, and NFRE), except for tillage-by-N fertilizer interaction effect on grain yield (Table 2-1). This two-way interaction effect on grain yield was mainly due to the control treatment which had greater yield in CT than in NT treatment while there was no significant difference in yield by tillage for fertilized treatments. For the same reason, grain yield when averaged across N fertilizer and year was greater in CT than in NT ($P=0.06$). There was no tillage effect on above-ground N uptake and NFRE. Agronomic responses did not differ by year. Fertilized treatments (AA-d and AA-s) had greater grain yield and above-ground N uptake compared to the control treatment without significant differences between them. In other words, when only fertilized treatments were considered, there was no significant N fertilizer effect on any agronomic variables, including NFRE.

Nitrous Oxide Emissions

Nitrous oxide fluxes increased after N application in both years (Figure 2-2). Both fertilized treatments in both tillage regimes had maximum flux and greatest monthly mean flux in the month of Jun in both years. Monthly mean fluxes were $\leq 53 \mu\text{g N m}^{-2} \text{ hr}^{-1}$ in both tillage treatments in 2010 and CT treatment in 2011. Both fertilized (AA-d and AA-s) treatments in NT treatment in 2011 had monthly mean fluxes in Jun reach about $100 \mu\text{g N m}^{-2} \text{ hr}^{-1}$.

A significant two-way interaction effect of tillage and N fertilizer on both area- and yield-based N_2O emissions was observed (Table 2-1) because both N_2O emission indices did not differ by tillage in the case of the control treatment in both years. In contrast, both fertilized treatments (AA-d and AA-s) had greater N_2O emission in NT than in CT in 2011 (only area-based N_2O emissions shown, Figure 2-3a). There were significant interaction effects of tillage and year on N_2O emissions and FIEF, but on yield-based N_2O emissions only at $P=0.07$. No-till increased all three emission indices compared to CT in 2011, and that was not the case in 2010 (Figure 2-3a). Both area- and yield-based N_2O emissions in fertilized treatments were greater than in the control treatment with no significant difference between them. There was no significant difference in FIEF by N fertilizer, but FIEF was greater in 2011 than in 2010.

Soil and Soil-water Nitrate Intensity

Soil NO_3^- in monthly samples (0-0.3 m) increased after fertilizer applications and reduced to baseline towards the end of August each year (Figure 2-4). Seasonal soil NO_3^- patterns were observed to be similar for both AA-d and AA-s treatments in the CT

treatment both years. However, soil NO_3^- accumulation in the AA-d was apparently greater than in AA-s during the season in the NT treatments each year. There was no significant difference in soil NO₂3I in upper 0.15 m or 0.30 m by year (Table 2-2). Significant two-way interaction effect of tillage and N source was found for soil NO₂3I in soil from both above-mentioned depths. At both depths, there was no difference in soil NO₂3I for the control and AA-s treatments by tillage while NO₂3I in soil from both depths were greater in NT than in CT for the AA-d treatment (only 0-0.30 m depth data shown, Figure 2-3b). Soil NO₂3I at both depths was greater in AA-d compared to AA-s in NT treatment in both years.

Soil-water NO₂3I was greater in 2010 when there was more precipitation than in 2011 and was greater in fertilized treatments than in the control (Table 2-2). There was no difference in soil-water NO₂3I intensity due to tillage.

Discussion

Effect of AA placement depth

Fujinuma et al (2011) reported greater N₂O emissions from shallower application (0.10 m) of AA compared to conventional AA application (0.20 m) in an excessively well drained loamy sand. In contrast, Breitenbeck and Bremner (1986) observed greater N₂O emissions with deeper AA application in clay loam soil. In the current study, no significant difference in N₂O emissions was observed by AA application depth in silt loam soil. Comparing and resolving the effects of AA placement on N₂O emissions is difficult since there are a few related studies and even within available studies, there are many other confounding factors affecting N₂O emissions. One distinguishing feature

among our study and those mentioned above is soil texture. Contrasting soil textures can be associated with soil properties that can affect N₂O production (Rochette et al., 2004). Figure 2-5 summarizes data from these three studies on N₂O emissions following AA placement at different depths.

Nitrous oxide emissions were found to be correlated with soluble organic carbon availability in coarse-textured soils and with soil NO₃⁻ accumulation in fine-textured soils (Chantigny et al., 2010). Fujinuma et al (2011) reported greater soil organic matter (SOM) at shallow depth and attributed greater N₂O emissions in AA-s treatment compared to AA-d to this stratification of SOM. Concentrated bands of AA, when applied, release SOM by its sterilizing effect on microbial populations (Tomasiewicz and Henry, 1985) and thus, the shallower depth would have greater dissolved organic carbon (DOC) after injection of AA (Venterea et al., 2010; Norman et al., 1988). This might have stimulated more nitrification-driven N₂O production in the AA-s treatment. In the case of Breitenbeck and Bremnar (1986), considering the soil texture where the experiment was conducted, it is likely that N₂O production was primarily due to denitrification. Less oxygen availability deeper in this fine textured soil might have resulted in greater N₂O emissions with depth.

In the current study, mean WFPS of the monthly soil samples at 0.00 – 0.15 and 0.15-0.30 m depth was in a range of 50 – 60 %, and mean soil WFPS of these samples from individual sampling date was always < 80 %. As Linn and Doran (1984a) noted, this implies N₂O production could be primarily nitrification-driven. Soil moisture of the two depths where AA was placed was statistically not different during the growing season each year. Soils at both depths of AA placement also had similar SOM content

(data not shown). Therefore, similar soil moisture and organic matter content at two depths could have caused similar nitrification-driven N₂O emissions under both AA applications.

However, N₂O emissions could have been derived from denitrification as well. Considering the silty loam texture of the soil used in this study and the potential for saturated conditions, anaerobic soil aggregates may be present where denitrification could drive N₂O production. In fact, N₂O emissions were found to be highly correlated to soil NO₃I from the upper 0.15 m as well as from the upper 0.30 m (

Table 2-3), which is consistent with other reports (Zebarth et al., 2012; Engel et al., 2010; Burton et al., 2008). Soil NO₃I was similar in both AA treatments in the CT treatment each year (Figure 2-3b). That would probably explain similar N₂O emissions under both AA applications in the CT treatment. However, the pattern of soil NO₃I segregated by N source, placement and year did not follow exactly that of N₂O emissions, especially for the AA-d treatment in NT (2010) and AA-s in NT (2011) (Figure 2-3a, b).

In the dry year of 2011, the AA-s treatment in NT emitted more N₂O emissions than observed NO₃I would suggest. In a dry year of 2011, possibly soil moisture could have been a limiting factor to N₂O production. The relatively wetter soil surface (0.05 m) in the NT treatment compared to CT during a period where peak fluxes occurred would have enhanced N₂O emissions in NT than in CT. In the current study, soil NO₂⁻ accumulation was not rigorously measured. Since NO₂⁻ is more proximal to N₂O emissions than NO₃⁻, soil NO₂⁻ intensity (NO₂I), if rigorously measured with special precautions due to its chemical instability (Maharjan and Venterea, 2013), might explain the elevated N₂O emissions in the AA-s treatments in NT in the dry year. That might

also explain why N₂O emissions did not differ in NT treatments by AA placement depth in 2011 even though NO₂3I differed by placement depth.

In 2010 when total seasonal precipitation was greater by 240 mm compared to 2011, soil surface (upper 0.05 m) was wetter than in 2011 which could promote reducing conditions to convert N₂O produced at deeper layer in NT, as in the case of the AA-d treatment, to N₂ during its upward movement to the soil surface. That could have caused the discrepancy between elevated NO₂3I and observed N₂O emissions in the AA-d treatment in NT in 2010 and thus, resulted into similar N₂O emissions under both AA treatments in NT treatment that year. Alternatively, lack of data on NO₂⁻ accumulation in soil may have limited our ability to explain these results. Application of AA can result in the accumulation of NO₂⁻ in soil at concentrations above 25 μg N g⁻¹ (Venterea and Rolston, 2000) and NO₂⁻ is a substrate for N₂O produced via nitrifier-denitrification (Wrage et al., 2001), chemodenitrification (Stevenson et al., 1970) and heterotrophic denitrification (Zumft, 1997). This signifies the importance of measuring soil NO₂I separately from NO₂3I to better understand the mechanisms involved in N₂O emissions (Maharjan and Venterea, 2013).

Following the trend of N₂O emissions, FIEF also did not differ by AA placement depth. In the current study, FIEF was estimated in relation to N₂O emissions in the control treatment and was about 0.3 %. If N₂O emission factors (EF) from fertilized treatments are estimated as N₂O emissions per applied N rate, independent of the control treatment, EF is about 0.5 % of applied N rate and is towards the lower end of the range of EF (0.3 – 3 %) published in IPCC guidelines for National Greenhouse Gas Inventory.

Placement depth of AA did not significantly change agronomic responses as was the case in Fujinuma et al (2011). Fernandez et al (2011) reported yield loss with pre-plant shallow (0.10 m) application of AA. However, AA was applied in seed rows unlike in the current study or Fujinuma et al (2011) where AA was applied between rows. Yield loss was the result of seedling injury and thus, it was recommended to avoid pre-plant shallow AA application directly under or near the corn rows. Since there were no differences in yield or N₂O emissions by placement depth, yield-scaled N₂O emissions also did not differ by AA placement depth in the current study.

Neither did soil-water NO₃I during the growing season differ by placement depth of AA. The total amount of NO₃⁻ leached would be greatly affected by the amount of drainage, but since both fertilized subplots were similarly treated, these values can be used as a measure to compare NO₃⁻ leaching potential in those fertilized subplots. Apparently, N leaching is not significantly affected by placement depth of AA.

Tillage effect

Greater N₂O emissions in NT than in CT for the AA-d treatment in 2011 can be explained by the fact that soil NO₃I was greater in NT than in CT for AA-d that year. The latter was true in 2010 as well but there was no difference in N₂O emissions by tillage for the AA-d treatment in 2010, most possibly because in 2010, upper layer soil was wetter (than in 2011) and might have reduced N₂O produced in the lower soil layer on its way up to soil surface. Similar soil NO₃I in both tillage systems for the AA-s treatment explains similar N₂O emissions in both tillage systems for AA-s in 2010.

Greater N₂O emissions are attributed to higher soil NO₃⁻ levels in other studies, too (Bronson et al., 1992; Snyder et al., 2009). Halvorson et al (2010) also noted greater N₂O emissions due to elevated NO₃⁻ levels in soil but in CT compared to NT in case of polymer-coated urea. Fertilizer was band applied on soil surface, followed by irrigation and PCU granules in CT were partially buried in the soil and many granules were suspended in the water and moved with the water out of the fertilizer band, thus allowing their quicker decomposition than in NT. Jacinthe and Dick (1997) and Kessavalou et al (1998) also observed greater N₂O emissions under CT compared to NT. However, there are other studies that reported greater N₂O emissions under NT compared to CT as in a dry year in the current study (Liu et al., 2006; Goodroad et al., 1984). Venterea et al (2005) observed that the effect of tillage on N₂O emissions varied by N sources in the same research station where the current study was conducted. Greater N₂O emissions were observed under NT compared to CT following broadcast urea in a two-year experiment. Emissions did not vary by tillage following urea-ammonium-nitrate and were greater in CT than in NT following AA application at 0.15 – 0.20 m depth in a one-year experiment. Vertical distribution of aerobic and facultative anaerobic microbial populations was observed to be greater in upper 0.07 m in NT compared to CT and over the 0.15-0.30 m depth; plowed soils contained more facultative anaerobes (Linn and Doran, 1984b). Venterea et al (2005) reasoned that AA injected to a depth, which was below the most active denitrifying zone in the NT treatment compared to right at the most active denitrification activity zone in CT may have resulted in greater N₂O emissions in CT than in NT. When these three years of N₂O emission data following AA application in the same research station (1 from Venterea et al., 2005 and 2 from the current study)

are considered together, the tillage effect on N₂O emissions following AA application varied by year. In 2004, N₂O emissions were greater in CT compared to NT (Venterea et al., 2005); in 2010, emissions did not vary by tillage and in 2011, emissions were greater in NT compared to CT.

In 2011 which was drier than 2004 and 2010, 7 wk period starting from May 24 through Jul 11 recorded greater N₂O fluxes in NT than in CT treatments. During that period, there were some differences in soil moisture by tillage. Out of 15 soil sampling events during that period, 10 had greater soil moisture in NT than in CT with a mean difference of 12% whereas in 5 sampling events, CT had greater soil moisture than in NT with a mean difference of only 6%. This might have enhanced N₂O production in the NT treatment compared to CT in the dry year of 2011 when soil moisture could possibly be a limiting factor to N₂O production. In normal years, N₂O emissions were either greater in CT than in NT or did not differ by tillage.

A significant tillage effect on grain yield was observed at $P = 0.06$ mainly due to gain in yield in the control treatment in CT each year. Greater yield in CT compared to NT was also observed by Venterea et al (2011) in the experiments conducted at the same research station as the current study. Similar differences in grain yield by tillage are attributed to cooler soil temperatures in NT in the spring, which may inhibit early-season plant development (Kaspar et al., 1987; Vyn and Raimbault; Vetsch and Randall, 2004). Other studies have reported the opposite (Ismail et al., 1994; Grandy et al., 2006). In the current study, no difference in soil temperature in the upper 0.05 m layer was observed and that possibly could have removed all possible effect of tillage on crop development and eventually on crop yield in fertilized treatments. However, a significant tillage effect

on yield was found in the control subplot, possibly due to mineralization of soil organic N in the CT treatment.

There was no significant difference in soil-water NO₃⁻ by tillage. Increased drainage and greater NO₃⁻ concentration in NT leachate were reported in several studies (Kanwar et al., 1988; Tyler and Thomas, 1977). In contrast, Byre et al (2000) observed no difference between CT and NT in amount of NO₃⁻ leached in two years, but in the third year, which had precipitation greater by 235 and 375 mm than in the previous two years, NT had more NO₃⁻ leached than in CT. Since CT disrupts soil structures, and destroys macropores in tilled layer, water in NT would move quicker through the soil profile. Petrovic (2004) and Morton et al (1988) found that abundant irrigation and/or precipitation can also greatly increase NO₃⁻ leaching depending on soil type. In the current study, drainage was not estimated and since, as other studies suggested, drainage can vary by tillage, any inference about total amount of NO₃⁻ leached in different tillage regimes is difficult to make.

Conclusions

In contrast to Fujinuma et al (2011) and Breitenbeck and Bremner (1986), no significant difference was observed in N₂O emissions by AA placement depth in this study. Comparing our study with these two reports, it appears that soil textures and consequently soils properties, including drainage affect N₂O emissions following AA application at different depths. In the current study, soil NO₂I was highly correlated to N₂O emissions but measuring soil NO₂I separate from NO₃I would explain the controls over N₂O emissions. When soil moisture is a limiting factor, tillage effect on soil

moisture can subsequently affect N₂O emissions, as seen in a dry year in the current study, where NT significantly increased N₂O emissions in fertilized treatments. Changes in placement depth also affect speed of AA application, tractor-fuel consumption and soil disturbance, which can have associated economic and environmental implications. Therefore, a full life-cycle analysis would be required to determine effects of AA placement depth in mitigating GHG emissions

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Table 2-1: Results of statistical analyses for different dependent variables as affected by year, N source and tillage, and their

Sources of Effect	Environmental Variables			Agronomic Variables		
	N ₂ O emissions (kg N ha ⁻¹)	Yield-based N ₂ O emissions (g N Mg ⁻¹ grain)	FIEF‡ (%)	Grain yield (Mg ha ⁻¹)	Above-ground N uptake (kg N ha ⁻¹)	NFRE‡ (%)
Year (Y)						
2010	0.71 (0.06)	66.4 (3.7)	0.25 (0.03) b	10.6 (0.5)	130.6 (8.6)	30.2 (5.2)
2011	0.91 (0.11)	81.3 (8.6)	0.43 (0.05) a	10.5 (0.5)	157.7 (12.6)	45.6 (6.7)
<i>Significance</i>	NS	NS	*	NS	NS	NS
N fertilizer† (N)						
Control	0.41 (0.02) b	51.6 (4.1) b	-	8.2 (0.5) b	98.6 (7.7) b	-
AA-d	1.01 (0.08) a	86.9 (8.0) a	0.35 (0.04)	11.9 (0.3) a	169.6 (11.6) a	39.4 (8.4)
AA-s	1.00 (0.09) a	83.0 (8.3) a	0.33 (0.06)	11.5 (0.3) a	164.1 (10.5) a	36.4 (6.8)
<i>Significance</i>	***	***	NS	***	***	NS
Tillage‡ (T)						
CT	0.71 (0.16) b	61.0 (14.4) b	0.24 (0.07) b	10.9 (2.6) a	151.4 (35.7)	33.2 (7.8)
NT	0.91 (0.11) a	86.7 (20.4) a	0.44 (0.13) a	10.1 (2.4) b	136.8 (32.2)	42.6 (10.0)
<i>Significance</i>	***	***	***	<i>P</i> = 0.06	NS	NS
T × N	*	*	NS	*	NS	NS
Y × N	NS	NS	NS	NS	NS	NS
Y × T	*	<i>P</i> = 0.07	*	NS	NS	NS
Y × T × N	NS	NS	NS	NS	NS	NS

interactions

† N fertilizer include control (no N), AA-d (deep-applied anhydrous ammonia), and AA-s (shallow-applied anhydrous ammonia).

‡ Tillage includes CT (conventional tillage) and NT (no till).

‡ FIEF – fertilizer-induced emission factor; NFRE – nitrogen fertilizer recovery efficiency

*** Significant at *P* < 0.001, ** at *P* < 0.01, * at *P* < 0.05 and NS – not significant

For each variable, means followed by the same letter are not significantly different (*P* < 0.05).

Table 2-2: Mean (standard error) of soil and soil-water N intensities during the season.

Sources of Effect	Soil-water NO ₂ I (g N kg ⁻¹ d)	Soil intensity (0.00-0.15 m) (g N kg ⁻¹ d)		Soil N intensity (0.00-0.30 m) (g N kg ⁻¹ d)	
		NO ₂ I	NH ₄ I	NO ₂ I	NH ₄ I
Year (Y)					
2010	1.15 (0.08) a	1.84 (0.29)	1.03 (0.05)	1.75 (0.21)	0.99 (0.05) a
2011	0.66 (0.05) b	2.13 (0.37)	0.93 (0.25)	1.64 (0.27)	0.73 (0.16) b
<i>Significance</i>	**	NS	NS	NS	*
N fertilizer† (N)					
Control	0.69 (0.10) b	0.87 (0.14) b	0.76 (0.11) b	0.82 (0.14) c	0.76 (0.11) b
AA-d	0.99 (0.11) a	2.87 (0.42) a	1.43 (0.32) a	2.50 (0.28) a	1.14 (0.21) a
AA-s	1.04 (0.09) a	2.21 (0.36) a	0.74 (0.07) b	1.75 (0.21) b	0.67 (0.08) b
<i>Significance</i>	**	***	**	***	*
Tillage‡ (T)					
CT	0.89 (0.09)	1.76 (0.28)	0.92 (0.14)	1.52 (0.28)	0.76 (0.08)
NT	0.92 (0.09)	2.21 (0.37)	1.04 (0.20)	1.87 (0.18)	0.96 (0.15)
<i>Significance</i>	NS	NS	NS	NS	NS
T × N	NS	*	NS	*	NS
Y × N	NS	NS	*	NS	*
T × Y	NS	NS	NS	NS	NS
Y × T × N	NS	NS	NS	NS	NS

† N fertilizer include control (no N), AA-d (deep-applied anhydrous ammonia), and AA-s (shallow-applied anhydrous ammonia).

‡ Tillage includes CT (conventional tillage) and NT (no till).

*** Significant at P < 0.001, ** at P < 0.01, * at P < 0.05 and NS – not significant

For each variable, means followed by the same letter are not significantly different (P < 0.05)

Table 2-3: Results of linear regression analysis for cumulative N₂O emissions versus soil N intensities of nitrite and nitrate (NO₂I) and ammonium (NH₄I) for all treatments and analyzed separately for conventional tillage (CT) and no-till (NT).

soil depth	Soil N intensity	All data	All data		All data		All data		
		both yrs	2010	2011	CT	NT	Control	AA-d	AA-s
0-15 cm	NO ₂ I	0.44 ***	0.49 **	0.48 **	0.27 *	0.41 **	0.47 *	0.29 NS	0.12 NS
0-30 cm	NO ₂ I	0.40 ***	0.70 ***	0.42 **	0.35 *	0.37 **	0.44 *	0.21 NS	0.06 NS
0-15 cm	NH ₄ I	0.05 NS	0.002 NS	0.09 NS	0.08 NS	0.13 NS	0.07 NS	0.05 NS	0.04 NS
0-30 cm	NH ₄ I	0.0003 NS	0.12 NS	0.04 NS	0.05 NS	0.03 NS	0.07 NS	0.0001 NS	0.17 NS

*** $P < 0.001$, ** $P < 0.01$, * $P < 0.05$

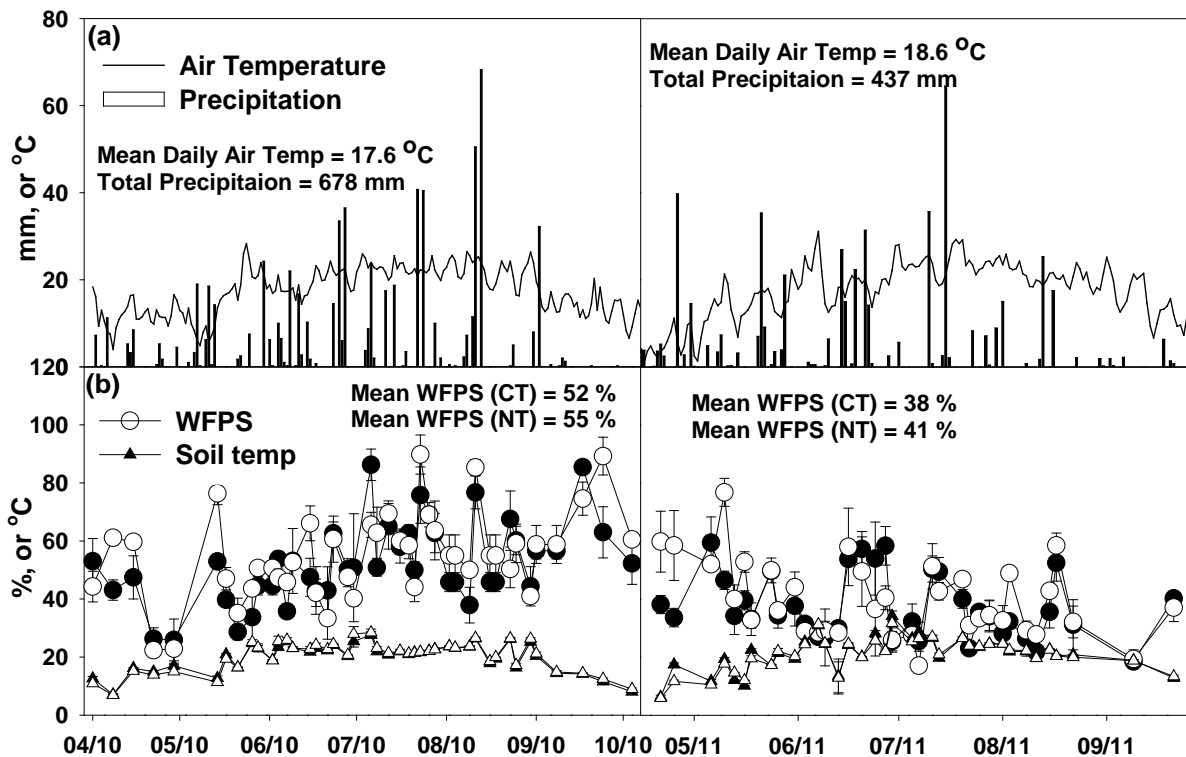


Figure 2-1: (a) Daily precipitation and air temperature, and (b) mean (with standard error) soil temperature and water-filled pore space (WFPS) at time of N₂O sampling.

†Open and filled symbols refer to no-till (NT) and conventional tillage (CT) systems.

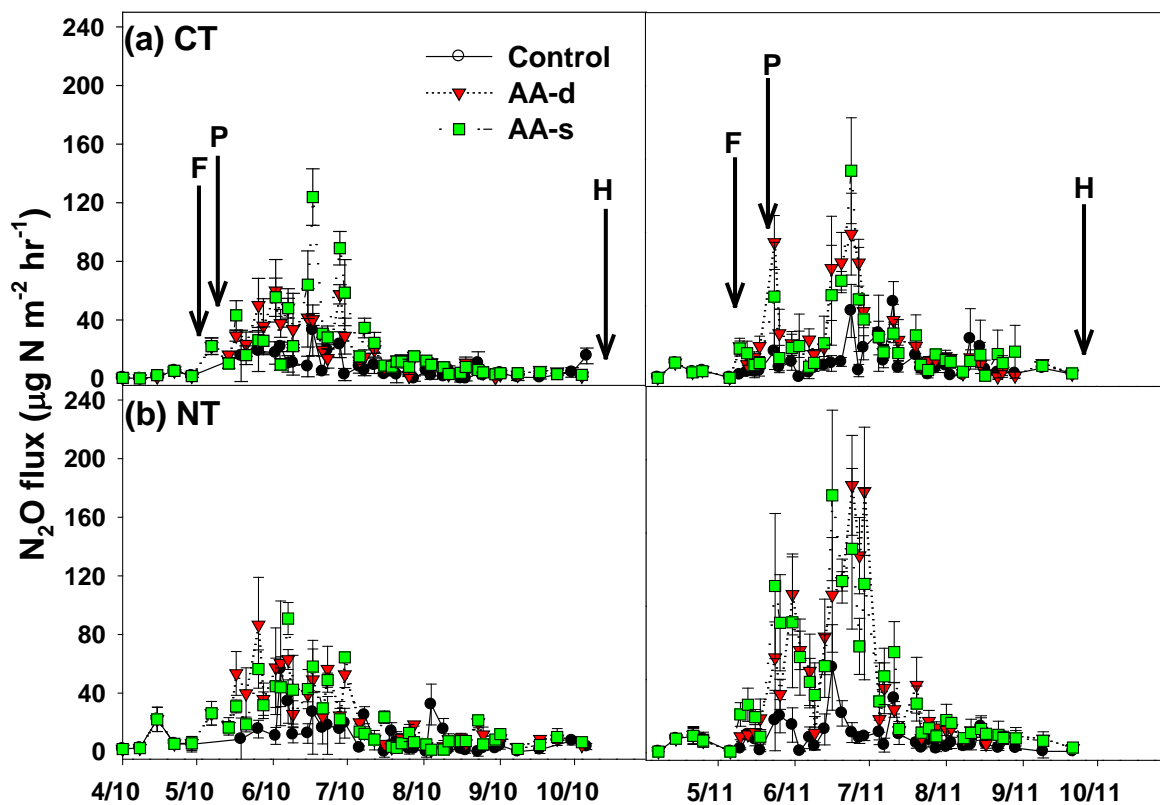


Figure 2-2: Mean (with standard error) growing season N_2O emissions in plots under conventional tillage (CT) and no-till (NT) systems with shallow and deep placement of anhydrous ammonia (AA-s and AA-d) and no-N (control). Bars with same lower case letters are not significantly different ($P < 0.05$). Downward-pointing arrows indicate dates of planting (P), fertilizer application (F) and harvest (H).

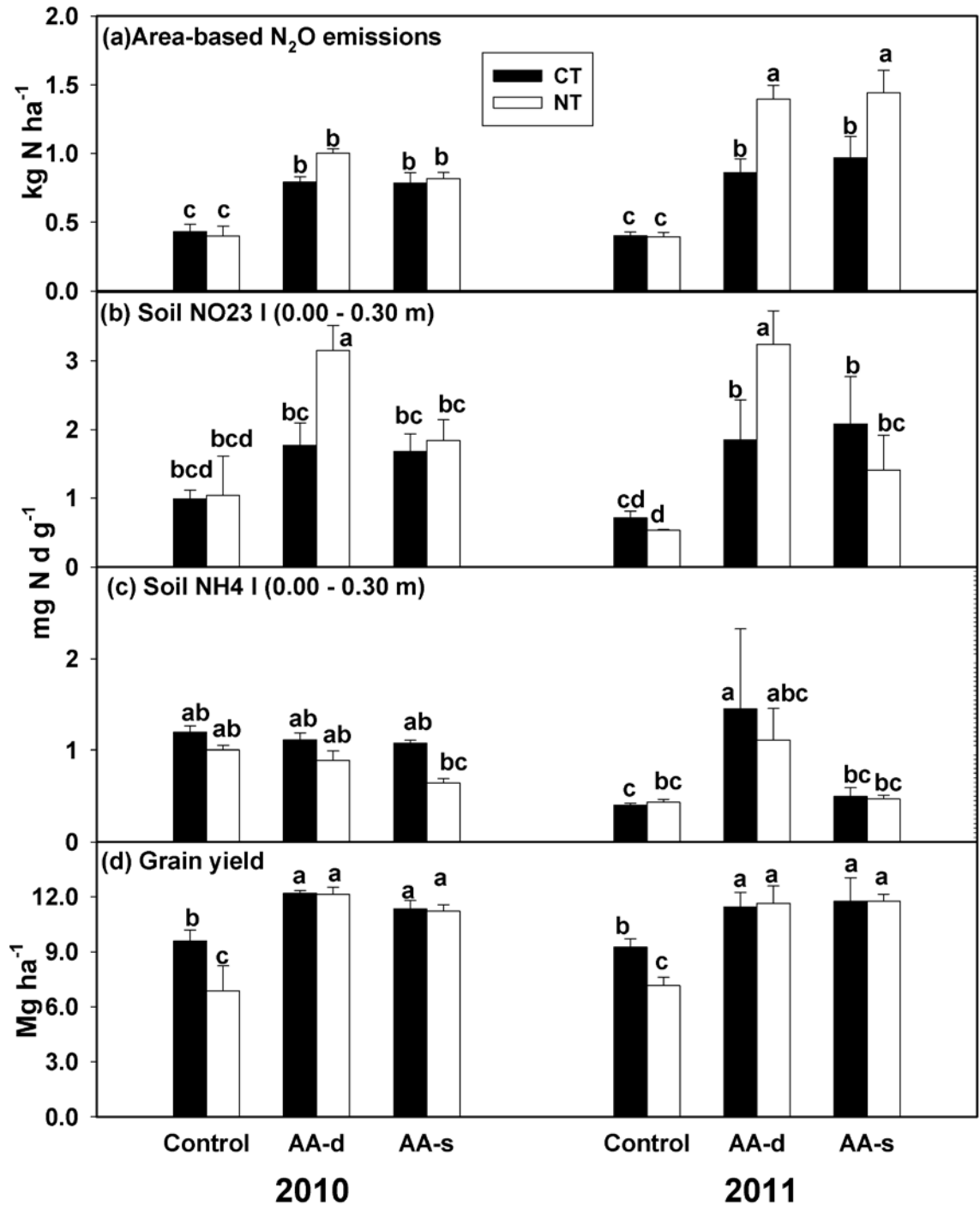


Figure 2-3: Mean (with standard error) (a) growing season N₂O emissions, (b) soil nitrite plus nitrate intensity (NO₂₃I), (c) soil ammonium intensity (NH₄I), and (d) grain yield in plots under conventional tillage (CT) and no-till (NT) systems with shallow and deep placement of anhydrous ammonia (AA-s and AA-d) and no-N (control). Bars with same lower case letters are not significantly different (P < 0.05).

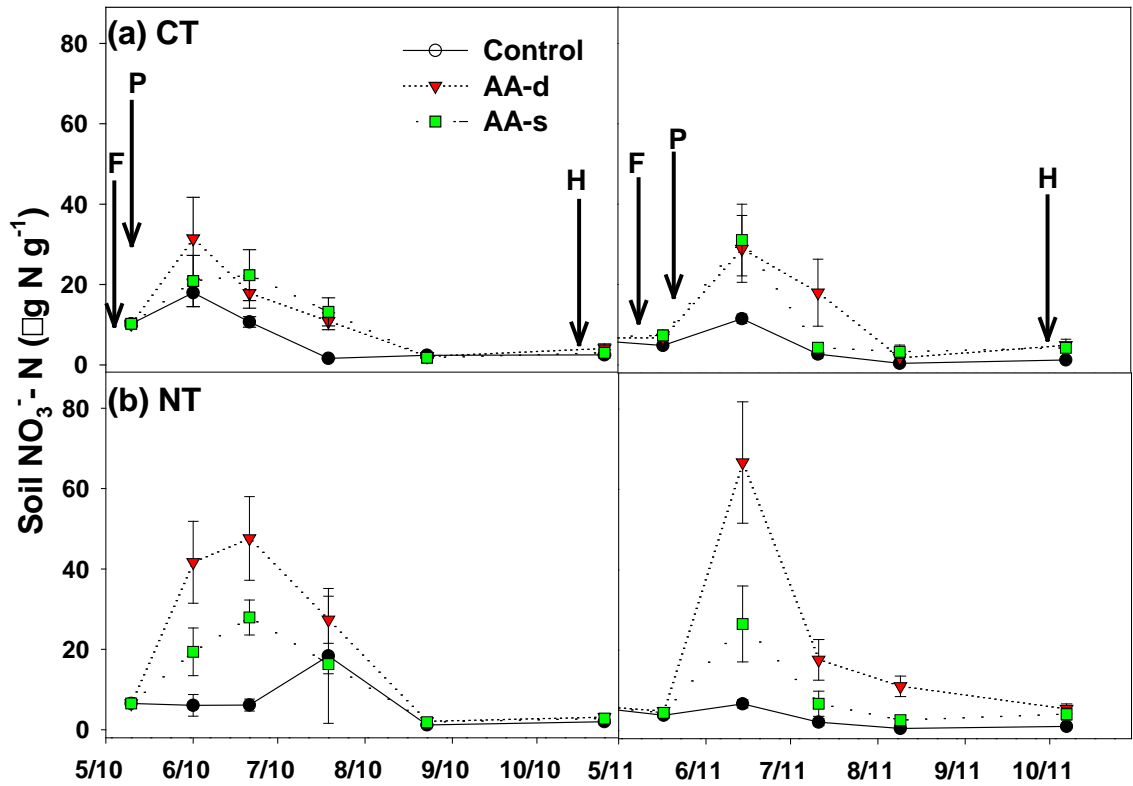


Figure 2-4: Mean (and standard error) soil nitrate (NO_3^-) concentrations in the upper 0-0.3 m depth in plots under conventional tillage (CT) and no-till (NT) that received shallow and deep placement of anhydrous ammonia (AA-s and AA-d) and no N (control) in 2010 and 2011.

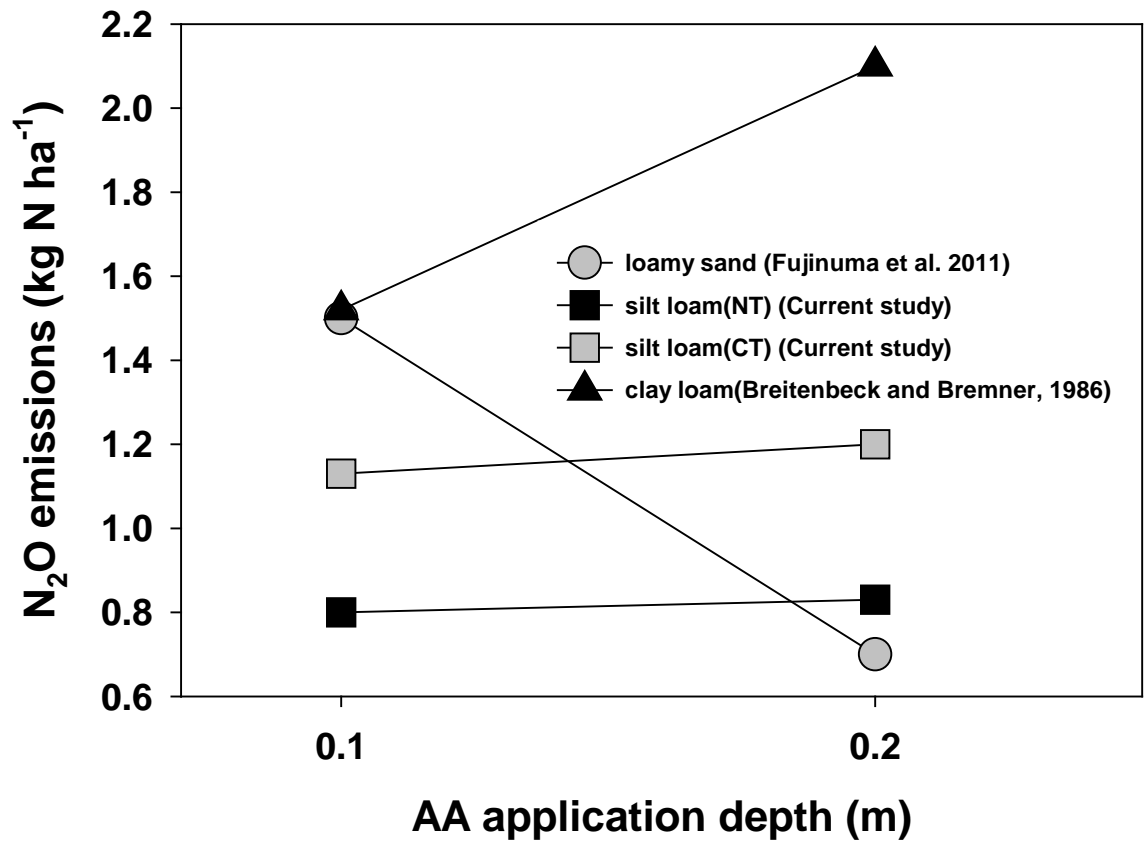


Figure 2-5: Cumulative N₂O emissions following anhydrous ammonia application at different depths in three different soil types; loamy sand (Fujinuma et al., 2011), silt loam (current study), and clay loam (Breitenbeck and Bremner, 1986).

Chapter 3 – Soil Inorganic Nitrogen Dynamics and Nitrous Oxide Emissions: Broadcast versus Band application of Conventional Urea and Controlled–release Fertilizers

Nitrogen (N) fertilizer management is a major factor affecting crop yield, N use efficiency (NUE), nitrous oxide (N₂O) emissions, and ammonia (NH₃) volatilization. Application of specialized fertilizers such as urea (CU) with urease and nitrification inhibitors (IU) and polymer–coated urea (PCU) and optimization of N placement may improve NUE and mitigate N loss. The objective of this study was to compare effects of different N sources and placement on N₂O emissions, NH₃ volatilization and crop yield in a corn cropping system. Evaluated N sources were PCU, IU, and CU applied either surface broadcast/incorporated (BI) or mid–row banded (MRB). Soil inorganic N accumulation was measured on a weekly basis during the growing season and soil nitrite (NO₂⁻), nitrate (NO₃⁻) and ammonium (NH₄⁺) intensities were estimated using soil N accumulation over time. MRB significantly increased N₂O emissions compared to BI for PCU and CU. Averaged over placement and years, N₂O emissions decreased in order of CU > PCU > IU. Significant amounts of N accumulation, including NO₂⁻, were observed in banded rows. Regression analysis showed that N₂O emissions were more strongly correlated to NO₂⁻ intensity than NO₃⁻ intensity. Compared to BI, MRB reduced NH₃ volatilization loss and the CU treatment had greater NH₃ loss than PCU or IU had. This study underscores the significance of the interacting effect of N source and placement that impacts N₂O emissions. The study also highlights the importance of measuring accumulation of soil NO₂⁻, a precursor to N₂O emissions, in our efforts to understand and mitigate N₂O emissions from agriculture.

Abbreviations: PCU, polymer-coated urea; IU, urea containing urease and nitrification inhibitors; U, urea; IU/U, a 50/50 mix of IU and U; NO₂I, soil nitrite intensity; NO₃I, soil nitrate intensity; NO₂₃I, soil nitrite plus nitrate intensity; NH₄I, soil ammonium intensity; FIEF, fertilizer-induced emission factor; NFRE, nitrogen fertilizer recovery efficiency; BI, broadcast/incorporation; MRB, mid-row banding.

Introduction

Increasing N fertilizer use in agriculture is contributing to rising N₂O emission, which is a potent greenhouse gas and also contributes to stratospheric ozone depletion (Ravishankara et al., 2009). Nitrogen loss through ammonia (NH₃) volatilization from fertilized agricultural land can also have adverse ecological impacts on environmental quality (EPA, 2011; Zaman et al, 2009). Upon depositing to ground, NH₃ can cause soil acidification (van der Eerden et al., 1998), become a secondary source of N₂O emission, and promote eutrophication of surface water bodies (EPA, 2011; Sutton et al., 2008). Optimization of N source and/or placement may be pivotal in achieving a best N management practice to mitigate NH₃ and N₂O loss without reducing or in a best case scenario, with gain in crop production.

Specialized N fertilizers including polymer-coated urea (PCU) and urea with chemical inhibitors (IU) are N sources, alternate to CU that are examined for mitigating N losses. Some field studies have reported the effectiveness of these products in improving plant NUE (Shoji et al., 2001; Freney et al., 1992), and reducing N₂O emissions (Halvorson et al., 2010; 2011; Hyatt et al., 2010; Bronson et al., 1992), and

NH₃ volatilization loss (Connel et al., 2011; Rochette et al., 2009; Chai and Bremner, 1987), while others have shown limited or no effect (Sistani et al., 2011; Venterea et al., 2011). There is also uncertainty regarding effects of fertilizer placement on N losses and crop response. Banded N placement has been reported to increase NUE (Hou et al., 2010; Malhi et al., 1996), and crop yields (Grant et al., 2001; Rees et al., 1997) compared to surface broadcast N, but there are mixed reports when band placement of N is compared to broadcast incorporated N (Fujinuma et al., 2011; Hou et al., 2010). Band placement of N has been reported to reduce NH₃ volatilization (Rochette et al., 2008; Sommer et al., 2004); however, there are reports suggesting greater NH₃ volatilization with banded urea compared to broadcast (Rochette et al., 2009). Banding of N fertilizers was found to increase N₂O emissions in irrigated corn (Halvorson et al., in press) and in a canola-based cropping system (Engel et al., 2010). Cheng et al (2006) reported significant reduction in N₂O emissions in banded PCU treatment compared to broadcast incorporated or banded CU with no difference between the latter two in a cabbage field. No differences were found between banded and broadcast urea in wheat production systems (Burton et al., 2008) or in Chinese cabbage (Hou and Tsuruta., 2003) in terms of N₂O emissions. Information is lacking on relative performance of different combinations of N source and placement on N losses in corn cropping systems and results available from different crop based studies are also not consistent. Study of temporal dynamics of soil inorganic N may provide some insights on N losses under varying conditions.

The role of NO₂⁻ as a precursor substrate for N₂O production is presented in several reports (Engel et al., 2010; Fukumoto and Inubushi, 2009; Campos et al., 2009; Alinsafi et al., 2008; Venterea, R. T., 2007). It is difficult to detect NO₂⁻ in soil after

broadcast urea (Engel et al., 2010) but concentrated band placement of N can result in localized NO_2^- accumulation. Free NH_3 in areas of elevated concentration of NH_4^+ can have a greater toxic effect on NO_2^- oxidizing bacteria than on NH_4^+ oxidizing bacteria by two orders of magnitude (Suthersan, S. and Ganczarczyk, J. J., 1986; Alleman, J. E., 1984). Therefore, when fertilizer is applied in concentrated bands, considerable NO_2^- accumulation in soil is observed (Van Cleemput and Samater, 1996). Engel et al (2010) attributed greater N_2O emissions with nested or banded N to significant soil NO_2^- accumulation. Possibly for the same reason, greater N_2O emissions were observed with banded anhydrous ammonia compared to broadcast urea as reported in Fujinuma et al., 2011. Correlation between N_2O emissions and NO_2^- accumulation has been reported for composting processes (Fukumoto and Inubushi, 2010; He et al., 2001), and in activated sludge (Alinsafi et al., 2008; Itokawa et al., 2001). There is a lack of information linking different N management in corn cropping system and subsequent soil NO_2^- -N accumulation that affects N_2O emissions.

The main objective of this study was to compare area- and yield-based N_2O emissions, NH_3 volatilization, grain yield, and NUE in corn plots each of which received either BI or MRB post-emergence application of one of fertilizers (CU, PCU or IU) over two consecutive growing seasons. The study also investigated temporal soil inorganic N dynamics during the growing season and the relationship of soil N (NO_2^- -N, NO_3^- -N and NH_4^+ -N) accumulation to N_2O emissions.

Materials and Methods

Site Description and Experimental Design

The site is located at the University of Minnesota's Research Farm in St. Paul, MN (44.99° N, 93.17° W), where the soil is a Waukegan silt loam containing 23 % sand, 55 % silt, and 22 % clay in the upper 0.15 m. 30-year Apr–Oct average precipitation and temperature at the site are 621 mm and 16.4°C respectively (MCWG, 2012). A two-year study was established in 2011 using a randomized complete block design with four blocks, each containing eight 5.3 m by 5 m plots. Corn was planted in all plots at a seeding rate of 95,660 ha⁻¹ on 25 Apr 2011 and 30 Apr 2012. Fertilizer treatments were CU (46% N w/w), PCU (44% N w/w) (ESN; Agrium Advanced Technologies, Loveland, CO), and IU, urea (46% N w/w) impregnated with the urease inhibitor N-(n-Butyl)-thiophosphoric triamide (NBPT) and the nitrification inhibitor dicyandiamide (DCD), (Super U; Agrotain International, St. Louis, MO). Separate plots in each block received each N source applied using both BI and MRB. One plot in each block served as a control treatment and received no added N. In this way, there were 7 different fertilizer treatments randomly assigned to each block in 2011. In 2012, one additional treatment received a 50:50 (by N wt.) mix of IU and CU (IU/CU) applied using MRB (8 treatments total). Each fertilized treatment received 180 kg N ha⁻¹, which is close to the recommended rate for South–Central Minnesota (Randall et al., 2008). All fertilizer treatments were applied after emergence at V6 stage (1 Jun 2011 and 5 Jun 2012). Broadcast treatments were incorporated (0.05 m depth) the same day using a cultivator which uniformly tilled (to 0.05 m depth) all the plots (including MRB treatments). In plots receiving the MRB treatment, following tillage on the same day, furrows (0.05–m deep and 0.05–m wide) were manually prepared in the middle of each row along a line

parallel to corn rows with a hoe, and fertilizers were hand-applied into the furrows which were then gently back-filled using rakes.

Nitrous Oxide Emissions

Soil-to-atmosphere N₂O fluxes were measured using non-steady state chambers (Venterea et al., 2010). Gas samples were collected once a week in May and Sept and twice a week in Jun through Aug in both years, for a total of 33 and 30 sampling dates in 2011 and 2012, respectively. Sampling was carried out within 24 hr of rain events in 43% of sampling events in 2011 and 45% in 2012. One acrylic chamber anchor (0.69 m × 0.34 m × 0.10 m deep) was installed in each plot centered between corn rows with the short side parallel to the corn row encompassing > 90% of the inter-row width while allowing for expansion of the above-ground corn root mass. On each sampling day, insulated and vented chamber tops (0.69 m × 0.34 m × 0.13 m high) were secured to anchors with 60-mm binder clips before gas sampling. Gas samples were collected after 0, 0.5, 1.0 and 1.5 h using a 12-mL polypropylene syringe. Samples were immediately transferred to glass vials sealed with butyl rubber septa (Alltech, Deerfield, IL) and analyzed within 1–2 wk using a headspace autosampler (Teledyne Tekmar, Mason, OH) connected to a gas chromatograph (GC) (model 5890, Agilent /Hewlett-Packard, Santa Clara, CA) equipped with an electron capture detector. The GC was calibrated with analytical grade standards (Scott Specialty Gases, MI) each day when samples were analyzed. Gas concentrations in molar mixing ratios determined by the GC were converted to mass per volume concentrations using ideal gas law and air temperatures at the sampling time. Gas fluxes were calculated from the rate of change of gas

concentration, chamber volume, and base area using linear regression (LR) or quadratic regression (QR) (Wagner et al., 1997) and using correction factors to account for suppression of the surface–atmosphere concentration gradient (Venterea, 2010). LR was used in place of QR when time series gas concentration data had completely linear or positive curvature, i.e., when second derivative of QR results were ≥ 0 (Venterea et al., 2009). The QR method was evaluated using the LINEST function in Excel (v. 2010, Microsoft).

Ammonia Volatilization

A chamber/acid trap method was used to compare relative rates of ammonia (NH_3) volatilization from the control and BI treatments both years and from the MRB treatments in 2012 only. Two stainless steel chamber anchors ($0.50 \text{ m} \times 0.29 \text{ m} \times 0.09 \text{ m}$ deep) were permanently installed in each plot centered between corn rows with the short side parallel to the corn row. On each day of measurement, two 0.14 m –diameter glass petri–dishes containing 50 mL of 0.2 N –sulfuric acid were placed inside each anchor and chamber tops ($0.50 \text{ m} \times 0.29 \text{ m} \times 0.10 \text{ m}$ high) were secured to anchors with 60–mm binder clips. After 24 to 72 h, acid traps were collected and analyzed for NH_4^+ –N using a flow–through injection calorimetric analyzer (Lachat, Loveland, CO). One of two chambers located in each plot was alternately covered to minimize disturbance of soil conditions. Because chamber placement for $\geq 24 \text{ h}$ was expected to alter soil temperature and moisture, this method was used primarily to compare relative differences in volatilization among treatments. Ammonia fluxes were calculated from the concentration of NH_4^+ –N captured, liquid volume of acid, chamber base area, and duration of

installation. The chambers encompassed 66% of the inter-row width, leaving approximately 0.1 m uncovered on either side of the chamber. For purposes of comparing treatments, we assumed that NH_3 volatilization rates in these uncovered areas in the MRB treatments could be approximated by rates measured in the control treatments in the corresponding block, and that rates in the uncovered areas in the BI treatments did not differ from the covered areas.

Yields and Plant Nitrogen Content

After physiological maturity, corn ears were manually harvested from all plants over a distance of 1.5 m in the middle two rows of each plot. Ears were dried, shelled, and further dried for 3 d at 65°C and weighed to obtain dry grain and cob yield. Stover was collected by cutting plants just above their crowns for all plants where corn ears were harvested. Stover was weighed, and six plants from each sub-plot were sub-sampled and ground, dried and weighed for moisture content. Grain, cob and stover samples were further ground with a grinding mill and analyzed for N content with an elemental N analyzer (VarioMax; Elementar, Hanau, Germany). Grain N uptake for each plot was calculated by multiplying grain yield by N content in grain sub-samples from that plot. Total above-ground N uptake for each plot was calculated by using above-ground biomass (grain, stover and cob) and N content in sub-samples of each of those components from that plot.

Soil Physical and Chemical Properties

Soil temperature was measured on each N₂O flux measurement day using temperature probes (Fisher, Hampton, NH) inserted to the 0.05–m depth within 1 m of the chambers. Soil water content and bulk density were determined on samples collected one from each block to the 0.05–m depth using metal cores (0.05–m diameter) within 1 hr of each flux measurement. Bulk density values were used together with gravimetric water content to estimate water–filled pore space (WFPS). Additional soil samples were collected once a wk starting one wk prior to fertilizer application until the end of season on a total of 11 dates in 2011 and 13 dates in 2012. Soil samples at depth intervals of 0–0.1 and 0.1–0.2 m were collected at different locations in the inter–row region within each plot using a 19–mm diameter coring tool (Oakfield Apparatus, Inc., Oakfield, WI). Both years, soil samples were collected from the mid–row (center) position (0.38 m from the corn row) in all treatments, and also at a distance of 0.20 m from the row (off–center position) in the MRB treatments. In 2011, additional soil samples were collected at a distance of 0.20 m from the row of BI treatments and 0.28 m from the row in the MRB treatments. These additional sampling locations were removed in 2012 based on t–tests showing no significant difference in soil N concentrations between the 0.20 and 0.28 m locations in the BI treatments or between 0.20 and 0.28 m locations in the MRB treatments. Cores from each plot were collected in plastic bags and stored in cooler during transportation from field to laboratory. On the day of collection, samples from each location within each plot were homogenized, and subsamples (~ 10 g) were extracted in 2 M KCl, pH adjusted to ~8 (Stevens and Laughlin, 1995), filtered, and analyzed for NO₂[–] and total NO₂[–] + NO₃[–] separately using a flow–through injection calorimetric analyzer (Lachat, Loveland, CO). The remaining soil sample was

refrigerated before sub-sampling (~ 10 g) for extraction in 2 M KCl (pH ~ 5.5), filtering, and analyzing for NH_4^+ using a flow-through injection calorimetric analyzer (Lachat, Loveland, CO). Two additional subsamples (~ 5 g) were used to determine soil moisture by oven-drying at 105°C and soil pH in a 1:1 (by wt.) mixture of soil and 1 M KCl.

Data Analysis and Statistics

Nitrous oxide fluxes measured on each sampling date were used to estimate cumulative area-based N_2O emissions using trapezoidal integration of flux versus time. The fertilizer-induced emissions factor (FIEF) (%) was calculated by subtracting cumulative area-based N_2O emissions in the control treatment in each block from that in each fertilized plot in the same block and then expressing the result as a percentage of the total amount of fertilizer N applied (180 kg N ha^{-1}). Yield-based N_2O emissions (kg N Mg^{-1} grain) were calculated by dividing cumulative area-based N_2O emissions by grain yield for each plot. Cumulative area-based NH_3 volatilized was estimated by trapezoidal integration of NH_3 fluxes over time. Yield-based NH_3 volatilized (g N Mg^{-1} grain) were calculated by dividing cumulative area-based NH_3 volatilized by grain yield for each plot. Crop NUE (kg grain kg^{-1} N) for each fertilized plot was determined by dividing grain yield in that plot by total N fertilizer applied (Zebarth et al. 2004). Nitrogen fertilizer recovery efficiency (NFRE) was calculated by subtracting the above-ground N uptake in the control treatment from that in N treatment and expressing the result as a percentage of applied N rate (Bock, 1984). Soil N intensities (g N kg^{-1} d), separately for $\text{NO}_2^- - \text{N}$, $\text{NO}_3^- - \text{N}$ and $\text{NH}_4^+ - \text{N}$ were determined for soil samples from each of different

locations by trapezoidal integration of corresponding soil N concentrations at that location versus time (Engel et al., 2010).

Effects of year, N source, and placement were determined using Proc Mixed in SAS with block, and block-by-year treated as random effects and N source, placement, and year as fixed effects (Littell et al., 2006; SAS, 2003). Whenever the main effect was significant, means comparisons were conducted using contrasts in SAS with significance criteria of $P < 0.05$. Because placement did not apply to the control treatment, it was excluded from the complete analysis. Separate statistical analyses were carried out for only MRB treatments in 2012 that included the IU/CU-MRB treatment and also for NH_3 emissions in 2012 only that included MRB treatments. Regression analysis (SAS, 2003) was conducted to determine the effect of soil N intensities on N_2O emissions.

Results

Climate and Soil Properties

Total precipitation during 1 May through 31 Oct in 2011 and 2012 were 664 mm and 513 mm, respectively, compared to a 30-yr average of 561 mm (MCWG, 2012) (Figure 3-1). A prolonged period of drier than normal conditions persisted from mid-Jun through Oct in 2012. From 20 Jun through 1 Oct, 174 mm of rain was recorded in 2012 compared to 471 mm in 2011. WFPS in the upper 0.05 m at the time of N_2O flux sampling was $\geq 40\%$ on 20 dates in 2011 compared to only 6 dates in 2012. Average daily air temperatures were 17.8°C and 18.2°C in 2011 and 2012 growing seasons respectively and corresponding soil temperatures measured at the time of N_2O flux sampling were 21.2 and 21.9°C (Figure 3-1).

Agronomic Responses

There were no significant treatment interaction effects on agronomic variables (grain yield, above-ground N uptake, NUE, and NFRE) (Table 3-1). Year had a significant effect on grain yield and NUE (2011 > 2012) (Table 3-1). There was a trend for a greater above-ground N uptake in 2011 than in 2012 ($P=0.07$). Grain yield, above-ground N uptake and NUE did not vary with N sources or placement (Table 3-1). There was no significant effect of year, N source or placement on NFRE, which was 52% when averaged across all years, N sources and placement. In 2012 when there was an additional treatment of IU/CU-MRB, agronomic variables did not vary by N source in MRB treatments (Table 3-2).

Nitrous Oxide Emissions

Daily N₂O fluxes increased within 1 to 2 wks after fertilizer application in both years (Figure 3-2a-b). Increased fluxes were observed until Jul end in BI treatments and until early Aug in MRB treatments. Fluxes in the BI treatment decreased to the flux in the control treatment in early Aug while fluxes in the MRB treatment decreased to baseline later in the season towards the middle of Aug. Maximum N₂O flux values under all N sources in MRB treatments were greater in 2011 than in 2012. Almost all (47 out of 50) flux measurements $> 100 \mu\text{g N m}^{-2} \text{hr}^{-1}$ occurred when WFPS was $< 60\%$ in 2011 and all (30) such fluxes occurred at WFPS $< 53\%$ in 2012.

There was a second-order interaction effect of N source and placement on area- and yield-based N₂O emissions, and FIEF (Table 3-1). Banding significantly increased both area- and yield-based N₂O emissions, and FIEF compared to BI for PCU and CU

but not for IU (Figure 3-3). Area-based N_2O emissions in different combinations of N source and placement decreased in the order of CU-MRB > PCU-MRB > IU-MRB (=CU-BI = IU-BI = PCU-BI). Averaged over years and placement, area- and yield-based N_2O emissions were significantly greater in CU compared to PCU or IU and area-based N_2O emissions were greater in PCU than in IU (Figure 3-3). Averaged across N sources and placement, area-based N_2O emissions were greater in 2011 than in 2012 (Table 3-1). Averaged across all years, N sources and placement, FIEF was 1% and the statistics and treatment effects on FIEF were identical to area-based N_2O emissions (data not shown). In 2012 when there was an additional treatment, area- and yield-based N_2O emissions and FIEF were significantly reduced in IU/CU-MRB compared to CU-MRB (Table 3-2).

Soil N Dynamics and Nitrogen Intensity

Figure 3-5 and Figure 3-5 show soil inorganic N dynamics and pH at upper 0.1 m of mid-row locations under different N sources and placement during 2011 and 2012, respectively. Significant amount of soil NO_2^- -N accumulation was found in MRB treatments in both years (Figure 3-5a; Figure 3-5a). Maximum soil NO_2^- N accumulation of $62 \mu\text{g N g}^{-1}$ soil and $44 \mu\text{g N g}^{-1}$ soil was measured in the CU-MRB treatment in 2011 and 2012 respectively. In 2011 when there was more soil moisture available due to greater precipitation than in 2012, PCU-MRB had maximum soil NO_2^- N accumulation of $72 \mu\text{g N g}^{-1}$ soil. In the dry year of 2012, NO_2^- N accumulation in PCU-MRB was less and similar to those in IU-MRB. Compared to BI, the MRB treatment had apparently greater concentrations of soil inorganic N during the season. In MRB treatment,

measured maximum values of soil $\text{NH}_4^+ - \text{N}$ were $1049 \mu\text{g N g}^{-1}\text{soil}$ in 2011 and $900 \mu\text{g N g}^{-1}\text{soil}$ in 2012 (Figure 3-5b; Figure 3-5b). Some amount of $\text{NO}_3^- - \text{N}$ was found in post-season soil samples from both BI and MRB treatments each year (Figure 3-5c; Figure 3-5c). Residual soil $\text{NO}_3^- - \text{N}$ was significantly greater in 2012 than in 2011 and in MRB treatments than in BI (data not shown).

Mean seasonal soil pH was significantly greater in MRB treatments than in BI when averaged over years and N sources. Soil pH in BI treatment over the season were between 5.6 to 6.1 in 2011 and between 5.7 to 6.4 in 2012 with an exception when the CU treatment had soil pH of 6.9 in one sampling event in 2012 (Figure 3-5d; Figure 3-5d). In MRB plots, increased soil pH was measured initially in a few sampling events and maximum soil pH was 7.4 in PCU and IU treatments in 2011 and 8.3 in CU treatment in 2012.

Soil N intensities under different treatments were calculated at different locations for 0–0.1 m and 0.1–0.2 m depths separately but reported for both depths combined together. Soil N intensities did not vary by year, except with NO_2^- intensity at center (mid-row) location, which was greater in 2011 than in 2012 (Table 3-3). All N intensities at mid-row locations were greater in MRB treatments compared to BI and the effect was opposite at off-center locations (0.20 m away from corn row).

Table 3-4 shows a three-way interaction effect of year, N source and placement on NO_2^- intensity at mid-row locations. Soil NO_2^- intensity did not differ by N sources in BI treatments in both years while it decreased in order of $\text{PCU} = \text{CU} > \text{IU}$ in 2011 and $\text{CU} > \text{IU} = \text{PCU}$ in 2012. Soil NO_2^- intensity in MRB treatments was greater than in BI treatments for PCU and CU in 2011 and only for CU in 2012. Linear correlation between

N₂O emissions and soil N intensity reflecting the seasonal N dynamics at the mid-row locations was stronger with soil NO₂⁻ N intensity than with soil NH₄⁺– N intensity or soil NO₃⁻ – N intensity (Table 3-5). Multiple regression analysis with NO₂⁻ N and NO₃⁻ – N intensity as two independent variables showed that there was not much improvement in correlation coefficient (r^2) values than with NO₂⁻ alone and t-values showed that the soil NO₂⁻ N intensity had a significant effect on N₂O emissions, unlike NO₃⁻ – N intensity.

Ammonia Volatilization

Ammonia volatilization reached its maximum value within a wk after CU–BI application each year while there was a lag in time for IU–BI in 2011 and for PCU–BI in both years in reaching maximum NH₃ volatilization (Figure 3-2b). There was an interaction effect of N source and year on area-based NH₃ volatilization (Table 3-1). In the CU–BI treatment, area-based NH₃ volatilization was significantly greater in 2011 than in 2012 (Table 3-5). Area-based NH₃ volatilization with the CU–BI treatment was significantly greater than in PCU–BI or IU–BI in 2011. Area-based NH₃ volatilization was greater in CU–BI than in PCU–BI (by 34%) and IU–BI (by 76%) in 2012. Expressed per unit grain yield, NH₃ volatilization decreased in order of CU > IU > PCU.

In 2012, when NH₃ volatilization was also measured in the MRB treatments, MRB greatly reduced both area- and yield-based NH₃ volatilization loss compared to BI (Table 3-1). When only MRB treatments in 2012 were compared, area-based NH₃ volatilization did not vary by N sources but yield-based NH₃ volatilization with CU was greater than in PCU or IU (Table 3-2).

Discussion

Nitrous Oxide Emissions

Area-based N₂O emissions were greater in 2011 than in 2012 and it is most likely due to the year 2011 being wetter than 2012. Most likely for the same reason, yield was greater in 2011 than in 2012. Since the difference in N₂O emissions between two years (2011 > 2012 by 117%) was comparatively greater than the difference in grain yield (2011 > 2012 by 39%), yield-based N₂O emissions were greater in 2011 than in 2012.

Averaged over years and N placement, both PCU and IU reduced area- and yield-based N₂O emissions and FIEF compared to CU. Between alternate N sources, IU reduced area-based N₂O emissions and FIEF compared to PCU. Many studies have shown effectiveness of PCU or IU over CU in reducing N₂O emissions (Halvorson et al, 2010; Shoji et al, 2001; Bremner et al, 1981). However, the effectiveness of PCU or IU is not consistent as has been seen in other studies (Sistani et al., 2011; Chu et al, 2007; Li et al, 2002). Climate conditions such as precipitation and site-specific conditions such as soil texture are likely to be important factors that affect N₂O emissions under different N sources.

Averaged over two years, MRB treatments had greater area- and yield-based N₂O emissions and FIEF compared to BI for PCU and CU, not for IU. In MRB treatments only, area-based N₂O emissions and FIEF decreased in order of CU > PCU > IU and yield-based N₂O emissions in order of CU > PCU = IU. The results of this study are consistent with several other reports (Halvorson et al., in press; Fujinuma et al., 2011; Engel et al., 2010; Cheng et al., 2002, 2006). However, there are reports which suggest no difference in N₂O emissions with broadcast incorporated or banded N (Burton et al.,

2008; Xou and Tsuruta., 2003), or less N₂O emissions with banded N compared to broadcast (Nash et al., 2012; Hultgreen and Leduc., 2003). Soil N accumulation may provide some insights on N₂O emissions under different fertilizer management, such as N source and placement.

In the current study, N₂O emissions were more strongly correlated to soil NO₂⁻ – N than to soil NO₃⁻ – N intensity. Multiple regression analysis also showed that the effect of NO₃⁻ – N intensity on N₂O emissions was not significant while that of NO₂⁻ – N intensity was. Peak N₂O fluxes were also observed in both years at soil WFPS below 60%, which according to Linn and Doran (1984) is well within WFPS range where nitrification is dominant over denitrification. This together with the soil N intensity results implies that oxidation of NH₄⁺ was likely the primary source of NO₂⁻, which in turn contributed to N₂O emissions, while denitrification of NO₃⁻ was less important as a source of N₂O. As Van Cleemput and Samater (1996) noted, band placement of fertilizers can induce “NH₃ toxicity” effect, where free NH₃ due to soil alkalinity favored by urea hydrolysis inhibits NO₂⁻ oxidation and causes NO₂⁻ accumulation in soil. Hawkins et al (2010) suggested that elevated soil pH can have a more important inhibiting effect on NO₂⁻ oxidation than free NH₃. Either way, NO₂⁻ accumulation in N banded soil can lead to higher N₂O emissions by reduction of NO₂⁻ and this effect of elevated rates of N₂O production associated with NO₂⁻ accumulation under highly aerobic soil conditions was reported by Venterea (2007). This could have been the case with CU–MRB and PCU–MRB treatments in the current study, where greater soil NO₂⁻ – N intensity in CU–MRB treatment compared to CU–BI (statistically significant in both yrs) and PCU–MRB compared to PCU–BI treatment (statistically significant in 2011)

corresponded to greater N₂O emissions. In the case of IU–MRB, the chemical inhibition of hydrolysis and nitrification seemed to have been effective in limiting N₂O production, as evidenced by soil NO₂⁻ – N intensity which was not significantly greater compared to IU–BI and that, in effect, likely led to N₂O emissions, comparable to that in IU–BI.

Soil NO₂⁻ – N accumulation in BI treatments during the season was always below 1 µg N g⁻¹ soil in both years with an exception of one sampling event each in both years, when CU treatment had NO₂⁻ – N accumulation of 11 and 9 µg N g⁻¹ soil in 2011 and 2012 respectively. These low values of NO₂⁻ – N accumulation in soil corresponded to N₂O emissions of ≤ 2.3 kg N ha⁻¹ in wet year 2011 and ≤ 1.6 kg N ha⁻¹ in dry year 2012. However, in MRB plots greater and persistent NO₂⁻ – N accumulation over the season led to greater soil NO₂⁻ –N intensity, which in turn corresponded to greater N₂O emissions, especially for CU in both years (6.2 and 3.4 kg N ha⁻¹ in 2011 and 2012 respectively), and PCU in 2011 (5.0 kg N ha⁻¹) when the season was wetter than in 2012. For IU in both years, soil NO₂⁻ intensity was smaller and corresponded to less N₂O emissions.

Table 3-5 shows a strong linear correlation between N₂O emissions and NO₂⁻ – N intensity each year and both years together. Such correlation between N₂O emissions and NO₂⁻ accumulation have been reported in the composting processes (Fukumoto and Inubushi, 2010; He et al., 2001), and in activated sludge (Alinsafi et al., 2008; Itokawa et al., 2001). The difference in NO₂⁻ –N accumulation and subsequent NO₂⁻ – N intensity during the season among different treatments underscores the potential for optimizing N banding intensity in order to achieve less extreme conditions that generate elevated N₂O production while preserving the other possible benefits of banding. In the current study,

it was found that IU–MRB did not cause substantial NO_2^- –N accumulation in both years and same was true for PCU–MRB in the dry year of 2012. This result suggests that IU is a best choice of N source where band placement of fertilizers is recommended and PCU is also recommendable for band application in a dry climatic condition. .

Ammonia Volatilization

Under favorable environmental conditions, broadcast urea is commonly reported to lose 30–50% of applied N through NH_3 volatilization (Vaio et al., 2008; Griggs et al., 2007; Martha et al., 2004; Antisari et al., 1996; Christianson et al., 1995) and sometimes, as high as 60% (Soares et al., 2012). Therefore, incorporation of urea mechanically or with water (rain or irrigation) is recommended to reduce volatilization loss (Dawar et al., 2011; Sommer et al., 2004; Sogaard et al., 2002; Rochette et al., 2001; Grant et al., 1996). In the current study, N fertilizers were either broadcast incorporated or band applied at 0.05 m depth and rain of 9 mm on the day of fertilizer application and another of 5 mm four days later occurred in 2011 and rainfall totaling 47 mm within two days of fertilizer application occurred in 2012. In both years, rainfall events might have moved N down in soil profile, thus helping to reduce volatilization loss which was $\leq 1\%$ of applied N.

In BI treatments, area–based NH_3 volatilization with the CU treatment was significantly greater than in PCU or IU in 2011 and was greater than in PCU (by 34%) and IU (by 76%) in 2012. Urease inhibitor such as NBPT used with IU in the current study is generally reported to reduce NH_3 volatilization compared to CU (Frame et al., 2012; Turner et al., 2011; Rochette et al., 2009; Chai and Bremner, 1987). When added to CU, NBPT inhibits the activity of urease enzyme by blocking three active sites of the

urease molecule (Manunza et al., 1999), and help reduce volatilization loss of N. Coated urea had also been reported to reduce NH_3 volatilization compared to uncoated urea (Connel et al., 2011; Francisco et al., 2011). Coated–urea is designed for slow release of N over the season, which subsequently renders small doses of urea solution for hydrolysis over time and prevents accumulation of significant amount of NH_4^+ in soil and rise in soil pH, thus reducing NH_3 volatilization. Yield–scaled NH_3 volatilization decreased in order of $\text{CU} > \text{IU} > \text{PCU}$ that implies that more NH_3 volatilization loss would occur in the same order for gain of equal agronomic production.

In 2012 when NH_3 volatilization loss was also measured in MRB treatments, MRB greatly reduced NH_3 volatilization compared to BI. Similar results were reported in other studies (Rochette et al., 2008; Sommer et al., 2004; Preez and Burger, 1987) while there are also reports suggesting greater NH_3 volatilization with banded urea compared to broadcast (Rochette et al., 2009). Volatilization loss of N is driven by the NH_3 source strength (concentration) and limited by the resistance to gas diffusion to atmosphere (Rochette et al., 2008). Hence it depends on a number of factors such as soil properties, including buffer capacity, climatic conditions, and management factors. Mixing fertilizers with soil, as in BI treatments in the current study, may be less efficient in reducing volatilization loss than placing fertilizers to the same depth as in MRB since a part of mixed–in fertilizer will be close to the surface and be susceptible for volatilization loss (Sommer et al., 2004). In the current study volatilization loss of N in BI treatments was $<1\%$ of applied N, which can be an underestimate, due to limitations of the acid–trap method used to measure it. However, band placement of fertilizers relatively reduced volatilization loss compared to BI in this study.

Mix of IU and CU (IU/CU)

Amending urea with additives is not a new N management practice. Urea amended with zeolite in corn cropping systems was reported to increase N uptake (Ahmed et al., 2010) and reduce NH_3 volatilization when used with sago waste water (Omar et al., 2011). Yield in a low input of urea but with organic additives was comparable to that in conventionally fertilized plots (Kramer et al., 2002). In the current study, the IU/CU–MRB treatment reduced NH_3 volatilization loss compared to any BI treatment and was more effective than CU–MRB in reducing N_2O emissions without compromising in agronomic production. The mix treatment was expected to provide N necessary for initial phases of corn growth due to early hydrolysis of CU and delayed but sustained N supply in later stages of growth from IU in the mix. This arrangement of N supply over the season with IU/CU-MRB treatment could have reduced soil NO_2^- accumulation at a given time compared to CU–MRB treatment, thus preventing substantial N_2O emissions. The results of this study showed some encouraging potential for the variable combination of CU with IU to mitigate N loss.

Conclusions

Band placement of fertilizers significantly increased N_2O emissions compared to BI for the PCU and CU treatments. Averaged across years and N placement, IU was effective in reducing area–based N_2O emissions and FIEF compared to CU or PCU. Greater soil NO_2^- – N accumulation corresponded to greater N_2O emissions. The current study showcases some potential to improve N management to mitigate N_2O emissions by avoiding substantial NO_2^- – N accumulation in fertilized soil. Band placement of

fertilizers was shown to have a positive effect on reducing NH₃ volatilization loss. Alternate N sources, PCU and IU, have potential in reducing NH₃ volatilization loss compared to CU. The mix of IU/CU in their variable combination is another potential way to reduce gaseous N losses and improve N management.

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Table 3-1: Results of statistical analyses for different dependent variables as affected by year, N source and placement, and their interactions.

Sources of Effects	Environmental variables						Agronomic variables			
	Area-based N ₂ O (kg N ha ⁻¹)	Yield-based N ₂ O (kg N Mg ⁻¹ grain)	Area-based † NH ₃ (kg N ha ⁻¹)	Yield-based † NH ₃ (g N Mg ⁻¹ grain)	Area-based ‡ NH ₃ (kg N ha ⁻¹)	Yield- § based NH ₃ (g N Mg ⁻¹ grain)	Grain yield (Mg ha ⁻¹)	Above-ground N uptake (kg N ha ⁻¹)	NUE (kg grain kg ⁻¹ N)	NFRE (%)
Year (Y)										
2011	3.3 (0.4) a	0.24 (0.03)	1.07 (0.25) a	78.7 (18.2)	NA	NA	14.1 (0.3) a	285 (13)	78.4 (1.7) a	64.8 (7.5)
2012	1.6 (0.2) b	0.17 (0.03)	0.52 (0.06) b	55.5 (7.9)	NA	NA	10.1 (0.4) b	244 (8)	56.3 (2.1) b	39.3 (5.7)
<i>Significance</i>	**	NS	NS	NS	NA	NA	**	NS	**	NS
N source† (N)										
Control	0.5 (0.1)	0.06 (0.01)	0.06 (0.02)	8.3 (3.9)	0.02 (0.00)	2.7 (0.3)	9.6 (0.8)	171 (13)	–	–
PCU	2.3 (0.2) b	0.18 (0.01) b	0.52 (0.05) b	41.7 (4.3) c	0.27 (0.11)	25.2 (10.2)	12.7 (0.8)	272 (17)	70.7 (4.1)	55.6 (7.8)
IU	1.6 (0.2) c	0.13 (0.01) b	0.56 (0.11) a	50.6 (9.4) b	0.21 (0.10)	22.8 (11.4)	12.0 (0.7)	277 (20)	66.7 (3.9)	58.7 (11.9)
CU	3.4 (0.2) a	0.30 (0.02) a	1.30 (0.33) a	108.9 (19.6) a	0.38 (0.13)	42.9 (15.9)	11.6 (0.7)	245 (19)	64.6 (3.6)	41.8 (12.5)
<i>Significance</i>	***	***	**	***	NS	NS	NS	NS	NS	NS
N Placement‡ (P)										
BI	1.6 (0.1) b	0.13 (0.01) b	NA	NA	0.52 (0.06) a	55.5 (7.9) a	12.1 (0.5)	263 (13)	67.3 (3.0)	50.9 (8.3)
MRB	3.3 (0.4) a	0.28 (0.04) a	NA	NA	0.05 (0.02) b	5.1 (1.4) b	12.1 (0.5)	268 (10)	67.3 (3.0)	53.2 (5.8)
<i>Significance</i>	***	***	NA	NA	***	***	NS	NS	NS	NS
Interaction										
N × P	**	**	NA	NA	NS	NS	NS	NS	NS	NS
N × Y	NS	NS	*	NS	NA	NA	NS	NS	NS	NS
N × Y × P	NS	NS	NA	NA	NA	NA	NS	NS	NS	NS

*** Significant at $P < 0.0001$, ** at $P < 0.01$, * at $P < 0.05$, and NS – not significant, NA – not applicable

†N sources include no N (control), polymer-coated urea (PCU), urea impregnated with inhibitors (IU) and conventional urea (CU). The control was not included as an N source in the overall analysis so that placement effects could be examined.

‡Placement includes BI– broadcast incorporation and MRB– mid-row banding

§ Only the BI treatments were measured both years; ¶ Placement effects on NH₃ emissions were analyzed only in 2012.

§ For each variable, means followed by the same letter are not significantly different ($P < 0.05$).

Table 3-2: Results of statistical analyses for different dependent variables as affected by N source in MRB treatments in 2012.

N source†	Environmental variables				Agronomic variables			
	Area-based N ₂ O (kg N ha ⁻¹)	Yield-based N ₂ O (kg N Mg ⁻¹ grain)	Area-based NH ₃ (kg N ha ⁻¹)	Yield-based NH ₃ (g N Mg ⁻¹ grain)	Grain yield (Mg ha ⁻¹)	Above-ground N uptake (kg N ha ⁻¹)	NUE (kg grain kg ⁻¹ N)	NFRE (%)
PCU	1.6 (0.4) b	0.15 (0.04) b	0.03 (0.00)	2.9 (0.1) b	11.5 (0.8)	2578 (11)	63.9 (4.5)	46.2 (13.8)
IU	1.0 (0.1) b	0.10 (0.01) b	0.03 (0.00)	2.9 (0.2) b	9.9 (0.9)	251 (25)	55.1 (5.0)	42.4 (18.7)
CU	3.4 (0.5) a	0.40 (0.11) a	0.09 (0.05)	9.4 (3.1) a	9.7 (1.7)	255 (27)	53.9 (9.4)	48.9 (19.2)
IU/CU	1.6 (0.3) b	0.15 (0.04) b	0.07 (0.03)	6.4 (2.1) ab	10.6 (0.7)	267 (8)	58.9 (3.9)	51.2 (12.7)
<i>Significance</i>	**	*	NS	*	NS	NS	NS	NS

†N sources include polymer-coated urea (PCU), urea impregnated with inhibitors (IU), conventional urea (CU) and mix of IU and CU (IU/CU).

§For each variable, means followed by the same letter are not significantly different ($P < 0.05$).

Table 3-3: Results of statistical analyses for soil N (NO_2^- –N, NO_3^- –N and NH_4^+ –N) intensity ($\text{g N kg}^{-1} \text{ d}$) at center and off-center locations as affected by year, N source and placement, and their interactions.

Source of Effects	NO_2^- –N intensity		NO_3^- –N intensity		NH_4^+ –N intensity	
	center†	off-center†	center	off-center	center	off-center
<u>Year (Y)</u>						
2011	16.2 (5.2) a	0.7 (0.2)	196 (35)	71.9 (10.0)	271 (71)	21.6 (2.1)
2012	6.8 (2.7) b	1.2 (0.2)	204 (29)	80.3 (15.9)	277 (54)	40.0 (7.7)
<i>Significance</i>	*	NS	NS	NS	NS	NS
<u>N source†</u>						
(N)						
Control	0.6 (0.1)	0.6 (0.1)	24.1 (0.9)	33.1 (5.6)	14.3 (2.2)	13.1 (2.0)
PCU	13.3 (6.2) a	0.8 (0.1) b	258 (50) a	94.6 (20.7)	305 (83)	31.6 (6.1)
IU	2.7 (0.8) b	0.7 (0.1) b	186 (28) ab	77.7 (14.8)	249 (68)	57.4 (32.1)
CU	18.6 (5.8) a	1.4 (0.3) a	156 (32) b	56.2 (10.2)	268 (83)	57.4 (8.8)
<i>Significance</i>	***	*	*	NS	NS	NS
<u>Placement‡</u>						
(P)						
BI	1.5 (0.3) b	1.2 (0.2) a	107 (13) b	108.9 (14.1) a	54 (6) b	45.6 (6.2) a
MRB	21.6 (5.0) a	0.7 (0.1) b	293 (30) a	43.4 (5.4) b	494 (47) a	16.0 (3.0) b
<i>Significance</i>	***	**	***	***	***	*
<u>Interaction</u>						
N × P	**	NS	NS	*	NS	NS
N × Y	**	NS	NS	NS	NS	NS
N × Y × P	**	NS	NS	NS	NS	NS

† N sources include no N (control), polymer-coated urea (PCU), urea impregnated with inhibitors (IU) and conventional urea (CU). The control was not included as an N source in the overall analysis so that placement effects could be examined.

‡ Placement includes BI– broadcast incorporation and MRB– mid-row banding

‡ Center and off-center locations are at 0.38 and 0.20 m away from corn row

§For each variable, means followed by the same letter are not significantly different ($P < 0.05$).

Table 3-4: Means (SE) for soil NO₂⁻–N intensity (g N kg⁻¹ d) where significant year-by-N source-by-placement treatment interaction effects were found.

N source†	2011		2011	
	BI	MRB	BI	MRB
Control	0.49 (0.00)	–	0.75 (0.02)	–
PCU	0.58 (0.03) c	48.2 (4.8) a	1.23 (0.33) c	3.07 (1.43) c
IU	0.53 (0.01) c	4.5 (1.8) c	1.10 (0.35) c	4.64 (1.34) c
CU	2.98 (1.16) c	40.8 (10.8) ab	2.37 (0.62) c	28.27 (9.10) b

† N sources include no N (control), polymer-coated urea (PCU), urea impregnated with inhibitors (IU) and conventional urea (CU). The control was not included as an N source in the overall analysis.

§ Means followed by the same letter are not significantly different ($P < 0.05$).

Table 3-5: Correlation coefficient (r^2) (and P values) for linear regression analyses of cumulative N₂O emissions versus different soil N intensity metrics determined in soil samples from the mid-row position and 0–0.2 m depth.

Soil N intensity	2011	2012	both yrs
NH₄⁺ – N	0.78 (0.009)	0.23 (0.23)	0.41 (0.01)
NO₂⁻ – N	0.82 (0.005)	0.86 (0.0008)	0.82 (< 0.0001)
NO₃⁻ – N	0.65 (0.03)	0.09 (0.46)	0.30 (0.04)
NO₂⁻ – N + NO₃⁻ – N	0.83 (0.03)	0.88 (0.005)	0.82 (< 0.0001)

Table 3-6: Means (SE) for cumulative area-based NH₃ volatilization in BI treatments where year-by-N source treatment interaction effects were found.

N source†	2011	2012
Control	0.10 (0.02)	0.02 (0.00)
PCU	0.53 (0.11) b	0.50 (0.05) b
IU	0.74 (0.02) b	0.38 (0.14) b
CU	1.93 (0.40) a	0.67 (0.06) b

† Control – no nitrogen, PCU – polymer-coated urea, IU – urea impregnated with inhibitors, and CU – conventional urea

§ Means followed by the same letter are not significantly different ($P < 0.05$).

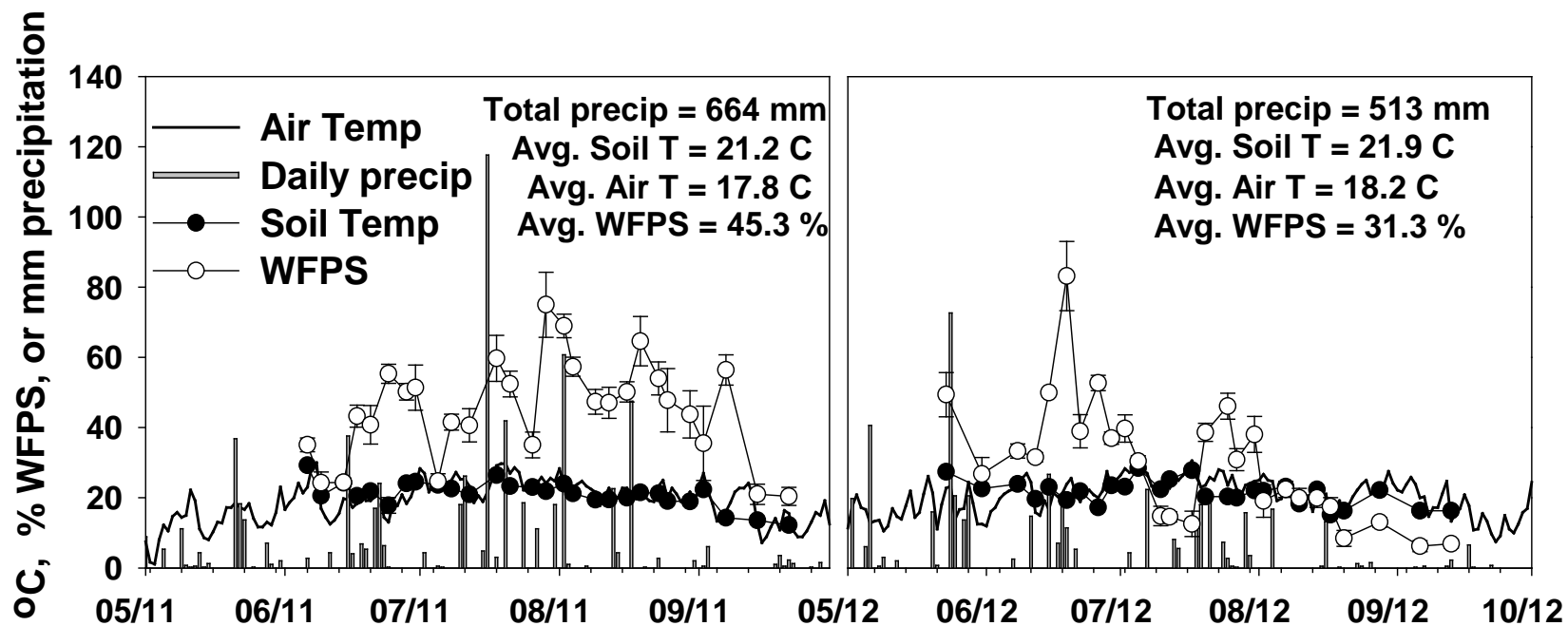


Figure 3-1: Daily precipitation, mean daily air temperature and mean (SE) soil temperature, and mean (SE) water-filled pore space (WFPS) at the 0.05-m depth at the time of N₂O sampling during 2011 and 2012.

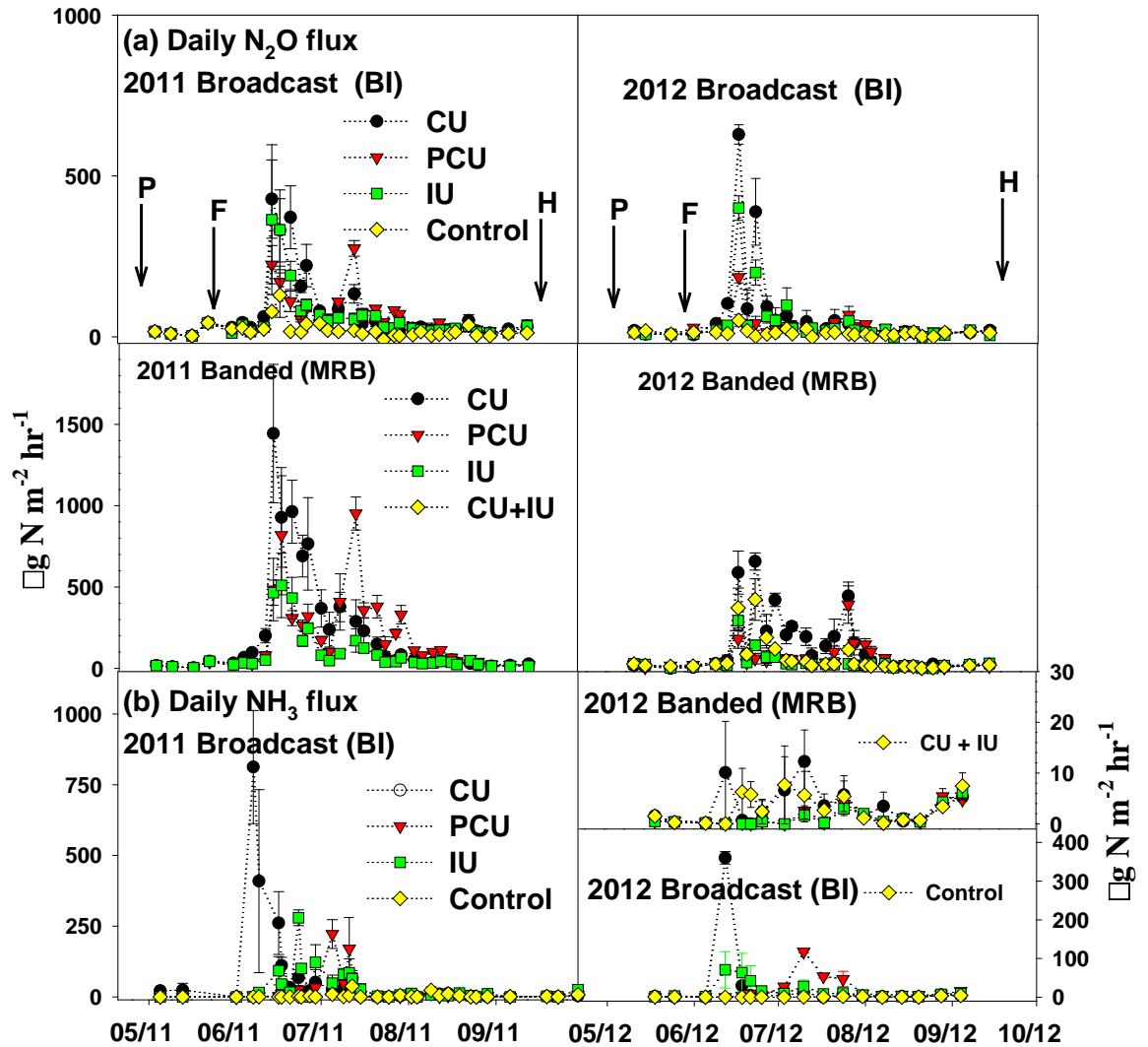


Figure 3-2: Mean (SE) N₂O emissions in (a) broadcast incorporation (BI) and (b) mid-row band (MRB) application of fertilizers and (c) mean (SE) NH₃ emissions in BI and MRB treatments under different N sources; no N (control), polymer-coated urea (PCU), urea impregnated with inhibitors (IU) and conventional urea (CU) during 2011 and 2012. Downward-pointing arrows indicate date of planting (P), fertilizer application (F) and grain harvest (H).

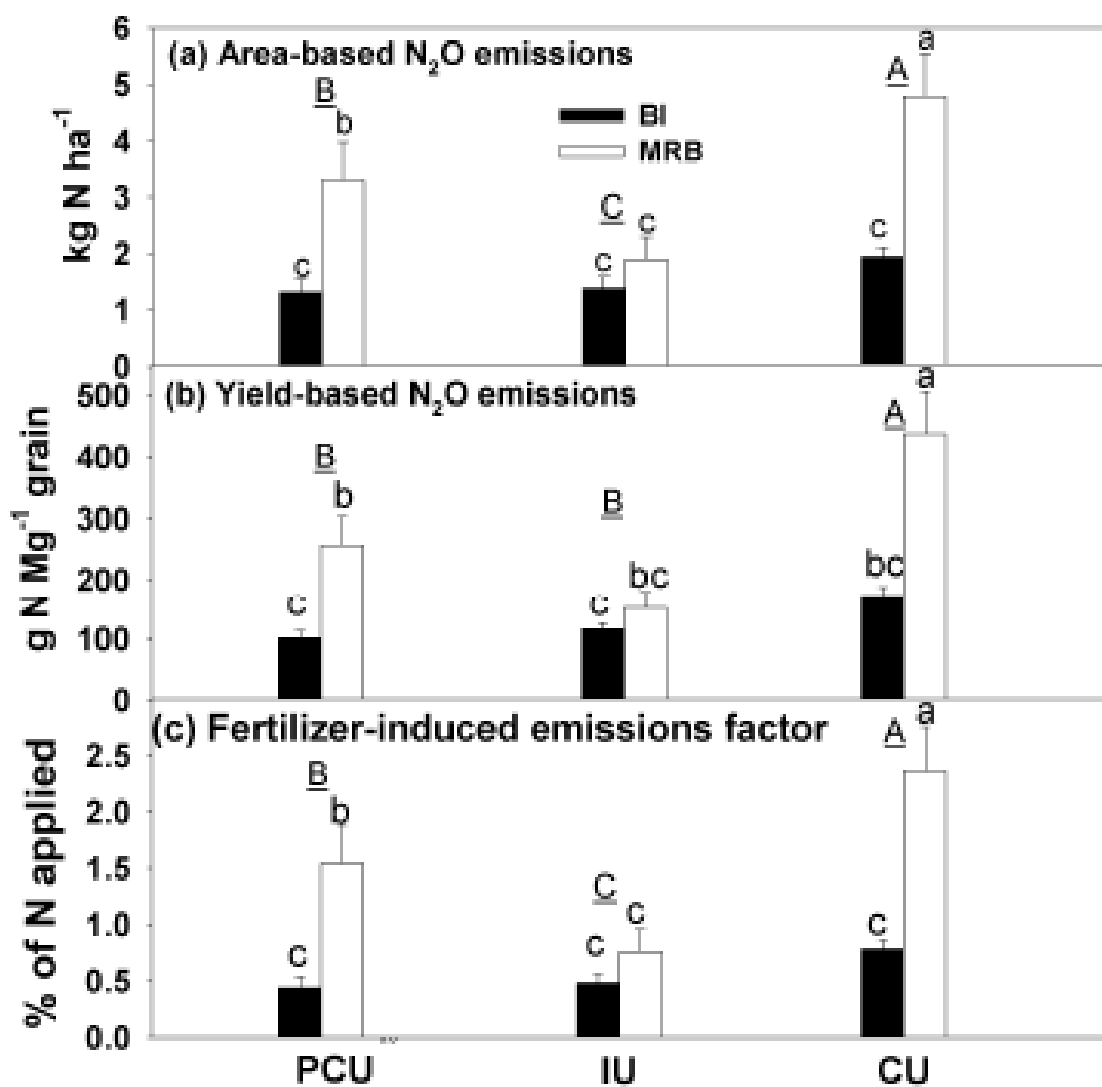


Figure 3-3: Mean (SE) cumulative N₂O emissions (a) expressed per unit of area, (b) per grain yield and (c) fertilizer-induced emissions factors (FIEF) in broadcast incorporated (BI) and mid-row banded (MRB) treatments under different N sources; no N (control), polymer-coated urea (PCU), urea impregnated with inhibitors (IU) and conventional urea (CU) during 2011 and 2012. For a quantity in each set of comparisons, bars with the same letters are not significantly different ($P < 0.05$). Lowercase letters refer to means comparison of all combinations of N source and placement. Underlined uppercase letters refer to means comparison of N sources.

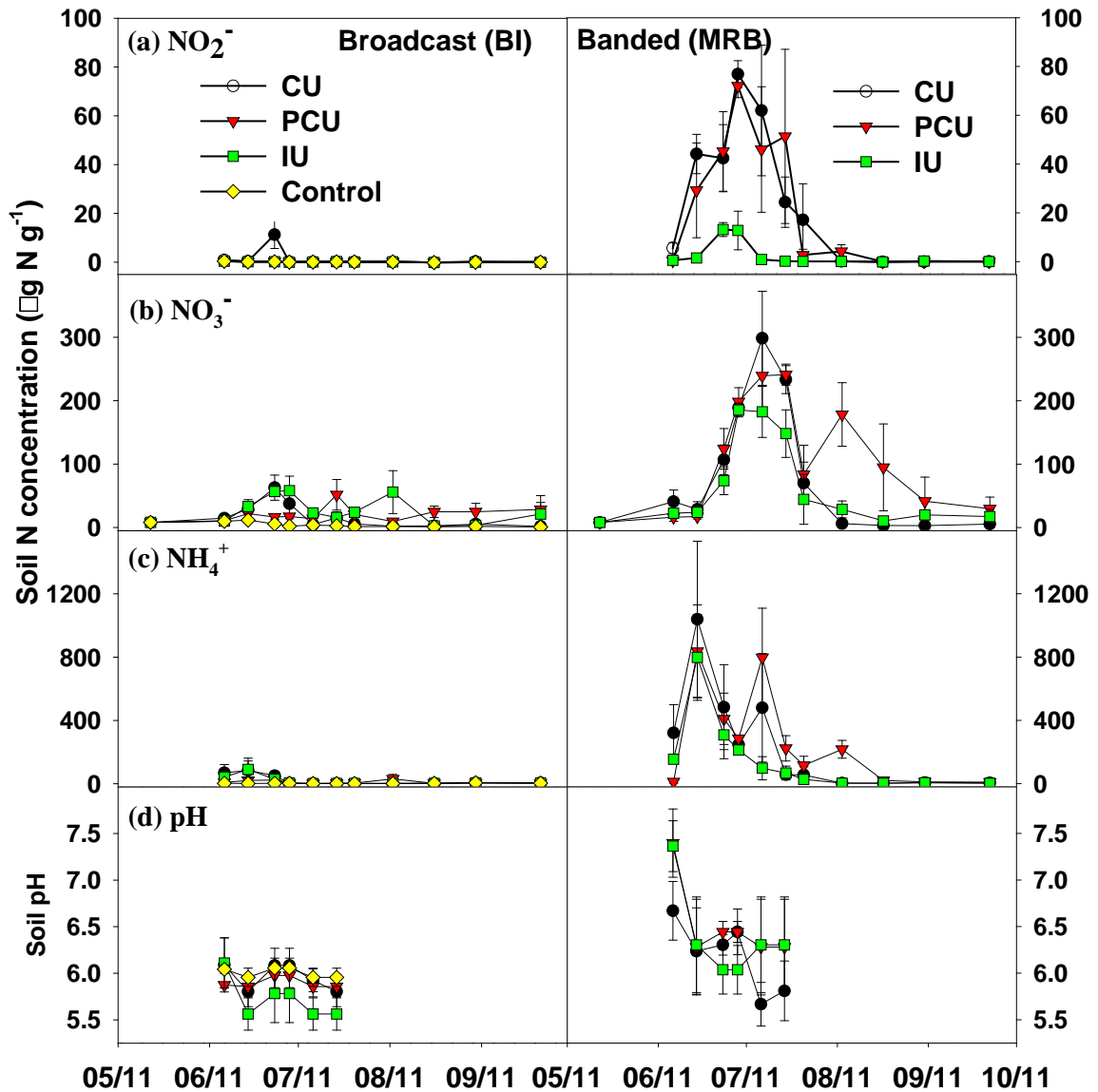


Figure 3-4: Mean (SE) soil concentrations of (a) nitrite (NO_2^-), (b) nitrate (NO_3^-) and (c) ammonium (NH_4^+) and (d) pH in the upper 0.10-m depth of the mid-row location in broadcast incorporated (BI) and mid-row banded (MRB) treatments under different N sources; no N (control), polymer-coated urea (PCU), urea impregnated with inhibitors (IU) and conventional urea (CU) during 2011.

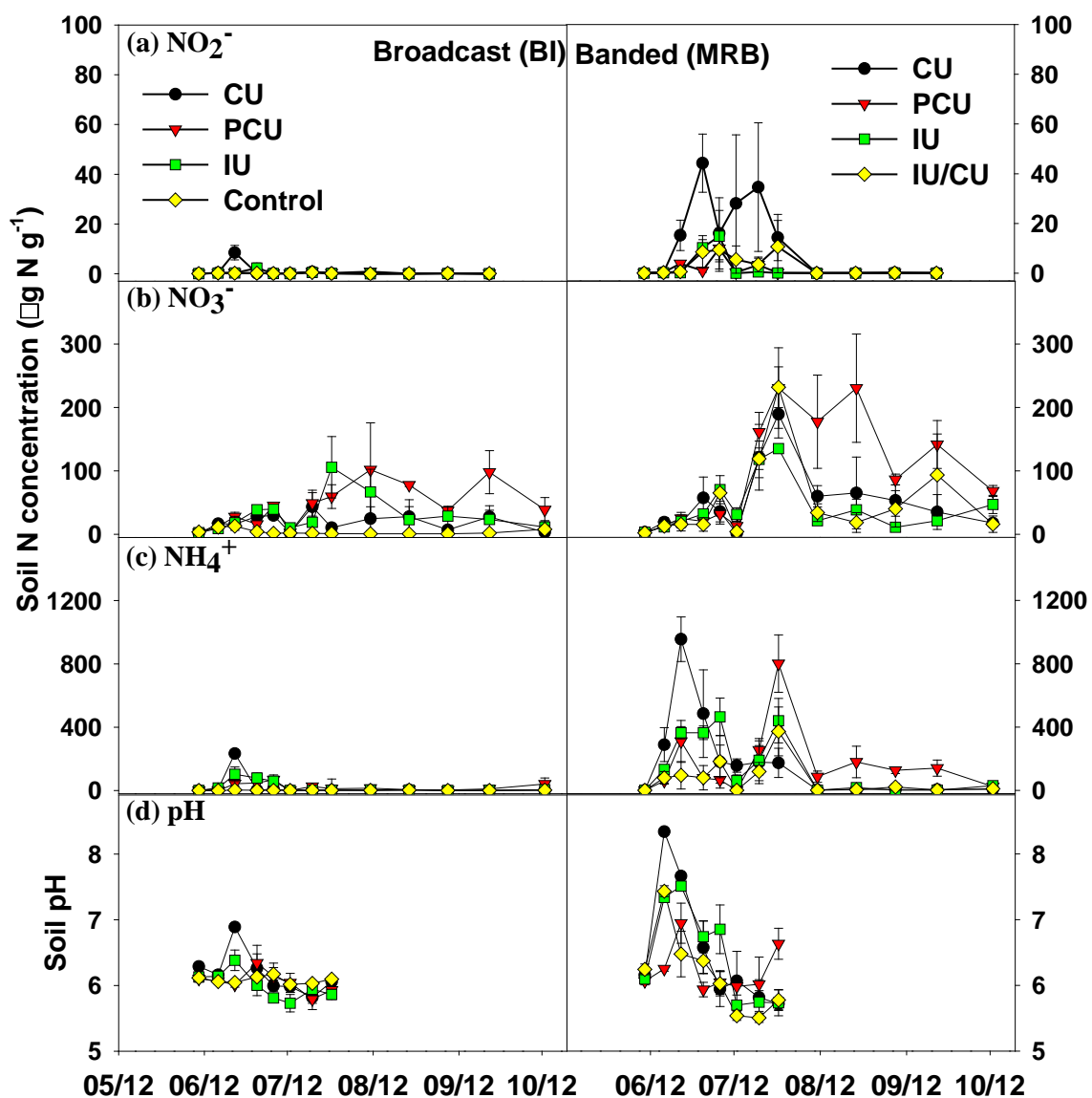


Figure 3-5: Mean (SE) soil concentrations of (a) nitrite (NO_2^-), (b) nitrate (NO_3^-) and (c) ammonium (NH_4^+) and (d) pH in the upper 0.10-m depth of the mid-row location in broadcast incorporated (BI) and mid-row banded (MRB) treatments under different N sources; no N (control), polymer-coated urea (PCU), urea impregnated with inhibitors (IU) and conventional urea (CU) during 2012.

Conclusions

Our results from three different research experiments show the significance/potential of optimizing management of N source, placement, tillage and irrigation in an effort to reduce N losses without decreasing yield, or in a best scenario with an increase in yield. Irrigation did not increase and in some cases decreased N_2O and NO_3^- losses when N losses were expressed on a yield-basis. Apparently, CU if split applied could perform on the level of (or better than) PCU or IU. However, when it was not split-applied and was applied one-time before planting as PCU and IU in the other experiment (Chapter 2), CU increased N_2O emissions and NH_3 volatilization compared to PCU or IU. Across all three N treatments (PCU, CU and IU), banding was effective in reducing NH_3 loss but increased N_2O emissions for the PCU and CU treatments. Our results suggest that banded application of IU could achieve benefits of banding without unintended consequences of increased N_2O emissions. The result showing that a banded 50/50 mix of IU/CU reduced N_2O points out that a mixed N source may provide a more economical N_2O mitigation strategy compared to using 100% of the IU product which generally has higher cost than CU. No significant difference in N_2O emissions, grain yield and NO_3^- leaching potential by AA placement depth observed in silt loam soils do not necessarily imply that there is no significance in considering placement depth for the AA treatment in relation to GHG mitigation efforts. Shift in placement depth does affect speed of AA application, tractor-fuel consumption and soil disturbance which can have associated economic and environmental implications. These factors need to be included

in analysis while determining the effects of AA placement depth in mitigating GHG emissions.

Results from these experiments point out the limitations of reporting environmental impacts of agricultural practices only on an area-scaled basis. Reporting yield-based N losses would simultaneously regard for both agronomic production and N losses. The wide range and high upper limit of indirect N₂O emission estimates from the experiment in sandy soils (Chapter 1) indicate the need of improved methods of quantifying indirect N₂O emissions in evaluating management effects on total GHG budgets. In the experiment (Chapter 3) where temporal soil NO₂⁻ concentrations were measured separately from NO₃⁻, the results emphasize the need for measuring soil NO₂⁻ concentrations separately from NO₃⁻ and suggest that it might provide more insight and management opportunities in mitigation of N₂O.

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