NITROGEN DYNAMICS IN SOILS FROM THE RED RIVER VALLEY OF THE NORTH

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Rakesh Awale

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The Supervisory Committee certifies that this ***disquisition*** complies with North Dakota State University's regulations and meets the accepted standards for the degree of

DOCTOR OF PHILOSOPHY

SUPERVISORY COMMITTEE:

Dr. Amitava Chatterjee
Chair

Dr. Hans Kandel

Dr. Thomas DeSutter

Dr. David Franzen

Approved:

August 11, 2015
Date

Dr. Frank Casey
Department Chair

ABSTRACT

The objectives of this study were to evaluate the effects of (i) N management on crop yield, N availability, and N losses from a silty clay having subsurface drainage, (ii) soil moisture and nitrification inhibitor nitrapyrin [2-chloro-6-trichloro methyl pyridine, NP] on N_2O emissions, and (iii) urea N-additives on NH_3 volatilization and N_2O emission losses from two contrasting soil textures (silty clay and sandy loam).

The mean yields for corn (*Zea mays* L.), wheat (*Triticum aestivum* L.), sugarbeet (*Beta vulgaris* L.), and soybean (*Glycine max* L.) were 7.4, 0.9, 47.0, and 2.6 Mg ha^{-1} in 2012, and were 8.3, 4.1, 38.3, and 3.0 Mg ha^{-1} in 2013, respectively, across N and drainage treatments. Applying recommended N-rate along with NP increased N availability to crops, particularly under the subsurface drained condition. Application of extra N-rate than recommended only increased N losses associated with N_2O and NH_3 emissions.

In the laboratory, N_2O emissions from urea applied at 250 kg N ha^{-1} to silty clay soil were 0.14, 0.96, and 4.00% of applied-N at 30, 60, and 80% WHC, respectively. At WHC $\leq$ 60%, NP reduced N_2O emissions by 2.6 to 4.8 fold compared to urea alone.

Ammonia volatilization was higher from sandy loam (0.7 to 4.3% of applied-N) than from silty clay (0.1 to 0.4% of applied-N). In sandy loam, applying urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT) and polymer coated urea (PCU) reduced NH_3 losses by 32.3% and 84.2%, respectively, compared to untreated-urea. In silty clay, NBPT reduced NH_3 volatilization by 71.4% relative to untreated-urea. N_2O emissions did not differ between soils, and were between 3.7 to 7.4% of applied-N. In sandy loam, NP, SuperU (urea containing NBPT and nitrification inhibitor dicyandiamide), and PCU reduced N_2O emissions by 23.5%, 43.8%, and 51.1%, respectively, compared to urea alone.

Within the scope of two years of the field study, subsurface drainage and N management influenced soil N availability more than crop yield, emphasizing the need for long term research on subsurface drainage effect on crop yield. Soil moisture, texture and N management exert strong influence on NH_3 volatilization and N_2O emission.

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GENERAL INTRODUCTION

Nitrogen (N) fertilization is essential in most cropping systems to optimize crop yields and economic returns (Belanger et al., 2001). However, N management is a challenge due to the fate of applied N fertilizer and uncertainties of weather (Dell et al., 2014). The N added to meet crop demand is subject to fixation in the soil along with losses through ammonia (NH_3) volatilization, nitrate (NO_3^-) leaching, and nitrous oxide (N_2O) emissions, with up to 98% of total N applied loss reported in the literature (Gioacchini et al., 2002). As a result of these N losses, the mean fertilizer-N recovery by crops ranges between 35 to 65% (Smil, 1999).

About 1.8 million ha of soils in the Red River Valley (RRV) of the North Dakota and northern Minnesota are poorly drained (USDA-NRCS, 2014). Poorly drained soils in the RRV are potentially highly productive; however, saturated soil conditions and flooding often limit production (Wiersma et al., 2010). Wet climatic periods and the preponderance of soluble salts in soils within the region have stimulated an interest among growers in installing subsurface (tile) drainage systems during the last 15 years (Cihacek et al., 2012; NDSU Extension Service, 2015).

Subsurface drainage removes excess gravitational water from the crop root zone and improves soil aeration and temperature, timeliness of field operations, field workability and trafficability, and agronomic yields (Kladivko et al., 2005). However, subsurface drainage can influence below ground N dynamics, N availability and losses, and thereby crop N uptake (Bouwman et al., 2010). Usage of N-additives (such as urease and/or nitrification inhibitors), slow-release polymer coated urea, and split-N application has a potential to minimize N losses and improve crop yields (Halvorson et al., 2014). Research on the combined effect of subsurface drainage and targeted N management on crop production in poorly drained soils in the RRV is limited.

LITERATURE REVIEW

Ammonia (NH_3) Volatilization

Globally, 46% of the N input for crop production comes from inorganic N fertilizers (Smil, 1999), and urea is by far the most common synthetic N fertilizer used because of its low cost relative to other N sources (Bierman et al., 2012). Ammonia (NH_3) volatilization is one of the major N loss pathways associated with the use of surface applied urea (Zaman and Blennerhassett, 2010) where nearly 81% of the anthropogenic NH_3 emissions results from agricultural activities in the United States (Aneja et al., 2008). In soils, urea quickly hydrolyzes into ammonium (NH_4^+) and carbonate (CO_3^-) in the presence of urease enzyme and water (Zerpa and Fox, 2011). Further, the NH_4^+ produced dissociates into gaseous NH_3 by combining with the hydroxyl ion (OH^-), formed from the reaction of CO_3^- with water. Research has shown that as much as 64% of the urea applied to the soil surface can be lost through NH_3 volatilization (Rochette et al., 2009), especially from calcareous soils with low cation exchange capacity (CEC) (Franzen et al., 2011; Francisco et al., 2011).

Ammonia volatilization is primarily driven by the difference in NH_3 partial pressure between the soil atmosphere and the air. Therefore, volatilization losses of NH_3 from surface applied N fertilizers depend on such factors that affect the partial pressure of NH_3 as initial soil pH, soil CEC, soil clay type and content, soil organic matter content, soil water content, temperature, and wind (Clay et al., 1990; Mkhabela et al., 2006; Pelster et al., 2012).

Increase in soil pH shifts the equilibrium reaction [NH_4^+ (soil) = NH_3 (soil) = NH_3 (gas)], by moving more NH_4^+ towards NH_3 form, resulting greater NH_3 emissions at higher pH (Mkhabela et al., 2006). Likewise, higher soil temperature increase soil concentration of NH_3 dissolved in soil water, leading to higher rate of NH_3 volatilization (Clay et al., 1990). High NH_3

losses are expected upon drying of soil (water evaporation) because of the rapid movement of urea fertilizer towards the soil surface (Al-Kanani et al., 1991). Studies have also found that NH_3 volatilization increases linearly as soil water content increases, until the soil reaches saturation, because of greater accumulation of NH_4^+ upon O_2 limitation with soil saturation (Singh et al., 2011). Hargrove (1988) reported that maximum NH_3 volatilization occurs when the soil water content is at field capacity. According to Francisco et al. (2011), soils higher in CEC can retain greater NH_4^+ to the higher negative charges at the exchange sites, and thus render lower NH_4^+ substrate availability for NH_3 loss as compared with soils with low CEC. Furthermore, the relative contribution to CEC of soil increases with organic matter and clay content, and thereby reducing NH_3 emissions from soils with higher organic matter and clay content than from the soils with low organic matter and clay content (Al-Kanani et al., 1991; Watson et al., 1994). Soil texture, therefore, has a significant role as to influence NH_3 volatilization due to variations in the soil factors that regulate it (NH_3 volatilization) (Pelster et al., 2012).

Management of N application can also have a profound effect on NH_3 volatilization. Application of N fertilizer can be expected to increase the NH_4^+ concentration, and thereby NH_3 volatilization, with losses much pronounced within the first few days of N application (Rawluk et al., 2001; Soares et al., 2012). Application of urease inhibitors and other controlled release urea fertilizers has a potential to reduce NH_3 volatilization losses. In a laboratory experiment with Typic Hapludox from Brazil, Soares et al. (2012) showed that the application of the urease inhibitor N-(n-butyl) thiophosphoric acid triamide (NBPT) reduced NH_3 volatilization losses between 54 and 78%, compared to untreated urea. Rochette et al. (2013) reported that NH_3 loss was 50% of applied N when urea was surface applied, while band placement of urea fertilizer decreased volatilization loss by 14% cm^{-1} soil depth and incorporating urea at depths >7.5 cm completely inhibited NH_3 emission. Jantalia et al. (2012) documented that immediate irrigation (16 to 19 mm of water) 1 d after N application is sufficient to limit NH_3 loss from surface applied N fertilizers to <4%. Therefore, soil incorporation of surface applied N fertilizers mechanically or from heavy rainfall (irrigation) after N application, and use of urease inhibitors can negate NH_3 volatilization losses (Engel et al., 2011; Holcomb et al., 2011).

Nitrous Oxide (N_2O) Emission

Nitrogen fertilization in agricultural cropping systems is responsible for approximately 70% of the total N_2O emissions (Kroeze et al., 1999). Nitrous oxide is the main precursor to the depletion of the stratospheric ozone layer as well as it promotes the greenhouse effect (Crutzen, 1981). Annual losses of N_2O account for 1-1.25% of the amount of N fertilizer applied (IPCC, 2006), however losses over 5% have also been reported (Crutzen et al., 2008; Glenn et al., 2012).

In soils, N_2O is produced mainly through the microbial processes of nitrification and denitrification which are primarily controlled by soil pH, soil aeration, soil texture, and the availability of oxidizable C sources and inorganic N substrates (NH_4^+ and NO_3^-) (Simek and Cooper, 2002; Senbayram et al., 2009; Hoben et al, 2011). Generally, the size of denitrifier community and total gaseous N production are higher at neutral or slightly alkaline soils than acidic soils, attributed to the smaller quantity of organic matter and mineral N availability to the denitrifiers at acidic condition (Simek and Cooper, 2002). According to Bateman and Baggs (2005), soil microsites become predominantly anaerobic at $\geq$ 60% soil water filled pore space (WFPS) and promotes greater N_2O emissions through denitrification process because of limited O_2 availability, while nitrification mainly regulates N_2O production below 60% WFPS. Chantigny et al. (1998) showed a linear response in N_2O production with N rates due to increased N availability. Nitrogen fertilization and soil water content, therefore, influence N_2O

fluxes. Large fluxes of N_2O shortly after N application and rainfall/irrigation events are usually reported in the literature (Gagnon et al., 2011; Menendez et al., 2012).

Poorly drained soils are deemed favorable for denitrification loss of N_2O due to extended periods of soil saturation oftentimes observed with high clay containing soils (Glenn et al., 2012; Asgedom et al., 2014). However, previous studies of soil texture effects on N_2O emissions have yielded contradictory results, with some noting greater emissions from fine-textured soils than coarse-textured soils (Sexstone et al., 1985; Rochette et al., 2008; Pelster et al., 2012), and others noting opposite results (Mkhabela et al., 2006; Jarecki et al., 2008). Sexstone et al. (1985) documented that the total N loss due to denitrification from the clay soil loam soil was double that of the sandy loam because of the longer duration of the enhanced denitrification rate, due to higher water retention in the clay loam soil. Furthermore, the lower O_2 diffusion rates, associated with the fine-texture silty clay soil, can yield more anaerobic microsites and enhance denitrification as compared with the sandy loam soil (Pelster et al., 2012). According to Pelster et al. (2012), the greater availability of easily mineralizable C in the silty clay soil than the sandy loam soil not only provides the necessary electron donor for denitrification, but it can also stimulate soil microbial respiration rates, deplete soil O_2, and thus enhance anaerobic microsites necessary for denitrification. Similarly, Rochette et al. (2008) observed exceptionally higher N_2O emissions from clayey than loam soil, attributed to denitrification favored by the decomposition of higher organic matter content in the clayey soil. The potential of higher organic C content in enhancing N_2O emissions is further validated by another study on two clay loam soils with different C contents, which demonstrated that higher C content of the temperate grassland soil favored denitrification as well as soil respiration rates compared to the lower organic C containing semiarid arable soil (Sanchez-Martin et al., 2008).

Conversely, lower N_2O emissions from fine-textured soil were also observed as a result of decreased gas diffusivity, favoring N_2O reduction (Weitz et al., 2001; Gu et al., 2012). Similarly, Jarecki et al. (2008) observed higher N_2O emissions in the sandy loam than in the clayey soil upon application of urea ammonium nitrate (UAN) or organic swine manure. The lower N_2O emissions associated the clayey soil was attributed to the fact that the clayey soil had higher soil CEC (26.7 $cmol_c$ kg^{-1}) than the sandy soil (10.6 $cmol_c$ kg^{-1}), which increased the adsorption of NH_4^+ at the exchange sites, and thus rendered lower N availability for N_2O production (Jarecki et al., 2008). Pain et al. (1990) also showed higher N_2O emissions in sandy than in clay soil due to higher nitrification observed in the sandy soil, which accumulated higher NO_3^- substrates for denitrification, when conditions became anaerobic. Mkhabela et al. (2006) showed that the higher soil pH in the sandy loam soil (5.7) as compared with the silty clay loam soil (4.7) favored denitrifier organisms and enhanced denitrification, which consequently produced 2.5 times higher N_2O emissions from the sandy loam soil than from the silty clay loam soil.

Nitrate (NO_3^-) Leaching

Nitrate (NO_3^-) is weakly held by soil, and thus is prone to leaching. Nitrate leaching is the downward movement of NO_3^- in the soil profile with percolating water. The leaching loss of NO_3^- can reduce crop yield due to depletion of available N in the root zone, and can also impair surface and ground water quality (Jaynes et al., 2001; Drury et al., 2009). The combination of factors such as soil texture, structure, water holding capacity, and permeability, the amount and timing of precipitation received, crop yield variations, and soil and N nutrient management impact the leaching loss of NO_3^- from soils (Kladivko et al., 2005; Randall and Vetsch, 2005). In a laboratory study with two contrasting soil textures (Greenville loam and Lakeland sand) using lysimeters, Singh et al. (2012) demonstrated that nearly 87% of applied urea N leached out from the Lakeland sand as NO_3^-, while the Greenville loam lost <1% of applied N because the latter had lower percolation rate (<1.0 mL h^{-1}) and heavier texture, compared to the former. Similarly, urea applied to the sandy loam soil (103 kg ha^{-1}) had 10 times higher NO_3^- losses than to the clay loam soil (10 kg ha^{-1}) (Gioacchini et al., 2002). In a subsurface drainage study in Minnesota, average flow-weighted NO_3^- concentration in the drainage water from corn (*Zea mays* L.) plots increased in the year (30.0 mg L^{-1}), following the preceding three years with dry periods (12.5 mg L^{-1}), due to carryover of unused fertilizer-N, and mineralized soil-N during the dry years (Randall et al., 2003). In poorly drained soils in central Iowa, Jaynes et al. (2001) studied the amount of NO_3^- leached in the subsurface drains from corn-soybean (*Glycine max* L.) rotation applied with three different N rates (low: 57-67 kg ha^{-1}; medium: 114-135 kg ha^{-1}, and high: 172-202 kg ha^{-1}). The authors found that, over four years, the NO_3^- mass loss in the subsurface drainage water from the low, medium, and high N rates were 29, 35, and 48 kg N ha^{-1}, respectively, with the latter (high N rate) being significantly greater than the former two N rates. Management of N application timing, and usage of nitrification inhibitors or slow release N fertilizers have potential to reduce NO_3^- leaching losses from agroecosystems (Randall et al., 2003; Randall and Vetsch, 2005; Nelson et al., 2009). Nelson et al. (2009) found that the slow release polymer coated urea (Environmentally Smart Nitrogen, ESN, Agrium Inc.) reduced the concentration of NO_3^- in soil water (at 45 cm depth collected by suction lysimeters) by 51 to 63% early in the corn growing season, compared to conventional urea. Applying nitrification inhibitor nitrapyrin [NP, (2-chloro-6-(trichloromethyl) pyridine), DOW AgroSciences] to the fall- or spring-applied anhydrous ammonia reduced NO_3^- leaching into subsurface drainage water by 13 to 18%, compared to untreated fall-applied anhydrous ammonia (Randall et al., 2003).

Subsurface (Tile) Drainage

Drainage and flooding are critical problem in the Red River Valley (RRV) of North Dakota and northern Minnesota due to the flat topography and dominant poorly drained clay soils (Jin et al. 2008). About 1.8 million ha of soils in the RRV are poorly drained (USDA-NRCS, 2014). Poorly drained soils in the RRV can produce high crop yields; however, saturated soil conditions and flooding often limit production (Wiersma et al., 2010; Kandel et al., 2013). Wet climatic cycle, increased crop and land prices, and the presence of soluble salts in soils within the region have stimulated an interest among growers in installing subsurface tile drainage systems during the last 15 years (Cihacek et al., 2012; NDSU Extension Service, 2015).

Subsurface tile drains are buried pipelines that remove excess gravitational soil water from agricultural fields to improve soil aeration and temperature, field workability and trafficability, and timeliness of agronomic operations, so that crop productivity in not unduly compromised (Chieng et al., 1987; Jin et al., 2008; Drury et al., 2009; Nelson et al., 2011). Subsurface drainage can accelerate soil N mineralization by improving soil aeration (Rochette et al., 2010; Gutinas et al., 2012), influence NH_3 volatilization by changing N substrate availability (Singh et al., 2011), increase NO_3^- leaching in the drains (Klocke et al., 1999; Randall et al., 2003), reduce denitrification loss of N_2O by eliminating water logging (Venterea et al., 2008), and thereby influence crop N uptake and crop productivity (Nelson et al., 2011).

Impact of subsurface drainage on crop productivity

Many studies conducted under a wide variety of soils have indicated significant crop yield improvements in soils with subsurface drainage that were not traditionally tile drained (Nelson et al., 2011). For instance, from a study over 10 years in a poorly drained Clermont silt loam soil in southern Indiana, Kladivko et al. (2005) found the corn yields were increased by 10 to 17% with subsurface drainage (5 m spacing) plots over non-drained plots – attributed to wetter soil conditions, delayed planting date, and lower plant population under non-drained plots. Similarly, in a Putnam claypan soil in northeast Missouri, Nelson et al. (2011) reported that subsurface drainage over four years increased soybean yield by 9 to 22% compared to without drainage. Another study conducted in similar soil by Nash et al. (2015) concluded that subsurface drainage reduced the potential denitrification N loss of conventional urea fertilizer during the early growing season, and thereby increased corn yield by 15 to 21% - presumably due to greater N uptake than when no drainage was present. In a study conducted in poorly drained Fargo silty clay, Hoppe (2013) reported a significant increase in soybean yield by 17% with subsurface drainage, compared to a non-drained condition, during one of two study years. In poorly drained Vallers loam and Hegne silty clay loam soils from the RRV, subsurface drainage not only reduced the incidence and duration of shallow water tables, but it also raised soil temperature up to 4°C during May and June, compared to non-drained soils (Jin et al., 2008). Faster soil warm-up in the spring can play an important role in crop growth and agronomic yield because soil temperature strongly influences seed germination, seedling emergence and growth, root development, and microbial activity in the soil (Eghball and Marranville, 1993; Agehara and Warncke, 2005). Similarly, Kandel et al. (2013) found that subsurface drainage increased the penetration resistance of a Fargo silty clay soil and therefore, the drained soil was capable of bearing a higher load carrying capacity, compared to the non-drained soil. And, improvement in field trafficability and workability can increase crop yields as the number of opportunity days to work the land increases (Chieng et al., 1987). Furthermore, the addition of control structures to the subsurface drainage technology has allowed the growers to regulate the flow of water through the drainage tiles, and thereby increase the retention of crop available water as well as N nutrient during the dry growing periods (Drury et al., 2009). The improvement in the use efficiency of water and N consequently increases crop yields (Fisher et al., 1999; Nelson et al., 2011; Nash et al., 2015).

Nevertheless, studies involving the effect of subsurface drainage systems on crop yields have often resulted inconsistent results. For example, in a Fargo silty clay, soybean and wheat (*Triticum aestivum* L.) yields were not improved with subsurface drainage compared to undrained treatments over two study years (Kandel et al., 2013). Similar results were also reported by Wiersma et al. (2010) for soybean and wheat in Vallers loam and Hegne silty clay loam soils, where the crop yields were not different between subsurface drained and non-drained treatments. The decrease of available water in the soil profile - caused due to rapid lowering of water table and for extended period of time with subsurface drainage - was attributed to the lack of response of drainage management in this study (Wiersma et al., 2010). In fact, the lack of crop yield response to subsurface drainage management is more evident during the moderate to extreme dry growing seasons, when abnormally poor crop growth conditions presumably limit crop yield potentials (Kladivko et al., 2005; Hoppe, 2013; Nash et al., 2015). Therefore, yield improvement with subsurface drainage is long term investment and may not be reaped in every year (Kladivko et al., 2005).

Impact of subsurface drainage on N mineralization and availability

Subsurface drainage has potential to improve soil aeration and temperature (Jin et al., 2008). Soil microclimate plays a very important role in regulating soil microbial activity, N mineralization rate, and N availability (Agehara and Warncke, 2005). According to Franzluebbers (1999), rate of N mineralization is maximum when the soil water filled pore space (WFPS) is between 50 to 60% because of maximum soil microbial activity at these water regimes, with the N mineralization rates subsequently declining near saturation due to O_2 limitations. Others have shown that N mineralization rate followed first order kinetics and that the response of N mineralization to temperature is generally described by exponential functions such as Arrhenius equations, with the rate doubling for each 10°C increase in temperature (Stanford and Smith, 1972). In poorly drained soils from the RRV of Minnesota, Wiersma et al. (2010) found that the grain protein content of wheat increased linearly with the drainage coefficient, attributed to the increment in available N from mineralization, and the larger volume of soil for plant roots to extract available N with the improvement in drainage. Besides, draining excess water can eliminate water logging conditions, which can reduce denitrification losses of N and thereby increase crop N availability (Nash et al., 2015).

Impact of subsurface drainage on N_2O emission

Poorly drained soils usually favor denitrification loss of N_2O because of extended periods of soil saturation, which leads to root-zone oxygen reduction through displacement of soil air by water (Sims, 2010; Nash et al., 2015). Installing subsurface drainage can eliminate the chance of water logging by lowering the water table, and thereby, reduce the denitrification N losses (Nelson et al., 2009; Tesfai et al., 2015). In Minnesota, Venterea et al. (2008) showed that the total corn growing season soil N_2O emissions were 50% lower from subsurface drained plots compared to non-drained plots because the former had lower soil water retention. In a recent study conducted in oat (*Avena sativa* L.)-barley (*Hordeum vulgare* L.) rotation in three contrasting soils with different drainage classes (poorly drained, imperfectly drained, and moderately well drained) in Norway, Tesfai et al. (2015) found that over two growing seasons, cumulative N_2O emissions ranged 6 to10 kg N_2O-N ha^{-1} in poorly drained soil, 4 to 12 kg N_2O-N ha^{-1} in imperfectly drained soil, and 0.2 to 0.9 kg N_2O-N ha^{-1} for moderately well drained soil.

Soil N_2O emissions from poorly drained soils were usually higher during the growing seasons, compared to moderately well drained soil because of relatively shallow ground water table and higher soil water content in the poorly drained soil (Tesfai et al., 2015). Similarly, Grossel et al. (2014) reported that the mean daily N_2O flux from tile-drained (3.6 g N_2O-N ha^{-1} d^{-1}) loamy soils in Central France was smaller than undrained soils (29 g N_2O-N ha^{-1} d^{-1}) because the average WFPS was 9% lower in the drained plots. Reduction in N_2O emission losses associated with the lowering of water table with subsurface drainage and/or soil water content can increase crop N uptake and improve yields (Nelson et al., 2009). Recently, Nash et al. (2015) reported that subsurface drainage in a Putnam claypan soil increased corn N uptake by 26% over non-drained treatment because drainage increased N availability in soil - due to the reduced saturated soil conditions during early corn growing season and low denitrification N loss.

Impact of subsurface drainage on NH_3 volatilization

Subsurface drainage may influence NH_3 volatilization rates by changing soil water and temperature regimes, and/or influencing the N substrate availability. Soil anaerobic conditions can decrease nitrification and thereby accumulate NH_4^+, which consequently results in greater amounts of NH_3 under an anaerobic soil environment (Singh et al., 2011). As such, in Al-Kanani et al. (1991) demonstrated that NH_3 volatilization rates increased linearly with the increase in soil water content until saturation in cultivated soils in eastern Canada. According to Clay et al. (1990), concentration of dissolved NH_3 in soil increase with soil temperature, therefore, NH_3 emission losses are greater with higher than lower soil temperature. Conversely, subsurface drainage can accelerate N mineralization in poorly drained high organic matter soils (Franzluebbers, 1999; Rochette et al., 2010), which can in turn increase NH_3 losses as N availability increases (Rawluk et al., 2001). Moreover, using subsurface drainage to lower soil water table provides surface soil water with more space to percolate down the soil profile that can incorporate fertilizer N into the soil, resulting in low NH_3 volatilization (Norman et al., 2003). There is no information as to the effect of the subsurface drainage on NH_3 volatilization ever published.

Impact of subsurface drainage on NO_3^- leaching

Nitrate leaching is the primary mechanism of N loss under well drained soils (Klocke et al., 1999; Gioacchini et al., 2002), whereas it may not be of agronomic concern under poorly drained soils, such as are found within the production areas of the RRV (Swenson et al., 1979). However, when tile drained, significant amounts of NO_3^- losses have also been reported from poorly drained soils (Jaynes et al., 2001; Randall et al., 2003; Drury et al., 2009). For example, in a clay loam soil in Minnesota, Randall et al. (2003) reported that up to 122 kg N ha^{-1} was lost as NO_3^- through subsurface drainage water in one year. Therefore, concentrations of NO_3^- in the subsurface drained water above the drinking water guideline (10 mg N L^{-1}) are often reported in the literature (Drury et al., 1996). Apart from soil texture, NO_3^- leaching also varies with the amount and timing of precipitation, crop yield variations, and soil and N nutrient management (Kladivko et al., 2005; Randall and Vetsch, 2005). Greater N losses to subsurface drains are often observed in years following a drought due to greater residual N in the soil profile (Randall et al., 2003).

In view of growing concern over the leaching of NO_3^- to groundwater and decreased crop N use efficiency (Jaynes et al., 2001), there is justification for minimizing NO_3^- loss from the tile drains by regulating the out-flow of drainage waters using controlled structures in the subsurface drainage technology (Drury et al., 2009). Controlled subsurface drainage has shown the potential to reduce NO_3^- concentrations in the drainage water (Drury et al., 1996; Fisher et al., 1999; Nelson et al., 2009; Nash et al., 2015).

Nitrogen Management Strategies

High clay containing, poorly drained soils in the RRV warrant targeted N management considerations (Asgedom et al., 2014). Development of effective management practices to maximize crop production is important in poorly drained soils because of their vulnerability for N losses (Randall et al., 2003). Losses of N from crop production fields can pollute soil and water quality, and can reduce agronomic yields (Crutzen, 1981; Drury et al., 2009). Management of N application using N-additives such as nitrification and/or urease inhibitors, controlled release stabilized N fertilizer sources, and split N application may reduce potential N losses from agroecosystems (Trenkel, 1997; Zaman and Blennerhassett, 2010; Jantalia et al., 2012; Dell et al., 2014; Halvorson et al., 2014).

Urease inhibitor

Urease inhibitors delay urea hydrolysis rate by blocking the enzyme urease - which catalyzes the hydrolysis reaction (Manunza et al., 1999). As a result, NH_4^+ availability as well as rise in soil pH is reduced, favoring low NH_3 production under these conditions (Dawar et al., 2011). The NBPT has been reported as one of the most efficient urease inhibitors in reducing NH_3 volatilization losses across a variety of soils, with a reduction range between 15 to 89% compared to untreated urea (Clay et al., 1990; Rawluk et al., 2001; Cantarella et al., 2008; Francisco et al., 2011; Soares et al., 2012). Usually, maximum NH_3 volatilization losses (up to 86% of total growing season NH_3 emissions) occur within first few days (7 to 9 d) of urea application, and application of NBPT can minimize this loss by 96% during this period (Rawluk et al., 2001). The delay in urea hydrolysis by urease inhibitor NBPT can also facilitate the movement of surface applied urea into sub-surface layer both vertically and laterally with water coming from rain or irrigation (Dawar et al., 2011). Movement of urea into sub-surface layers decreases NH_3 loss due to greater incorporation of NH_4^+ into soil exchange complex (Sigunga et al., 2002; Rochette et al., 2014). Therefore, under soil conditions where high NH_3 emissions occur, the urease inhibitor NBPT could not only reduce NH_3 losses, but also provides farmers with at least a certain time period (a week) to schedule management practices (such as irrigation, tillage) in order to reduce N loss via volatilization (Grant et al., 1996; Francisco et al., 2011). However, significant NH_3 losses may occur from the NBPT-treated urea in the later growing periods provided the low crop uptake and the N-fertilizer is not incorporated into the soils by rainfall (irrigation) or manually by 10 to 15 days because the urea from the NBPT-treatment may eventually become available (Cantarella et al., 2008; Akiyama et al., 2010). The duration of the inhibition of urease hydrolysis caused by NBPT, and its (NBPT) extent in reducing NH_3 emissions may differ depending upon the soil texture and environmental conditions (Rawluk et al., 2001; Gioacchini et al., 2002; Engel et al., 2011). Moreover, as the NBPT-treated urea might become available for hydrolysis during the later growing periods, N losses via N_2O emission and/or NO_3^- leaching might also prevail during the periods of favorable soil conditions (Jarecki et al., 2008; Sanchez-Martin et al., 2008).

Nitrification inhibitor

Nitrification inhibitors such as Nitrapyrin (NP) and dicyandiamide (DCD) interfere with the nitrification of NH_4^+ to NO_3^- (Chen et al., 2010a). Therefore, these inhibitor compounds have potential to reduce NO_3^- leaching losses (Randal et al., 2003; Randal and Vetsch, 2005) as well as denitrification losses of N_2O (Soares et al., 2015; Omonode and Vyn, 2013), but may accelerate NH_3 volatilization (Gioacchini et al., 2002). In their meta-analysis review, Wolt

(2004) and Akiyama et al. (2010) have shown that the application of nitrification inhibitors to N-fertilizers potentially reduces N_2O emission losses by 30 to 51% compared to untreated N sources. Similarly, in a vertisol in Indonesia, the application of DCD to urea reduced cumulative corn growing season N_2O emissions by 56%, compared with urea alone (Jumadi et al., 2008). The concentrations of NO_3^- in soil water at 90 cm depth measured over a spring wheat growing season in Minnesota were lower with NP than conventional urea (Thapa et al., 2015). Nevertheless, the efficiency of nitrification inhibitors may vary with the interplay of various factors including soil physico-chemical properties (texture, pH, organic matter), soil environmental conditions (moisture, temperature), and N management (Wolt, 2000; Gioacchini et al., 2002; Randall et al., 2003). For example, Gioacchini et al. (2002) reported that application of DCD increased NO_3^- leaching loss by 48% in clay loam soil and by 24% in sandy loam soil, attributed to enhanced soil N mineralization due to priming effect caused by the retention of NH_4^+ for a longer period of time. Cumulative growing season N_2O emissions in spring wheat were similar between urea plus NP and untreated urea (Thapa et al., 2015).

In principle, the mechanism to the increase in NH_3 emissions by the nitrification inhibitors involves (i) the higher retention of NH_4^+ concentration in the soil for a longer time, (ii) the maintenance of higher pH induced from the reduction in nitrification, and (iii) the release of extra soil organic N caused by a priming effect resulted from higher NH_4^+ concentration (Gioacchini et al., 2002; Zaman and Blennerhasset, 2010; Soares et al., 2012). For instance, Rodgers (1983) documented higher NH_3 losses of 20 to 68% when urea was treated with DCD in different English soils. Similar stimulating effect of NP on NH_3 losses from urea was also observed by Bundy and Bremner (1974) in three soils in Iowa, where the NP treatment lost 11 to 34% applied N as NH_3 while the untreated urea lost only 3 to 9% of applied N. Nonetheless, the extent of the stimulating effect of nitrification inhibitors on NH_3 volatilization may differ with soil texture due to relative rate of inhibitor degradation as influenced by soil characteristics such as organic matter and clay content (Hendrickson and Keeney, 1978; Wolt, 2000; Singh et al., 2008).

Urease plus nitrification inhibitor

Nitrification inhibitors have potential to reduce N_2O emission and NO_3^- leaching losses (Randall et al., 2003; Omonode and Vyn, 2013). However, the accumulation of NH_4^+ in soils for a longer time may enhance NH_3 volatilization (Bundy and Bremner, 1974; Rodgers, 1983). Therefore, in order to minimize the effect of nitrification inhibitors on the tradeoff between increased NH_3 volatilization, and reduced N_2O emissions and NO_3^- leaching, recently, there has been a growing interest in the treatment of both urease and nitrification inhibitors to the N fertilizers (Zaman et al., 2008; Parkin and Hatfield, 2013; Halvorson et al., 2014).

Many studies have shown that the application of both urease inhibitor and nitrification inhibitor to urea-based fertilizers is associated with a significant reduction in NH_3 volatilization and N_2O emissions over a wide variety of soils due to inhibition of urea hydrolysis reaction by NBPT (Zaman and Blennerhassett, 2010; Jantalia et al., 2012). Nevertheless, the influences of the combined application of both of these inhibitors on NH_3 volatilization and/or N_2O emissions are not consistent (Gioacchini et al., 2002; Dell et al., 2014). For example, in irrigated corn grown in Fort Collins clay in Colorado, Jantalia reported that SuperU (urea stabilized with NBPT and DCD, Koch Agronomic Services) decreased NH_3 volatilization losses by 88-95% compared to un-treated urea. Recently, Thapa et al. (2015) also found that the SuperU reduced cumulative NH_3 volatilization by 26% compared to conventional urea, over a spring wheat growing season in a Bearden silt loam in Minnesota. Likewise, the proportions of applied-N lost via NH_3

volatilization from urea + NBPT + DCD and untreated urea to an acidic Brazilian soil were 17% and 28%, respectively, the latter being significantly higher than the former (Soares et al., 2012). However, in their other experiment with the same soil, the NH_3 losses were not different between urea + NBPT + DCD treatment (33% of applied N) and untreated urea (37% of applied N) (Soares et al., 2012). These authors argued that the retention of higher NH_4^+ and higher soil pH caused by DCD, and not by the interference of DCD on NBPT, increased NH_3 losses from the urea + NBPT + DCD treatment that was comparable to the NH_3 emission from the untreated urea (Soares et al., 2012). Conversely, Zaman et al. (2008) pointed out the DCD influenced the efficiency of NBPT, and thus resulted 29% increment in NH_3 losses with urea + NBPT + DCD treatment over untreated urea, both applied to a sandy loam soil in New Zealand. Moreover, DCD maintains NH_4^+ for longer time in soils, and can promote extra release of soil organic N due to priming effect, and thereby increase NH_3 volatilization (Gioacchini et al., 2002). These studies illustrate that the combined effect of urease and nitrification inhibitor can vary with soil characteristics (Watson et al., 1994).

Studies involving the combined use of both urease and nitrification inhibitors have documented significant reduction in N_2O emissions and NO_3^- leaching in a wide variety of soils, attributed to the N inhibition characteristics of both of the inhibitors (Zaman et al., 2008; Zaman and Blennerhassett, 2010; Sanz-Cobena et al., 2012). In silt loam soil, Zaman and Blennerhassett (2010) reported that the NBPT + DCD reduced N_2O losses by 55% compared with untreated urine fertilizer. Similarly, a stabilized urea fertilizer containing NBPT and DCD, SuperU, reduced N_2O emissions on an average by 46% compared with urea and by 21% compared with urea ammonium nitrate (UAN) in corn-based cropping system in Colorado (Halvorson et al., 2014). Thapa et al. (2015) reported that the SuperU reduced cumulative N_2O emission by 50%, compared to conventional urea in a Bearden silt loam soil in Minnesota. In the same study, the concentrations of NO_3^- in soil water at 90 cm depth measured during the growing season was less with SuperU than conventional urea (Thapa et al., 2015). In contrast, few studies have also reported that application of NBPT + DCD to conventional N fertilizers had no response in N_2O emissions, possibly due to inherent soil organic N mineralization contributing significantly to N_2O productions (Parkin and Hatfield, 2013), or excessive dry soil condition (Dell et al., 2014). For instance, Gioacchini et al. (2002) found that, compared to untreated urea, the treatment of NBPT + DCD to urea increased NO_3^- leaching losses in sandy loam (by 57%) and clay loam soils (by 36%) due to enhanced soil N mineralization upon application of the inhibitors.

Controlled release polymer coated urea (PCU)

Controlled release polymer coated urea (PCU) fertilizers, such as ESN, are coated with a soluble membrane that acts as a diffusion barrier which controls the release of N based on soil water content (Trenkel, 1997; Hyatt et al., 2010). A slow N releasing nature of these fertilizers allow growing plants with an opportunity for extended period of N uptake from soils until later periods of the growing season, leaving less N substrate for potential N losses associated with NH_3 volatilization (Rochette et al., 2009), N_2O emission, and NO_3^- leaching (Nelson et al., 2009; Halvorson et al., 2014).

Nevertheless, research evaluating the effect of PCU fertilizers on N losses (NH_3 volatilization, N_2O emission, and NO_3^- leaching) compared to conventional N fertilizers has yielded contradictory results with some noting reduced N losses with PCU than conventional N sources (Hyatt et al., 2010; Akiyama et al., 2010), while others have reported equal or higher N losses with PCU (Parkin and Hatfield, 2013; Dell et al., 2014; Soares et al., 2015). For instance, in a corn field in Brazilian Oxisol, Pereira et al. (2009) found that application of PCU reduced

NH_3 losses by 50%, compared to conventional urea. In different studies conducted in clay loam soils under irrigated corn-based cropping systems in Colorado, PCU reduced N_2O emissions on an average by 42% compared with urea, and by 14% compared with UAN (Halvorson et al., 2014). In contrast, Jantalia et al. (2012) reported stimulation of NH_3 loses from the PCU by 38 to 67% compared to urea, upon application on clay loam soil. The authors further suggested the necessity to evaluate NH_3 losses for extended period of time with PCU since NH_3 fluxes from this N fertilizer increases from around 6 wk (Jantalia et al., 2012). Based on a four year study with rainfed corn production in central Pennsylvania, Dell et al. (2014) concluded that the PCU fertilizers may not be effective to reduce N_2O emissions during the dry growing periods. According to Soares et al. (2015), a combination of factors such as time of N release from PCU, soil microclimate, and N uptake by plants can influence N availability in soils and N losses. Moreover, the temporal dynamics in N release rates from the PCU depends on soil texture. Halvorson and Del Grosso (2012) documented that PCU constantly had lower soil NO_3^- than urea during 2 months after N application in clay loam soil. Likewise, Parkin and Hatfield (2013) observed soil NO_3^- accumulation from PCU was lower than that from urea during the first 37 d following fertilizer applications in soils from Iowa. Recently, in a laboratory incubation of silt loam soil moistened to 30% WFPS, Dell et al. (2014) showed that the PCU delayed NH_4^+ accumulation and the subsequent buildup of NO_3^- until 2-3 wk, compared to urea. And, the following periods had higher NO_3^- concentration with the PCU than the urea treatment (Dell et al., 2014).

Soil NO_3^- test and split N application

Soil NO_3^- tests are important techniques for estimating the amount of inorganic N required for optimizing crop yields (Zebarth and Paul, 1997; Belanger et al., 2001). As such, the preplant soil NO_3^- test (PPNT) - taken just prior to a planting crop -usually measures the residual inorganic N content in soils with some early season N mineralization (Belanger et al., 2001). The PPNT does not reflect N cycling during the growing season, and therefore, may not be suitable for soils possessing high potential of mineralization-immobilization (Chen et al., 2010b; Rochette et al., 2010). Conversely, the mid-season soil NO_3^- tests (such as pre-sidedress soil NO_3^- test, PSNT) are found to be better correlated with crop yields than the PPNT (Magdoff, 1991). Therefore, the assessment of soil mineral N throughout the crop growing period improves our knowledge on N availability to crops (Chen et al., 2010b). An accurate assessment of soil NO_3^- during the crop growing season allows growers not only to improve fertilizer N recommendation, but also to protect against excessive N escaping to the environment.

Crop N demand is usually low during early growth stages, and there is a general consensus among researchers on the application of fertilizer N at the time of high crop demand - usually several weeks after crop emergence (Parkin and Hatfield, 2010). Therefore, applying N in split doses or side-dress application later in the growing season can improve the coordination between soil N availability and crop N demand, and thereby reduce N losses (Randall et al., 2003). Errebhi et al. (1998) showed that minimizing N application at planting and applying the majority of N at emergence and hilling stage in potato (*Solanum tuberosum* L.) reduced the amount of NO_3^- lost via leaching. Recently, Maharjan et al. (2014) reported that applying urea fertilizer in two to three doses, over two corn growing seasons in a Hubbard loamy sand in Minnesota, increased corn yield by 10.5% and N uptake by 13.5%, compared with pre-plant applied stabilized urea fertilizers (PCU or SuperU) at similar N rate. In the same study, split N application reduced N_2O emission and NO_3^- leaching losses by 17 and 29%, respectively, than the pre-plant applied PCU (Maharjan et al., 2014). However, applying N fertilizer in split doses to synchronize with the periods of high crop N demand may not always improve crop yields (Randall et al., 1997), and may even increase N loss when the soil conditions become more conducive (Venterea and Coulter, 2015).

Impact of Management on Crop Productivity

The N-additives have potential to limit N losses to the environment, increase N availability, and thereby may improve crop yields; however their effectiveness are not consistent as the N release rates from these N fertilizers varies with soil and environmental conditions (Gioacchini et al., 2002; Randall et al., 2003; Zaman et al., 2008; Jantalia et al., 2012; Parkin and Hatfield, 2013; Halvorson et al., 2014; Dell et al., 2014; Soares et al., 2015). Randall and Vetsch (2005) documented that, over six study years in clay loam, corn grain yields for fall-applied ammonia, fall-applied ammonia + NP, spring-applied ammonia, and spring-applied ammonia + NP were 10.1, 10.7, 10.8, and 11.0 Mg ha^{-1}, respectively, with the corresponding fertilizer N recovery of 47, 56, 56, and 61%, respectively. Similarly, Burzaco et al. (2014) reported that over two growing seasons, side-dress application of UAN at the V6 corn growth stage increased N uptake by 8%, on average, compared to pre-plant applied UAN. In the same study, the authors also found the application of NP to UAN increased the use efficiency of N by corn by 17% (Burzaco et al., 2014). In poorly drained claypan soil in northeastern Minnesota, Nash et al. (2015) reported that PCU fertilizer increased corn yields by 20% compared to conventional urea because PCU mitigated denitrification N loss potential in a saturated soil environment. According to Hyatt et al. (2010), PCU fertilizer can be a viable alternative N application strategy to split-applied urea in irrigated potato because PCU fertilizers are less expensive and can reduce soil N_2O emissions with no yield reduction relative to split-applied urea fertilizer.

Conversely, Halvorson et al. (2012) studied the effect of four N-stabilized fertilizers [ESN, Duration III (a polymer coated urea, Agrium Inc.), SuperU, and stabilized UAN with AgrotainPlus (containing NBPT and DCD, Koch Agronomic Services] on irrigated no-till corn in Colorado, and found that, over two years, the N-stabilized fertilizers did not improve corn yield but reduced N_2O emissions by 31 to 53% compared to conventional urea. Similarly, Dell et al. (2014) did not find any difference in corn yield among ESN, SuperU, stabilized UAN with AgrotainPlus, cation-stabilized amine-N, untreated UAN, and conventional urea over four years. The lack of efficiency of the N-stabilized fertilizers in this study was attributed to the reduced crop N demand from drought stress during the growing periods (Dell et al., 2014). Grain yield and protein concentration in winter wheat, grown in the drier regions of Canadian prairies, were similar among broadcast applied urea, ammonium nitrate, and NBPT-treated urea (Mckenzie et al., 2010). In the same study, PCU reduced grain yield by 6% and protein concentration by 3%, on average, compared to non-treated N sources due to excessive delay in N release observed with the PCU (Mckenzie et al., 2010).

Nitrogen Management under Subsurface Drainage Condition

The benefits of installing subsurface drainage systems to poorly drained soils seem quite appealing. However, subsurface drainage influences below ground N dynamics (Bouwman et al., 2010). Moreover, the growing concern about NO_3^- contamination of surface waters by subsurface drained fields in crop production has prompted the development of effective N management practices to reduce NO_3^- loss in the drainage water. The combination of subsurface drainage and targeted N management such as N-additives or split N application in poorly drained soils in the RRV may greatly reduce the N loss potential, increase N availability in soil, improve crop N uptake, and increase crop production. Simultaneous measurements of yield, N availability, and N losses as influenced by the interaction of N management and subsurface drainage or soil water regimes have not been intensively studied in the RRV. Chaput (2014) reported no yield improvements in corn in two subsurface drained soils (Fargo and Cresbard) in the RRV with the use of N-additives (NP, PCU, NBPT + DCD) or split N application over two dry years. Therefore, research is needed to evaluate if the combination of subsurface drainage and N fertilizer management practices can increase crop production while reducing the potential of N loss from poorly drained soils in the RRV.

Objectives

The objectives of this study were as follows:

(i) To evaluate the effects of N management on crop yield, N availability, and N losses via NH_3 volatilization, N_2O emissions and NO_3^- leaching from a Fargo silty clay having subsurface drainage,

(ii) To evaluate the effects of soil moisture and nitrification inhibitor nitrapyrin on N_2O emissions, and

(iii) To evaluate the effects of urea N-additives on NH_3 volatilization and N_2O denitrification losses from two contrasting soil textures (Fargo silty clay and Ulen sandy loam) from the RRV.

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NITROGEN DYNAMICS AND CROP PERFORMANCE IN FARGO SILTY CLAY SOIL UNDER SUBSURFACE DRAINAGE

Abstract

Installing tile drainage facilitates early planting and field operations, and tiling has tremendously increased in the Red River Valley (RRV) due to recent wet cycles. This experiment studied tile drainage and N management effect on corn (*Zea mays* L.), wheat (*Triticum aestivum* L.), sugarbeet (*Beta vulgaris* L.) and soybean (*Glycine max* L.) production in a naturally poorly drained Fargo soil. Application of recommended N rate with nitrification inhibitor nitrapyrin [2-chloro-(6-trichloromethyl) pyridine] increased soil inorganic N levels during the mid-crop growing season, particularly under the tile drained condition. Applying urea with urease inhibitor N-(n-butyl) thiophosphoric triamide increased soil N availability early during the wheat growing period under the tile-drained condition. Average corn, wheat, sugarbeet, and soybean yields were 7.4, 0.9, 47.0, and 2.6 Mg ha^{-1} in 2012, and were 8.3, 4.1, 38.3, and 3.0 Mg ha^{-1} in 2013, respectively, across N management and drainage. Yield responses to drainage and N management were limited due to abnormally dry growing periods along with large inherent soil N mineralization. In 2013, application of recommended N-fertilizer increased corn and wheat yields on average by 27.6 and 18.0%, respectively. Under sugarbeet in 2012, applying higher than recommended N rate increased root impurity (% sucrose loss to molasses) by 8%. Also, the higher N rates were usually associated with greater N_2O emissions, with the recorded maximum daily N_2O surface flux rate of 105 g N_2O-N ha^{-1} d^{-1}. Addition of fertilizer-N increased NH_3 volatilization losses up to 1.7% of the applied N. Tile drainage and N management influenced soil N availability more than crop yield during two years of study. A long-term study is needed to investigate the fertilizer N use efficiency under tile drainage.

Introduction

About 1.8 million ha of soils in the Red River Valley (RRV) of the North are poorly drained (USDA-NRCS, 2014), which has led to increased adoption of subsurface drainage (Kandel et al., 2013). Subsurface drainage can provide agronomic benefits through the gravimetric water removal, reduced surface runoff, and improved trafficability (Sims, 2010). However, shifting water regimes influences below ground N dynamics through changes in soil moisture and temperature (Bouwman et al., 2010).

Soil water content has significant influence on N mineralization rates (Gutinas et al., 2012). Subsurface drainage accelerates organic N decomposition by improving soil aeration (Rochette et al., 2010). Optimum N rates for crop production can vary greatly among years based on N mineralization rates and possible N losses (Leiros et al., 1999). A precise estimate of N mineralized in soils under subsurface drainage, hence is critical in determining rate of N fertilizer application required to optimize crop yield and minimize environmental N losses (Dessureault-Rompre et al., 2013).

Subsurface drainage has potential to reduce denitrification loss of nitrous oxide (N_2O) from agricultural fields (Dusenbury et al., 2008). Poorly drained soils favor denitrification loss because of root-zone oxygen reduction through displacement of soil air by water (Gagnon et al., 2011). Installing subsurface drainage can eliminate the chance of water logging by lowering the water table, and thereby, the denitrification N losses (Venterea et al., 2008). Apart from soil aeration, the availability of inorganic N substrates is also an important factor that controls the dynamics of soil N_2O emissions (Gagnon et al., 2011). Large pulses of N_2O production at times immediately following N application and/or heavy rainfall events are not uncommon (Dusenbury et al., 2008). Denitrification loss of N_2O from agricultural soils increases with N application rates

(Hoben et al., 2011). These studies suggest the necessity of revisiting N fertilizer application rates based on N requirement of crops, grown in soils with subsurface drainage tile lines.

Nitrate (NO_3^-) leaching is a major concern in subsurface drained soils (Klocke et al., 1999; Jaynes and Colvin, 2006). Annual rainfall, crop yield variations, and soil and nutrient management, in part or combination, govern NO_3^- leaching loss (Randall et al., 2003; Randall and Vetsch, 2005). Greater NO_3^- losses to subsurface tile drains are observed in years following a drought due to greater residual N in the soil profile (Kladivko et al., 2005). Balancing the amount of N required for optimum crop growth while minimizing NO_3^- loss under subsurface drainage is a major challenge in the RRV.

Ammonia (NH_3) volatilization is another major N loss pathways associated with the use of surface applied NH_4^+ based fertilizers (Engel et al., 2011). Ammonia volatilization from soils depends on soil water and temperature, texture and cation exchange, pH, wind speed, and surface coverage by residue (Bouwmeester et al., 1985; Clay et al., 1990). Soil water regimes have a strong impact on the NH_4^+ transport through profile and subsequently on the availability of NH_4^+ substrate for NH_3 volatilization (Singh et al., 2011). Subsurface drainage may increase the potential of soil NH_3 volatilization by maintaining the soil water content at field capacity; however, the extent of control mechanism is still not understood (Nash et al., 2015). Further, clay soils generally adsorb more NH_4^+ and limit NH_3 emissions, but the extent of control mechanism is still not understood (Griggs et al., 2007; Gu et al., 2013).

Soil N supply is proportional to crop yield and quality (Halvorson and Hartman, 1974). Insufficient N limits crop yield, but excessive amounts of N can deteriorate air and water quality (Crutzen, 1981; Randall et al., 2003; Soares et al., 2012). Application of fertilizer-N has generally shown to increase crop yields but it also increases N losses, especially when fertilizer-

N is applied in excess of crop requirements (Malhi and Lemke, 2007; Engel et al., 2011). Therefore, N management practices that co-ordinate peak mineral N availability during the periods of rapid crop N uptake is important not only to improve the agronomic yields but also to lessen the impacts of lost N from the agricultural systems into the environment (Parkin and Hatfield, 2010).

One way to tighten the synchrony between rapid crop N uptake and N availability could be through the addition of urease and/or nitrification inhibitors to the urea fertilizers (Parkin and Hatfield, 2013; Dell et al., 2014). Urease inhibitors [e.g. N-(n-butyl) thiophosphoric tiramide, NBPT) delay urea hydrolysis rate by blocking the enzyme urease (Manunza et al., 1999), and nitrification inhibitors (e.g. nitrapyrin, NP) impede NH_4^+ oxidation to NO_3^- (Omonode and Vyn, 2013). These N-inhibitors thus can create an opportunity for the grower to manage the synchronization of mineral N release from urea fertilizers during rapid the crop growing period. Moreover, reducing the availability of NH_4^+ and/or NO_3^- in soils when crop N requirement is small, the application of N-inhibitors has the potential to reduce N losses via volatilization (Engel et al., 2011), leaching (Randall and Vetsch, 2005), and denitrification (Parkin and Hatfield, 2013). Consequently, crop yields are increased due to greater use efficiency of the applied N (Randall et al., 2003). Application of N fertilizers in split doses could be another approach to co-ordinate maximum crop N uptake and thereby increase N use efficiency (Maharjan et al., 2014).

Fertilizer-N recommendations are usually based on the amount of N available at the beginning of growing season such as preplant soil NO_3^- test (PPNT) (Zebarth and Paul, 1997). The PPNT measures carry-over NO_3^- in soils from previous growing season in addition to some early growing season mineralization. However, substantial amount of soil N mineralization is deemed possible during the crop growing season, which is less considered (Rochette et al., 2010). Since the PPNT does not indicate soil N cycling during crop growth stages, the application of N based on single soil N test before planting could result in under- or over-use of N fertilizers (Belanger et al., 2001). Conversely, the mid-season soil NO_3^- tests (such as pre-sidedress soil NO_3^- test, PSNT) are found to be better correlated with crop yields than the PPNT (Magdoff, 1991). Therefore, monitoring mineral N contents in soils during the growing season can improve our knowledge on N availability for crops (Chen et al., 2010b).

A field experiment was conducted during the 2012-2013 growing seasons to determine changes in N availability and losses under tile drained soils for different N rates and management under corn, wheat, sugarbeet, and soybean production in high clay soils of North Dakota, USA. Simultaneous measurements of yield and N losses as influenced by interaction of management practices and tiles drainage have not been intensively studied in the RRV. We hypothesize that crop yields would be increased under tiles drainage condition due to increase in the N availability under favorable soil water level. The primary objectives of this field experiment were determining the interactions of tiles drainage and N fertilizer management practices on (1) crop yield and quality, (2) inorganic soil N availability, (3) denitrification loss of N in the form of N_2O, (4) soil water NO_3^- concentration at 60 cm soil depth, and (5) NH_3 volatilization loss of N from a Fargo silty clay soil. In addition the suitability of in-season soil inorganic N measurements to determine supplemental fertilizer N needs in these crops was also assessed.

Materials and Methods

Description of experimental site

Field experiments were located at North Dakota State University research site (46.93°N, 96.85°W) near Fargo, North Dakota, USA. Broadly, the site has Fargo silty clay soil and is classified as Fine, smectitic, frigid Typic Epiaquerts with 0-1% slope (Soil Survey Staff, 2014). Subsurface drainage tiles were installed at the 2.5 ha experimental area in 2008. The area was divided into eight units of 61 m long by 54 m wide, each unit consisted of seven lateral subsurface drainage tile lines. Tile lines of 10 cm in diameter were installed at a depth of 90 cm with a spacing of 7.6 m, and with a drainage coefficient of 7.5 mm d^{-1}.

Each unit was controlled via a water table control structure (Agri-Drain Corp, Adair, Iowa). Four of the units had the control structures open to represent subsurface drainage and the remaining four units had the control structures closed to represent undrained field conditions.

Field experiments and experimental design

At the experimental site, corn, wheat, sugarbeet, and soybean were grown in rotation during the 2012-2013 growing seasons, and all crops were planted each year. A randomized complete block design was used with four replicates in split-plot arrangement with drainage (undrained and subsurface drained) as the main plot factors and N fertilizer management (Table 1) as the sub plot factors in each crop for both years.

N management in corn

In 2012, the N fertilizer treatments consisted of (i) 180 kg N ha^{-1} at preplant in the form of urea (Urea180), (ii) 224 kg N ha^{-1} at preplant in the form of urea (Urea224), (iii) 224 kg N ha^{-1} at preplant in the form of urea plus nitrification inhibitor nitrapyrin [2-chloro-(6-trichloromethyl) pyridine] (NP, trade name Instinct,17.6% by weight active ingredient solution, DOW AgroSciences) (Urea224 + NP), and (iv) split application of 112 kg N ha^{-1} at preplant in the form of urea, and 112 kg N ha^{-1} at 6 leaf stage in the form of urea ammonium nitrate (UAN) [Split (Urea112 + UAN112)]. For 2013, the N fertilizer treatments were (i) control (0 kg N ha^{-1}), (ii) 134 kg N ha^{-1} at preplant in the form of urea (Urea134), (iii) 134 kg N ha^{-1} at preplant in the form of urea plus NP (Urea134 + NP), and (iv) 67 kg N ha^{-1} at preplant in the form of urea plus 67 kg N ha^{-1} at 6 leaf stage in the form of UAN streamed between the rows [Split (Urea67 + UAN67)]. Each main plot (drained and undrained) comprised of four individual corn plots with four different N treatments resulting in 32 experimental units each year (2 drainage factors x 4 N-treatments x 4 replications).The NP was applied to the soil based on an area basis (451 g NP ha^{-1} soil).

N management in wheat

In 2012, the N fertilizer treatments in wheat included: (i) control (0 kg N ha^{-1}), (ii) 146 kg N ha^{-1} at preplant as urea (Urea146), (iii) 146 kg N ha^{-1} at preplant as urea plus urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT, trade name Agrotain Ultra, 26.7% by weight active ingredient solution, Koch Agronomic Services) (Urea146 + NBPT), and (iv) 146 kg N ha^{-1} at preplant as urea plus NP (Urea146 + NP). In 2013, the N treatments were (i) control (0 kg N ha^{-1}), (ii) 112 kg N ha^{-1} at preplant as urea (Urea112), (iii) 112 kg N ha^{-1} at preplant as urea plus NP (Urea112 + NP), and (iv) 202 kg N ha^{-1} at preplant as urea (Urea202). Wheat crop consisted of a total of 32 experimental units (2 drainage factors x 4 N-treatments x 4 replications) in both years. The NBPT was mixed with urea based on urea weight (835 mg NBPT kg^{-1} urea).

N management in sugarbeet

For sugarbeet, the N fertilizer treatments consisted of application of (i) control (0 kg N ha^{-1}), (ii) 146 kg N ha^{-1} at preplant as urea (Urea146), (iii) 146 kg N ha^{-1} at preplant as urea plus NP (Urea146 + NP), and (iv) 180 kg N ha^{-1} at preplant as urea (Urea180) in both years. These resulted in a total of 32 experimental units (2 drainage factors x 4 N-treatments x 4 replications) in both years. The NP was applied to soil based on an area basis (451 g NP ha^{-1} soil).

N management in soybean

The N fertilizer treatments for soybean included (i) control (0 kg N ha^{-1}), (ii) 26 kg N ha^{-1} at preplant as urea (Urea26), (iii) 26 kg N ha^{-1} at preplant as urea plus NP (Urea26 + NP), and (iv) 39 kg N ha^{-1} at preplant as urea plus NP (Urea39 + NP) in 2012. However, in 2013, the N fertilizer treatments were (i) control (0 kg N ha^{-1}), (ii) 26 kg N ha^{-1} at preplant as urea (Urea26), and (iii) 39 kg N ha^{-1} at preplant as urea plus NP (Urea39 + NP). These resulted in a total of 32 experimental units (2 drainage factors x 4 N-treatments x 4 replications) in 2012 and 24 experimental units (2 drainage factors x 3 N-treatments x 4 replications) in 2013. The NP was applied to the soil based on an area basis (451 g NP ha^{-1} soil).

Field operations

In both years, corn was planted in the experimental field sections that were under soybean in the previous years. The plots were cultivated to a depth of 7.6 cm once in the fall following the harvest of soybean, and again in the spring before planting corn with a one-pass field cultivator. The preplant urea fertilizers were uniformly broadcasted by hand and incorporated immediately with the field cultivator on April 26 in 2012 and on May 15 in 2013. Corn hybrid PH-8640 RIB was planted on April 30 in 2012 and on May 15 in 2013 at the rate of 88000 seeds ha^{-1} with a 1010 John Deere seed planter (John Deere, Moline IL). The seeds were placed 3.8 cm deep with 15 cm in-row (seed to seed) spacing and 76 cm between-rows (row to row) spacing, such that four corn rows were included in an individual corn plot size of 6.1 m long by 3.0 m wide. For the split N treatments, the UAN was side-dress applied on June 4 in 2012 and on June 18 in 2013. All of these corn rows were machine harvested at physiological maturity on Oct. 9, and Oct. 24, respectively in 2012 and 2013. Corn grain yields were determined at the moisture contents of 15.0% in both years.

Wheat followed soybean in 2012, and sugarbeet or soybean in 2013. The plots were cultivated to a depth of 7.6 cm in the fall after crop harvest, and once again in the spring before planting wheat with a one-pass field cultivator. Urea fertilizers were uniformly broadcasted by hand and incorporated immediately with the field cultivator on April 11 in 2012 and on May 15 in 2013. The hard red spring wheat variety Prosper was planted on April 11, 2012 and May 16, 2013 at the rate of 3.95 million pure live seeds ha^{-1} with a 1010 John Deere seed planter. The seeds were placed 3.8 cm deep with 18 cm row spacing. An individual experimental unit (sub-plot) measured 6.1 m long by 1.5 m wide. In 2012, a glyphosate drift from the nearby soybean plots burned down the wheat plants. Therefore, wheat was re-seeded again on May 31 in 2012. Wheat was machine harvested at physiological maturity on Aug. 29, and Aug. 19, respectively in 2012 and 2013. Wheat grain yields were determined at the moisture contents of 13.5% in both years.

In 2012, sugarbeets were grown in the field sections previously under corn whereas in 2013, wheat preceded sugarbeets. The required rates of urea fertilizers were uniformly broadcasted by hand on May 10 and May 29, respectively in 2012 and 2013. The fertilizers were then incorporated using a Triple K field cultivator with rolling basket. On the same day, sugarbeet variety Crystal 985 Roundup Ready was planted with a John Deere Max Emerge II planter to an individual sub-plot size of 6.1 m long by 3.4 m wide. The seeds were placed 3.2 cm deep with 56 cm row spacing and 7.6 cm in-row spacing. The plots were thinned manually to maintain a plant population of 156500 plants ha^{-1} for the first year only. Glyphosate herbicide [N-(phosphonomethyl) glycine, in the form of potassium salt] (trade name Roundup WeatherMAX, 48.8% by weight active ingredient solution, Monsanto Canada Inc.) was applied on June 22 in 2012, and on July 6 in 2013 at the rate of 3.5 L ha^{-1} (1.71 kg a.i.ha^{-1}). Two middle rows from each plot were machine harvested and on Sept. 17 in 2012, whereas the beets were harvested manually (3.1 m long each from two middle rows) on Oct. 24 in 2013. The beets were weighed instantly (gross sugarbeet root yield) and subsamples of the sugarbeet roots were sent to American Crystal Sugar Quality Tare Lab, East Grand Forks, MN, USA for yield determinations and quality analyses. From this data, net sugarbeet root yield was calculated after subtracting the external root impurities (tare %) from the gross sugarbeet root yield. The net sugarbeet root yield hereafter is referred to as sugarbeet (root) yield.

For both years, soybeans were planted to the field strips previously cropped with corn. The plots were cultivated in the fall after crop harvest and again in the following spring before planting soybean. Soybean variety PFS 12R06 was planted on May 11, 2012 and May 16, 2013 at the rate of 432000 seeds ha^{-1}. The seeds were placed approximately at 4.5.cm deep with 36 cm row spacing. Each individual sub-plot (experimental unit) measured 6.1 m long by 1.5 m wide. Urea fertilizers were uniformly broadcasted by hand on May 15 and May 17, respectively in 2012 and 2013. Roundup WeatherMax herbicide, at the rate of 2.4 L ha^{-1} (1.58 kg ha^{-1}), was applied through TeeJet 8001 XR nozzle tips in 93.5 L ha^{-1} spray volume at 200 kPa spray pressure. The herbicide applications were made within a few days after planting before crop emergence, at V3 growth stage, and at full bloom (R2) growth stage in both years. Soybeans were harvested using a Wintersteiger Classic plot (Wintersteiger Ag., Ried, Austria) combine after physiological maturity on Sept. 24 and Oct. 2, respectively in 2012 and 2013. Grains yields were determined at the moisture contents of 13.0% in both years.

Basic soil properties

Before planting sugarbeets, three soil cores - up to a depth of 120 cm with depth intervals of 0-30, 30-60, and 60-120 cm - were collected using a truck mounted probe (3.6 cm internal diameter) and composited per replicate block in order to determine initial soil inorganic N levels (Maynard et al., 2008). Also, separate soil cores (1.9 cm diameter) were taken from the upper 30 cm soil surface from each individual sugarbeet plots to determine bulk density (Blake and Hartge, 1986), organic matter (Combs and Nathan, 1998), soil pH and EC (Thomas, 1996), cation exchange capacity (Chapman, 1965), particle size analysis (Elliott et al., 1999), Olsen-P (Frank et al., 1998), and available K (Warncke and Brown, 1998). The basic soil physical and chemical properties are presented in Table 2. Besides, three soil cores with depth intervals of 0-15, and 15-30 were also collected per each replicate block from each crop at the first soil sampling events in both years to determine bulk density (Blake and Hartge, 1986). The average bulk densities from each crop were used to calculate their respective growing season soil inorganic N contents as well as water filled pore space (discussed below).

Growing season soil inorganic N content

After planting, soil samples were collected by hand using a soil probe (2 cm internal diameter) from the upper 30 cm soil profile - with 15 cm increments for both growing season in all crops. For all crops, soil samples were collected at a monthly interval in 2012, whereas collected at a bi-weekly interval for the first two months and then at a monthly interval until harvest in 2013. Two to four soil cores were collected from between crop rows and composited for each sub-plot. The samples were transferred to the laboratory in a cooler and stored at -4°C until analyzed. In the laboratory, soil inorganic N (NH_4^+ and NO_3^-) contents were determined according to Maynard et al. (2008). Field moist soil (6.5 g) was extracted with 25 mL of 2M KCl after shaking the mixture for 30 min in a reciprocal shaker. The soil suspension was then centrifuged for 5 min and filtered through a Whatman no. 2 filter paper. The extracts were then analyzed for inorganic N using an Automated Timberline TL2800 Ammonia Analyzer

(Timberline Instruments, CO, USA). Soil NH_4^+ and NO_3^- concentrations (mg kg^{-1}) in the 0-15 cm and 15-30 cm depth were multiplied by respective (depth-wise) bulk densities to express them into area basis (kg ha^{-1}). The inorganic N contents at the two depth intervals were summed to obtain NH_4^+ and NO_3^- contents for the upper 30 cm soil profile. Finally, both the NH_4^+ and NO_3^- contents were added together to obtain total inorganic N contents for 0-30 cm soil depth.

Soil water filled pore space

Soil moisture contents in the soil samples were determined by gravimetric weight loss on heating a sub sample at 105°C for 24 h. These were used to calculate the bulk density of the soil cores and to convert the inorganic N concentrations to dry weight basis. Water filled pore space (WFPS) in the top 0-30 cm soil was calculated from the following equation:

$$\%\ \text{WFPS} = (\text{SMC x BD}) / [1 - (\text{BD/PD})] \text{ x } 100 \qquad (1)$$

where, SMC is the soil moisture content (g g^{-1}), BD is the bulk density (Mg m^{-3}) measured per each crop in each year, and PD is the particle density (2.65 Mg m^{-3}).

Measurement of N_2O emission

Nitrous oxide flux measurements were conducted only during the 2012 growing season. The N_2O emission rates from surface soil was measured using semi-permanent vented static PVC chamber (25.4 cm internal diameter and 10 cm height) method following the GRACEnet project protocol outlined by Parkin and Venterea (2010). A polyvinyl chloride (PVC) anchor ring with beveled edge was inserted into the soil between crop rows in each sub-plot. The germinating crops, if any, inside the PVC rings were plucked out during anchor installation. Gas samples were collected at four instances for both corn (52, 78, 87, and 100 d after fertilizer application) and sugarbeet (35, 42, 54, and 73 d after fertilizer application), whereas the samples were taken only twice in wheat (62 and 71 d after fertilizer application). Gas samples were taken in between 0800 h and 1200 h of the day assuming to represent the average flux of the day. On the observation day, the height of the anchor ring above the soil surface was recorded, in order to calculate the headspace volume after chamber enclosure. A chamber was placed on the anchor and gas samples (30 mL) were collected from the chamber headspace at 0, 15, and 30 min with a graduated polypropylene syringe. The samples were then transferred to 12 mL pre-evacuated glass serum vials and transported to the laboratory for analysis. In addition, soil temperature and volumetric soil water content at the 6 cm depth, adjacent to each gas chamber, were also measured by using GS3 soil moisture-temperature sensor (Decagon Devices, Inc., Pullman, WA 99163). All the gas samples were analyzed within 24 h, using a DGA 42-Master gas chromatograph (Dani Instruments, Milan, Italy), fitted with an electron capture detector (ECD). The ECD was operated at 300 °C, He carrier gas at 10 mL min^{-1}, Hayesep N 80/100 mesh (0.32 cm diameter x 50 cm length) and Porapak D 80/100 mesh (0.32 cm diameter x 200 cm length) columns in an oven operated at 80 °C. Assuming a linear increase in gas concentration, flux was calculated using the following equation:

$$F = kd\ (273/T)\ (V/A)\ (\Delta C/\Delta t) \tag{2}$$

where, F is the rate of gas emission (mass $ha^{-1}d^{-1}$), k is unit conversion, d is gas density (g cm^{-3}) at 273 °K, T is the air temperature (°K), V is the chamber volume (cm^3), A is soil area covered by chamber (cm^2) and $\Delta C/\Delta t$ is the rate of change of concentration over 15 and 30 min intervals (Ginting et al. 2003).

Measurement of NH_3 volatilization loss

In 2013, NH_3 volatilization losses from the N fertilizers were measured from corn and sugarbeet plots using semi-static open chambers as described by Jantalia et al. (2012). A chamber was installed in the middle of each sub-plot in between the crop rows. The chambers were secured in an upright position on the soil surface using wire stakes, surrounded by rubber bands. Ammonia volatilization measurements were taken six times (5, 9, 19, 27, 33, and 40 d after N application), and five times (19, 22, 25, 32, and 60 d after N application) from corn and sugarbeet, respectively. On the day of measurement, the foam strips and the acid solution were collected, stored in 0.5 L mason jars containing 125 mL of 2 M KCl solution, and new traps were replaced. The sampled traps were transferred to the laboratory, where they were immediately extracted with 250 mL of 2 M KCl solution. The extracts were analyzed for NH_3 concentration using the ammonia analyzer as described above. Cumulative NH_3 volatilization loss from each sub-plot was obtained by adding NH_3 produced at individual days within the sub-plot.

Measurement of soil water NO_3^- concentration

Samples of the soil water at 60 cm soil depth were collected from the middle of each plot between rows using suction lysimeters (68 cm in length and 2.2 cm diameter; Irrometer Company, Inc., CA, USA) during the 2013 sugarbeet growing season. The suction lysimeters were installed on June 13, 2013 (15 d after treatment application) and were allowed to equilibrate for a week such that the first water sample collected (22 d after treatment application) was discarded, and not used for data analysis. Then onwards sampling was conducted for a total of 9 times during the growing season (26, 29, 33, 36, 40, 47, 54, 62, 71 d) after treatment application). Using a hand pump, a vacuum of -60 kPa was applied to the tubes and maintained for a period until the time of water sampling. Water samples inside the lysimeters were extracted using a polypropylene syringe, collected into polypropylene conical tubes, and transferred to the laboratory for analyses. In the laboratory, NO_3^- concentrations in the water samples were analyzed using the ammonia analyzer. The lysimeters were devoid of water samples in all of the drained plots on 26 d, as well as in all of the plots (drained and undrained) on 47, 62, and 71 d.

Chlorophyll meter reading, leaf sampling and analyses

Leaf chlorophyll meter readings and leaf-N concentrations were measured in all crops during 2013 growing season. In corn, chlorophyll meter readings were taken on July 23 (silking stage) using a hand held chlorophyll meter SPAD-502 Plus (Konica Minolta Optics, Inc., Japan). Altogether, 20 to 25 leaves from corn plants within a sub-plot were randomly measured by the meter approximately at the midway of the leaves, and average readings were recorded (Scharf et al., 2002). On July 31, about 25 corn leaves - lying below and opposite the ears - were randomly collected from the corn plants, and dried at 65°C for a week. In wheat, about 25 uppermost leaves were measured for leaf chlorophyll meter readings on July 23, and nearly 50 to 55 uppermost leaves were sampled on July 31 for leaf-N analysis. Leaf tissue-N concentration in sugarbeet tops were measured on July 30. Within each sub-plot, 25 to 30 fully developed recently matured leaves were sampled and dried at 65°C for a week. Leaf chlorophyll meter readings were measured from 20 to 25 leaves from sugarbeet plants on August 12. In soybean, chlorophyll meter readings on the uppermost trifoliate soybean leaves (25 in number) were measured on July 22 (R4 stage). Soybean leaf tissue-N concentration was determined on July 30 (R6 stage). Within each sub-plot, 25 to 30 uppermost trifoliate leaves were sampled and dried at 65°C for a week. All the dried leaf samples from the crops were ground in a Thomas Wiley mill to pass a 2 mm screen, and subsamples were sent to AGVISE Laboratories, Northwood, North Dakota for total N determination.

Statistical analyses

Data were analyzed separately for crops using a RCBD in a split-plot arrangement with drainage and N-fertilizer management as main factors for the analysis of variance as calculated by SAS PROC GLM (version 9.3, SAS Institute Inc., Cary, NC, USA). The growing season soil

NH_4^+ and NO_3^- contents, N_2O emission rates, NH_3 volatilization losses, and soil water NO_3^- concentration data were tested separately for each sampling date. Mean separations were tested using Fisher's least significant difference at alpha level≤0.05. However, during the 2012 growing season, precipitation was comparatively lower than the 30 yr average (Figure 1) and water table depth did not reach the level to cause any flow in the tile lines. For this reason, tile effect was not considered and only N management effect on crop and soil parameters were compared during the 2012 growing season. Crop yields were regressed against the total soil inorganic N contents - measured throughout the growing seasons - using Minitab statistical software (version 17, Minitab Inc., PA, USA) with linear and quadratic regression models. Similarly, crop yields were also regressed with leaf-N concentrations and chlorophyll meter readings with linear and quadratic regression models using Minitab. However, only the significant relationships ($P \leq 0.05$) are presented.

Results

Weather conditions and soil water filled pore space

Daily precipitation and mean air temperature during the 2012 and 2013 growing seasons recorded at the research site by the Fargo NDAWN station are presented in Figure 1 (NDAWN, 2015). In 2012, the growing season precipitation totaled 53% of the long-term (1981-2010) normal precipitation. Consequently, the crops were under visible drought stress during the growing period. In contrast, the 2013 growing season was relatively wet compared to the normal years, but the distribution was uneven. More than half of the total season precipitation fell within the first two months of the growing season in 2013. As a result, the entire plot area was intermittently flooded during May and June of 2013. July and August were relatively dry and the crops were under some drought stress. The last part of the 2013 growing season had above normal rainfall. Growing season air temperatures were between 7 and 25°C in 2012, which is slightly higher than the normal years. In 2013, air temperatures during the growing season ranged similar to that of the normal years, and ranged between 7 to 22°C.

In 2012, growing season soil WFPS ranged from 50 to 77% across all the crops (Figure 2). Regardless of drainage, soil WFPS was slightly higher in 2013 than 2012 growing season and ranged between 51 to 89% under undrained conditions and between 51 to 87% under drained conditions, across all the crops. The soil WFPS reflected the precipitation pattern in 2013 (Figure 3). During the first two months, soil WFPS ranged between 65 to 89%, across all the crops. Soil WFPS measured for the next two months dropped down to as low as 51% in wheat, with a maximum value of 73% recorded in corn. The later part of the growing season again observed a gradual increase in WFPS in all crops (67 to 83%), except in wheat. Nevertheless, the WFPS for the drainage treatment did not differ significantly across the growing season in all crops.

Growing season soil inorganic N (NH_4^+ and NO_3^-) dynamics under corn

In 2012, management of N application had no influence on soil NH_4^+ as well as NO_3^- contents throughout the growing season (Figure 4). Highest NH_4^+ contents were recorded in soils sampled on 7 d in all N-treatments. On this day, about 76 kg NH_4^+ ha^{-1} was measured in soil applied with nitrapyrin (Urea224 + NP), while the urea-N fertilizers applied without NP did not exceed 42 kg N ha^{-1} in soils, regardless of N rates. After 7 d, soil NH_4^+ contents in all the N treatments declined gradually, and measured less than 11 kg ha^{-1} at harvest (i.e. on 169 d). The disappearance of NH_4^+ from soils in the N-fertilizer treatments coincided well with the accumulation of NO_3^- in soils. About 44 kg NO_3^- ha^{-1} were recorded for soils sampled on 7 d**,** when averaged across the N treatments. Soil NO_3^- levels in the N treatments increased nearly by

6 times on 62 d. Also on the same day, the highest NO_3^- contents were recorded in all N treatments. At harvest, the soils had about 86 kg NO_3^- ha^{-1} on average.

In 2013, soil inorganic N contents among the N treatments varied with drainage conditions (Figure 5). Soil NH_4^+ contents in the N treatments peaked on 37 d, irrespective of drainage, however. For the soils sampled on 37 d, under undrained condition, Urea134 + NP had significantly higher soil NH_4^+ level (25 kg N ha^{-1}) than split N application (16 kg N ha^{-1}) or unfertilized control (11 kg ha^{-1}), the latter two treatments being similar. Application of Urea134 also increased soil NH_4^+ level (23 kg N ha^{-1}) over the control, however, it did not differ either from Urea134 + NP or split-N application. All the N-fertilized treatments released similar NH_4^+ levels to that of unfertilized control after 50 d. In contrast, under drained condition, the Urea134 + NP accumulated the highest NH_4^+ in soils on 22 d than rest of the N treatments. By 37 d, the N-fertilized treatments released similar NH_4^+ levels (21 kg N ha^{-1} on average), but were significantly higher than unfertilized control (12 kg N ha^{-1}). Nevertheless, the split N treatment increased soil NH_4^+ level in the latter part of the growing season, particularly under drained condition. On 64 d, under drained condition, the split N treatment had higher NH_4^+ level (28 kg NH_4^+ ha^{-1}) than unfertilized control, but did not differ from the application of Urea134 with or without NP.

The patterns of NO_3^- release in soils differed with N management as well as with drainage in 2013 (Figure 5). Application of N fertilizers generally increased soil NO_3^- contents over the unfertilized control under both drainage conditions. The Urea134 treatment released maximum NO_3^- contents in soils on 22 d (129 and 75 kg ha^{-1} for undrained and drained conditions, respectively) whereas the application of NP to urea (Urea134 + NP) delayed peak NO_3^- releases in soils until 37 d (110 and 133 kg ha^{-1} for undrained and drained conditions, respectively). The peak NO_3^- for split N treatment was measured on 123 d for undrained condition (62 kg ha^{-1}) and on 37 d for drained condition (75 kg ha^{-1}). Soil NO_3^- contents in the N fertilized treatments did not differ among each other until 22 d, regardless of drainage. By 37 d, application of NP had significantly higher soil NO_3^- level than untreated urea treatments (Urea134 and Split-N) under both drainage conditions. This effect of NP was short-lived, since the NO_3^- levels from Urea134 + NP were similar to that of split N treatment by 50 d. For the soil sampled on 50 d, the Urea134 released greater NO_3^- content compared with Urea134 + NP and split N. Nevertheless, under undrained condition, the split N treatment released more NH_4^+ than Urea134 on 123 d.

Growing season soil inorganic N (NH_4^+ and NO_3^-) dynamics under wheat

In 2012, management of N application had no influence on soil NH_4^+ contents throughout the growing season (Figure 6). Soil NH_4^+ contents peaked on 11 d in all N treatments, with the NH_4^+ levels ranging between 51 kg ha^{-1} in the unfertilized control to 91 kg ha^{-1} in the Urea146 treatment. The NH_4^+ levels declined gradually afterwards, and averaged 4 kg ha^{-1} across all the N treatments at harvest (i.e. on 140 d). The decrease in the NH_4^+ content in the soil was accompanied by an increase in NO_3^- content. Soil NO_3^- significantly increased due to the application of N fertilizers over the unfertilized control after 75 d following treatment application. However, the application of inhibitors (NBPT or NP) to urea had no influence on soil NO_3^- contents as compared to untreated urea throughout the growing season. Soil NO_3^- contents across N sources averaged 242 kg ha^{-1} on 75 d, which dropped slightly to 193 kg ha^{-1} at harvest.

Soil mineral N releases from the N treatments were influenced by drainage in 2013 (Figure 7). Under undrained condition, application of NP to urea (Urea112 + NP) significantly accumulated higher soil NH_4^+ level than untreated urea (Urea112 and Urea202) and unfertilized control treatments until 12 d after treatment application. After 21 d, the NH_4^+ levels for all the N treatments were similar. In contrast, under drained condition, application of N fertilizers (with or without NP) increased soil NH_4^+ contents over the unfertilized control on 12d. On this day, however no differences were observed among N-fertilized treatments. On 21 d, the Urea202 had the highest NH_4^+ content than rest of the N treatments. After 21 d, soil NH_4^+ levels in the N-fertilized treatments dropped to the levels similar to that of unfertilized control.

Soil NO_3^- contents among the N treatments differed significantly until 33 d under both drainage conditions during the 2013 wheat growing season (Figure 7). Compared with unfertilized control, the Urea112 increased NO_3^- contents in soils until 33 d under undrained condition, but only until 12 d under tile-drained condition. In Urea112, the peak NO_3^- contents of 99 and 112 kg ha^{-1} were recorded on 12 d, for undrained and tile-drained conditions, respectively. Application of NP to urea (Urea112 + NP) had responses similar to untreated Urea112 for both drainage conditions, with peak soil NO_3^- contents (111 and 96 kg ha^{-1} for undrained and drained conditions, respectively) measured on 12 d. Applying higher N rate (Urea202), however, buildup NO_3^- levels in soils significantly as compared with Urea112 from 21 to 33 d, irrespective of drainage. For the same periods (21 to 33 d), the Urea202 had greater NO_3^- accumulation in soils than Urea112 + NP, but only under tile-drained condition. The Urea202 had its peak NO_3^- released in soils on 12 d for undrained condition (124 kg ha^{-1}), and on 21 d for tile-drained condition (190 kg ha^{-1}). After 46 d, soil NO_3^- contents in all the N-treatments did not exceed 10 kg ha^{-1}, under both drainage conditions.

Growing season soil inorganic N (NH_4^+ and NO_3^-) dynamics under sugarbeet

Soil inorganic N content (NH_4^+ and NO_3^-) measured during the 2012 sugarbeet growing season is shown in Figure 8. There were no significant differences in soil NH_4^+ contents among the N treatments throughout the growing season. Nonetheless, soil NH_4^+ levels increased from an average value of 6 kg ha^{-1} measured on 1 d to 56 kg ha^{-1} on 48 d. Soil NH_4^+ contents dropped sharply afterwards, with less than 5 kg ha^{-1} recorded in the N treatments, on average. Soil NO_3^- contents in the N treatments mirrored the NH_4^+ release patterns. The measured soil NO_3^- contents in all the N treatments were below 25 kg ha^{-1} on 1 d after treatment application. Soil NO_3^- levels increased drastically and maximum soil NO_3^- contents were recorded on 48 d in all treatments including unfertilized control. For the soils sampled on 48 d, NO_3^- contents was the lowest with unfertilized control (65 kg ha^{-1}), Urea180 (252 kg ha^{-1}) was higher than Urea146 (172 kg ha^{-1}), and Urea146 + NP (194 kg ha^{-1}) did not differ from Urea180 and Urea146. Soil NO_3^- declined gradually onwards, with less than 15 kg ha^{-1} evident after 111 d in all treatments.

Ammonium release in soils from the N treatments differed with drainage in 2013. Differences in NH_4^+ contents among N treatments were limited to the soils sampled on 7 d for both drainage conditions, however (Figure 9). On 7d, under undrained treatment, the Urea146 + NP and Urea180 had significantly higher NH_4^+ contents in soils than the unfertilized control. In contrast, under undrained condition, soil NH_4^+ level was the highest with Urea146 among the N treatments on 7 d. Nonetheless, elevated levels of soil NH_4^+ were recorded for the N treatments on 30 d after treatment application under both drainage conditions. Across the N treatments, the NH_4^+ levels on this day ranged between 57 to 127 kg ha^{-1} under undrained condition, and between 71 to 93 kg ha^{-1} under drained condition. After 78 d, soil NH_4^+ levels were less than 2 kg ha^{-1} in all treatments, regardless of drainage.

Soil NO_3^- contents generally increased with N application over the unfertilized control treatment under both drainage conditions during the 2013 growing season (Figure 9). Among the N-fertilized treatments, Urea180 significantly increased soil NO_3^- levels than Urea146 from 30 to

48 d, particularly under drained condition. Nevertheless, soil NO_3^- contents for all the N-fertilized treatments peaked on 15 d, regardless of drainage management, which ranged from 137 to 174 kg ha^{-1} under undrained condition and from 121 to 194 kg ha^{-1} under drained condition. The NO_3^- levels were similar between with or without NP application, regardless of N rate throughout the growing season under both drainage conditions. Soil NO_3^- levels in the N-fertilized treatments returned to the levels that of control treatment by 71 d under both drainage conditions.

Growing season soil inorganic N (NH_4^+ and NO_3^-) dynamics under soybean

Application of N fertilizers - regardless of source and rate - had no influence on soil NH_4^+ contents during the 2012 soybean growing season, except at harvest (Figure 10). Soil NH_4^+ measured during the early 2012 soybean growing season exhibited huge variations within the N treatments, resulting in lack of significant differences among them. At 24 d after treatment application, the unfertilized control had 4 kg NH_4^+ ha^{-1}, whereas soil NH_4^+ for the N-fertilized treatments averaged 18 kg ha^{-1}. At harvest (on 114 d), Urea39 + NP had the highest NH_4^+ in soils among the N treatments. On the other hand, soil NO_3^- varied considerably among N treatments during the 2012 soybean growing season (Figure 10). On 24 d, soil NO_3^- levels among all the N treatments were similar and averaged 28 kg ha^{-1}. By 55 d, the NO_3^- levels increased nearly by 2 fold in the control treatment to 7 fold in the Urea39 + NP treatment. On 55 d, soil NO_3^- levels for the N treatments ranked in the order: Urea39 + NP > Urea 26 = Urea 26 + NP > Control. At harvest, soil NO_3^- content measured in Urea 39 + NP (43 kg N ha^{-1}) was the highest among all the N treatments.

During the 2013 growing season, soil NH_4^+ contents under soybean did not exceed 20 kg ha^{-1} across drainage and N management (Figure 11). Under undrained condition, however, the

NH_4^+ content increased with Urea39 + NP over the unfertilized control until 34 d. During this period, Urea26 treatment had either similar or less soil NH_4^+ levels than Urea39 + NP. On the other hand, under drained condition, application of N fertilizer had no influence on soil NH_4^+ contents throughout the growing season.

Soil NO_3^- release patterns from the N treatments also varied with drainage in 2013 (Figure 11). Under drained condition, the Urea26 increased NO_3^- levels in soils than control until 12 d, whereas the Urea39 + NP extended the NO_3^- levels until 21 d. For the soils sampled on 21 d, the Urea39 + NP had significantly higher NO_3^- level than Urea26. On the other hand, there were no significant differences in soil NO_3^- levels among the N treatments throughout the growing season under undrained condition. Nevertheless, the N treatments accumulated maximum levels of NO_3^- on 12 d under both drainage conditions, followed by gradual decline in NO_3^- then onwards. On 12 d, soil NO_3^- levels ranged from 158 to 185 kg ha^{-1} under undrained condition and from 85 to 165 kg ha^{-1} under drained condition across the N treatments.

Crop yields

In 2012, corn yield averaged 7.37 Mg ha^{-1} with no significant difference among the N treatments (Table 3). In 2013, the yields increased with the application of fertilizer-N over the unfertilized control on average by 2.32 Mg ha^{-1} under undrained condition and by2.24 Mg ha^{-1} under drained condition (Table 4). The yields for the N-fertilized treatments [(Urea134, Urea134 + NP, and split (Urea67 + UAN67)] did not differ among each other under both undrained and drained conditions, and averaged 8.29 Mg ha^{-1} and 8.25 Mg ha^{-1}, respectively. Drainage management had no influence on corn yields across the N treatments.

The average wheat yield for the N treatments was 0.87 Mg ha^{-1} (878 kg ha^{-1}) during the 2012 growing season (Table 5). Wheat yields did not differ among the N treatments in this year.

However, in 2013, yields improved by the application of N fertilizers as compared with the control treatment in the undrained plots on an average by 0.90 Mg ha^{-1} (Table 6). In contrast, management of N application had no effect on wheat yield in the drained plots. Wheat yields in the drained plots ranged between 3.19 to 3.82 Mg ha^{-1} whereas the yields ranged between 3.46 to 4.44 Mg ha^{-1} in the undrained plots. Wheat yields did not differ between undrained and drained plots across the N treatments.

Under sugarbeet, N management had no effect on sugarbeet root yield and sucrose concentration in 2012 (Table 7). In 2012, the sugarbeet root yield averaged 46.4 Mg ha^{-1}, with net sucrose concentrations of 16.6%. In 2013, mean sugarbeet root yield (38.3 Mg ha^{-1}) and sucrose concentration (14.1%) were comparatively lower than 2012. Drainage and N management did not influence sugarbeet root yield, sucrose concentration, and percentage of sucrose loss to molasses (SLM %) in 2013 (Table 8). Nevertheless, increasing N rate rather tended to increase impurity in beet roots, with significant differences observed in 2012. In 2012, the SLM % increased ($P<0.0.5$) with Urea180 by 8 and 15% compared to Urea146 and control, respectively.

Soybean yields were significantly influenced ($P<0.0.5$) by N management during the 2012 growing season (Table 9). In 2012, the unfertilized control treatment produced the highest grain yield of 2.99 Mg ha^{-1} among all the N treatments. Application of N reduced the grain yields by 19.1 and 23.7% at the N rates of 25 kg ha^{-1} + NP, and 39 kg ha^{-1} + NP, respectively, as compared with the unfertilized control. In 2013, drainage management and N application had no influence on soybean yield. The soybean yields were 2.98 and 2.92 Mg ha^{-1} for undrained and drained conditions, respectively, in 2013.

Relationship between soil inorganic N and crop yield

The suitability of soil NO_3^- as well as total inorganic N (NH_4^+ + NO_3^-) contents - measured at 0-30 cm depth during growing season - as a predictor of N supply to their respective crop yields were evaluated using regression analysis. In 2012, soybean grain yield was related to soil total N (NH_4^+ + NO_3^-) at 55 d ($R^2 = 0.21$; $P = 0.008$) with a linear regression model (Figure 12). In 2013, there were statistically significant ($P \leq 0.05$) quadratic relationships between crop grain yield and soil inorganic N content measured during early to mid-growing season for corn (Figure 13) and wheat (Figure 14). In corn, the relationships were generally improved by including soil NH_4^+ content in the quadratic model as compared with the NO_3^- content alone, whereas the inclusion of NH_4^+ content had no effect in the relationships in wheat.

The proportion of variability explained by the relationships (R^2-value) decreased with time in corn, whereas in wheat the R^2-value (i.e. 47%) was the highest with the relationship obtained for soils sampled at 33 d. In corn, almost 51% of the variability in grain yield could be accounted by soil total N (NH_4^+ + NO_3^-) measured at 22 d. The proportion of variability explained declined to 48% on 37 d and 28% on 50 d in corn. The critical mineral N contents for maximum grain yields were 124, 111, and 45 kg ha^{-1} for the soils sampled at 22, 37, and 50 d, respectively under corn. Under wheat, the critical soil NO_3^- contents obtained from the quadratic relationships for maximum wheat grain yields at 12, 21, and 33 d were 142, 123, and 74 kg ha^{-1}, respectively. For the particular day, crop yields increased with increasing mineral N content up to the critical values, with no further improvement in yields above these values.

Sugarbeet root yield as well as its yield parameters (sucrose content, and SLM %) were not related to inorganic N contents in soils, sampled at any date in both years (data not shown).

N_2O emissions

In all crops, N_2O fluxes measured during the mid-growing season in 2012 were highly variable within the N treatments. Consequently, no significant differences were observed among the treatments on any sampling date in any crop (Table 10 to 13).

In corn, the elevated N_2O emissions were recorded on 54 d after N application (Table 10) in response to a total of 28 mm of precipitation that occurred on June 13-14 (52-53 d after N application) (Figure 1), with the Urea224 treatment exhibiting the largest flux of 105 g N_2O-N d^{-1} ha^{-1}. Cumulative precipitation for the following 3 wk period totaled only 9 mm. Consequently, the emission rates measured on 78 d after N application did not exceed 10 g N_2O-N d^{-1} ha^{-1} in any of the N treatments. The N_2O flux rates increased to about 27 g N_2O-N d^{-1} ha^{-1} on average across N treatments on 87 d, owing to 20 mm of total precipitation received on July 24-25 (86-87 d after N application). By 100 d, the N_2O rates averaged 8 g N_2O-N d^{-1} ha^{-1} on average across N treatments. Among the N treatments, Urea224 had the highest total N_2O emissions during the measurement period. The total N_2O emitted across the measurement period from Urea224 was higher than Urea180 by 24.4%, Urea224 + NP by 19.6%, and split N application by 26.4%.

Under wheat, for the measurement taken on 62 d after N application, the small precipitation events (<2 mm) for the preceding 2 wk period likely limited the N_2O flux rates, with an average of 5 g N_2O-N d^{-1} ha^{-1} across N treatments (Table 11). The emission rates increased by 3 fold (17 N_2O-N d^{-1} ha^{-1}), on average by 71 d, coinciding with a total of 20 mm of total precipitation occurred on July 24-25 (69-70 d after N application). The total emissions of N_2O for the N treatments were in the decreasing order: Urea146 > Urea146 + NBPT > Urea146 + NP > Control.

Similar to corn and wheat, N_2O emissions from the sugarbeet plots were also characterized by the total amount of precipitation received during the measurement periods, with the flux values ranging between 10 to 36 g N_2O-N d^{-1} ha^{-1} across N treatments (Table 12). Although not different significantly, generally the N_2O fluxes were always the highest with Urea180, and the least with the unfertilized control, throughout the measurement periods. Among the N treatments, soils applied with Urea180 released more total N_2O. The total N_2O emissions from Urea180 were higher than Urea146 by 27.8% and Urea146 + NP by 18.6%.

In soybean, N_2O flux measurement was conducted at only one instance on 72 d after treatment application (Table 13). Across the treatments, the N_2O flux rates measured on this day were low (< 9 g N_2O-N ha^{-1} d^{-1}), probably attributed to a small precipitation (<8 mm) the occurred on this day.

NH_3 volatilization

In corn, cumulative NH_3 volatilization losses varied significantly among N treatments in 2013 under both undrained and drained conditions (Table 14). Volatilization losses of NH_3 increased with N application over the unfertilized control, irrespective of drainage management. And, the losses of NH_3 were more pronounced with the application of nitrapyrin to urea (Urea134 + NP) than without NP application (Urea134). Under undrained condition, NH_3 volatilization loss with Urea134 + NP were 67% higher than control treatment, while the loss from Urea146 treatment was intermediate between them. Under drained condition, Urea146 emitted 61% greater NH_3 than control, and the corresponding increment with Urea146 + NP over the control was 68%. The percent N fertilizer applied lost as NH_3 for Urea134 and Urea134 + NP were 0.96 and 1.84% under undrained condition, and were 1.47 and 2.01% under drained condition, respectively. Ammonia volatilization losses for drainage treatments were not significantly different across the N treatments.

In Sugarbeet, cumulative losses of NH_3 did not respond to drainage in 2013 (Table 15). However, application of N significantly increased NH_3 losses compared to unfertilized control treatment, under both undrained and drained conditions. The Urea146 had 38 and 46% higher NH_3 losses compared with the control treatments, respectively under undrained and drained conditions. Emissions of NH_3 were more pronounced with higher N application rate. With Urea180, cumulative NH_3 losses were 41% and 56% higher than control under undrained and drained conditions, respectively. No significant differences were observed in NH_3 emissions between Urea146 and Urea180, regardless of drainage management. Across drainage, the mean cumulative NH_3 volatilization loss was 1.6 kg ha^{-1} from N application, representing less than 0.5% of applied N fertilizers.

Soil water NO_3^- concentration

Soil water NO_3^- concentration (mg L^{-1}) measured at the 60 cm soil depth during the 2013 sugarbeet growing season for the N treatments under undrained and subsurface drained conditions are presented in Figure 16. Soil water NO_3^- concentration tended to be lower under subsurface drained than undrained condition across the N treatments. Under undrained condition, peak concentration in Urea146, Urea146 + NP, and Urea180 were 96, 75, and 85 mg L^{-1}, respectively, whereas the corresponding peak concentrations for these treatments under subsurface drained condition were 53, 69, and 63 mg L^{-1}, respectively. Generally, NO_3^- concentration increased with N application over the control treatment irrespective of drainage management. Compared to the control, application of nitrapyrin to urea (Urea146 + NP) accumulated more NO_3^- under subsurface drained condition, while the application of urea without nitrapyrin (Urea146) accumulated greater NO_3^- under undrained condition. However, there were no differences in NO_3^- concentrations among the N fertilized treatments throughout the measurement period for both drainage conditions.

Leaf chlorophyll meter reading and N concentration

Leaf chlorophyll meter reading and N concentration measured during mid-growing season were influenced by N management in corn (Table 16) and wheat (Table 17). In corn, application of Urea134, with or without NP, significantly increased both chlorophyll reading as well as leaf-N over the control, regardless of drainage management. Among the N-fertilized treatments, split N application either had statistically lower or similar values as compared to applying the entire N at planting. In wheat, the highest values for chlorophyll reading and leaf-N concentration resulted from the application of higher N rate (Urea202). The chlorophyll readings for Urea202 were significantly different from that of the control treatments under both drainage conditions, whereas the differences for leaf-N were significant only under drained conditions between Urea202 and control. Neither drainage nor N management had any influence on the chlorophyll meter reading as well as leaf N-concentration in sugarbeet (Table 18) and soybean (Table 19).

Linear regression models were used to explain the relationships between chlorophyll reading and crop yield ($R^2 = 0.47$; $P < 0.001$ for corn, and $R^2 = 0.26$; $P = 0.005$ for wheat), and between leaf-N concentration and yield ($R^2 = 0.21$; $P = 0.009$ for corn, and $R^2 = 0.34$; $P < 0.001$ for wheat) (Figure 15). Sugarbeet root yield as well as its yield parameters, and soybean grain yield were neither related with chlorophyll reading nor with leaf-N concentration in 2013 (data not shown).

Discussion

Soil inorganic N dynamics during the 2012 growing season

Soil inorganic N (NH_4^+ as well as NO_3^-) transformations among the N treatments remained similar under corn as well as under wheat, suggesting similar patterns of N release from the N treatments during the dry growing period. Besides, the mineral N levels were highly variable within N treatments throughout the growing season, as evident from the large error bars (Figure 4 and Figure 6). Soil inherent N mineralization probably contributed to the large within-treatment variation in the mineral N levels among the N treatments, and no significant differences in mineral N levels were observed (Kolberg et al., 1999; Carpenter-Boggs et al., 2000). Nevertheless, under sugarbeet, applying higher N rate of 180 kg ha^{-1} increased NO_3^- level in soil as compared with the recommended N rate of 146 kg ha^{-1} during the mid-growing season. Similarly under soybean, application of higher N rate with nitrification inhibitor increased soil NO_3^- level during the mid- growing season and at the harvest. The increment in soil mineral N availabilities in these crops rather reduced yield quality in sugarbeet root, and grain yield in soybean. Moreover, the excess NO_3^- availabilities are prone to higher N losses, since no improvements in yields were seen. This is further supported by a slightly higher N_2O emissions associated with the higher urea N rate of 180 kg ha^{-1} as compared with the 146 kg ha^{-1} N rate in sugarbeet.

Soil mineral N (NH_4^+ + NO_3^-) measured at the harvest exceeded 100 and 200 kg ha^{-1} under corn and wheat, respectively suggesting that carryover of N to the subsequent year may occur. In fact, these are reflected in the measured NO_3^- values of 130 kg ha^{-1} on average in the following sugarbeet plots prior to planting in 2013. In all crops, the total soil mineral N measured during growing season exceeded the actual amount of N applied through the N fertilizers, owing to large inherent soil organic N mineralization (Power et al., 1974; Rochette et al., 2010). This is further supported by the fact that the control treatments (without any added N) measured nearly proportionate quantity (in wheat) or more than half (in sugarbeet) the recommended N rates during the mid-crop growing season. These spatial and temporal variations in the soil N supply further stress the necessity of soil testing throughout crop growing period in order to assess the amount of available N required corresponding to the fertilization scheme precisely, such that crop yields are not limited by N deficiency and insignificant amount of applied N enters into the environment.

Soil inorganic N dynamics during 2013 growing season

During the 2013 growing season, the patterns of N release from the N sources varied with drainage. Studies have shown that N release from N sources increases with soil moisture, with maximum soil microbial activity for maximum N mineralization observed between 50 to 60% WFPS (Franzluebbers, 1999; Agehara and Warncke, 2005). In the present study, across the crops, soil WFPS measured during 2013 growing season fluctuated between 51 to 89% under undrained condition, and between 51 to 87% under drained condition, with slightly lower water contents seen in the latter during the growing season. Therefore, the differential patterns in N release from the N sources with drainage could be attributed to these variations in soil water contents.

In general, the application of NP accumulated more NH_4^+ content, and delayed NO_3^- buildup as compared with untreated urea, indicating that the NP hindered nitrification activity (Chen et al., 2010a). Our results are in line with previous studies that have shown that the urea fertilizers without NP lead to a rapid accumulation of mineral N (NH_4^+ and NO_3^-) in soils than when NP is co-applied (Omonode and Vyn, 2013). Nevertheless, the effects of NP were not consistent throughout all the crops under investigation, probably due to high spatial variation in soil inherent soil N mineralization across the site as well as due to varying amounts of N uptake by these crops, as evident from varying proportions of leaf tissue N concentrations measured across crops (Table 16 to 19). Moreover the presence of large organic matter content, high soil pH (Table 2), and early-season wet soil conditions at the study site could have also influenced the efficacy of NP (Hendrickson et al., 1978; Chen et al., 2010a; Parkin and Hatfield, 2010).

Split N application released slightly higher mineral N during the latter corn growing period. This was expected. Application of higher N rates generally increased soil mineral N level as compared to the recommended N rates regardless of sources in all crops, except corn. There were no appreciable improvements in yields in these crops with the increase in soil mineral N level from higher N rates. These results indicate that excess application of N should be avoided not only to attain higher gross revenue but also to reduce the risk of N losses to the environment (Randall et al., 2003).

Crop yield and yield parameters during the 2012 growing season

Nitrogen fertilization had no influence on yields in any crop in 2012, suggesting that soil residual N and/or organic N mineralization were sufficient to supply crop N needs (Dell et al., 2014). Moreover, the 2012 growing season was excessively dry than the normal years, and crops were visibly under some drought stress which likely reduced crop N needs. Also, the movement of N into the active root zone might have also been hindered within the dry topsoil, which consequently led to poor root N uptake (Ray et al., 2005).

Nevertheless, significant yield reduction was observed with N fertilization in soybean, but only during the 2012 growing season. In 2012, soybean yield decreased by 3 kg ha^{-1} for every 1 kg ha^{-1} increment in soil test total N measured at 55 d after fertilizer application (Figure

12). Two explanations are deemed plausible to the yield reduction in soybean with N fertilization. Firstly, due to the induction of iron deficiency chlorosis (IDC) in soybean caused by high NO_3^- levels in soil from N fertilization (Wiersma, 2010; Bloom et al., 2011; Buetow and Kandel, 2015). High NO_3^- in soil not only inhibits Fe acquisition by roots due to high pH at the root surface (Nikolic and Romheld, 2003), but greater assimilation of NO_3^- by plants may also led to an increased apoplastic pH - which in turn decreases the rate of reduction of Fe III to Fe II (Kosegarten et al., 1999). In the current study, N-fertilization significantly increased soil NO_3^- levels than the unfertilized control plots during the 2012 soybean growing season (Figure 10), that could have induced IDC in soybeans and consequently reduced grain yield. The other reason why the yields may have been lower with the N application is that the soybean plants were taller compared with the control, and had a larger crop canopy utilizing more of the soil water during the growing season and possibly running out of available soil water for pod fill (Al-Ithawi et al., 1980; Wingeyer et al., 2014). Application of N fertilizers has shown to increase aboveground soybean biomass compared to without any N application (Ray et al., 2005; Osborne and Riedell, 2006a). With sufficient precipitation, N application at the same site increased soybean yield in 2014 (Buetow and Kandel, 2015). According to Osborne and Riedell (2006b), soybean yield response to applied N depends on environmental conditions during the growing season, with larger response to applied N usually evident in growing seasons receiving adequate precipitation, while the seasons not receiving adequate precipitation may not respond to applied N.

In sugarbeet, the application of N tended to increase impurity in beet roots. The SLM % significantly increased with higher N application rate (Urea180) than recommended N rate (Urea146) or control. Studies have confirmed that excess N fertilization, above recommended rate, usually lowers purity indexes with depressed sucrose concentrations (Halvorson and

Hartman, 1974; Anderson and Peterson, 1988). Excess N fertilization can stimulate sugarbeet top growth beyond the point where maximum root yields are attained and thereby direct photosynthates into regenerating canopy rather than into the root storage (Anderson and Peterson, 1988).

In wheat, the delayed crop re-planting considerably reduced grain yields as compared with the usual wheat grain yields of 4.4 Mg ha^{-1} for the study area (Kandel et al., 2013).

Crop yields were also similar among the N fertilized treatments, regardless of N source and N rate in all the crops. Proportionate quantities of mineral N, released from the various N sources in corn (Figure 4) as well as in wheat (Figure 6), could be related with similar N uptake among the N sources, resulting in no yield differences among them. In sugarbeet and in soybean, soil NO_3^- availabilities differed significantly among different N sources during mid-growing season, however, crop growth stress caused by extended period of dry growing season (Figure 1) could have reduced N demand in these crops, and consequently no differences in yields were observed.

Crop yield and yield parameters during the 2013 growing season

Drainage had no influence on yields in any crops. Several studies have indicated significant crop yield improvements under subsurface drainage compared with undrained conditions due to improvement in soil environment and/or N availability for crops with drainage (Chieng et al., 1987; Kladivko et al., 2005; Jin et al., 2008; Sims, 2010; Hoppe, 2013; Nash et al., 2015). In these studies, however, the yield responses to drainage were observed only during wet years or the years receiving normal precipitation during the majority of the growing season, while drainage was irresponsive during the moderate to extreme dry growing seasons. Therefore, crop yield response to drainage management depends upon the amount and the pattern of precipitation received during the growing season. In the present study, although the 2013 growing season received greater precipitation than normal years, the distribution was uneven with dry mid-growing season (Figure 1). Higher than normal precipitation received in May (141 mm) and June (199 mm) months caused visible standing water intermittently in some parts of the experimental field. However, subsurface drainage did not lower WFPS remarkably within the surface soil (0- 30 cm depth) throughout the 2013 growing season under any crops (Figure 3), possibly because of the high capillary water associated with the fine-textured soil at the research site. Moreover, July and August precipitation totaled only 26 mm and 12 mm, respectively, causing visible stress in crops which consequently lowered crop N demand. Hence, similar soil water regimes and drier mid-season growing conditions might be connected with lack of yield response under subsurface drained condition in 2013 (Wiersma et al., 2010).

Application of N improved corn and wheat yields over their respective control treatments, but the yields were similar among the N-fertilized treatments under both drainage conditions. These results suggest the necessity of N application regardless of N sources in order to optimize crop yields (Black, 1993).The necessity of N fertilization to optimize crop yields is further reflected in the significant quadratic relationships obtained between soil mineral N availabilities measured during early to mid-growing season and yields for both crops (Figure 13 and 14). For example, in corn, grain yields increased with increasing N availability (measured at 37 d) to a critical value of 111 kg N ha^{-1}. Above this level, however, corn yield appeared not to depend on soil mineral N up to 120 kg N ha^{-1} and yield declined gradually for even higher soil mineral N levels.

Crops yields were similar among the N management treatments under both drainage conditions in sugarbeet as well as in soybean, regardless of significant differences in soil N availabilities observed among the N treatments during the growing season in both crops. In both crops, the chlorophyll readings as well as the leaf-N concentrations measured during the mid-growing season were similar among N treatments, indicating proportionate amount of N uptakes. Under sugarbeet plots, the soil residual NO_3^- contents measured prior to N application averaged 130 kg ha^{-1} (Table 2), and more than 100 kg ha^{-1} (NH_4^+ + NO_3^-) were measured in soils during the mid-growing season (48 to 71d) in the control plots (Figure 9). Therefore, lack of yield differences observed among N management treatments in sugarbeet could be attributed to large amount of soil residual N from previous growing season and organic N mineralization that could have contributed the required crop N demands. While in soybean, in addition to large residual NO_3^-, the biological N_2 fixation possibly provided crop N needs. Moreover, the drier mid-growing season in 2013 promoted crop stress, consequently lowering N demand.

Relationships of crop yields with soil and plant parameters

Results from the regression analysis indicates that in corn the total soil inorganic N (NH_4^+ + NO_3^-) measured during 22 to 37 d appears to be most suitable for use to determine if additional fertilizer-N is required for corn grain production in silty clay soils. Pre-sidedress soil NO_3^- test (PSNT) for predicting N requirement to optimize crop yields has already been a proven technology (Magdoff, 1991; Belanger et al., 2001). In corn, the PSNT is usually conducted during 5-6 corn leaf stage since this period coincides with rapid corn N uptake. However, under soil conditions, where significant amount of NH_4^+ can accumulate until 5-6 corn leaf stage, simultaneous determination of both NH_4^+ as well as NO_3^- can have better precision in estimating crop N needs (Zebarth and Paul, 1997). However, such an improvement in estimating N needs for optimizing yield by the inclusion of NH_4^+ to the PSNT was not observed for wheat. The proportion of variability accounted in wheat yield (R^2-values) remained higher or unchanged with soil NO_3^- content than with total soil inorganic N ($NH_4^+ + NO_3^-$) (Figure 14) from early to mid-growing season, possibly because of small NH_4^+ content relative to NO_3^- due to nitrification observed after 12 d. Nevertheless, the best quadratic relationship ($R^2 = 0.47$; $P < 0.001$) between wheat yield and NO_3^- content was observed for the soils sampled during 33 d.

Different critical values were obtained with the tested quadratic models for different soil sampling dates for both corn and wheat. The values declined as the crop growth progressed were expected because of crop N uptake with the progression of crop growth. Given that corn yields were most precisely estimated with the soil total mineral N during 22 to 37 d, we suggest the critical mineral N range of 111 to 124 kg ha^{-1} deemed necessary during this period for obtaining the maximum corn yield. For wheat, soil NO_3^- content of 74 kg ha^{-1} on 33 d is critical for obtaining maximum grain yield. Above these critical values, the yields declined with soil mineral N availability suggesting diminishing returns upon increasing N availability (Zebarth and Paul, 1997). The excess soil mineral N during the latter periods of growing season when crop uptake is small can also be subjected to losses via denitrification or leaching.

Both, corn and wheat yields were linearly correlated with their respective chlorophyll meter readings and leaf-N concentrations. Results of the present study indicate that leaf chlorophyll meter reading and leaf-N concentration measured during the mid-growing season could be used to estimate and/or predict N needs for maximum grain yields in corn and wheat (Moraghan et al., 2003).

N_2O emissions

Soil N_2O fluxes measured across crops followed precipitation pattern and events that occurred during the 2012 growing season, with larger N_2O flux rates observed during the measurement periods receiving 20 to 28 mm of precipitation. Larger N_2O flux rates in response to the precipitation events - as a consequence of increased soil saturation - are commonly reported in the literature (Gagnon et al., 2011; Parkin and Hatfield; 2013). However, except for one of the flux measurement days in corn, soil N_2O fluxes remained mostly below 36 g N_2O-N ha^{-1} d^{-1} across the crops, throughout the measurement period. These results are comparable to those reported by Liebig et al. (2010) for silt loam soils in Mandan, North Dakota, where peak values varied from 19 to 27 g N_2O-N ha^{-1} d^{-1} in spring wheat - fallow and spring wheat - safflower (*Carthamustinctorius* L.) - rye (*Secalecereale* L.) cropping systems. In contrast, daily N_2O fluxes in the present study are comparatively lower than the reported peak values of 740 g N_2O-N ha^{-1} d^{-1} for silt loam soils in Indiana by Omonode and Vyn (2013). Poorly drained soils usually favor denitrification because of O_2 inhibition in these soils upon soil saturation (Nash et al., 2011). In general, N_2O emissions are lower from soils with less than 60% water filled pore space (WFPS), increases slowly between 60 and 80% WFPS, and then increase more rapidly above 80% WFPS (Bateman and Baggs, 2002). Spikes in N_2O emissions are, therefore, commonly observed after rainfall and/or irrigation events (Asgedom et al., 2014). In the present study, soil WFPS measured at 0-30 cm depth during 2012 growing season for crops never exceeded 77%, and remained mostly below 60%. The growing season received about 50% or less precipitation than the normal years, and the maximum daily precipitation received was 25 mm in the whole growing season. Therefore, the dry growing period in 2012 could have restricted N_2O emissions in our study as opposed to others that have commonly reported larger spikes in N_2O production following rainfall and/or irrigation events greater than 70 mm (Omonode and Vyn, 2013). Moreover, lower gas diffusivity and/or higher cation exchange capacity associated with fine-textured soils in the study site may have also limited N_2O production (Gu et al., 2013).

Soil N_2O fluxes did not differ among the N management treatments. Studies have shown that application of mineral N fertilizers tends to cause positive and linear N_2O emissions because of greater inorganic N substrate availability (Chantigny et al., 1998; Halvorson et al., 2008). Soil NO_3^- content measured at 0-30 cm soil depth in all crops was generally higher with the N-fertilized treatments as compared to the control plots. At the similar N rates, availability of NO_3^- in soils increased with the application of nitrification inhibitor NP as compared with urea alone during the mid-growing season for sugarbeet and soybean crops. However, due to inconsistence in temporal release of mineral N from the applied fertilizers as well as soil inherent N mineralization and due to episodic nature of N_2O emission induced by rainfall events, N_2O emissions did not vary among different N fertilizer sources during the dry growing season in 2012 (Rochette et al., 2010; Parkin and Hatfield, 2013).

NH_3 volatilization

Cumulative NH_3 volatilization losses between the drainage treatments were similar across the N treatments, in both corn and sugarbeet. However, in the present study, differences in soil WFPS between drained and undrained plots were not significant throughout the 2013 growing season in both corn and sugarbeet. Approximately, 46 of precipitation fell within the next 5 d after N application under corn, and about 70 mm of precipitation fell on the day after N application under sugarbeet, which could have considerably incorporated the N fertilizer, regardless of drainage. Moreover, the N fertilizers were incorporated manually at 15 cm soil depth after N application. Therefore, soil incorporation of N fertilizer by high rainfall and/or manually after N application could have also limited NH_4^+ substrate availability, regardless of drainage (Rochette et al., 2013). And considering proportionate amounts of NH_4^+ transport from the soil surface down to soil profile, NH_3 emissions from subsurface drained and undrained plots are unlikely to be different (Norman et al., 2003).

Application of N increased NH_3 losses as compared to unfertilized control regardless of drainage conditions under both corn and sugarbeet. A higher NH_3 emission is expected from N-fertilized treatments due to greater availability NH_4^+ substrate in the fertilized plots (Figure 5 and 9). Under corn, across drainage, NH_3 volatilization losses from Urea134 and Urea134 + NP were about 1.4 and 1.7% of the total applied N. Similarly, under sugarbeet, the N-fertilized treatments had almost two times higher NH_3 emissions than control, and represent approximately 0.4 and 0.5% of the total applied N lost as NH_3 respectively from Urea146 and Urea180, across drainage. These results are comparable to the reported values of 2.3±0.4% for surface applied urea for clay loam soil at a simulated irrigation of 16 to 19 mm of precipitation applied after 1 d of urea application (Jantalia et al., 2012) and 2.8% for sandy loam soils at 21.4 mm of simulated rain applied after 1 d of N application (Holcomb et al., 2011). As in these studies, high precipitation (46 and 70 mm in corn and sugarbeet, respectively) received shortly after N application considerably incorporated fertilizer N into soil and restricted NH_3 volatilization (Rochette et al., 2013). Higher CEC associated with high clay soil at the research site could have also limited the NH_4^+ substrate required for volatilization (Griggs et al., 2007). Furthermore, the urea were incorporated into soils shortly after their application in our study, which would reduce NH_3 loss because of increased contact of urea with soil exchange complex, and where it is converted to the stable NH_4^+ form (Norman et al., 2003).

In corn, NH_3 emissions were slightly higher from the soil applied with Urea134 + NP than with Urea134. Nitrification inhibitor NP increases NH_4^+ substrate availability, and thus can enhance NH_3 loss (Gioacchini et al., 2002). Although, the availability of NH_4^+ tended to be greater with the application of NP during the early growing period, it apparently was not enough to significantly influence NH_3 volatilization under wet early growing season, when most of the NH_4^+ would have already been stabilized to the soil exchange complex (Jantalia et al., 2012).

Soil water NO_3^- concentration

Soil water NO_3^- concentration at 60 cm depth was highly variable. However, across all the N treatments, the concentrations of NO_3^- were slightly lower under subsurface drained than undrained condition throughout the measurement period. A consistently lower NO_3^- concentration with subsurface drainage could in part be due to N uptake by sugarbeet crop. The measurement of leaf chlorophyll conducted at 54 d revealed that, across the N treatments, the spad values were slightly higher for the subsurface drained sugarbeet plots compared to undrained plots. Sugarbeet N demand is usually high from the early growth period until canopy growth phase for the development of above-ground plant parts, during which maximum N is assimilated (Martin, 2001).

Nitrate concentration generally increased with N fertilization over the control, irrespective of drainage management. The lower NO_3^- levels with the control treatments were expected. Under subsurface drained condition, application of NP accumulated significantly greater soil water NO_3^- levels than the control, while the urea treatments without NP were only slightly greater than control. Under undrained condition, the soil water NO_3^- concentration appeared not to depend on NP but N fertilization. In the present study, the extraction of soil water for the determination of NO_3^- concentration began only after 29 d following N application due to untrafficable soil condition at the study site. Despite the delayed measurements, under subsurface drained condition, the NO_3^- concentration tended to be slightly higher with the application of Urea146 + NP than without NP treatments (Urea146 and Urea180). Since nearly a third of the total growing season precipitation fell within the initial 30 d (Figure 1), considerable losses of N were deemed possible through denitrification without NP application during these initial 4 wk period (Chen et al., 2010; Omonode and Vyn, 2013). These results suggest the efficacy of nitrification inhibitor NP to conserve more NO_3^- in soils with subsurface drainage condition, which otherwise could have potentially lost through denitrification without the application of NP.

Conclusions

Our experiment showed the need for long term studies of subsurface drainage and N management on crop yields and quality, and N losses in the RRV. Although contrasting weather patterns occurred during the 2012 and 2013 growing seasons, our study emphasized that across intense wetting and drying cycles, subsurface drainage and N management can have pronounced effects on N availability under silty clay soils. Within the scope of this two year study, yield benefits with subsurface drainage were limited. Apart from the high cation exchange associated with the soil under investigation, mechanical incorporation of fertilizer-N into soils can considerably restrict NH_3 volatilization from these soils, with a possibility of up to 1.74% loss from the applied-N. Inherent soil N mineralization appears to be an important factor controlling crop yields, and therefore assessment of soil mineral N during crop growth period appears to be important to improve our knowledge on N availability for crops. The research results may provide important information to growers considering suitable N management and use of subsurface drainage systems within this region.

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Table 1. Nitrogen fertilizer management treatments applied in 2012 and 2013 growing seasons in the crops.

Crops	2012	2013
Corn	(i) 180 kg N ha^{-1} at preplant as urea (Urea180), (ii) 224 kg N ha^{-1} at preplant as urea (Urea224), (iii) 224 kg N ha^{-1} at preplant as urea plus Nitrapyrin (Urea224 + NP), (iv) 112 kg N ha^{-1} at preplant as urea plus 112 kg N ha^{-1} at 6 leaf stage as UAN [Split (Urea112 + UAN112)]	(i) Control (0 N), (ii) 134 kg N ha^{-1} at preplant as urea (Urea224), (iii) 134 kg N ha^{-1} at preplant as urea plus Nitrapyrin (Urea134 + NP), (iv) 67 kg N ha^{-1} at preplant as urea plus 67 kg N ha^{-1} at 6 leaf stage as UAN [Split (Urea67 + UAN67)]
Wheat	(i) Control (0 N), (ii) 146 kg N ha^{-1} at preplant as urea (Urea146), (iii) 146 kg N ha^{-1} at preplant as urea plus NBPT (Urea146 + NBPT), (iv) 146 kg N ha^{-1} at preplant as urea plus NP (Urea146 + NP),	(i) Control (0 N), (ii) 112 kg N ha^{-1} at preplant as urea (Urea112), (iii) 112 kg N ha^{-1} at preplant as urea plus Nitrapyrin (Urea112 + NP), (iv) 202 kg N ha^{-1} at preplant as urea (Urea202)
Sugarbeet	(i) Control (0 N), (ii) 146 kg N ha^{-1} at preplant as urea (Urea146), (iii) 146 kg N ha^{-1} at preplant as urea plus Nitrapyrin (Urea146 + NP), (iv) 180 kg N ha^{-1} at preplant as urea (Urea202)	(i) Control (0 N), (ii) 146 kg N ha^{-1} at preplant as urea (Urea146), (iii) 146 kg N ha^{-1} at preplant as urea plus Nitrapyrin (Urea146 + NP), (iv) 180 kg N ha^{-1} at preplant as urea (Urea202)
Soybean	(i) Control (0 N), (ii) 26 kg N ha^{-1} at preplant as urea (Urea26), (iii) 26 kg N ha^{-1} at preplant as urea plus Nitrapyrin (Urea26 + NP), (iv) 39 kg N ha^{-1} at preplant as urea plus Nitrapyrin (Urea39 + NP)	(i) Control (0 N), (ii) 26 kg N ha^{-1} at preplant as urea (Urea26), (iii) 39 kg N ha^{-1} at preplant as urea plus Nitrapyrin (Urea39 + NP)

Nitrapyrin, NP; N-(n-butyl) thiophosphoric triamide, NBPT.

Table 2. Basic soil characteristics in the surface 0-30 cm depth at the experimental site measured in sugarbeet plot during the 2012 and 2013 growing seasons.

Soil Properties[†]	2012	2013
Sand (g kg^{-1})	17 ± 3[‡]	17 ± 5
Silt (g kg^{-1})	359 ± 47	374 ± 61
Clay (g kg^{-1})	624 ± 89	609 ± 77
Bulk density (Mg m^{-3})	1.22 ± 0.11	1.23 ± 0.06
pH	8.24 ± 0.27	8.32 ± 0.38
EC (dS m^{-1})	1.59 ± 0.56	1.54 ± 0.62
Organic matter (g kg^{-1})	71.8 ± 1.7	70.7 ± 2.3
NO_3-N, kg ha^{-1} (0-30 cm)	36 ± 9	130 ± 31
NO_3-N, kg ha^{-1} (30-60 cm)	13 ± 8	59 ± 22
NO_3-N, kg ha^{-1} (60-120 cm)	44 ± 9	83 ± 28
Olsen-P (mg kg^{-1})	14.5 ± 8.5	26.5 ± 10.2
Available-K (mg kg^{-1})	333 ± 47	447 ± 45
Cation exchange capacity ($cmol_c$ kg^{-1})	NA[¶]	37.1 ± 2.3

[†] Soil properties measured for 0-30 cm soil depth, unless stated.

[‡] Values are mean ± standard deviations.

[¶] Not analyzed.

Table 3. Corn grain yield as affected by N management in 2012.

N fertilizer	Corn Grain Yield[†]
	---Mg ha^{-1}----
Urea180	7.78 ± 0.55
Urea224	7.19 ± 0.56
Urea224 + NP	6.99 ± 0.59
Split (Urea112 + UAN112)	7.54 ± 0.50
LSD (α=0.05)[‡]	NS[§]

[†] Values are means ± standard error (n=8); Different lowercase letters within a column indicate significant difference at 0.05 level of significance.

[‡] Least significant difference (LSD) values at α=0.05.

[§] NS, nonsignificant.

Table 4. Corn grain yield as affected by N management under undrained and drained conditions in 2013.

N fertilizer	Corn Grain Yield[†]	
	Undrained	Drained
	------------------Mg ha^{-1}------------------	
Control	5.97 ± 0.41 b	6.01 ± 0.27 b
Urea134	8.79 ± 0.37 a	8.33 ± 0.57 a
Urea134 + NP	8.65 ± 0.59 a	8.59 ± 0.68 a
Split (Urea67 + UAN67)	7.42 ± 0.19 a	7.84 ± 0.57 a
LSD (α=0.05)[‡]	1.43	0.86

[†] Values are means ± standard error (n=4); Different lowercase letters within a column indicate significant difference at 0.05 level of significance.

[‡] Least significant difference (LSD) values at α=0.05.

Table 5. Wheat grain yield as affected by N management in 2012.

N fertilizer	Wheat Grain Yield[†]
	----Mg ha^{-1}----
Control	0.69 ± 0.04 a
Urea146	0.98 ± 0.16 a
Urea146 + NBPT	0.88 ± 0.18 a
Urea146 + NP	0.96 ± 0.11 a
LSD (α=0.05)[‡]	NS[§]

[†] Values are means ± standard error (n=8); Different lowercase letters within a column indicate significant difference at 0.05 level of significance.

[‡] Least significant difference (LSD) values at α=0.05.

[§] NS, nonsignificant.

Table 6. Wheat grain yield as affected by N management under undrained and drained conditions in 2013.

N fertilizer	Wheat Grain Yield[†]	
	Undrained	Drained
	-------------------Mg ha^{-1}-----------------	
Control	3.46 ± 0.25 b	3.19 ± 0.24 a
Urea112	4.44 ± 0.08 a	3.73 ± 0.35 a
Urea112 + NP	4.32 ± 0.12 a	3.72 ± 0.47 a
Urea202	4.33 ± 0.14 a	3.82 ± 0.43 a
LSD (α=0.05)[‡]	0.57	NS[§]

[†] Values are means ± standard error (n=4); Different lowercase letters within a column indicate significant difference at 0.05 level of significance.

[‡] Least significant difference (LSD) values at α=0.05.

[§] NS, nonsignificant.

Table 7. Nitrogen management effects on sugarbeet yield and quality parameters during the 2012 growing season.

N fertilizer	Root Yield[†]	SLM[†‡]	Net Sucrose[†]
	--Mg ha^{-1}--	--------------------%-------------------	
Control	47.5 ± 3.0	1.65 ± 0.08 c	16.8 ± 0.3
Urea146	47.9 ± 2.9	1.80 ± 0.06 bc	16.8 ± 0.3
Urea146 + NP	45.2 ± 2.8	1.85 ± 0.08 ab	16.8 ± 0.3
Urea180	47.3 ± 2.8	1.95 ± 0.06 a	15.9 ± 0.4
LSD (α=0.05)[§]	NS[¶]	0.15	NS

[†] Values are means ± standard errors (n=8). Different lowercase letters within a column indicate significant difference at 0.05 level of significance.

[‡] SLM = sucrose loss to molasses, a measure of impurity content.

[§] Least significant difference (LSD) values at α=0.05.

[¶] NS, nonsignificant.

Table 8. Drainage and N management effects on sugarbeet yield and quality parameters during the 2013 growing season.

N fertilizer	Root Yield[†]		SLM[†‡]		Net Sucrose[†]	
	U[§]	D[¶]	U	D	U	D
	----------Mg ha^{-1}--------		--------------------------------%---------------------------			
Control	39.4 ± 1.6	36.7 ± 2.2	1.54 ± 0.14	1.69 ± 0.20	14.5 ± 0.4	14.4 ± 0.4
Urea146	40.1 ± 0.5	41.0 ± 1.1	1.58 ± 0.05	1.81 ± 0.12	14.3 ± 0.5	13.5 ± 0.6
Urea146 + NP	39.6 ± 0.6	37.0 ± 1.7	1.74 ± 0.08	1.67 ± 0.08	13.8 ± 1.6	14.3 ± 0.2
Urea180	36.7 ± 1.0	35.8 ± 3.8	1.73 ± 0.10	1.68 ± 0.12	14.0 ± 0.1	13.9 ± 0.5
LSD (α=0.05)[#]	NS[††]	NS	NS	NS	NS	NS

[†] Values are means ± standard error (n=4); Different lowercase letters within a column indicate significant difference at 0.05 level of significance.

[‡] SLM = sucrose loss to molasses, a measure of impurity content.

[§] U = undrained condition.

[¶] D= drained condition.

[#] Least significant difference (LSD) values at α=0.05.

[††] NS, nonsignificant.

Table 9. Drainage and N management effects on soybean grain yield (Mg ha^{-1}) in 2012 and 2013.

N fertilizer	Soybean Grain Yield†		
	2012	2013	
		Undrained	Drained
	------------------------------Mg ha^{-1}------------------------------		
Control	2.99 ± 0.18 a	2.81 ± 0.40	2.85 ± 0.23
Urea26	2.64 ± 0.20 ab	3.05 ± 0.18	2.87 ± 0.25
Urea26 + NP	2.42 ± 0.19 b	-	-
Urea39 + NP	2.28 ± 0.09 b	3.07 ± 0.24	3.04 ± 0.28
LSD (α=0.05)‡	0.38	NS§	NS

†Values are means ± standard errors (2012: n=8; 2013: n=4).Different lower case letters within the same column indicate significant difference at 0.05 level of significance.

‡Least significant difference (LSD) values at α=0.05.

§NS, nonsignificant.

Table 10. Soil N_2O fluxes as influenced by N management during the 2012 corn growing season.

N fertilizer	Days after treatment application				
	52 d	78 d	87 d	100 d	Total
	--------------------------- (g N_2O-N ha^{-1} d^{-1})† ---------------------------				
Urea180	74 ± 12	4 ± 1	25 ± 4	7 ± 1	110
Urea224	105 ± 69	7 ± 4	26 ± 12	11 ± 2	145
Urea224 + NP	74 ± 18	10 ± 2	28 ± 12	5 ± 1	117
Split (Urea112 + UAN112)	73 ± 17	7 ± 4	21 ± 10	6 ± 1	107
LSD (α=0.05)‡	NS§	NS	NS	NS	-

†Values are means ± standard error (n=4).

‡Least significant difference (LSD) values at α=0.05.

§NS, non-significant.

Table 11. Soil N_2O fluxes as affected by N management during the 2012 wheat growing season.

N fertilizer	Days after treatment application		
	62 d	71 d	Total
	---------------- (g N_2O-N ha^{-1} d^{-1})----------------		
Control	3 ± 1	15 ± 4	19
Urea146	5 ± 1	22 ± 5	27
Urea146 + NBPT	6 ± 1	17 ± 3	23
Urea146 + NP	6 ± 1	16 ± 2	22
LSD (α=0.05)‡	NS§	NS	-

†Values are means ± standard error (n=4).

‡Least significant difference (LSD) values at α=0.05.

§NS, non-significant.

Table 12. Soil N_2O fluxes as influenced by N management during the 2012 sugarbeet growing season.

N fertilizer	Days after N application				
	35 d	42 d	54 d	73 d	Total
	------------------------------N_2O flux (g ha^{-1} d^{-1})[†]------------------------				
Control	10 ± 3	13 ± 4	13 ± 3	13 ± 4	50
Urea146	20 ± 4	15 ± 9	23 ± 5	18 ± 4	76
Urea146 + NP	17 ± 5	16 ± 4	24 ± 5	28 ± 13	86
Urea180	24 ± 7	17 ± 1	36 ± 17	29 ± 5	106
LSD (α=0.05)[†]	NS[§]	NS	NS	NS	-

[†] Values are means ± standard errors (n=4).

[‡] Least significant difference (LSD) values at α=0.05.

[§] NS, non-significant.

Table 13. Nitrogen management influences on soil N_2O flux measured on July 6th, 2012 (72 d after treatment application) under soybean.

N fertilizer	N_2O flux (g ha^{-1} d^{-1})
Control	9 ± 3
Urea26	5 ± 2
Urea39 + NP	7 ± 2
LSD (α=0.05)[†]	NS[§]

[†] Values are means ± standard errors (n=4).

[‡] Least significant difference (LSD) values at α=0.05.

[§] NS, non-significant.

Table 14.Cumulative NH_3 volatilization losses from N fertilizers under undrained and drained conditions over 40 days of measurement during the 2013 corn growing season.

N fertilizer	Cumulative NH_3 loss[†]		Emission Factor	
	Undrained	Drained	Undrained	Drained
	------------kg ha^{-1}---------		-----------%-----------	
Control	1.22 ± 0.13 b	1.26 ± 0.12 b	-	-
Urea134	2.51 ± 0.39 ab	3.23 ± 0.20 a	0.96	1.47
Urea134 + NP	3.69 ± 1.27 a	3.95 ± 1.19 a	1.84	2.01
LSD (α=0.05)[‡]	1.79	1.63	-	-

[†] Values are means ± standard error (n=4); Different lowercase letters within a column indicate significant difference at 0.05 level of significance.

[‡] Least significant difference (LSD) value at α=0.05.

Table 15.Cumulative NH_3 volatilization losses from N fertilizers under undrained and drained conditions during the 2013 sugarbeet growing season.

N fertilizer	Cumulative NH_3 loss[†]		Emission Factor	
	Undrained	Drained	Undrained	Drained
	--------------kg ha^{-1}----------		-----------%----------	
Control	0.89 ± 0.11 b	0.77 ± 0.02 b	-	-
Urea146	1.44 ± 0.09 a	1.43 ± 0.14 a	0.38	0.45
Urea180	1.51 ± 0.15 a	1.75 ± 0.14 a	0.41	0.54
LSD (α=0.05)[‡]	0.35	0.46	-	-

[†] Values are means ± standard error (n=4); Different lowercase letters within a column indicate significant difference at 0.05 level of significance.

[‡] Least significant difference (LSD) value at α=0.05.

Table 16. Drainage and N management effects on corn leaf chlorophyll reading and tissue-N concentration measured 72 d and 80 d after treatment application, respectively during the 2013 growing season.

N fertilizer	Chlorophyll meter reading[†]		Leaf-N concentration[†]	
	Undrained	Drained	Undrained	Drained
	----------Spad units----------		----------------%----------------	
Control	45.8 ± 4.0 b	45.5 ± 0.7 b	2.45 ± 0.06 b	2.11 ± 0.16 b
Urea134	52.2 ± 1.1 a	54.0 ± 1.9 a	2.65 ± 0.06 a	2.65 ± 0.08 a
Urea134 + NP	55.2 ± 0.8 a	55.2 ± 1.2 a	2.62 ± 0.03 a	2.66 ± 0.09 a
Split (Urea67 + UAN67)	49.5 ± 1.9 ab	50.4 ± 1.9 b	2.47 ± 0.03 b	2.50 ± 0.05 a
LSD (α=0.05)[‡]	5.5	4.9	0.11	0.19

[†] Values are means ± standard error (n=4); Different lowercase letters within a column indicate significant difference at 0.05 level of significance.

[‡] Least significant difference (LSD) values at α=0.05.

Table 17. Drainage and N management effects on wheat leaf chlorophyll reading and tissue-N concentration measured 72 d and 80 d after treatment application, respectively during the 2013 growing season.

N fertilizer	Chlorophyll meter reading[†]		Leaf-N concentration[†]	
	Undrained	Drained	Undrained	Drained
	-----------spad units-------------		----------------%------------------	
Control	39.4 ± 0.7 b	38.6 ± 1.0 b	2.53 ± 0.11 a	2.27 ± 0.11 b
Urea112	39.0 ± 0.9 b	40.9 ± 0.9 ab	2.63 ± 0.11 a	2.45 ± 0.17 ab
Urea112 + NP	40.2 ± 0.3 ab	40.9 ± 1.2 ab	2.59 ± 0.15 a	2.64 ± 0.11 ab
Urea202	41.4 ± 0.5 a	42.4 ± 0.5 a	2.84 ± 0.13 a	2.82 ± 0.08 a
LSD (α=0.05)[‡]	1.3	2.4	NS[§]	0.4

[†] Values are means ± standard error (n=4); Different lowercase letters within a column indicate significant difference at 0.05 level of significance.

[‡] Least significant difference (LSD) values at α=0.05.

[§] NS, non-significant.

Table 18. Drainage and N management effects on sugarbeet leaf chlorophyll reading and tissue-N concentration measured 54 d and 62 d after treatment application, respectively during the 2013 growing season.

N fertilizer	Chlorophyll meter reading[†]		Leaf-N concentration[†]	
	Undrained	Drained	Undrained	Drained
	------------Spad Units----------		-----------------%----------------	
Control	39.9 ± 1.2 a	40.9 ± 0.8 a	4.54 ± 0.04 a	4.52 ± 0.05 a
Urea146	41.0 ± 1.1 a	42.4 ± 1.1 a	4.55 ± 0.05 a	4.54 ± 0.13 a
Urea146 + NP	41.7 ± 1.1 a	42.4 ± 1.2 a	4.62 ± 0.03 a	4.63 ± 0.05 a
Urea180	41.4 ± 0.6 a	42.8 ± 0.6 a	4.43 ± 0.06 a	4.61 ± 0.06 a
LSD (α=0.05)[‡]	NS[§]	NS	NS	NS

[†] Values are means ± standard error (n=4); Different lowercase letters within a column indicate significant difference at 0.05 level of significance.

[‡] Least significant difference (LSD) values at α=0.05.

[§] NS, non-significant.

Table 19. Drainage and N management effects on soybean leaf chlorophyll reading and tissue-N concentration measured 67 d and 75 d after treatment application, respectively during the 2013 growing season.

N fertilizer	Chlorophyll meter reading[†]		Leaf-N concentration[†]	
	Undrained	Drained	Undrained	Drained
	------------Spad units----------		-----------------%----------------	
Control	41.6 ± 0.6 a	43.5 ± 0.7 a	4.89 ± 0.05 a	4.78 ± 0.09 a
Urea26	41.7 ± 0.8 a	41.9 ± 1.0 a	4.85 ± 0.08 a	4.77 ± 0.10 a
Urea39 + NP	42.4 ± 0.3 a	43.2 ± 0.6 a	4.87 ± 0.08 a	4.83 ± 0.04 a
LSD (α=0.05)[‡]	NS[§]	NS	NS	NS

[†] Values are means ± standard error (n=4); Different lowercase letters within a column indicate significant difference at 0.05 level of significance.

[‡] Least significant difference (LSD) values at α=0.05.

[§] NS, non-significant.

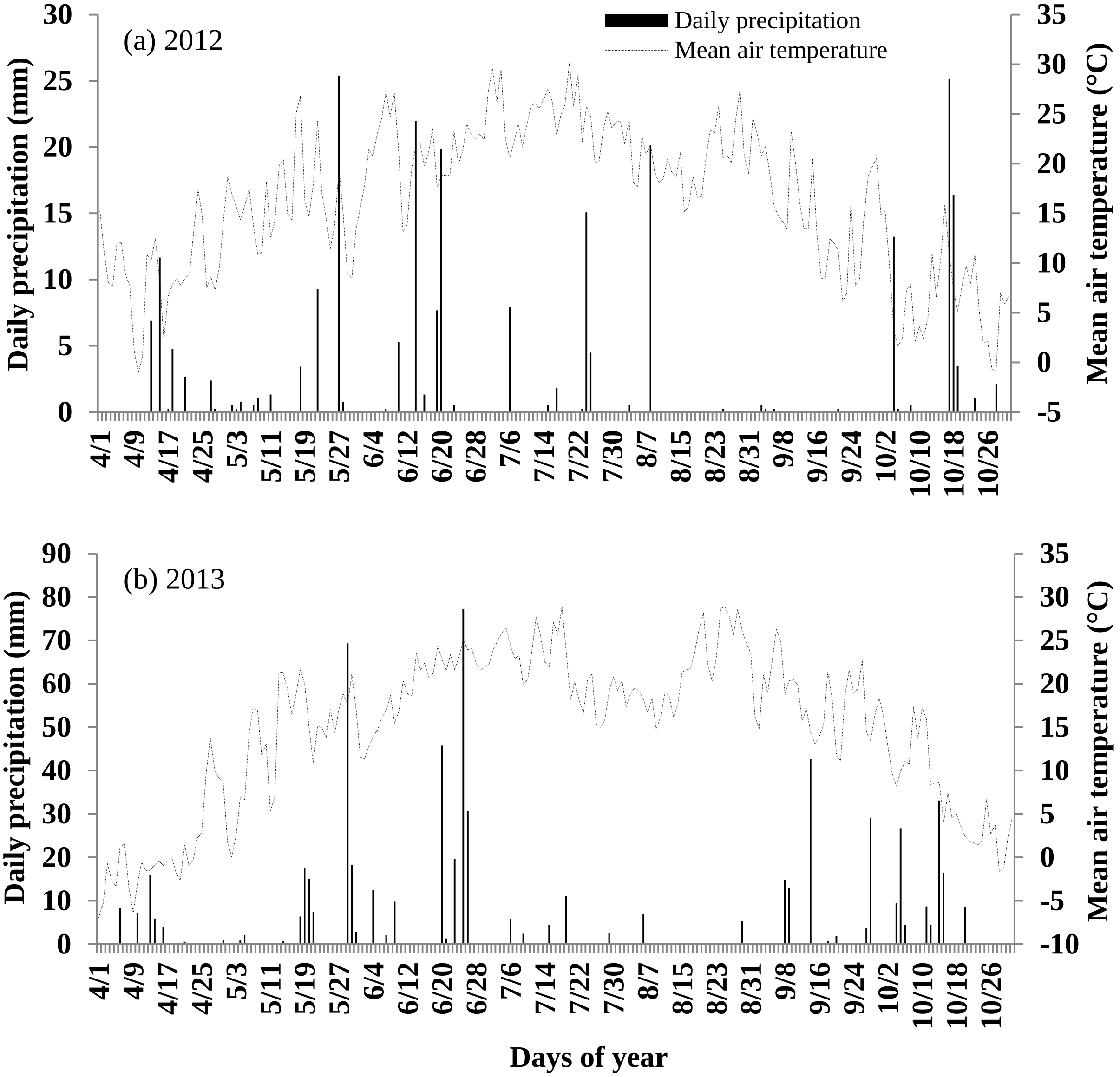

Figure 1. Daily precipitation and mean air temperature for the (a) 2012, and (b) 2013 growing seasons at the research site recorded by Fargo NDAWN station (NDAWN, 2015).

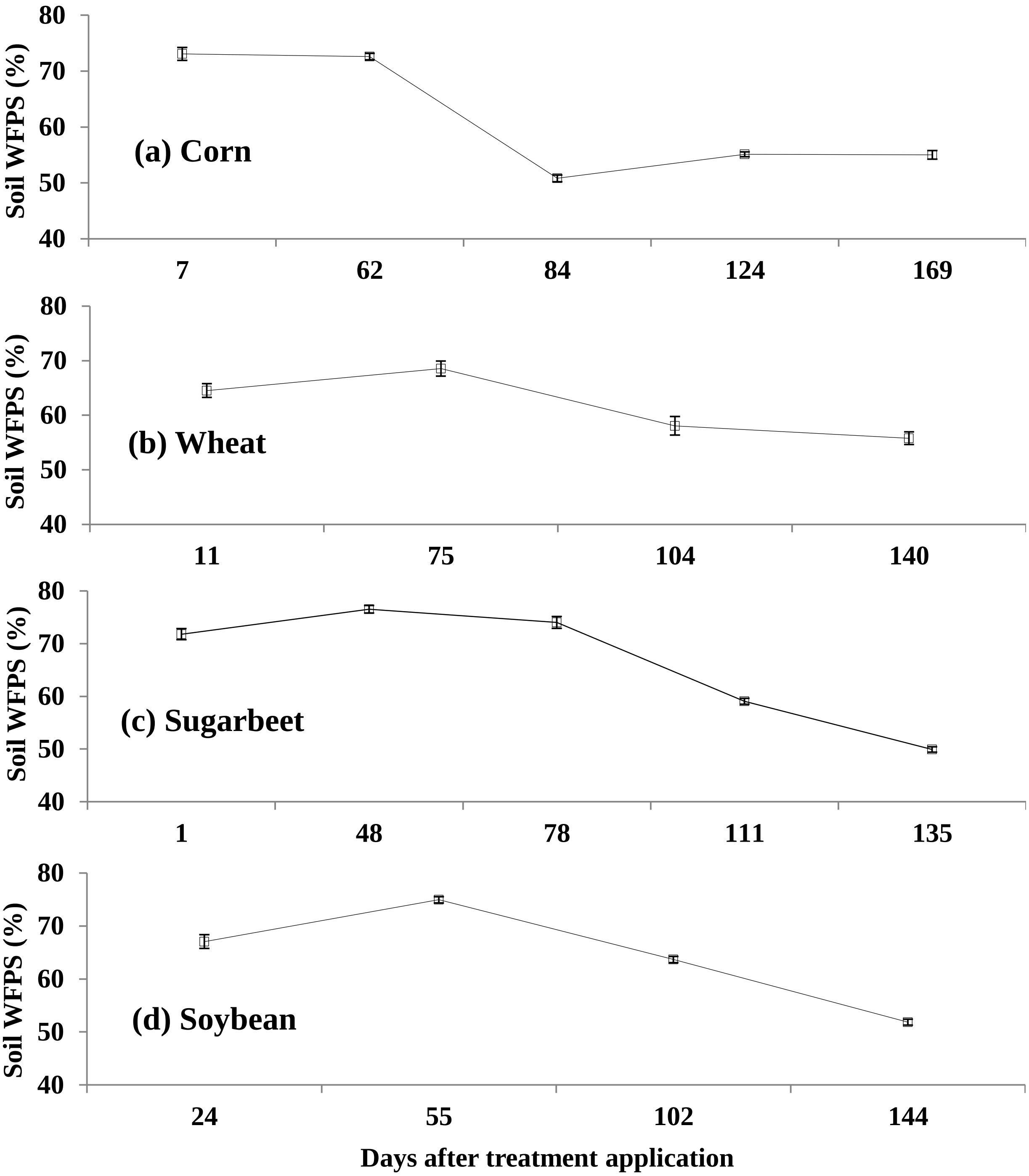

Figure 2. Soil water filled pore space (WFPS, %; 0-30 cm depth) measured during (a) corn, (b) wheat, (c) sugarbeet, and (d) soybean growing season in 2012. Bars represent standard errors (n=32).

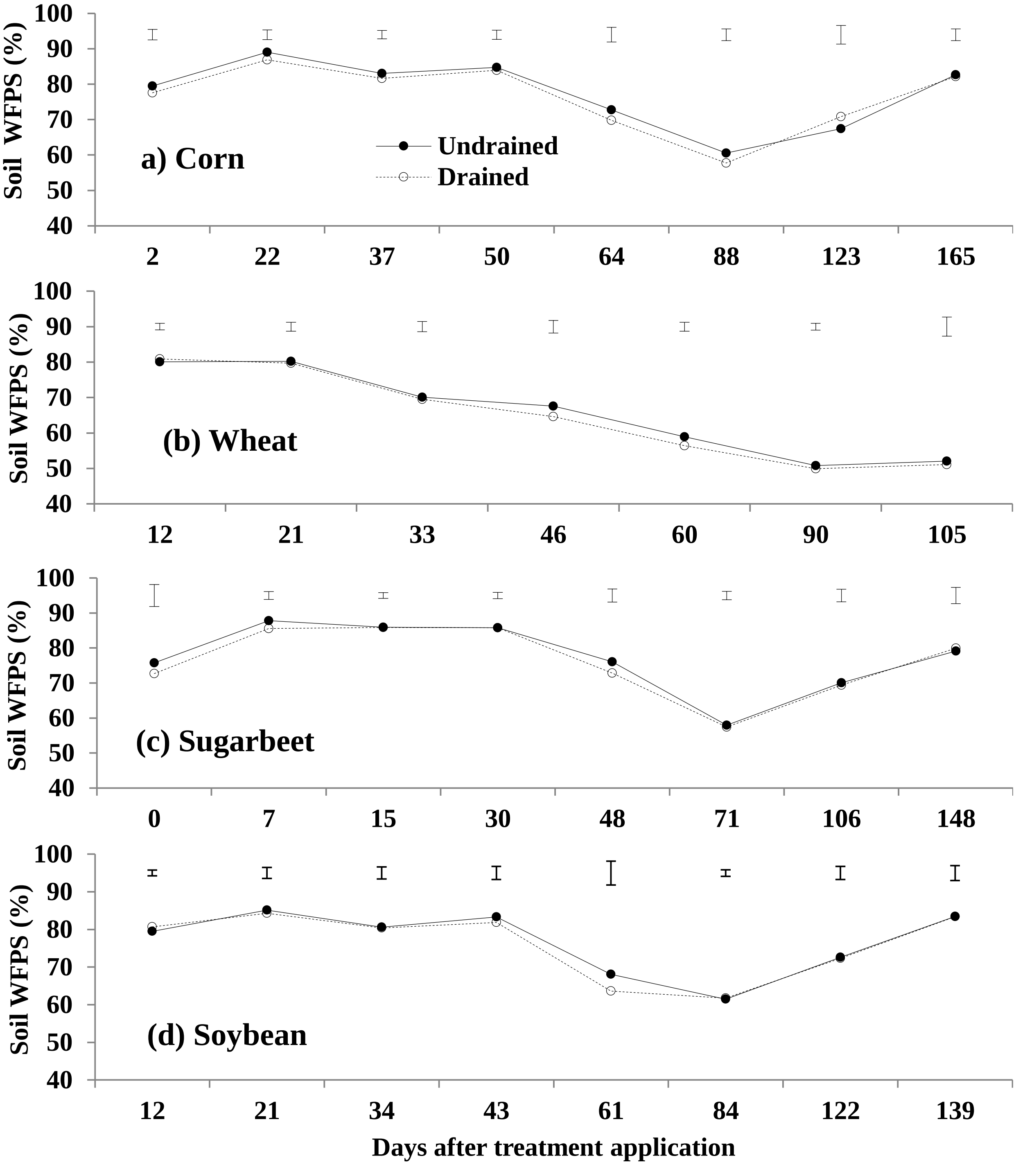

Figure 3. Soil water filled pore space (WFPS, %; 0-30 cm depth) measured for undrained and drained plots during (a) corn, (b) wheat, (c) sugarbeet, and (d) soybean growing season in 2013. Bars represent least significant difference values at 0.05 level of significance for the day (n=16**)**.

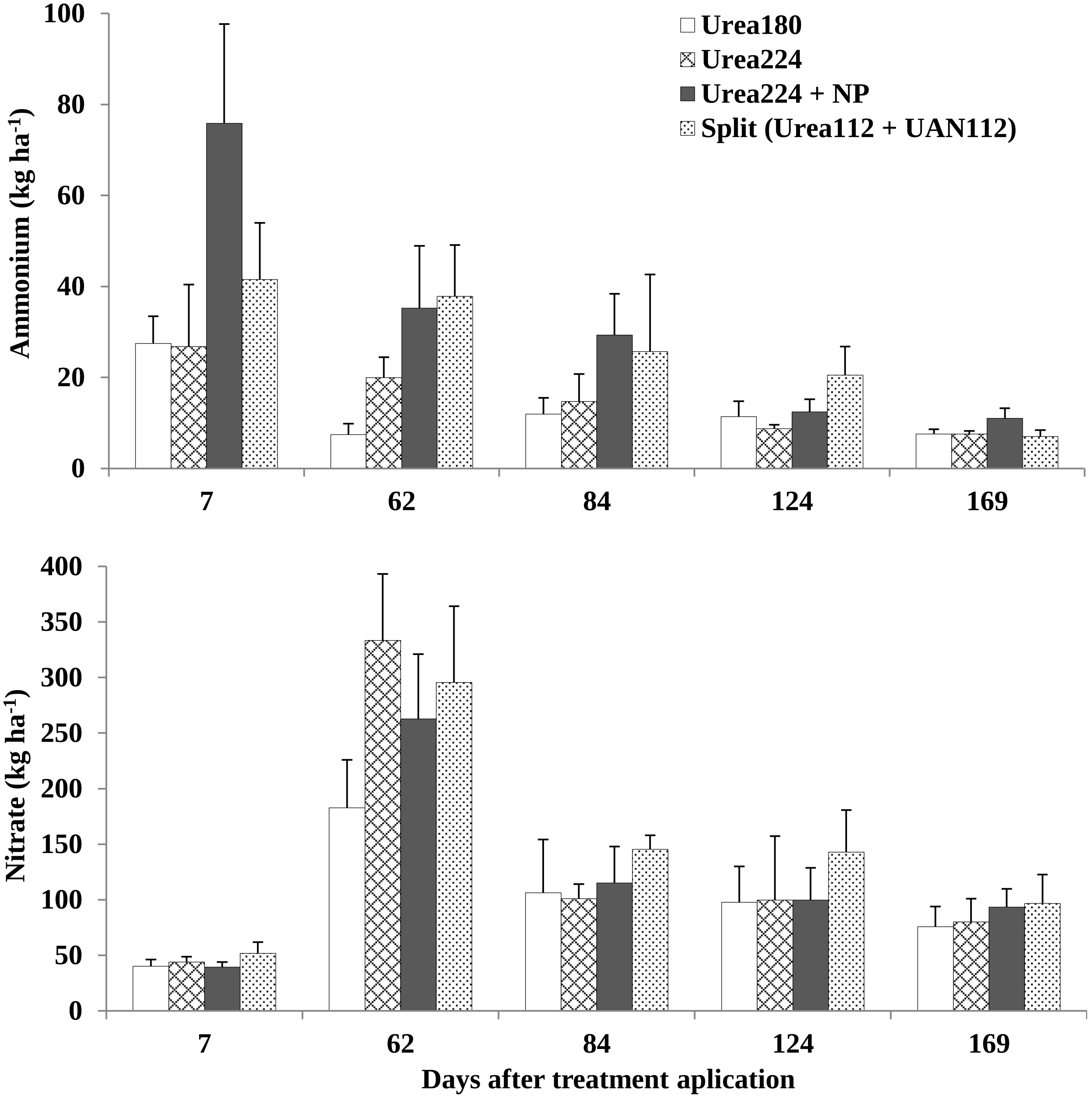

Figure 4. Temporal soil ammonium (NH_4^+) and nitrate (NO_3^-) dynamics at 0-30 cm soil depth for N treatments over a corn growing season in 2012. Bars represent standard errors (n=8). Different lower case letters within a day indicate significant difference at 0.05 level of significance.

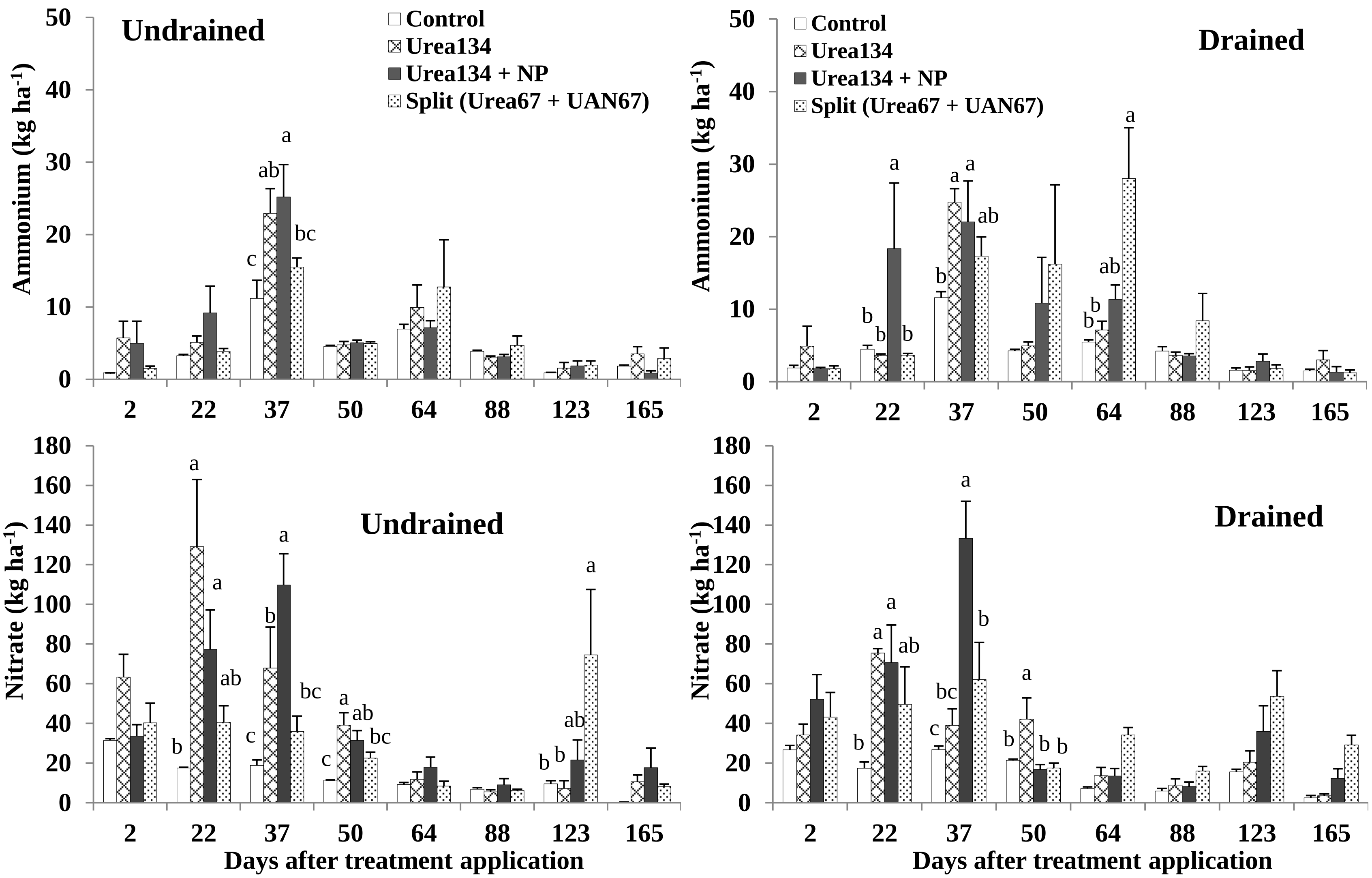

Figure 5. Temporal soil ammonium (NH_4^+) and nitrate (NO_3^-) dynamics at 0-30 cm soil depth for N treatments under undrained and drained conditions over a corn growing season in 2013. Bars represent standard errors (n=4). Different lower case letters within a day indicate significant difference at 0.05 level of significance.

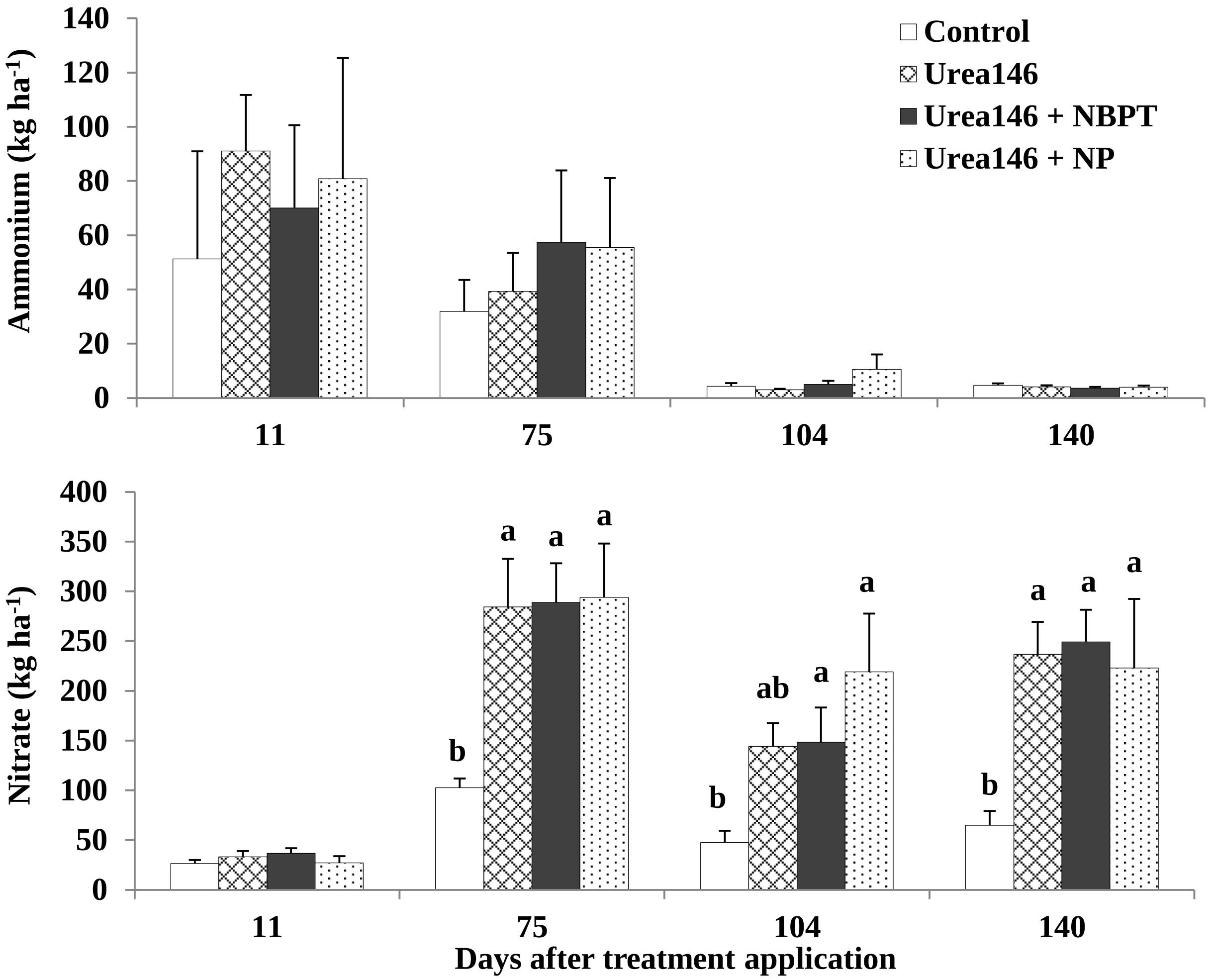

Figure 6. Temporal soil ammonium (NH_4^+) and nitrate (NO_3^-) dynamics at 0-30 cm soil depth for N treatments over a wheat growing season in 2012. Bars represent standard errors (n=8). Different lower case letter within a day indicate significant difference at 0.05 level of significance.

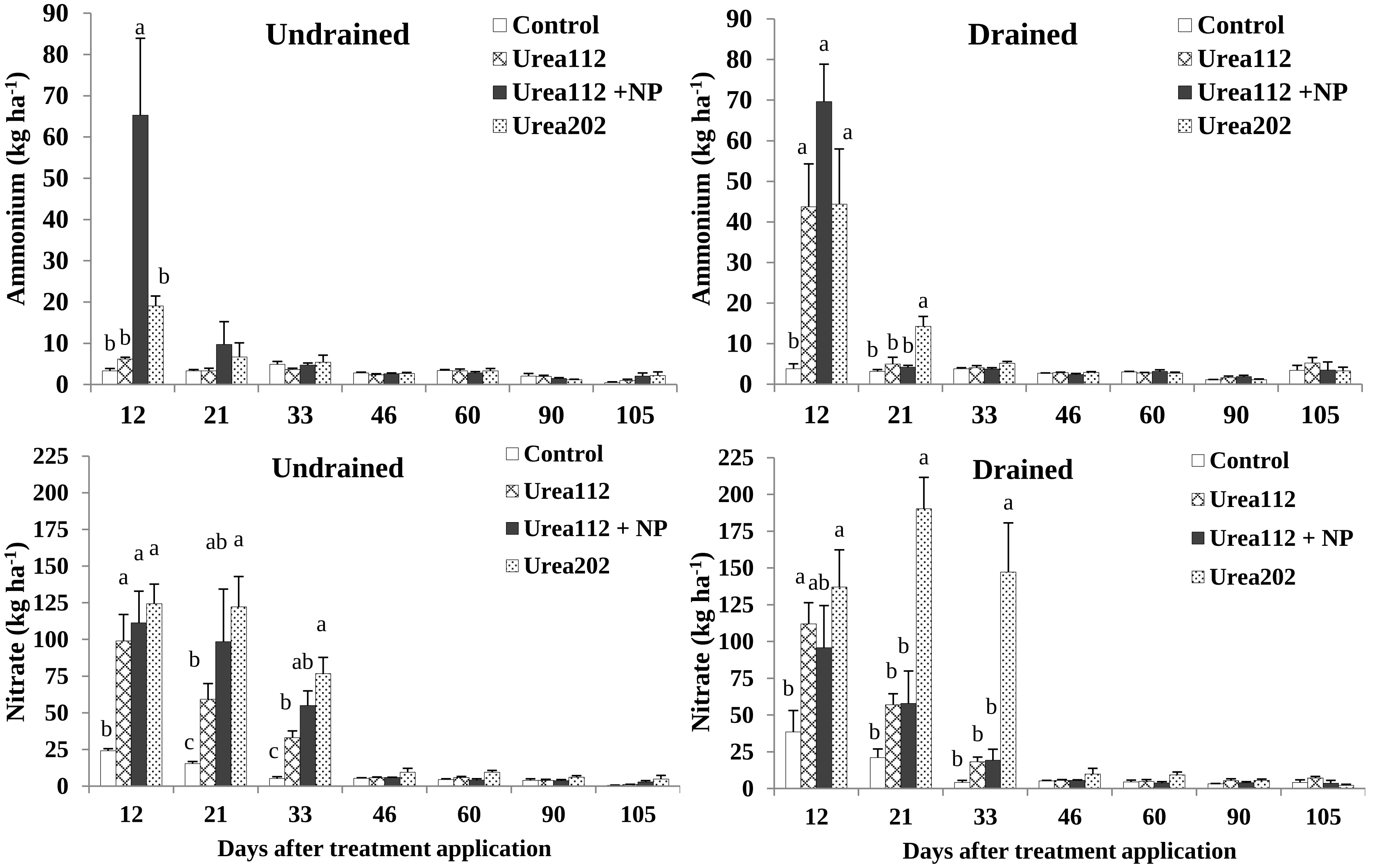

Figure 7. Temporal soil ammonium (NH_4^+) and nitrate (NO_3^-) dynamics at 0-30 cm soil depth for N treatments under undrained and drained conditions over a wheat growing season in 2013. Bars represent standard errors (n=4). Different lower case letters within a day indicate significant difference at 0.05 level of significance.

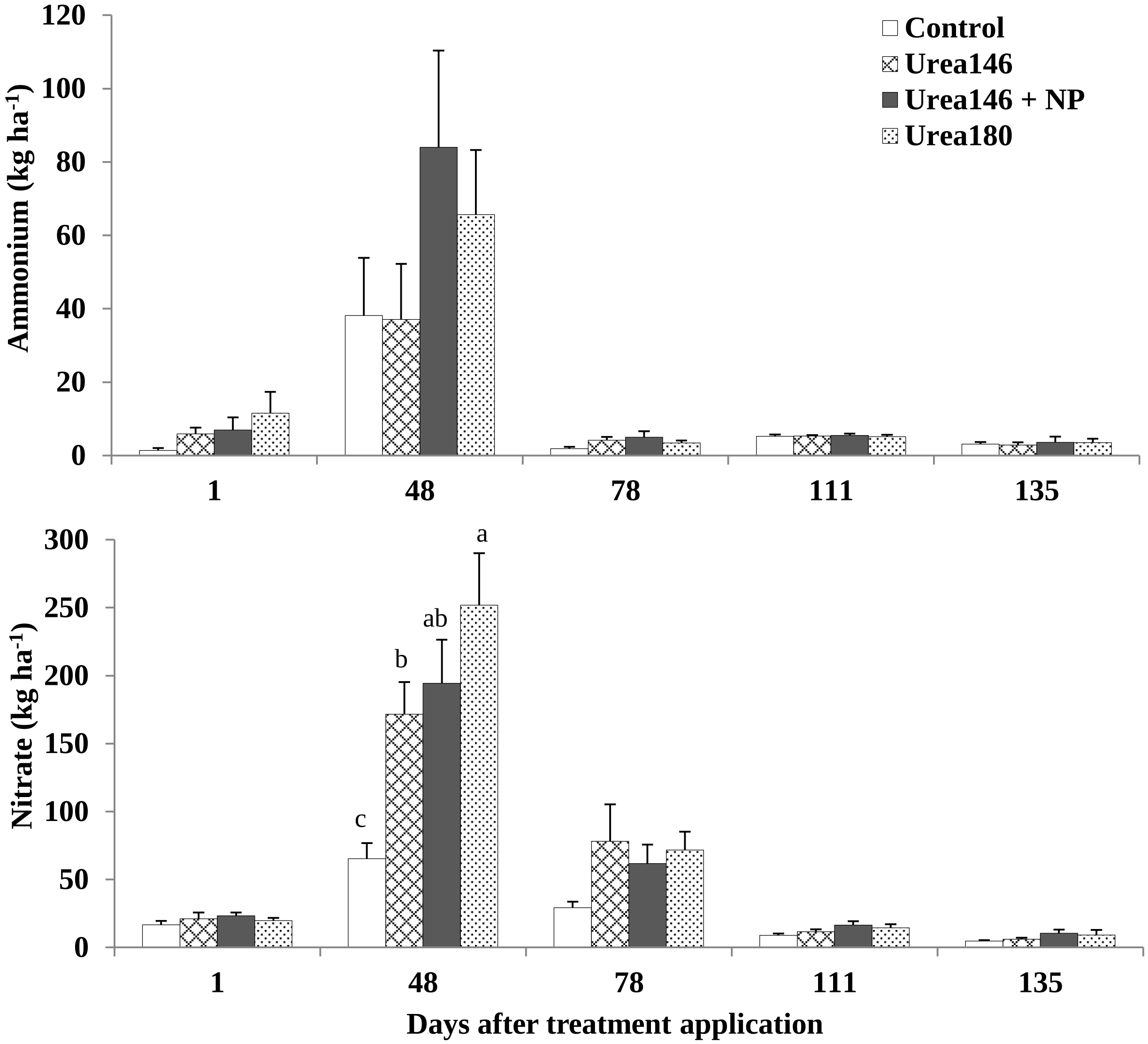

Figure 8. Temporal soil ammonium (NH_4^+) and nitrate (NO_3^-) dynamics at 0-30 cm soil depth for N treatments over a sugarbeet growing season in 2012. Bars represent standard errors (n=8). Different lower case letters within a day indicate significant differences at 0.05 level of significance.

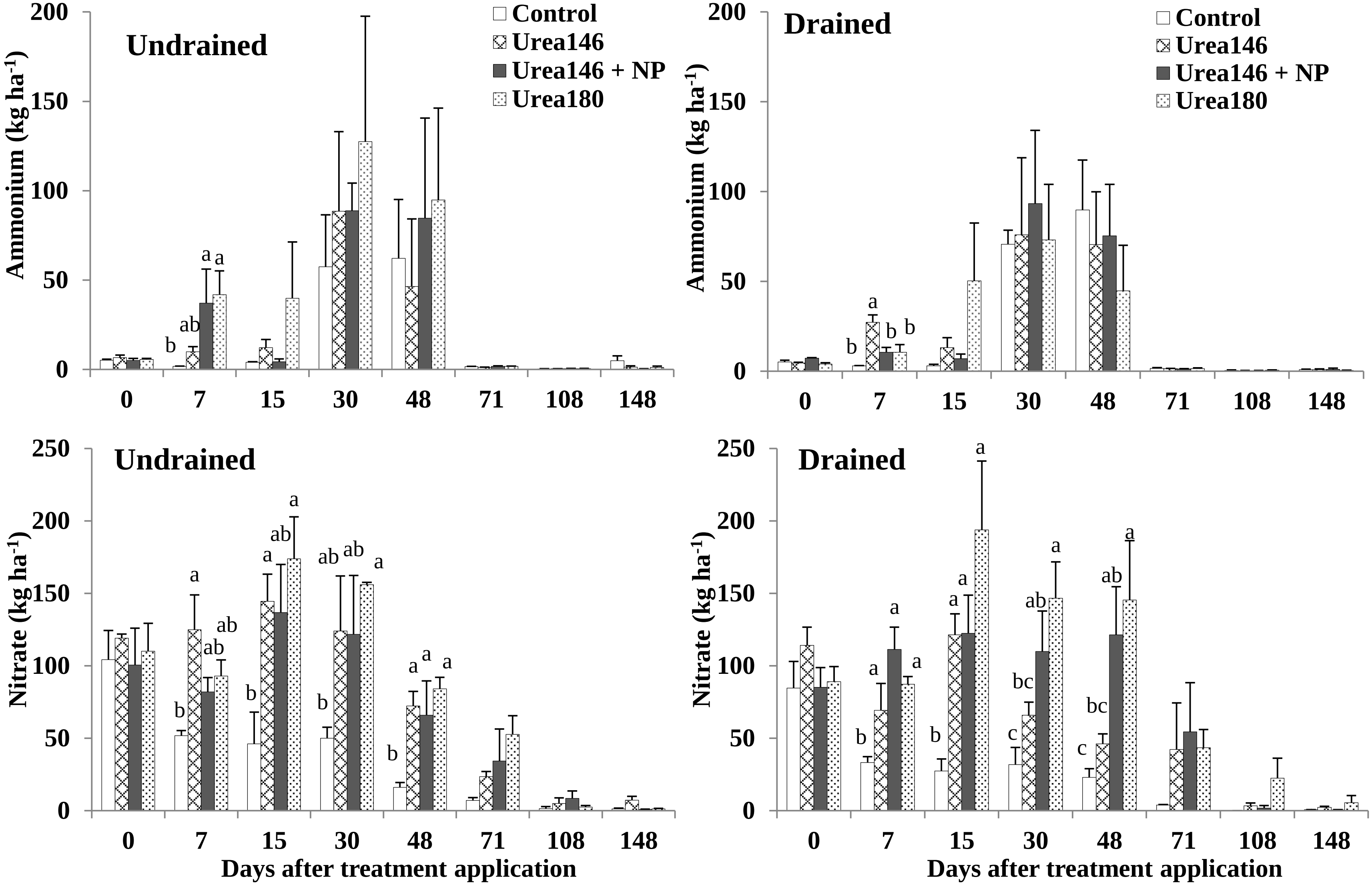

Figure 9. Temporal soil ammonium (NH_4^+) and nitrate (NO_3^-) dynamics at 0-30 cm soil depth for N treatments under undrained and drained conditions over a sugarbeet growing season in 2013. Bars represent standard errors (n=4). Different lower case letter within a day indicate significant difference at 0.05 level of significance.

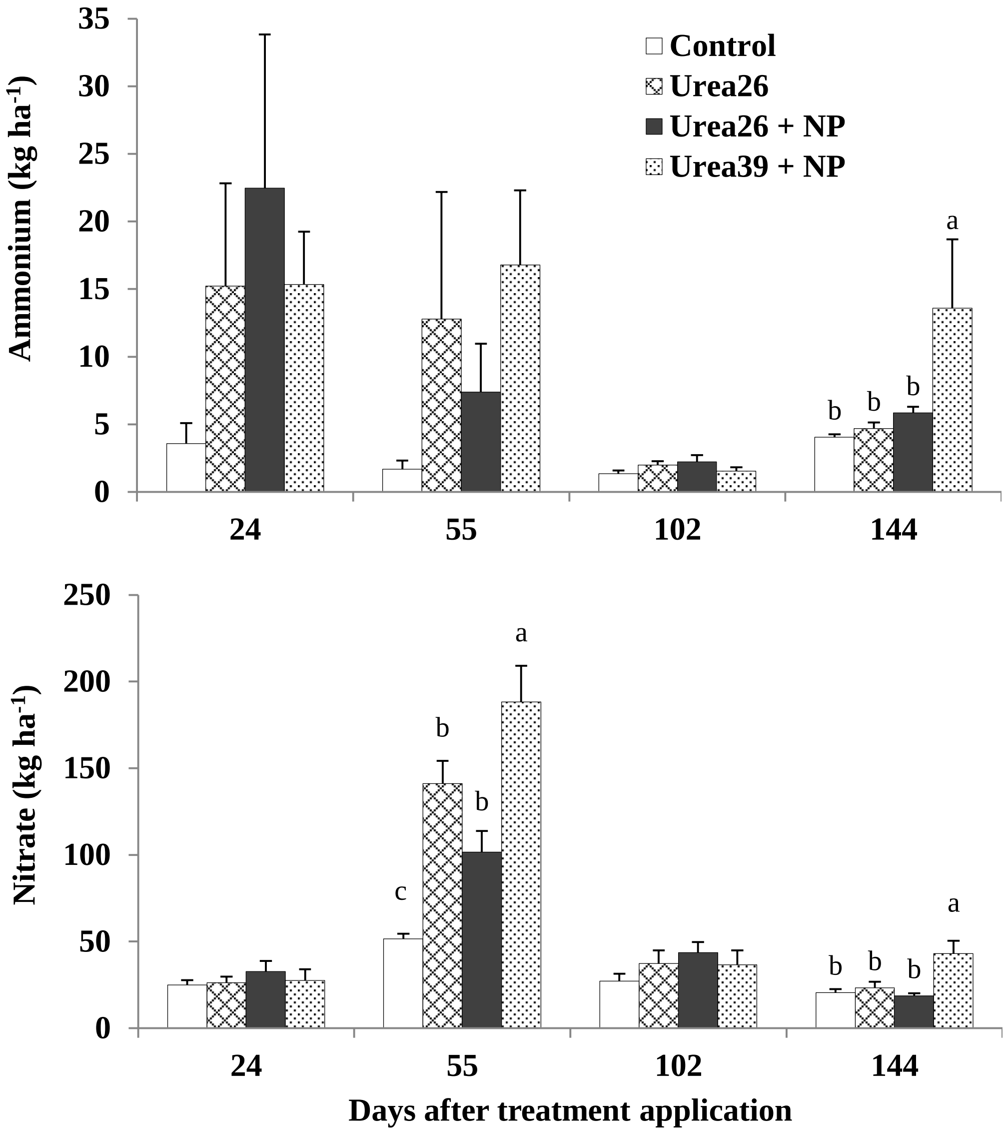

Figure 10. Temporal soil ammonium (NH_4^+) and nitrate (NO_3^-) dynamics at 0-30 cm soil depth for N treatments over a soybean growing season in 2012. Bars represent standard errors (n=8). Different lower case letters within a day indicate significant differences at 0.05 level of significance.

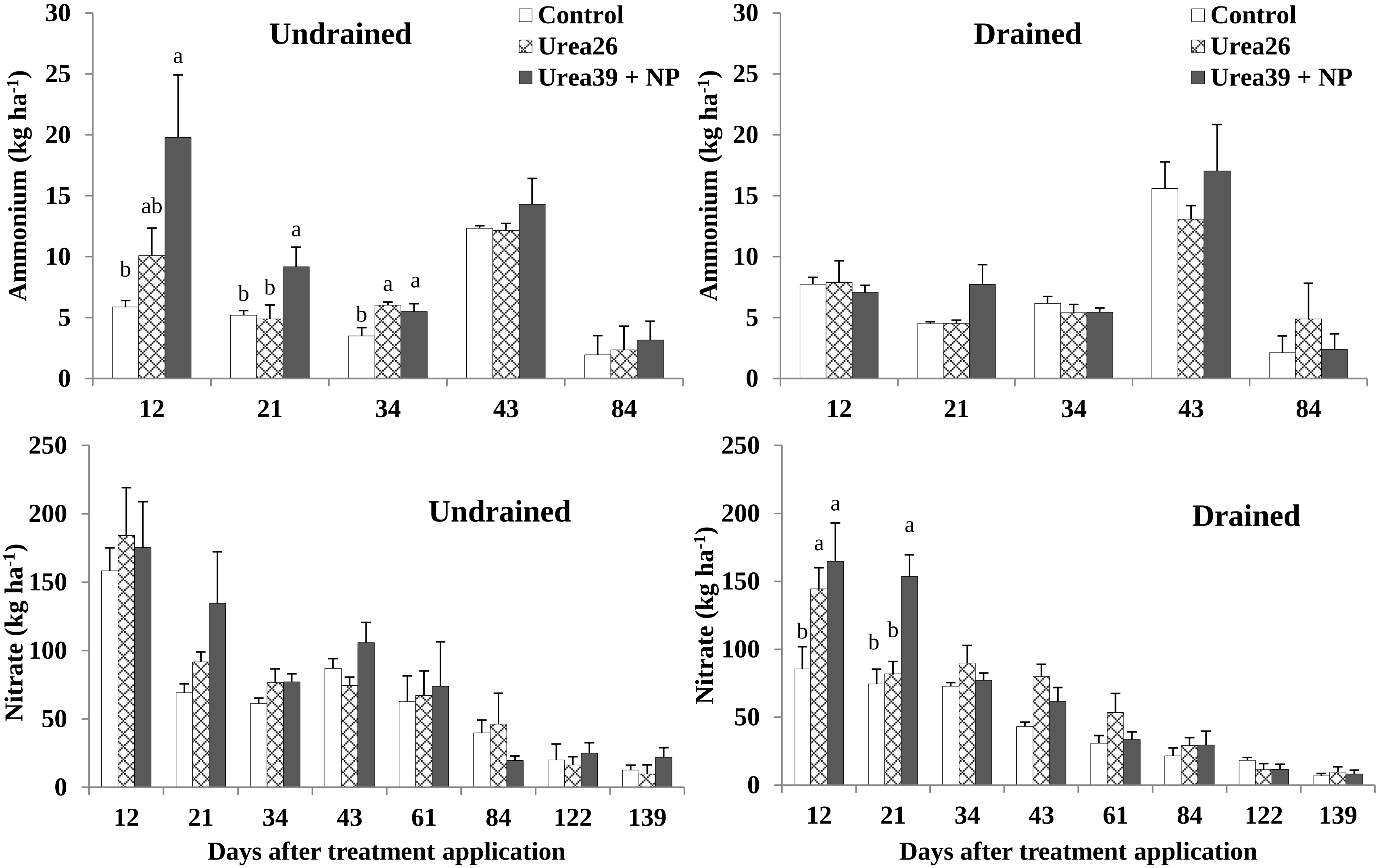

Figure 11. Temporal soil ammonium (NH_4^+) and nitrate (NO_3^-) dynamics at 0-30 cm soil depth for N treatments under undrained and drained conditions over a soybean growing season in 2013. Bars represent standard errors (n=4). Different lower case letter within a day indicate significant differences at 0.05 level of significance.

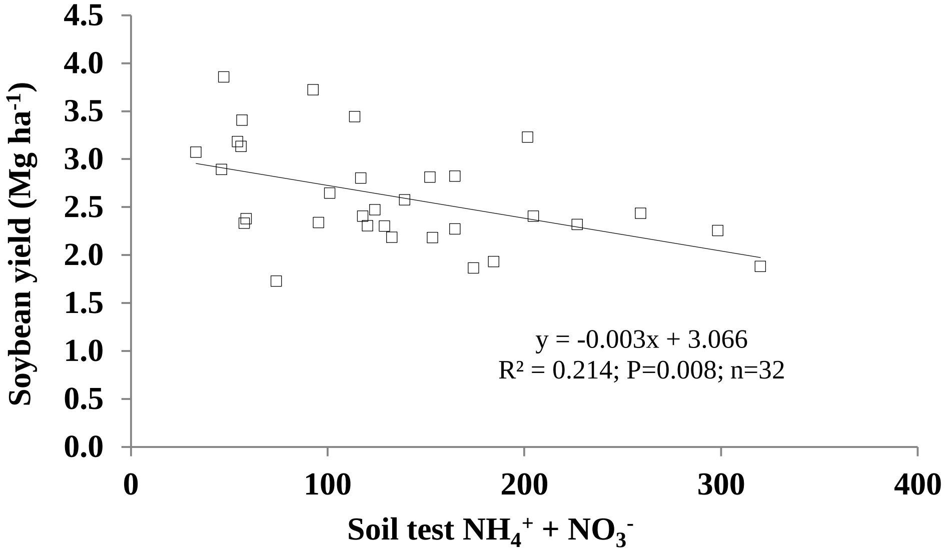

Figure 12. Relationship between soybean grain yield and soil NH_4^+ plus NO_3^- measured 55 d after treatment application during the 2012 soybean growing season.

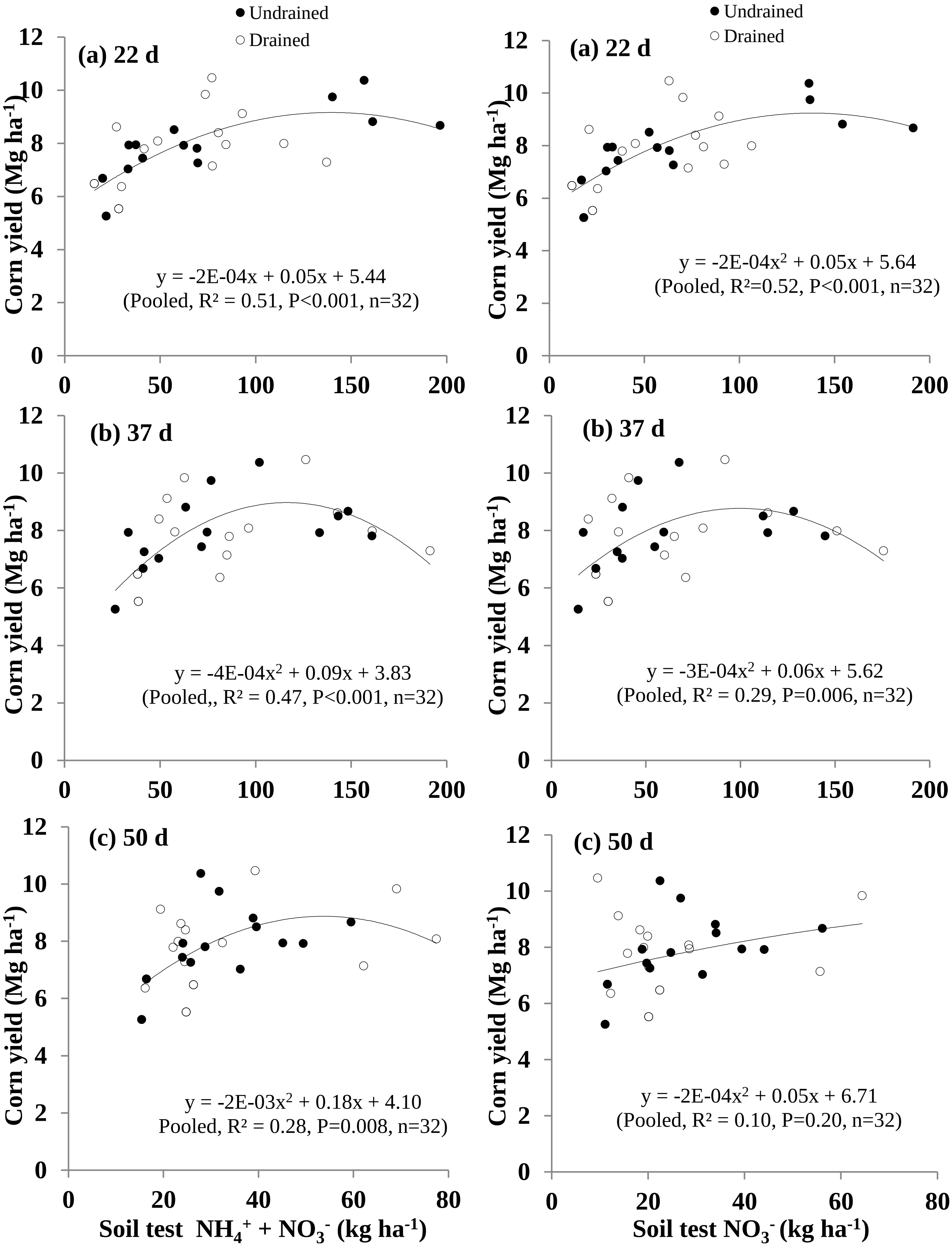

Figure 13. Relationship between corn grain yield and soil NH_4^+ plus NO_3^- or NO_3^- measured (a) 22 d, (b) 37 d, and (c) 50 d after treatment application during the 2013 corn growing season.

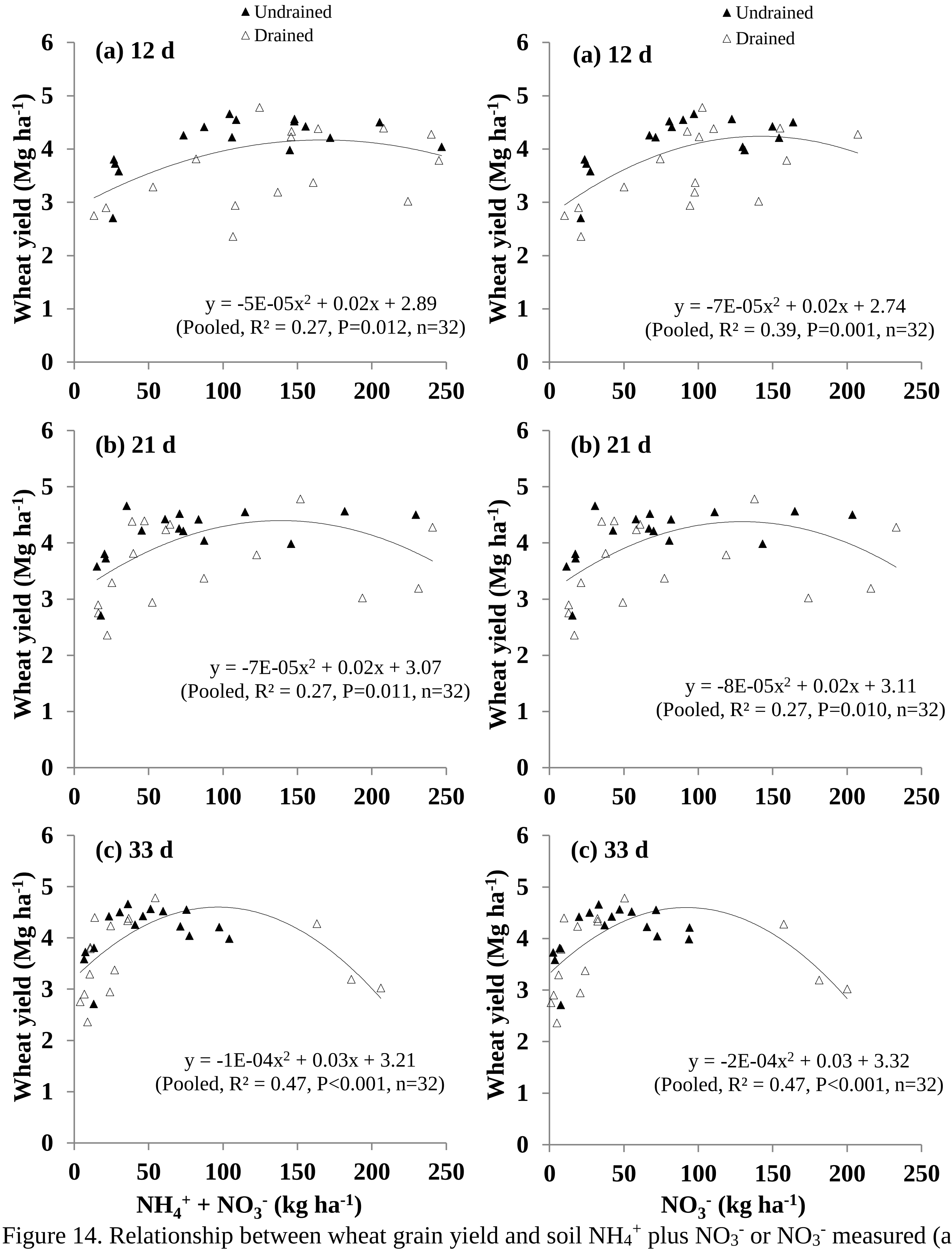

Figure 14. Relationship between wheat grain yield and soil NH_4^+ plus NO_3^- or NO_3^- measured (a) 12 d, (b) 21 d, and (c) 33 d after treatment application during the 2013 wheat growing season.

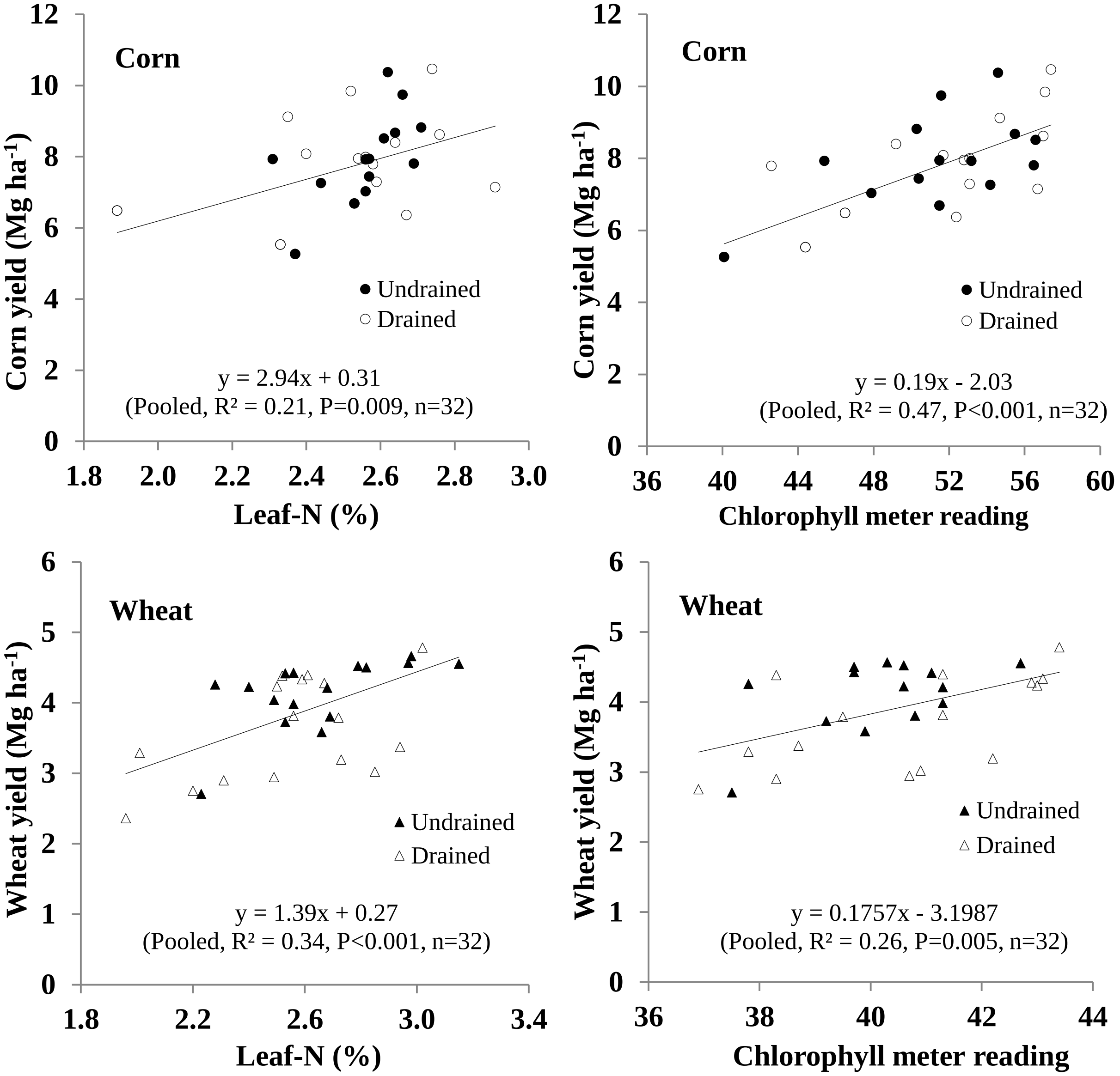

Figure 15. Relationship between crop grain yield and leaf-N concentration or chlorophyll meter reading measured in corn and wheat during the 2013 growing season.

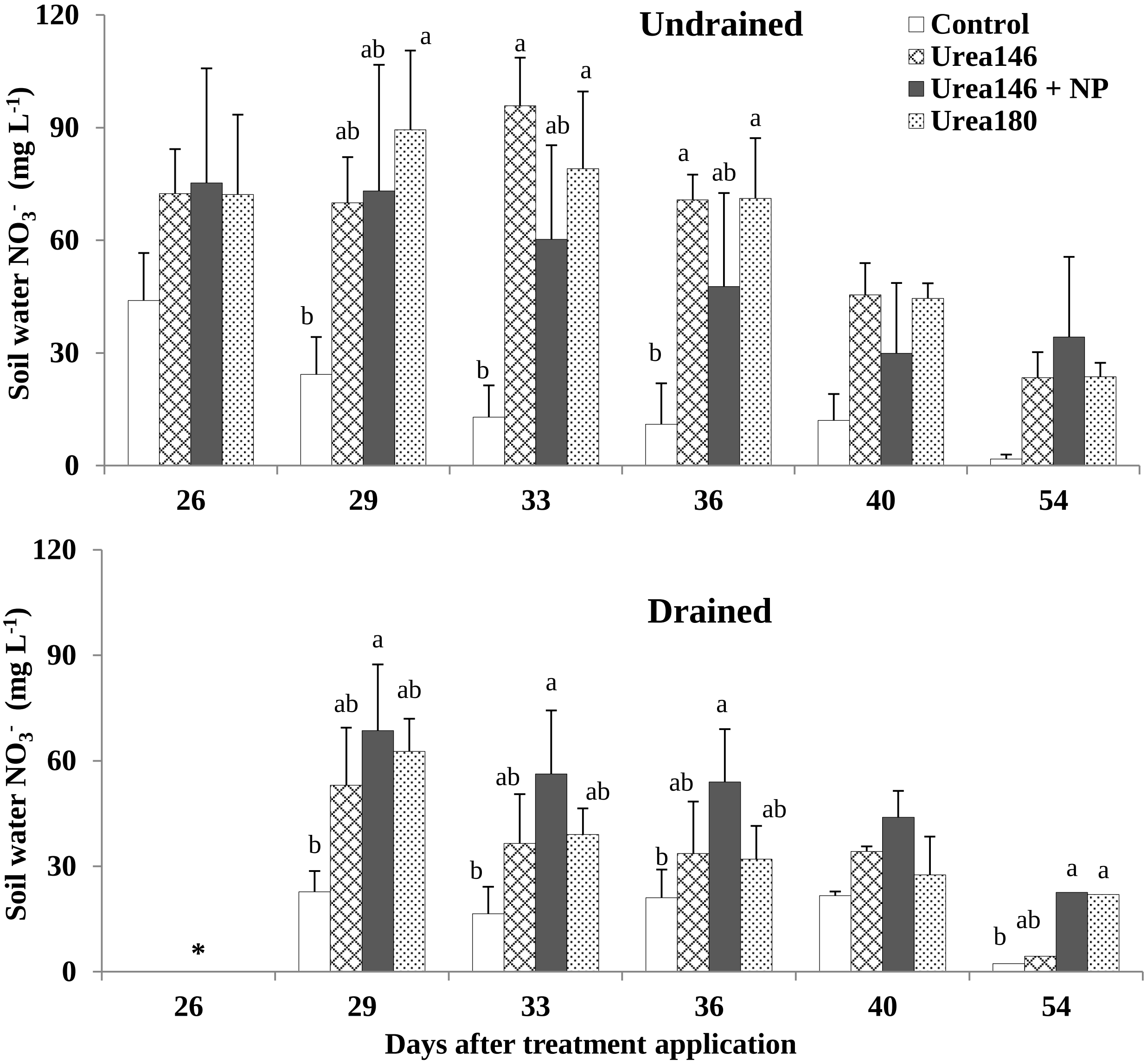

Figure 16. Soil water NO$_3^-$ concentration (mg L^{-1}) measured during the 2013 sugarbeet growing season as influenced by N management under undrained and drained conditions. Bars represent standard errors (n=4). Different lower case letter within a day indicate significant difference at 0.05 level of significance. *****Not available for the day.

SOIL MOISTURE CONTROLS THE DENITRIFICATION LOSS OF UREA-NITROGEN FROM SILTY CLAY SOIL[1]

Abstract

Relative control of soil moisture [30%, 60%, and 80% water holding capacity (WHC)] on nitrous oxide (N_2O) emissions from Fargo-Ryan soil, treated with urea at 0, 150, and 250 kg N ha^{-1} with and without nitrapyrin [2-chloro-(6-trichloromethyl) pyridine] (NP), was measured under laboratory condition for 140 days. Soil N_2O emissions significantly increased with increasing N-rates and WHC levels. Urea applied at 250 kg N ha^{-1} produced the highest cumulative N_2O emissions and averaged 0.6, 3.9, and 15.9 mg kg^{-1} at 30, 60, and 80% WHC, respectively. At WHC $\leq$ 60%, addition of NP to urea significantly reduced N_2O losses by 2.6 to 4.8 fold. Additions of NP to urea reduced N_2O emission at rates similar to the control (0 N) until 48 days for 30% WHC and 35 days for 60% and 80% WHC. These results can help devise urea-N fertilizer management strategies in reducing N_2O emissions from silty-clay soils.

Introduction

Nitrogen (N) fertilization is one of the main sources of anthropogenic nitrous oxide (N_2O) emissions (Asgedom et al., 2014). Urea [$CO(NH_2)_2$] (46% N) is the most commonly used synthetic nitrogenous fertilizer (Bierman et al., 2012) and its usage is expected to increase further to meet food demands (Snyder et al., 2009). Urea-N fertilizers increase NH_4^+ and NO_3^- substrates

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The material in this chapter was co-authored by Rakesh Awale and Amitava Chatterjee. Rakesh Awale had primary responsibility for the collection and analyses of samples, and was the primary developer of the conclusions that are advanced here. Amitava Chatterjee served as proofreader and checked the math in the statistical analysis conducted by Rakesh Awale.

in soils and consequently N_2O emissions, predominantly through denitrification (Senbayram et al., 2009). Denitrification of urea-N is a major N leakage from agricultural systems and can significantly reduce crop recovery of applied N (Gagnon et al., 2011) as well as promote the greenhouse effect (Crutzen, 1981).

Management of N-fertilizers for abatement of N_2O production from agricultural soils has been a primary focus for the last few decades (Burzaco et al., 2013). Higher N-fertilizer rates than recommended for optimum crop production are often used by farmers as an insurance against yield loss (Vanotti and Bundy, 1994). Studies have indicated that the increased use of N-fertilizers usually increases soil N_2O emissions due to increased availability of mineral N substrates (Ma et al., 2010; Hoben et al., 2011). Therefore, optimization of fertilizer N-rates, without compromising economic yields, may be the most practical means for achieving decreased N_2O emissions. Another way to reduce denitrification loss of urea-N fertilizer is the usage of nitrification inhibitors such as nitrapyrin [2-chloro-(6-trichloromethyl) pyridine] (NP) (Burzaco et al., 2013). Nitrapyrin delays the nitrification process and reduces soil N_2O emissions by limiting N substrate for denitrification (Omonode and Vyn, 2013).

Nitrogen fertilizer rates and nitrification inhibitor influences on N_2O emissions can interact with several soil environmental conditions (Chantigny et al., 1998; Halvorson et al., 2008; Gagnon et al., 2011). These interrelationships have confounded attempts to quantify gaseous N-loss from agricultural soils (Menendez et al., 2012). Soil water content is the dominant factor influencing denitrification loss of soil mineral N (Bateman and Baggs, 2005). According to Khalil et al. (2002), soil water regimes regulate the availability and diffusion of oxygen (O_2) as well as NH_4^+ and NO_3^- substrates in soils and consequently the N_2O emissions. Studies have shown that N_2O losses after N addition increase with increasing soil water content and are greatest when the soil moisture level exceeds 60% of water filled pore space (WFPS) (Bateman and Baggs, 2005) or 65% water holding capacity (WHC) (Senbayram et al., 2009). Greater N_2O fluxes from arable soils following excessive rainfall, irrigation, and spring thaw events are common (Gao et al., 2013). However, soil water regulation of N_2O emissions after N application may vary with site specific soil characteristics that influence soil aeration (Skiba and Ball, 2002).

Studies of the effects of soil moisture regimes and urea-N fertilizer rates in conjunction with nitrification inhibitors on N_2O emissions from clay soils of the Red River Valley (RRV) are relatively few (Asgedom et al., 2014). The RRV is the leading area of crop production in the United States. Therefore, the region exhibits high potential for N_2O emissions due to extensive use of urea-N fertilizers (Bierman et al., 2012). Moreover, high clay and organic matter contents of poorly drained soils within this region are deemed favorable for denitrification loss of N_2O (Glenn et al., 2012). A few studies conducted recently within the RRV of Manitoba, Canada, have documented variable N_2O emission factors (EFs) (percent N emitted as N_2O-N from the applied N-fertilizer), ranging from 0.75 to 3.8% (Glenn et al., 2012; Gao et al., 2013; Asgedom et al., 2014). The reported ranges differ considerably from the current default N_2O EF of 1.0% from annual application of N-fertilizer, as estimated by the IPCC (2006). These divergent results not only necessitate an approximation of EFs on the basis of site specific soil characteristics and N-management practices employed, but also highlight the need for the development of best N-management practices in order to lower N_2O emissions from high clay soils. Thus, a laboratory incubation study was conducted with the objective to evaluate the effects of soil moisture regimes and urea N-fertilizer rates, with and without additions of NP, on emissions of N_2O from silty clay soil from the RRV.

Materials and Methods

Soil

Surface soil at 0-15 cm depth was collected from the North Dakota State University research farm (46.93°N, 96.85°W), 8 km northwest of Fargo in North Dakota, USA. The soil was poorly drained Fargo silty clay, and classified as Fine, smectitic, frigid Typic Epiaquerts (Soil Survey Staff, 2014). Soil was air-dried and finely ground in a mechanical grinder to pass through a 2 mm sieve. The air-dried soil had 2% sand, 47% silt and 51% clay, 6.8% organic matter, pH (1:2.5 H_2O) of 8.24, EC (1:2.5 H_2O) of 1.6 dS m^{-1}, 2.7 mg NH_4^+ kg^{-1}, and 34.6 mg NO_3^- kg^{-1}. Water holding capacity of the sieved soil was determined as the water retained after 2 h of draining excess water from 10 g soil (dry equivalent weight, 7% w/w), which had initially been saturated with de-ionized water (Harding and Ross, 1964).

Experimental approach

Soil incubations were conducted in 1 L mason jars following the procedure as described by Mukome et al. (2013). The experimental design was a completely randomized design in a split plot arrangement with four replications. The whole plot treatments were soil moisture regimes (30, 60, and 80% WHC) and the sub-plot treatments were N-fertilizers. The N-fertilizer treatments include urea-N rates of 0 kg N ha^{-1} (N_0), 150 kg N ha^{-1}(N_{150}), 250 kg N ha^{-1}(N_{250}), 150 kg N ha^{-1} plus nitrapyrin [NP, 2-chloro-6-(trichloromethyl) pyridine, trade name Instinct, 17.6% by weight active ingredient solution, DOW AgroSciences] (NP_{150}), and 250 kg N ha^{-1} plus NP (NP_{250}). Nitrapyrin was applied to the soil based on an area basis (451 g NP ha^{-1} soil) at the manufacturer's recommended rate of 2.5 L ha^{-1}. One hundred grams (dry equivalent weight) of sieved soils were weighed into mason jars. Urea-N fertilizers, 52 and 86 mg per 100 g soil (equivalent to 150 and 250 kg N ha^{-1} respectively on weight basis for 5 cm deep soil) with and without NP, were amended to soil surface. De-ionized water (31, 63, and 84 mL) was uniformly added to soil surface using pipette to adjust the soils to 30, 60, and 80% of WHC, respectively. Unfertilized control (0 N) treatments were also established at each soil moisture level. The mason jars were closed with air-tight lids, fitted with gas sampling ports (butyl rubber septum) and incubated at 21±1 °C for 140 d. Soil water contents were regularly monitored by weighing the jars, and the required amounts of de-ionized water were added whenever necessary.

Measurement of N_2O emissions

Gas samples were taken from the mason jars on days 1, 2, 4, 5, 7, 10, 12, 16, 20, 24, 35, 48, 68, 84, 115, and 140 after treatment additions. On the measurement days, headspace air in the jar was mixed by withdrawing and injecting twice using a polypropylene syringe, and finally 30 mL gas sample was collected and transferred to 12 mL pre-evacuated glass serum vials for determination of N_2O concentration. Following gas sampling, the mason jars were aerated, replenished with de-ionized water (if needed) to maintain the soil water regimes, and closed again for further incubation until 140 d. The gas samples were analyzed within 24 h using a DGA-42 Master Gas Chromatograph (Dani Instruments, Milan, Italy) fitted with a ^{63}Ni electron capture detector (ECD). The ECD was operated at 300 °C, and He carrier gas was supplied at 10 mL min^{-1} to columns consisting of Hayesep N 80/100 mesh (0.32 cm diameter x 50 cm length) and Porapak D 80/100 mesh (0.32 cm diameter x 200 cm length) in an oven operated at 80 °C. The N_2O concentrations were converted into mass units assuming ideal gas relations and expressed as micrograms N_2O-N produced between sampling dates per kilogram of soil. Cumulative N_2O produced (mg kg^{-1} soil) from individual jars during the experiment was computed from the summation of N_2O emissions during each sampling period from the corresponding jars. The percent N emitted as N_2O-N from the applied urea-N treatments (% emission factor, EF) during the experiment was calculated using the following equation:

$$\% \text{ EF} = (N_2O_{fert} - N_2O_{control})/\text{N-applied} \times 100 \tag{3}$$

where N_2O_{fert} and $N_2O_{control}$ are the cumulative N_2O emissions from fertilized N treatments and control (N_0), respectively (Gagnon et al. 2011). The headspace N_2O concentrations measured between the sampling dates were divided by the elapsed time to obtain daily N_2O fluxes (μg N_2O-N kg^{-1} d^{-1}).

Measurement of soil residual inorganic N

Following the last N_2O sampling, replicate soils (dry equivalent mass of 5 g each) from each jar were extracted with 25 mL of 2 *M* KCl solution (Maynard et al., 2008). The extracts were analyzed for total inorganic N (NH_4^+ + NO_3^-) using an automated Timberline TL2800 Ammonia Analyzer (Timberline Instruments, CO, USA). Gravimetric soil water content was used to express soil residual inorganic N contents on a dry mass basis.

Data analysis

The effects of soil WHC and N-fertilizers on daily N_2O flux, cumulative N_2O emissions, % EF, and soil residual inorganic N were analyzed by ANOVA and the Fisher’s least significant difference using the ANOVA procedure of SAS (SAS Institute, version 9.3, 2002-2010). All statistical comparisons were made at the 95% significance level.

Results

The effects of soil WHC levels, N-treatments, and WHC x N-treatment interaction were all significant ($P<0.05$) for N_2O emission rates, cumulative N_2O emissions, percent EFs, and soil residual inorganic N contents.

Effect of soil moisture content

Daily N_2O emissions from N-fertilizer treatments at different soil WHC levels are presented in Figure 17. Soil N_2O fluxes from different urea-N treatments increased with increasing soil WHC levels. Soil N_2O emissions from N_0 at all WHC levels were low (<0.3 µg kg^{-1} d^{-1}) with the exception of initial peaks observed at 60% and 80% WHC levels on 1 d of incubation. At soil WHC ≤ 60%, emissions reached maximum on 5 d with N_{150} (43 and 354 µg kg^{-1} d^{-1} at 30% and 60% WHC, respectively) and N_{250} (58 and 564 µg kg^{-1} d^{-1} at 30% and 60% WHC, respectively). In contrast, the peak N_2O emissions lagged at 80% WHC and were observed on 7 d for N_{150} (527 µg kg^{-1} d^{-1}), and on 10 d for N_{250} (1022 µg kg^{-1} d^{-1}). After peak emissions, at WHC ≤ 60%, N_2O fluxes decreased gradually and approached to that of N_0 after 16 to 20 d of incubation; whereas at 80% WHC, emissions continued - although with smaller rates - until 68 d with N_{150} and 84 d with N_{250}.

Cumulative N_2O emissions from the N-treatments at different WHC levels measured over 140 d of incubation are presented in Table 20. Soil WHC level had significant effect on N_2O emissions ($P<0.05$). Across the N-treatments, cumulative N_2O emissions followed the decreasing order of 80% WHC > 60 % WHC > 30% WHC, with an exception with N_0 (Table 20). With N_0, cumulative N_2O emissions at 60% WHC and 80% WHC were similar ($P<0.05$), but both were higher than at 30% WHC. Except with N_0, cumulative N_2O emissions from urea-N treatments were significantly ($P<0.05$) greater at 80% WHC than at 30% and 60% WHC levels. At 80% WHC, cumulative emissions varied from 4.1 to 15.9 mg kg^{-1}. When comparing the same N-treatments, emissions at 80% WHC were 4 to 8.5 times higher than at 60% WHC, while were of 1.2 to 2.0 orders in magnitude than at 30% WHC. On the other hand, cumulative N_2O emissions from N-treatments at 60% WHC were generally larger (7 to 15 times) than at 30% WHC; however the differences were only significant with N_0 and N_{150}.

The percentages of applied N emitted as N_2O increased with increasing soil WHC levels (Table 21). The EFs at 30% WHC were the least and varied from 0.03 to 0.14%. Increasing soil moisture level to 60% had only slight increases in EFs (ranging from 0.35 to 1.23%) when comparing same N-treatments. In contrast, the EFs increased dramatically at 80% WHC as compared to both at 30% and 60% WHC levels, and the differences were significant ($P<0.05$). The EFs at 80% WHC varied from 1.7 to 4.0%.

Soil residual inorganic N contents in the N-treatments were in the range of 64 to 394 mg kg^{-1} at 30% WHC, 111 to 390 mg kg^{-1} at 60% WHC, and 3 to 180 mg kg^{-1} at 80% WHC (Table 22). The inorganic-N contents were significantly ($P<0.05$) lower with the soils adjusted at 80% WHC than at 60% or 30% WHC across all N-fertilizer levels. There were no significant differences in inorganic N contents at 30 and 60% WHC across N-treatments, with an exception with N_0. Under N_0, the mean inorganic N content of 111 mg kg^{-1} at 60% WHC was significantly ($P<0.05$) higher than the mean value of 64 mg kg^{-1} at 30% WHC. The N_0 always had the least mean residual inorganic N contents among the N-treatments at all soil WHC levels.

Effect of fertilizer-N and nitrification inhibitor

Additions of Urea-N with and without NP generally increased N_2O emissions as compared to control (Figure 17, Table 20). And, the NP addition to urea-N reduced N_2O fluxes as compared to urea-N applied alone, only for the initial periods of incubation. Both the NP treatments (NP_{150} and NP_{250}) consistently lowered the N_2O emissions to the levels statistically similar ($P>0.05$) to N_0 until 48 d of incubation at 30% WHC, whereas until 35 d at soil WHC $\geq$ 60%. After these certain incubation periods, the NP treatments generally increased N_2O

emissions compared to without NP additions. Nonetheless, the magnitudes in N_2O emissions from NP treatments increased with soil WHC levels. At 30% WHC, emissions from both the NP treatments were below 1.1 $\mu g\ kg^{-1}\ d^{-1}$; whereas at 60% WHC, emissions reached maximum of 19 and 44 $\mu g\ kg^{-1}\ d^{-1}$ with NP_{150} and NP_{250}, respectively. In contrast, at 80% WHC, the maxima in N_2O fluxes observed for NP_{150} and NP_{250} were 140 $\mu g\ kg^{-1}\ d^{-1}$and 220 $\mu g\ kg^{-1}\ d^{-1}$, respectively.

On average, cumulative emissions were 1.4 to 3.8 times greater in magnitude at N-rates of 250 kg ha^{-1} than at 150 kg ha^{-1}, irrespective of NP additions. However, the differences in cumulative N_2O emissions between the N-rates (150 vs. 250 kg ha^{-1}) were only significant ($P<0.05$) at 30 and 80% WHC levels, and without NP additions. At 30% and 80% WHC levels, N_{250} had higher cumulative N_2O emissions than N_{150} by 50 and 74%, respectively. Among the N-fertilizer treatments, N_{250} produced the highest cumulative N_2O at all WHC levels with mean emissions of 0.6, 3.9, and 15.9 mg kg^{-1}at 30, 60, and 80% WHC, respectively.

Addition of NP significantly ($P<0.05$) reduced cumulative N_2O emissions compared to without NP when comparing same N-fertilizer rates at ≤ 60% WHC levels, but not at 80% WHC (Table 20). And, the reductions were much pronounced at 30% WHC than at 60% WHC. On average, at 30% WHC, urea-N co-applied with NP had 4.3 fold lower cumulative N_2O emissions than without NP; whereas at 60% WHC, the NP treatments reduced cumulative N_2O emissions by only 2.6 fold than without NP. In sharp contrast, at 80% WHC, addition of NP to urea significantly ($P<0.05$) increased cumulative N_2O emissions by 2 fold than urea-N applied without NP at the rate of 150 kg ha^{-1}, while there was no response of NP additions to cumulative N_2O emissions at the urea-N rate of 250 kg ha^{-1}.

When compared between low (150 kg N ha^{-1}) and high (250 kg ha^{-1}) N-rates, differences in the percent EFs were only significant ($P<0.05$) at 80% WHC and without addition of NP. At

80% WHC, the EF with N_{250} (4.00%) was higher than with N_{150} (1.70%). Nonetheless, when comparing the same N-rates at soil WHC ≤ 60%, application of NP showed significant ($P<0.05$) reductions in EFs than without NP. At 30% WHC, the EF decreased from 0.12% with N_{150} to 0.03% with NP_{150}, and decreased from 0.14% with N_{250} to 0.03% with NP_{250}. Similarly, at 60% WHC, addition of NP with urea reduced EFs from 1.23% to 0.42% at N-rate of 150 kg ha^{-1}, and from 0.96% to 0.35% at N-rate of 250 kg ha^{-1}. On the other hand, at 80% WHC, additions of NP had no response on percent EF when comparing same N-rates. Across the urea-N rates without NP, the EFs averaged 0.13, 1.09, and 2.85% at the soil WHC levels of 30, 60, and 80%, respectively; whereas across the urea-N rates with NP, the EFs averaged 0.03, 0.39, and 3.47%, at the soil WHC levels of 30, 60, and 80%, respectively.

Generally, the residual inorganic-N contents increased with increasing N-rates but the differences were only significant ($P<0.05$) at soil WHC of ≥60% (Table 22). Application of NP had slight increases in the residual inorganic N contents than without NP, when comparing the same N-rates across all the soil WHC levels.

Discussion

Our study showed that the daily N_2O fluxes as well as cumulative N_2O emissions from urea-N treatments generally followed an order: 30% WHC < 60% WHC < 80% WHC. These results support earlier findings that soil N_2O emissions increase with increasing soil moisture levels due to increased restriction in O_2 availability and diffusion (Khalil et al., 2002; Bateman and Baggs, 2005; Chen et al., 2010; Menendez et al., 2012). In their isotopic N-labelling study, Senbayram et al. (2009) showed that almost all of N_2O emissions were derived from denitrification of ammonium sulfate (360 kg N ha^{-1}) in soils adjusted at 85% WHC (76% WFPS), and emissions at 85% WHC were significantly higher than at 65% WHC. According to

Bateman and Baggs (2005), soil microsites become predominantly anaerobic at ≥ 60% WFPS and promotes greater N_2O emissions through denitrification process because of limited O_2 availability. In our current study, any attempts were not made to partition the source of N_2O emissions; however, it can be assumed that considerably higher N_2O emissions at 80% WHC than at ≤60% WHC are primarily produced during denitrification. The measured residual inorganic N at the end of the incubation was usually higher in soils at ≤ 60% WHC than soils at 80% WHC, across all N-treatments. And, considerably higher N loss through denitrification at 80% WHC than at ≤ 60% WHC could be related with such differences in residual inorganic N. The differences of N_2O emissions at the same urea-N application rates but with different soil WHC levels, thus demonstrate the importance of soil moisture in determining N_2O emissions from soils when mineral-N substrate is not limited. Nonetheless, increasing the urea-N application rate however intensified N_2O emissions, owing to increased availability of N-substrates (Khalil et al., 2002). Soil moisture also regulated the time and durations of N_2O emissions. At 80% WHC, the applied urea-N rates (without NP additions) had an extended period (68 to 84 d) of N_2O emissions as compared to only 16 to 20 d at WHC levels ≤ 60%. These results highlights that soil moisture may be a key factor for large N_2O emissions from fertilized arable soils.

The cumulative emissions of N_2O from soils generally increased with N-rate, with an increment in total emissions by 2.5 fold (without NP) and 1.5 fold (with NP) at N-rate of 250 kg ha^{-1} than the N-rate of 150 kg ha^{-1} when averaged across all the soil WHC levels. Our results are in agreement with previous studies that have also reported greater emissions of N_2O at higher than at lower N-rates due to greater availability of mineral N substrates with higher N-rates (Chantigny et al., 1998; Hoben et al., 2011; Gao et al., 2013). In the present study, at all WHC levels, generally higher soil residual inorganic N contents were found with the high N-rates as compared with the low N-rates, indicating greater substrate availability during the incubation for N_2O emissions. Our findings suggest that reduction in the use of urea-N rates seems a promising way of reducing N_2O emissions from silty clay soil, and thus the results can be useful in devising urea-N fertilizer management decisions in crop production.

Co-application of nitrification inhibitors with urea-N fertilizers is one of the management options to lower N_2O emissions (Omonode and Vyn, 2013). Our results demonstrated that NP addition to urea was able to suppress N_2O emissions as long as 35 d at WHC levels ≥ 60% and 48 d at 30% WHC. The results are in agreement with that reported by Chen et al. (2010), which demonstrated that application of NP inhibited nitrification effectively until 42 d under laboratory conditions and thereby reduced N_2O emission rates for this period of soil incubation. However, the differences in durations in the suppression of N_2O emissions by NP at different WHC levels in our study suggests the reduction in performance of NP with increasing soil water content (Wolt, 2000). Nonetheless, daily N_2O fluxes with NP treatments increased significantly during the later periods of the incubation with much larger N_2O rates observed for 80% WHC than 30% or 60% WHC. Moreover, at 80% WHC, the flux rates continued until 140 d (55 and 88 $\mu g\ kg^{-1}\ d^{-1}$ with NP_{150} and NP_{250}, respectively). The current study was conducted in the absence of any growing plants. The continued flux could be related with the availability of mineral N substrates under the absence of crop N uptake.

Application of NP had 77% and 62% reductions in cumulative N_2O emissions than without NP application from the soils at 30% and 60% WHC, respectively, consistent with the values reported by Chen et al. (2010) for clay loam soils. However, at 80% WHC, no such reductions were observed with the application of NP suggesting poor performance of the inhibitor at higher WHC levels (Wolt, 2000; Menendez et al., 2012). Further, the lack of reductions in cumulative N_2O emissions with NP could be due to the longer duration (140 d) of the incubation period. The inhibitory effect of NP has been well established, however, studies have documented that NP are capable of reducing N_2O emissions as long as 6 wk under laboratory conditions (Chen et al., 2010). In the present study, at 80% WHC, both the NP treatments reduced N_2O emissions until 5 wk after the onset of the experiment, with significantly larger N_2O emissions observed then onwards until the termination of the study. Similar emissions were also observed for soils at 60% WHC; however, the emission rates were much smaller as compared to the soils at 80% WHC. This stresses the fact that long-term measurements of N_2O fluxes are essential when comparing the effects of different fertilizers.

Across the N-rates and WHC levels, the percentage of applied N emitted as N_2O was 1.36% without NP application and was 1.94% with NP application, which are comparatively higher than the EF values of 0.68% obtained for sandy loam soils under laboratory condition by Senbayram et al. (2009) and of 0.73% obtained for clay loam soils under arable condition by Gao et al. (2013). The differences observed in the percent EFs among these studies could partly be explained due to differences in soil texture and/or duration of the incubation. Nonetheless, the variations in percent EFs obtained in the current research for different N-sources (with and without NP) emphasizes the necessity of reconsidering the default N_2O emission factor of 1% of applied fertilizer-N, as suggested by the IPCC (2006).

Conclusions

A considerable amount of applied urea-N is subjected to denitrification loss above 60% WHC, with an increased potential of N_2O-N loss with increasing N-rates in silty clay soils. Denitrification loss of applied urea-N is both agronomic and environmental concerns. Efficient

N-fertilizer managements for reducing N_2O-N emissions include optimization of urea-N rates, usage of nitrification inhibitors (such as nitrapyrin), and avoiding N-application at the times of excessive rainfall, irrigation, or spring thaw events. Therefore, the findings from our current study have important implications for the development of N-management strategies for reducing N_2O emissions in the RRV regions and elsewhere, predominant with high clay containing poorly drained soils. Moreover, the results can be beneficial in devising estimates of N_2O production as a consequence of urea-N fertilizer managements within the RRV of the North.

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Table 20. Cumulative N_2O emissions from N fertilizers over 140 days of incubation at three soil moisture regimes.

N fertilizers[†]	Cumulative N_2O Emissions		
	30% WHC	60% WHC	80% WHC
	------------------------mg N_2O-N kg^{-1} soil------------------------		
N_0	0.0 ± 0.0 dB[‡]	0.1 ± 0.0 bA	0.1 ± 0.0 cAB
N_{150}	0.3 ± 0.0 bB	3.1 ± 0.5 aA	4.1 ± 0.4 cA
N_{250}	0.6 ± 0.0 aB	3.9 ± 0.3 aB	15.9 ± 2.2 aA
NP_{150}	0.1 ± 0.0 cdB	1.1 ± 0.3 bB	9.0 ± 3.1 bA
NP_{250}	0.1 ± 0.0 cB	1.5 ± 0.8 bB	12.8 ± 0.9 abA

[†] N fertilizers are N_0 (control, 0 N), N_{150} (150 kg N ha^{-1}), N_{250} (250 kg N ha^{-1}), NP_{150} (150 kg N ha^{-1} + Nitrapyrin), NP_{250} (250 kg N ha^{-1} + Nitrapyrin).

[‡] Values are means ± standard errors (n=4); Different lowercase letters within a column and different uppercase letters within a row indicate significant differences at 0.05 significance level.

Table 21. Percent emission factors (% EFs) for the N fertilizers at three moisture regimes.

N fertilizers[†]	Emission Factor		
	30% WHC	60% WHC	80% WHC
	---------------------------------%-----------------------------------		
N_{150}	0.12 ± 0.01 aB[‡]	1.23 ± 0.23 aA	1.70 ± 0.18 bA
N_{250}	0.14 ± 0.02 aB	0.96 ± 0.08 aB	4.00 ± 0.57 aA
NP_{150}	0.03 ± 0.01 bB	0.42 ± 0.15 bB	3.08 ± 0.95 abA
NP_{250}	0.03 ± 0.01 bB	0.35 ± 0.20 bB	3.86 ± 0.85 aA

[†] N fertilizers are N_0 (control, 0 N), N_{150} (150 kg N ha^{-1}), N_{250} (250 kg N ha^{-1}), NP_{150} (150 kg N ha^{-1} + Nitrapyrin), NP_{250} (250 kg N ha^{-1} + Nitrapyrin).

[‡] Values are means ± standard errors (n=4); Different lowercase letters within a column and different uppercase letters within a row indicate significant differences at 0.05 significance level.

Table 22. Soil residual inorganic N content measured at 140 d of incubation as influenced by N fertilizers at three moisture regimes.

N fertilizers[†]	Soil Residual Inorganic N		
	30% WHC	60% WHC	80% WHC
	----------------------------mg kg^{-1} soil------------------------		
N_0	64 ± 2 cB[‡]	111 ± 19 cA	3 ± 0 cC
N_{150}	268 ± 10 bA	266 ± 12 bA	56 ± 4 bcB
N_{250}	361 ± 7 abA	363 ± 18 aA	180 ± 4 aB
NP_{150}	356 ± 83 abA	278 ± 7 bAB	98 ± 42 bB
NP_{250}	394 ± 5 aA	390 ± 10 aA	167 ± 13 aB

[†] N fertilizers are N_0 (control, 0 N), N_{150} (150 kg N ha^{-1}), N_{250} (250 kg N ha^{-1}), NP_{150} (150 kg N ha^{-1} + Nitrapyrin), NP_{250} (250 kg N ha^{-1} + Nitrapyrin).

[‡] Values are means ± standard errors (n=4); Different lowercase letters within a column and different uppercase letters within a row indicate significant differences at 0.05 significance level.

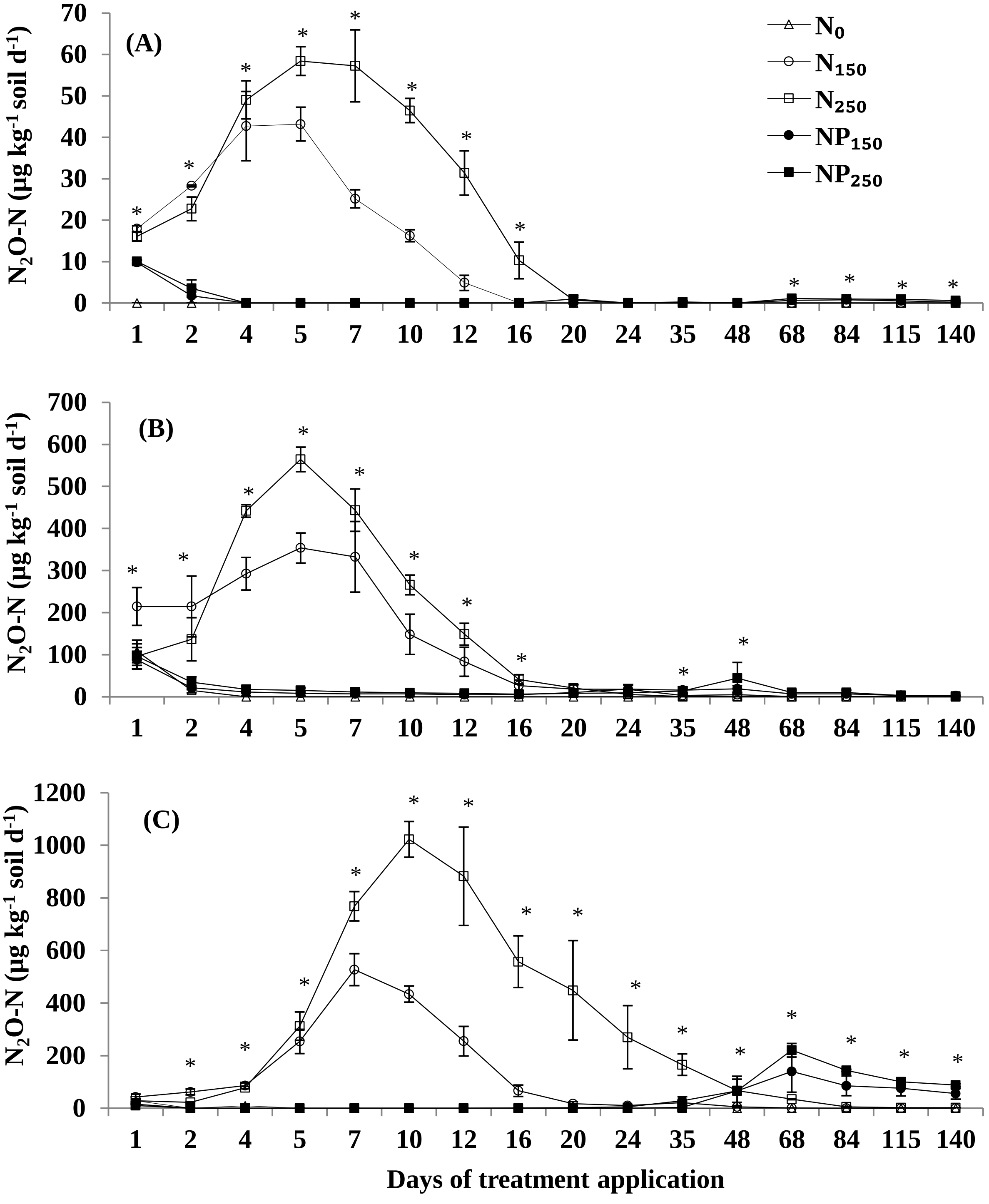

Figure 17. Daily soil N_2O fluxes after N fertilizer [N_0 (Control, 0 N), N_{150} (150 kg N ha^{-1}), N_{250} (250 kg N ha^{-1}), NP_{150} (150 kg N ha^{-1} + nitrapyrin), and NP_{250} (250 kg N ha^{-1} + nitrapyrin)] application at (A) 30% WHC, (B) 60% WHC, and (C) 80% WHC over 140 days of incubation. Error bars are standard errors (n=4). *Significant at α=0.05. Please note the large differences in y-axis scaling.

UREA N-STABILIZERS INFLUENCE AMMONIA VOLATILIZATION AND NITROUS OXIDE EMISSION FROM TWO CONTRASTING SOILS[2]

Abstract

Potentials of nitrogen (N) management additives to control N loss vary with soil texture. A laboratory experiment was conducted with an aim to quantify and compare ammonia (NH_3) volatilization and nitrous oxide (N_2O) losses with (i) control, (ii) urea, urea treated with (iii) urease inhibitor, NBPT [N-(n-butyl) thiophosphoric triamide], (iv) nitrification inhibitor, nitrapyrin (NP) [2-chloro-6-trichloro methyl pyridine], (v) urea stabilized with NBPT and nitrification inhibitor dicyandiamide (SuperU), and (vi) slow release N-fertilizer polymer coated urea (PCU) amendments from Ulen sandy loam and Fargo silty clay soils. Cumulative NH_3-N losses from the sandy loam soil ranged from 0.7 to 4.3% of applied-N, and were higher than those from the silty clay soil (0.1 to 0.4% of applied-N). In the sandy loam soil, compared to urea, the NBPT and the PCU treatments reduced NH_3-N volatilization by 32.3% and 84.2%, respectively, whereas the NP and the SuperU increased NH_3-N by 98.7% and 20.3%. However, in the silty clay soil, only the NBPT treatment exhibited significant reduction in NH_3-N losses of 71.4%, relative to urea. Emissions of N_2O-N did not differ between the soils across all the N-fertilizers, and ranged between 3.7 to 7.4% of applied-N. Nonetheless, in the sandy loam soil, NP, SuperU, and PCU treatments significantly reduced N_2O-N emissions by 23.5%, 43.8%, and 51.1%, respectively compared to urea. Depending upon soil conditions, choice of suitable N-source can be the best management strategy for reducing NH_3 and/or N_2O emissions.

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[2] The material in this chapter was co-authored by Rakesh Awale and Amitava Chatterjee. Rakesh Awale had primary responsibility for the collection of soil samples and the laboratory analyses of samples. Rakesh Awale was the primary developer of the conclusions that are advanced here. Rakesh Awale also drafted and revised all versions of this chapter. Amitava Chatterjee served as proofreader and checked the math in the statistical analysis conducted by Rakesh Awale.

Introduction

Urea [$CO(NH_2)_2$] is the most common synthetic nitrogenous (N) fertilizer because of its low cost relative to other N sources (Bierman et al., 2012). However, a major disadvantage associated with the use of urea is gaseous losses of N via ammonia (NH_3) volatilization and nitrous oxide (N_2O) emissions (Zaman and Blennerhassett, 2010). Almost 81% of anthropogenic NH_3 emissions (Aneja et al., 2008) and 70% of total N_2O emissions (Kroeze et al., 1999) result from agricultural activities.

Research has shown that as much as 64% of the urea applied to the soil surface can be lost through NH_3 volatilization (Rochette et al., 2009b), especially from calcareous soils with low cation exchange capacity (CEC) (Mkhabela et al., 2006; Francisco et al., 2011). Annual losses of N_2O generally account for 1-1.25% of the amount of N-fertilizer applied (IPCC, 2006), however higher amounts have been reported (Crutzen et al., 2008; Glenn et al., 2012). Both, NH_3 volatilization and N_2O emission losses have economic implications (Rochette et al., 2009b; Hyatt et al., 2010) and can deteriorate environmental quality (Crutzen, 1981; Soares et al., 2012).

Ammonia volatilization and N_2O emissions from surface applied N-fertilizers can vary with soil textures. In general, the size of denitrifier community and total gaseous N production are higher at neutral or slightly alkaline soils than acidic soils, attributed to the smaller quantity of organic matter and mineral-N availability to the denitrifiers at acidic condition (Simek and Cooper, 2002). Soils with high CEC adsorb greater amount of NH_4^+ to the exchange sites and thus reduce NH_4^+ availability for productions of NH_3 and N_2O (Jarecki et al., 2008; Francisco et al., 2011). Soil clay and organic matter contents can also influence emissions of NH_3 and N_2O because of their relative contribution to the CEC (Watson et al., 1994). Soil texture effects on gaseous emissions of NH_3 and N_2O is explicit, however, the magnitudes of N losses are still uncertain due to the interplay of various factors that regulate these losses (Francisco et al., 2011; Pelster et al., 2012).

Additions of N management additives have been proposed in order to reduce N losses associated with NH_3 volatilization and N_2O emissions from agroecosystems (Zaman and Blennerhassett, 2010; Jantalia et al., 2012; Halvorson et al., 2014). The N-(n-butyl) thiophosphoric tiramide (NBPT) has been reported as one of the most efficient urease inhibitors in reducing NH_3 volatilizations across a variety of soils (Clay et al., 1990; Rawluk et al., 2001; Soares et al., 2012). However, the duration of the inhibition of urease hydrolysis caused by NBPT, and its potential in reducing NH_3 emissions may differ depending upon the soil texture and environmental conditions (Rawluk et al., 2001; Gioacchini et al., 2002; Engel et al., 2011).

Nitrification inhibitors, such as 2-chloro-(6-trichloromethyl) pyridine (Nitrapyrin, NP), and dicyandiamide (DCD), suppress the ammonia monooxygenase enzyme responsible for the oxidation of NH_4^+ to NO_2^- (Chen et al., 2010). However, the accumulation of NH_4^+ in soils for a longer time may enhance NH_3 volatilization (Bundy and Bremner, 1974; Rodgers, 1983). Therefore, in order to minimize the effect of nitrification inhibitors on the tradeoff between increased NH_3 volatilization and reduced N_2O emissions, recently, there has been a growing interest in the treatment of both urease and nitrification inhibitors to N fertilizers (Zaman et al., 2008; Parkin and Hatfield, 2013; Halvorson et al., 2014). Nevertheless, the influences of the combined application of both of these inhibitors on NH_3 volatilization and/or N_2O emissions are not consistent (Gioacchini et al., 2002; Dell et al., 2014). Conversely, Zaman et al. (2008) pointed out the DCD influenced the efficiency of NBPT, and thus resulted 29% increment in NH_3 losses with urea + NBPT + DCD treatment over urea alone. Moreover, DCD maintains NH_4^+ for longer time in soils, and can promote extra release of soil organic N due to priming effect, and thereby increase NH_3 volatilization losses (Gioacchini et al., 2002). The inconsistent results related with the combined treatment of both urease and nitrification inhibitors are not limited to NH_3 losses. A number of field studies have reported that application of NBPT plus DCD to conventional N fertilizers had no response in N_2O emissions, possibly due to inherent soil organic N mineralization contributing significantly to N_2O productions (Parkin and Hatfield, 2013), or excessive dry soil condition (Dell et al., 2014).

Polymer coated urea (PCU) fertilizers release mineral N gradually in soils via diffusion through their coating (Trenkel, 1997; Hyatt et al., 2010). Such a slow releasing nature of these fertilizers has shown to reduce both NH_3 volatilization (Rochette et al., 2009a) as well as N_2O emission losses (Akiyama et al., 2010; Halvorson et al., 2014). Studies have also shown that the PCU fertilizers can accumulate mineral N in soils during the later periods, and consequently increase gaseous emissions of NH_3 (Jantalia et al., 2012) and N_2O (Soares et al., 2015; Parkin and Hatfield, 2013).

Urea N-additives have potential to delay NH_4^+ and NO_3^- transformations in soils relative to urea. However, the effectiveness of these N fertilizer sources has been shown to differ with soil physical and chemical properties, which has perplexed researchers recently. A better insight of the influences of these N sources on NH_3 volatilization and N_2O emissions from soils is deemed necessary in order to minimize N escaping to the environment. Also, effective N losses reduction technology is required, not because the magnitude of gaseous N losses is certain, but precisely because it is not, as evident from the varying proportions of N losses reported in the literature (IPCC, 2006; Zaman et al., 2008; Glenn et al., 2012; Soares et al., 2012). The objective of this study therefore was to examine how urea N-additives and stabilized urea fertilizers affect NH_3 volatilization and N_2O emission losses from two contrasting soils.

Materials and Methods

Soils used for the study

Two different soils were collected from the 0-15 cm surface layer of unfertilized borders of agricultural fields in Ada, northwest Minnesota (47.33°N, 96.39°W) and Mapleton, eastern North Dakota (46.82°N, 97.21°W). The soils are classified as Ulen sandy loam (Sandy, mixed, frigid Aeric Calciaquolls), and Fargo silty clay (Fine, smectitic, frigid Typic Epiaquerts) (Soil Survey Staff, 2014). The soils were air dried, ground to pass a 2 mm sieve, and analyzed to determine their physical and chemical properties (Table 23). Soil pH and electric conductivity (EC) of 1:2.5 soil: water extract were determined electrometrically (Thomas, 1986); organic matter by loss on ignition method (Combs and Nathan, 1998); soil texture by hydrometer method (Elliott et al., 1999); CEC by sodium acetate method and available potassium (K) by ammonium acetate method (Chapman, 1965); nitrate (NO_3^-) content was measured according to Maynard et al. (2008); and water holding capacity (WHC) of the sieved soil was determined following Harding and Ross (1964).

Experimental approach

Ammonia volatilization and N_2O emission losses were quantified from four different stabilized urea fertilizer sources as well as untreated urea (460 g N kg^{-1}), surface applied to two contrasting soils under controlled laboratory conditions. The N-stabilizer products were the urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT) (trade name Agrotain Ultra, 26.7% by weight active ingredient solution, Koch Agronomic Services), the nitrification inhibitor nitrapyrin (NP) [2-chloro-(6-trichloromethyl) pyridine] (trade name Instinct, 17.6% by weight active ingredient solution, Dow AgroSciences), urea stabilized with NBPT and nitrification inhibitor dicyandiamide (DCD) (Trade name SuperU, 460 g N kg^{-1}, Koch Agronomic Services), and the controlled release polymer coated urea-N fertilizer (PCU) (Environmental Smart Nitrogen, 440 g N kg^{-1}, Agrium Inc.). The NBPT was mixed with urea based on urea weight (835 mg NBPT kg^{-1} urea) and the NP was applied to soil based on an area basis (451 g NP ha^{-1} soil).

Experiments were carried out in 1-L mason jars under controlled laboratory conditions following the procedure as described by Singurindy et al. (2006), with a slight modification. One hundred grams (air-dry equivalent) of each soil was weighed into the mason jars, and amended with 36 mg N (equivalent to 670 kg N ha^{-1} on a soil weight basis, assuming a bulk density of 1.23 g cm^{-3}) of the N-fertilizer treatments (except control, 0 N applied) onto the soil surface. A higher rate of N than usual field N application rates was used in our study for the precision in weighing the N fertilizers, which could be applied to the smaller quantity (i.e. 100 g each) of soil. Therefore, the results obtained in this study may not represent an actual field situation, and one should be careful while relating our results to the actual field situations. The N fertilizer treatments include: (i) control (ii) urea (without N-additives), (iii) urea with NBPT, (iv) urea with NP, (v) urea stabilized with NBPT and DCD (SuperU), and (vi) PCU, with four replicates, arranged randomly in the two soils (Ulen sandy loam and Fargo silty clay). This resulted in a total of 48 experimental units (2 soil textures x 6 N treatments x 4 replications). Following the addition of N treatments, the soils were moistened to 60% WHC by dripping approximately 35 mL and 59 mL of de-ionized water (equivalent to 7.7 and 12.9 mm rainfall, respectively) to Ulen sandy loam and Fargo silty clay soils, respectively, through the jar walls using burette. The target soil WHC level of 60% was chosen for the study in order to account N_2O productions via different soil processes at this water content level (Bateman and Baggs, 2005). The mason jars were closed with airtight lids, fitted with gas sampling ports (butyl rubber septum), and were incubated at constant temperature of 20°C for 126 d in the laboratory. Inside the mason jar, a 30 mL plastic cup, containing 20 mL of 0.5 *M* H_3PO_4 (acid trap to capture NH_3), was also hung above the soil surface from the jar lid (Picture 1). During the incubation, the soil moisture content was maintained unchanged by monitoring the weight changes of mason jars and adding de-ionized water, whenever necessary.

Measurement of nitrous oxide, carbon dioxide, and ammonia emissions

Air samples for the determination of N_2O and CO_2 were collected from the mason jars on days 2, 4, 6, 8, 11, 17, 21, 28, 42, 63, 89, and 126 after treatment additions. On every sampling date, headspace air in the jar was mixed by withdrawing and injecting twice using a polypropylene syringe, and finally 30 mL air sample was collected and transferred to 12 mL pre-evacuated glass serum vials. Within 24 h of their collection, the samples were analyzed for N_2O and CO_2 concentrations using a DGA-42 Dani Master gas chromatograph fitted with ^{63}Ni-electron capture detector (ECD) and flame ionization detector (FID) with a methanizer, respectively. The ECD and the FID were both operated at 300°C, and He carrier gas was supplied at 10 mL min^{-1} to columns consisting of Hayesep N 80/100 mesh (0.32 cm diameter x 50 cm length) and Porapak D 80/100 mesh (0.32 cm diameter x 200 cm length) in an oven operated at 80°C. The N_2O and CO_2 concentrations were converted into mass units assuming ideal gas relations and expressed as micrograms N_2O-N and milligrams CO_2-C produced between sampling dates per kilogram of soil, respectively. The headspace N_2O and CO_2 concentrations measured between the sampling dates were divided by the elapsed time to obtain daily N_2O (μg N_2O-N kg^{-1} moist soil d^{-1}) and CO_2 fluxes (mg CO_2-C kg^{-1} moist soil d^{-1}). Cumulative N_2O-N produced (mg kg^{-1} moist soil) from individual jars during the experiment was computed from the summation of N_2O emissions during each sampling period from the corresponding jars. Nitrous oxide emissions calculated as N_2O-N, hereafter referred to as N_2O for simplicity.

Ammonia volatilization losses were measured the same day as the determination of N_2O emissions, until 89 d after treatments application, with an assumption that volatilization losses from these urea-based N-fertilizers can extend as long as 11 wk after N-application (Gioacchini et al., 2002; Cantarella et al., 2008; Jantalia et al., 2012). Following air sampling, jar lids were carefully opened, and acid traps were collected and replaced with fresh traps. The jar lids were closed again for further incubation, shortly (2-min) after aeration. The collected traps were extracted with 50 mL of 2 *M* KCl solution by shaking the mixture in a reciprocal shaker for 10 min at 180 oscillations per min. The extracts were then analyzed for NH_4^+ concentrations using an Automated Timberline TL2800 Ammonia Analyzer (Timberline Instruments, CO, USA). Daily fluxes of NH_3 (µg NH_3-N kg^{-1} moist soil d^{-1}) were calculated by dividing the NH_3-N emitted between the sampling dates by the elapsed time, and cumulative NH_3-N losses (mg NH_3-N kg^{-1} moist soil) during entire incubation was computed from the summation of NH_3 emissions during all sampling periods. Ammonia emissions calculated as NH_3-N, hereafter referred to as NH_3 for simplicity.

The percent N emitted as N_2O or NH_3 from the applied N-treatments (% emission factor, EF) during the experiment was calculated using the following equation:

$$\%\ \text{EF}\ (N_2O \text{ or } NH_3) = (C_f - C_c)/\text{N-applied X } 100 \tag{4}$$

where, C_f and C_c are the cumulative N_2O or NH_3 emissions from N-amended and control treatments, respectively (Jumadi et al., 2008).

Soil residual inorganic N

Residual inorganic-N contents in the soils were determined at the end of the incubation, following the last N_2O sampling. Replicate soils of 5 g (dry equivalent mass) each from individual jars were extracted with 25 mL of 2 *M* KCl solution (Maynard et al., 2008). The extracts were analyzed for total inorganic N (NH_4^+ + NO_3^-) using the Ammonia Analyzer. Gravimetric soil water content was used to express soil residual inorganic N contents on a dry mass basis.

Statistical analysis

The data for cumulative emissions of NH_3 and N_2O, %EF, soil residual inorganic N, and daily fluxes of CO_2 were subjected to analysis of variance according to a split-plot arrangement with a completely randomized design (CRD) using PROC GLM of SAS (version 9.3, SAS Institute, 2002-2010) assuming fixed soil texture and N-fertilizer effects. The soil textures were assigned as the whole plot factor, and the N-fertilizers - with 4 replications, arranged randomly over the whole plots - as the sub-plot factors. The daily NH_3 and N_2O data were tested separately for each sampling date by soil texture using the GLM procedure of SAS assuming the fixed N-fertilizer effects in a CRD. Means were compared using Fisher's least significant differences when there was a significant treatment effect at the 95% significance level.

Results

Ammonia volatilization

Daily NH_3 fluxes after treatment application

Daily NH_3 fluxes observed in the sandy loam soil were much larger as compared with those in the silty clay soil (Figure 18). In both soils, the highest NH_3 fluxes were observed with urea, and urea + NP treatments, occurred on 4 d after the application of the fertilizers. On this day, in the sandy loam soil, NH_3 fluxes from urea, and urea + NP treatments were 2665 µg N kg^{-1} d^{-1}, and 2709 µg N kg^{-1} d^{-1}, respectively, whereas only 160 µg N kg^{-1} d^{-1} and 185 µg N kg^{-1} d^{-1} evolved in the silty clay soil, respectively from the urea and urea + NP treatments. Daily NH_3 fluxes did not differ between urea and urea + NP treatments for the initial 4 d in both soils, however both these treatments had significantly higher emissions than other N-treatments for this period. Following peak emissions, fluxes from the urea treatments decreased sharply, and came back to the levels similar to the emissions from the control treatments by 21d in the sandy loam soil, and by 17 d in the silty clay soil. On the other hand, in the sandy loam soil, NH_3 emissions from the urea + NP treatment - although decreased gradually after peak emissions - were significantly higher than that of the other treatments until 28 d, and approach to that of control by 42 d. In the silty clay soil, the fluxes from urea + NP were higher than from other treatments (except SuperU) until 17 d, and reduced to the levels similar to the control by 28 d. The fluxes from urea + NP and SuperU treatments were similar for the period from 11- to 17-d in the silty clay soil.

In both soils, the addition of NBPT to urea reduced the peaks of the NH_3 emissions, delaying them until 8 d. Nevertheless on 8 d, in the sandy loam soil, NH_3 flux from urea + NBPT (980 µg kg^{-1} d^{-1}) was still significantly lower as compared to urea (1175 µg kg^{-1} d^{-1}), whereas the fluxes (28 µg kg^{-1} d^{-1} for urea + NBPT and 43 µg kg^{-1} d^{-1} for urea) were similar between them in the silty clay soil. In the former soil, significant increases in NH_3 fluxes were observed for urea + NBPT with respect to urea after 11 d until 17 d.

The SuperU treatment also delayed the peak emissions (1495 µg kg^{-1} d^{-1} in sandy loam and 64 µg kg^{-1} d^{-1} in silty clay) with respect to urea in both soils until 8 d. After 8 d, daily fluxes from the SuperU treatment significantly increased over urea until 42 d in the sandy loam soil, and until 17 d in the silty clay soil. When compared with urea + NBPT, in the sandy loam soil, the SuperU had constantly higher NH_3 fluxes from the onset of the incubation until 42 d, after which the emissions from these treatments were similar. In the silty clay soil, daily NH_3 fluxes from urea + NBPT and SuperU were similar for the initial 6 d, followed by significantly higher emissions in the SuperU treatment until 21 d. However, daily fluxes from SuperU were constantly lower than urea + NP until 28 d in the sandy loam soil, and until 8 d in the silty clay soil.

Daily NH_3 fluxes from the PCU treatment were significantly lower than that of urea until 17 d in the sandy loam soil, whereas only until 4 d in the silty clay soil. In fact, in the sandy loam soil, the PCU had the least daily NH_3 fluxes among all the N-amended treatments for the initial 17 d.

Cumulative NH_3 volatilization

Cumulative amounts of NH_3 volatilized from N-fertilizer treatments were significantly different for the two soils (Table 24 and 25). Emissions from the sandy loam soil were 3 to 18 times greater than from the silty clay soil, except for the control treatment. In both soils, the N-amended treatments had greater NH_3 volatilization losses than the control. Cumulative NH_3 lost for the urea treatment in the sandy loam soil was 4.3% of the N-applied, whereas only 0.2% of the urea-N applied was lost as NH_3 in the silty clay soil. Addition of urease inhibitor NBPT to urea significantly reduced the volatilization losses both from the sandy loam and the silty clay soils by 32.3% and 71.4%, respectively. Volatilization losses from the urea + NBPT treatment represent to only 2.9% and 0.1% of the N-applied in the sandy loam soil and the silty clay soil, respectively. In contrast, application of urea + NP, and SuperU caused significant increases (by 98.7% and 20.3% respectively) in NH_3 losses with respect to the urea treatment, particularly in the sandy loam soil. Nevertheless, in both soils, NH_3 losses with the SuperU treatments were still significantly lower as compared to urea + NP. The amounts of NH_3-N volatilized from PCU represented 0.7% and 0.2% of the applied-N in sandy loam and silty clay soils, respectively. In the sandy loam soil, this corresponds to 84.2% reduction in NH_3 volatilization compared with the urea treatment; however, the emissions were similar between these two treatments (urea and PCU) in the silty clay soil. In the sandy loam soil, the PCU had the least NH_3 volatilization losses among the N-amended treatments.

Nitrous oxide emissions

Daily N_2O fluxes after treatment application

Unlike NH_3 fluxes, daily N_2O emissions following N-application from the two soils followed different patterns (Figure 19). In the sandy loam soil, daily N_2O fluxes in the treatments remained lower during the first 4 d, ranging from 2 to 16 µg N kg^{-1} d^{-1}. Daily N_2O fluxes from urea and PCU increased by 6 d, and both exhibited their peak N_2O emissions on 21 d. In contrast, N_2O fluxes increased by only 11 d in urea + NBPT and SuperU treatments, and by 17 d in the urea + NP treatment. Nevertheless, all of these three treatments had their peak emissions on 21 d, similar to urea and PCU treatments. On 21 d, N_2O fluxes were highest with urea (1947 µg N kg^{-1} d^{-1}) and urea + NBPT (1955 µg N kg^{-1} d^{-1}), intermediate with urea + NP (973 µg N kg^{-1} d^{-1}) and PCU (850 µg N kg^{-1} d^{-1}), and least with SuperU (477 µg N kg^{-1} d^{-1}). Following their peak emissions, daily N_2O fluxes from all the N-amended treatments decreased sharply. The N_2O fluxes from urea, urea + NBPT, and PCU treatments approached to the levels similar to the emissions from the control treatments on 63 d, while the emissions from the treatments containing nitrification inhibitors (urea + NP and SuperU) were constantly higher than the rest of the treatments from 63 d until the end of the incubation.

In the silty clay soil, maximum daily N_2O fluxes were observed on 2 d for all treatments, including control. On this day, the N_2O fluxes, however, did not differ among the treatments, and ranged from 1525 µg N kg^{-1} d^{-1} in the urea + NP treatment to 2020 µg N kg^{-1} d^{-1} in the PCU treatment. Daily N_2O fluxes from all the N-amended treatments declined sharply until 6 d, showed linear increases again by 8 d, exhibited second peak emissions on 21 d, and declined gradually until the end the incubation. The N_2O fluxes from the control also declined sharply until 6 d and remained significantly low (< 33 µg N kg^{-1} d^{-1}) afterwards until the end of the incubation compared with the N-amended treatments. On 21 d, the fluxes from the N-amended treatments were similar among each other and ranged between 477 to 751 µg N kg^{-1} d^{-1}. Significant differences in N_2O fluxes among the N-amended treatments were only observed for the period from 8- to 17-d. For the period from 8- to 11-d, N_2O fluxes from urea and urea + NBPT were statistically similar, but both were higher than those from urea + NP, SuperU, and PCU treatments. The fluxes from the latter three treatments remained similar for this period (from 8- to 11-d). The urea + NBPT had the highest N_2O fluxes on 17 d among the treatments.

Cumulative N_2O emissions

Cumulative emissions of N_2O were similar between the two soil textures across all the N-fertilizers, with an exception for the control treatment, where the silty clay soil control had significantly higher emissions than that the sandy loam soil control (Table 26). The analysis of variance for cumulative N_2O emissions showed significant effect for N-fertilizer in the sandy loam soil (Table 24 and 26). In the sandy loam soil, cumulative N_2O emissions from all the N-amended treatments were significantly higher than the control. Urea had the highest cumulative N_2O emissions, corresponding to 7.4% of the applied-N. The addition of nitrification inhibitor NP to urea significantly reduced N_2O emissions by approximately 23.5%, resulting in a loss of

5.7% of the N-applied in the urea + NP treatment. The reduction was much pronounced (43.8%), with SuperU with respect to urea alone treatment. However, addition of NBPT alone to urea had no response in cumulative N_2O emissions. The PCU showed the least cumulative N_2O emissions among the N-amended treatments, representing to only 3.7% of the N-applied emitted as N_2O. When compared with urea-N treatment, N_2O emissions from the PCU was more than 50% less.

In the silty clay soil, cumulative N_2O emissions also increased as a result of N-application over the control. However, unlike the sandy loam soil, cumulative N_2O emissions were similar among the N-amended treatments. Here, the emissions from the N-amended treatments ranged from 22.4 to 30.6 mg N kg^{-1}, corresponding to 4.5 to 6.8% of the applied-N.

Carbon dioxide fluxes

Daily CO_2 fluxes measured from the soils on 2 d and 21 d following the application of N-treatments are shown in Figure 20. On 2 d, CO_2 fluxes from the silty clay soils (53.6 to 61.6 mg kg^{-1} d^{-1}) were higher than those from the sandy loam soils (6.9 to 9.3 mg kg^{-1} d^{-1}), for all the N-treatments including control. However, the fluxes did not differ among the N-treatments in both soils. By 21 d, the CO_2 fluxes increased sharply in the sandy loam soil (9.4 to 19.7 mg kg^{-1} d^{-1}), whereas the fluxes declined remarkably in the silty clay soil (22.7 to 25.2 mg kg^{-1} d^{-1}). On this day, across the N-treatments, CO_2 fluxes were similar between the soils type, except control. Emission of CO_2 from the sandy loam control was higher than from the silty clay control on 21 d. In the sandy loam soil, CO_2 fluxes from N-amended treatments were higher than control, with no differences among them. There were no significant differences in CO_2 fluxes among N-treatments in the silty clay soil.

Residual inorganic N content

Of the two analyzed N-forms, nitrate form of N (NO_3^-) was the only prevalent residual inorganic-N form present in all the soils at the end of the incubation. Hence, the residual inorganic-N herein is referred to as residual NO_3^-. Residual soil NO_3^- contents were considerably higher in the silty clay soil than in the sandy loam soil for all N-treatments (Table 27). Also, the NO_3^- contents varied significantly among the N-treatments, particularly in the sandy loam soil. In the sandy loam soil, the highest amount of residual NO_3^- was retained in the PCU treatment. In the sandy loam, residual NO_3^- contents did not differ among urea with or without any inhibitor treatments. However, the mean NO_3^- values in these treatments ranged between 15.4 to 18.0 mg kg^{-1}, and were higher than the zero-N control. In the silty clay soil, all the N-amended treatments had higher NO_3^- at the end of the incubation as compared with un-amended control treatment; however, no significant differences among N-amended treatments were seen, with mean values ranging from 27.5 to 36.7 mg NO_3^- kg^{-1}.

Discussion

Ammonia volatilization

Ammonia volatilization losses were significantly influenced by soil texture, with greater losses observed in the sandy loam soil (0.7 to 8.6% of applied-N) than in the silty clay soil (0.1 to 0.4% of applied-N), across all the N-amended treatments. Previous studies have shown that NH_3 volatilization form surface applied N-fertilizers can vary with initial soil pH, CEC, clay content, and organic matter (Hargrove, 1988; Sigunga et al., 2002; Francisco et al., 2011). Increase in soil pH shifts the equilibrium reaction [NH_4^+ (soil) = NH_3 (soil) = NH_3 (gas)], by moving more NH_4^+ towards NH_3 form, resulting greater NH_3 emissions at higher pH (Mkhabela et al., 2006). Relatively higher NH_3 volatilization losses from the sandy loam soil than from the silty clay soil can be attributed to higher soil pH, and lower CEC, organic matter, and clay content in the former soil as compared with the latter soil (Table 23).

Temporal pattern of NH_3 emission rates also varied among the N sources in both soils. More than 50% of the total cumulative NH_3 emissions occurred during the first 4 d of urea application in both soils as a result of accelerated urea hydrolysis within this period (Zaman and Blennerhassett, 2010). The proportion increased to 91% and 84% in the sandy loam soil and the silty clay soil, respectively by 8 d. Volatilization losses mostly occurred within the first few days of N-fertilizer application (Knight et al., 2007; Sigunga et al., 2002; Zaman et al., 2008; Zaman and Blennerhasset, 2010; Soares et al., 2012).

For the period from 11 d until 17 d in the sandy loam soil, NH_3 emissions from the NBPT increased overcoming the urea alone treatment, indicating urea hydrolysis in the later periods. Cantarella et al. (2008) found that delay in rainfall and/or irrigation by 10 to 15 d resulted into significant amount of volatilization losses from the NBPT-treated urea, and extended until 35 d, even though at a slower pace. However, this phenomenon was completely absent in the silty clay soil in the present study, illustrating differential patterns of NBPT efficacy associated with different soil textures (Gioacchini et al., 2002). Overall, the application of NBPT to urea reduced NH_3 losses from soils by 32 to 78%, consistent with the reduction range of 15 to 89% in the previously published studies (Rawluk et al., 2001 (28 to 88%); Cantarella et al., 2008 (15 to 78%); Zaman et al., 2008 (45%); Soares et al., 2012 (60%); Francisco et al., 2011 (25 to 89%).

Addition of nitrification inhibitors, such as NP and DCD, to urea-N fertilizers reduces nitrification rates, which in turn can enhance NH_3 volatilization (Rodgers, 1983). In our study, the addition of NP to urea almost doubled the NH_3 volatilization losses in the sandy loam soil, while an incremental tendency was observed in the silty clay soil. Nevertheless, the variations in

NH_3 losses in soils due to NP application could at least in part be explained by differences in soil characteristics influencing the effectiveness of nitrification inhibitors (Hendrickson and Keeney, 1978; Wolt, 2000; Singh et al., 2008). The SuperU treatment (containing both NBPT and DCD) showed higher daily fluxes as well as the overall cumulative NH_3 emissions, particularly in the sandy loam soil. This indicates that NBPT in combination with DCD was not as effective, in reducing NH_3 losses, as when it was used alone (Montemurro et al., 1998). Polymer coated urea had the least cumulative NH_3 emissions among the N-sources in the sandy loam soil, resulting in a reduction of 81% in NH_3 loss when compared to the urea alone treatment. Such reduction in NH_3 losses from PCU compared to regular urea are in agreement with previously reported reductions of 50-60% (Pereira et al., 2009; Rochette et al., 2009a). In contrast, few studies have also reported that NH_3 fluxes from the PCU increases from around 6-wk, suggesting the necessity to evaluate NH_3 losses for extended period of time with this N-fertilizer (Jantalia et al., 2012). This later incremental trend in NH_3 fluxes from the PCU was not evident in our study. In the present study, NH_3 fluxes from the PCU either remained significantly lower than urea for the first 17 d and 4 d in sandy loam and silty clay soil, respectively, or were similar to that of urea, afterwards, until the end of the incubation in both soils. In fact, emissions from the PCU were comparable to the control treatments after 11 d for both soils. Therefore, mineral N could have diffused slowly out of the PCU granules, similar to those observed by Rochette et al. (2009a), resulting in the reduction in NH_3 losses. Moreover, residual NO_3^- contents measured at the end of the incubation were the highest for PCU in the sandy loam soil, whereas in the silty clay soil, the PCU had slightly higher inorganic-N than other N-sources. The accumulation of NO_3^- at the end of the study further corroborates to the slow N-releasing property of the PCU, given that little NH_3 as well as N_2O emitted with this treatment.

The proportions of applied-N emitted as NH_3 from each N-source, applied to the sandy loam soils, are similar to the previously reported values of 4.2% for urea, 1.9% for urea-treated with NBPT, and 5.7% for urea-treated with NBPT and DCD (Zaman et al., 2008); 7 to 9% for urea-treated with DCD (Zaman and Blennerhassett, 2010); and 0.76% for PCU (Knight et al., 2007). However, these are lower than those reported by others (Gioacchini et al., 2002; Rochette et al., 2009a; Soares et al., 2012) probably because of variation in factors that affect NH_3 volatilization, such as soil physico-chemical properties, experimental conditions, and NH_3 quantification method between these studies. In our study, 35 mL de-ionized water (corresponding to 7.7 mm rain) was added to the sandy loam soils shortly after N-treatment application in order to adjust the soils at 60% WHC. The applied water could have incorporated the surface amended N-fertilizers into the soil, which considerably restricted NH_3 emissions from the soils (Holcomb et al., 2011; Jantalia et al., 2012) as compared with the other studies (Soares et al., 2012), where the adjustment of soil moisture preceded N-fertilizer application. The restriction in NH_3 emissions was much pronounced in the silty clay soil upon addition of 59 ml water (corresponding to 12.9 mm rain), in which less than 0.5% of the applied-N was lost as NH_3, regardless of N-fertilizer sources. Moreover, in the present study, there was no air exchange in the jars, as opposed to others (Soares et al., 2012) that have quantified NH_3 losses under constant regulation of air pressure inside the volatilization chambers. Removal of NH_3-laden headspace air inside the jar can reduce the NH_3 partial pressure above the soil and thus can increase NH_3 volatilization (Mkhabela et al., 2006).

Nitrous oxide emissions

Earlier investigations have shown that soil N_2O emission rates can be limited by both C and N availabilities, depending upon soil characteristics (Weitz et al., 2001; Sanchez-Martin, 2008). In fact, these limitations on N_2O emissions from the soils are reflected across the incubation period in the current study. The N_2O fluxes remained significantly lower for the initial 4 d of incubation for all the N-treatments in the sandy loam soil, whereas the silty clay soil exhibited highest emissions during this period. Thus, the initial burst of N_2O emissions observed in the silty clay soil, but not in the sandy loam soil could at least in partly be explained by increased C and N mineralization of organic matter rich silty clay soil (Franzluebbers et al., 2000; Pelster et al., 2012). This is further supported by the fact that the control treatment too had such a burst in N_2O emissions (proportionate to those from the N-amended treatments) during the first few days of incubation in the silty clay soil - driven possibly by the flush in mineralization of organic matter rich silty clay soil upon wetting. About 96% of the total N_2O emission from the control treatment in the silty clay soil was produced during the first 6 d of incubation. And, the proportions ranged between 47 to 58% for the N-amended treatments. Following the first week of incubation, N_2O emissions from both the soils gradually increased and peaked on 21 d. The N_2O fluxes observed in the sandy loam soils on 21 d were generally higher than those observed in the silty clay soils. On this day, in the silty clay soil, we observed similar soil respiration rates among the N-treatments (Figure 20). However, the N-amended treatments had significantly higher N_2O production rates over the control. These illustrate that factors other than readily available carbon, might have accounted for the increase in N_2O emissions during later periods of the incubation in this soil. Similarly, it appears that C was not limiting for N_2O production in the later periods of incubation in the sandy loam soil, because CO_2 fluxes were proportionate to those observed in the silty clay soil.

Given that soil C was not limited in the latter period of incubation, it is likely that differences in N availability could have controlled N_2O production. Earlier works have shown that soil N_2O emissions were significantly correlated with NO_3^- availability (Weitz et al., 2001; Khalil et al., 2009). Moreover, in the present study, increases in soil N_2O fluxes well complimented with the gradual decrease in the NH_3 fluxes (Figure 18 and 19). And, given that NH_3 emissions from the soils declined by the 3rd week of incubation, it can be assumed that the remaining NH_4^+ were converted into NO_3^- or immobilized into the soil colloids. This further strengthens our assumption that soil N_2O fluxes were primarily limited by mineral-N availability. Higher soil CEC in the silty clay soil than in the sandy loam soil would adsorb greater NH_4^+ to the exchange sites, and thus reduce NO_3^- availability necessary for denitrification (Jarecki et al., 2008; Francisco et al., 2011). The potential for N limitation for N_2O emissions by high soil CEC is further implicated by another study by De Visscher et al. (1998) that demonstrated higher N_2O emissions associated with low CEC-soil than from high CEC-soil because the former retained less NH_4^+ than the latter soil. Nevertheless, the magnitude of NH_4^+ retention and/or its conversion into NO_3^- could have differed among the N-fertilizers sources (Dell et al., 2014). These are reflected in differential amounts of N_2O losses from the N-fertilizers in the soils studied, ranging from 3.7 to 7.4% of applied-N across soil textures and N-fertilizers. This lower range of N-loss was observed for PCU treatment in the silty clay soil, similar to the highest N_2O EF of 3.8% reported by Glenn et al., 2012. Clearly, the proportions of N-applied lost through N_2O emissions are considerably higher than the default EF value of 1-1.25% quoted by IPCC (2006). The differences in the % EF obtained in this study from those reported values could at least in part be explained due to differences in the length of N_2O evaluation as well as the measurement conditions (field vs laboratory) among these studies.

Application of NBPT to urea had no influence on N_2O emissions in both soils because NBPT only delays urea hydrolysis reaction, and does not inhibit it completely (Cantarella et al., 2008). Urea treated with NP, and both with NBPT and DCD (SuperU) significantly reduced N_2O emissions in the sandy loam soil. About 5.7% and 4.2% of the applied-N was lost as N_2O from urea + NP and SuperU treatments, respectively, whereas the loss amounted to 7.4% in the urea treatment. Such variations in the additive effect of NBPT and DCD in reducing N_2O emissions compared to the use of only nitrification inhibitor was also observed by Zaman and Blennerhasset (2010). Because it takes certain time for urea to get hydrolyzed upon the action of NBPT, urea transformation is much slower under the influence of the combined use of both urease and nitrification inhibitors than when only nitrification inhibitor is used, which only retains the readily available NH_4^+ from its conversion into NO_3^- (Zaman et al., 2008; Zaman and Blennerhassett, 2010). Overall, the effect of NP in reducing N_2O losses (23.5%) in our study were comparable to the reported average of 51% in their meta-analysis by Wolt (2004), and 30 to 50% by Akiyama et al. (2010). Performance of NP varies with the interplay of various factors including soil physico-chemical properties (texture, pH, organic matter), environmental conditions (moisture, temperature), and N-fertilization practice (source, form, rate, placement) (Wolt, 2000). The reduction in N_2O losses of 43.8% observed with the SuperU (urea + NBPT + DCD) are in agreement with that reported for sandy clay loam soil by Sanz-Cobena et al. (2012). Both, urea + NP and SuperU treatments produced similar N_2O fluxes following 42 d after fertilizer application, possibly because the effects of these inhibitors had faded out due to their degradation (Wolt, 2000; Singh et al., 2008; Chen et al., 2010).

The PCU showed the least cumulative N_2O emissions among the N-amended treatments in the sandy loam soil, resulting in a reduction of 51% in N_2O loss when compared to the urea alone treatment. Our results are in agreement with earlier studies that have also observed N_2O reduction with PCU (by 42%) compared with urea (Halvorson et al., 2014). The potential of

PCU for reducing N_2O emissions is based on the premise that it releases N very slowly by diffusion through a semi-permeable polymer membrane (Trenkel, 1997; Hyatt et al., 2010). Such a gradual release of mineral-N from the PCU granules in our study too likely limited substrate availability for N_2O productions in the sandy loam soils. The higher accumulation of residual NO_3^- content with the PCU treatments in the sandy loam soil (Table 26) could also be related to lower N_2O emission losses in this treatment relative to the others. Nevertheless, the PCU was not effective in abating N_2O losses in the silty clay soil. Earlier investigations on the temporal dynamics in N-release rates from the PCU have yielded inconsistent results. Halvorson and Del Grosso (2012) documented that PCU constantly had lower soil NO_3^- than urea during 2-mo after fertilizers addition in clay loam soil. Likewise, Parkin and Hatfield (2013) observed soil NO_3^- accumulation from PCU was slower than that from urea during the first 37 d following fertilizer applications. Rochette et al. (2009a) observed a very slow apparent release of mineral-N from the PCU granules during 25 d period in silty clay loam soil. Recently, in a laboratory incubation of silt loam soil moistened to 30% WFPS, Dell et al. (2014) showed that the PCU delayed NH_4^+ accumulation and the subsequent buildup of NO_3^- compared to urea until 2-3 wk, and then onwards, the NO_3^- concentration in the PCU increased over the urea treatment. Therefore, because of such inconsistencies in the N-nutrient release pattern and duration, it is not unexpected that effectiveness of PCU in reducing N_2O emissions differed with soil textures in our study (Dell et al., 2014). Indeed, the literature regarding the potential of PCU in reducing N_2O emissions is mixed, with some noting reduction in N_2O emissions with PCU than conventional fertilizers (Hyatt et al., 2010; Akiyama et al., 2010; Halvorson et al., 2014), while others have reported equal or higher N_2O losses with PCU (Parkin and Hatfield, 2013; Dell et al., 2014; Soares et al., 2015). Moreover, in the current study, inorganic-N produced from inherent soil-N mineralization could have also provided significant N substrate fueling N_2O production in the organic matter rich silty clay soil (Khalil et al., 2009; Parkin and Hatfield, 2013).

Conclusions

Our study demonstrated that the beneficial effect of treating urea with urease inhibitor NBPT may be limited only to reducing NH_3 volatilization losses from soils. Under soil conditions favoring high NH_3 emissions, application of urea with nitrification inhibitors NP, and SuperU (urea stabilized with both urease inhibitor NBPT and nitrification inhibitor DCD) brings about an increase in NH_3 losses. However, these inhibitors seem favorable in abating N_2O emissions in sandy loam, low organic matter soils. Application of the slow-release polymer coated urea fertilizer would be the most effective strategy to control both NH_3 volatilization and N_2O emissions, particularly in sandy loam soils. The potential of urea-N stabilizers and slow release fertilizers may be restricted in soils, containing high organic matter content. Depending upon soil conditions, selection of suitable N-source can be a viable management practice for reducing NH_3 and/or N_2O emissions.

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Table 23. Physical and chemical properties of soils (0-15 cm) used in the study.

Soils	pH	EC[†]	OM[‡]	NO_3^-	Available K	CEC[§]	Soil texture		
							Sand	Silt	Clay
		dS m^{-1}	%	------mg kg^{-1}------		cmol$_c$ kg^{-1}	---------g kg^{-1}---------		
Sandy loam	8.29	0.13	2.1	2.1	131	10.4	814	103	93
Silty clay	7.27	1.16	3.8	34.8	544	43.4	62	454	494

[†] Electrical conductivity; [‡] Organic matter; [§] Cation exchange capacity.

Table 24. Results of general ANOVA on cumulative emissions of ammonia (NH_3-N) and nitrous oxide (N_2O-N) and residual inorganic N contents.

Source of variation	NH_3-N volatilization		N_2O-N emissions		Residual Inorganic N	
	F value	*P* value	F value	P value	F value	P value
Soil texture (S)	3790.9	<0.0001	8.8	0.0252	67.4	0.0002
N fertilizer (N)	253.6	<0.0001	22.2	<0.0001	22.1	<0.0001
S x N	222.3	<0.0001	0.7	0.6074	2.7	0.0376

Table 25. Cumulative emissions of ammonia (NH_3-N) over 89 d from various surface amended N fertilizers on two contrasting soils.

N fertilizers[†]	Cumulative NH_3-N emissions[‡]		Differences from urea[§]
	mg kg^{-1}	% of N-applied	%
		Sandy loam	
Control	0.7 ± 0.2 f	-	-
Urea	16.5 ± 0.4 c	4.3 ± 0.1 c	-
Urea + NBPT	11.4 ± 0.3 d	2.9 ± 0.1 d	-32.3
Urea + NP	32.1 ± 0.9 a	8.6 ± 0.2 a	+98.7
SuperU	19.7 ± 0.9 b	5.2 ± 0.3 b	+20.3
PCU	3.2 ± 1.0 e	0.7 ± 0.2 e	-84.2
LSD ($P \le 0.05$)[¶]	2.2	0.7	-
		Silty clay	
Control	0.5 ± 0.1 d	-	-
Urea	1.2 ± 0.2 ab	0.2 ± 0.0 ab	-
Urea + NBPT	0.7 ± 0.1 cd	0.1 ± 0.0 b	-71.4
Urea + NP	1.8 ± 0.3 a	0.4 ± 0.1 a	+85.7
SuperU	1.1 ± 0.2 bc	0.1 ± 0.0 b	-14.3
PCU	1.1 ± 0.1 bc	0.2 ± 0.0 ab	-14.3
LSD ($P \le 0.05$)	0.5	0.2	-

[†] NBPT, N-(n-butyl) thiophosphoric tiramide; NP, nitrapyrin; PCU, polymer coated urea.

[‡] Values (means ± standard error, n=4) followed by different lowercase letters in the same column within each soil texture differ significantly ($P \le 0.05$).

[§] (-) reduction, (+) increase.

[¶] Least significant difference (LSD) values provided for 0.05 level of significance.

Table 26. Cumulative emissions of nitrous oxide (N_2O-N) over 126 d from various N fertilizers amended on two contrasting soils.

N fertilizers[†]	Cumulative N_2O-N emissions[‡]		Differences from urea[§]
	mg kg^{-1}	% of N-applied	%
		Sandy loam	
Control	0.1 ± 0.0 e	-	-
Urea	27.3 ± 2.6 a	7.4 ± 0.7 a	-
Urea + NBPT	24.0 ± 3.4 ab	6.5 ± 0.9 a	-12.1
Urea + NP	20.9 ± 2.4 bc	5.7 ± 0.6 ab	-23.5
SuperU	15.4 ± 1.3cd	4.2 ± 0.4 bc	-43.8
PCU	13.5 ± 2.4 d	3.7 ± 0.7 c	-51.1
LSD ($P \leq 0.05$)[¶]	6.2	1.8	-
		Silty clay	
Control	6.0 ± 0.8 b	-	-
Urea	30.6 ± 2.8 a	6.8 ± 0.9 a	-
Urea + NBPT	25.1 ± 2.0 a	5.2 ± 0.6 a	-22.4
Urea + NP	22.2 ± 5.4 a	4.5 ± 1.3 a	-34.1
SuperU	22.5 ± 2.9 a	4.5 ± 0.6 a	-32.9
PCU	22.4 ± 2.0 a	4.5 ± 0.7 a	-33.3
LSD ($P \leq 0.05$)	9.5	3.0	-

[†] NBPT, N-(n-butyl) thiophosphoric tiramide; NP, nitrapyrin; PCU, polymer coated urea.

[‡] Values (means ± standard error, n=4) followed by different lowercase letters in the same column within each soil texture differ significantly ($P \leq 0.05$).

[§] (-) reduction, (+) increase.

[¶] Least significant difference (LSD) values provided for 0.05 level of significance.

Table 27. Residual inorganic N content measured for the soils at the end of incubation.

N fertilizers[†]	Sandy loam	Silty clay
	----------------mg kg^{-1}[‡]----------------	
Control	0.3 ± 0.0 c	3.6 ± 1.2 b
Urea	17.6 ± 2.6 b	27.5 ± 5.8 a
Urea + NBPT	18.3 ± 3.6 b	36.5 ± 2.3 a
Urea + NP	15.4 ± 2.5 b	36.7 ± 4.5 a
SuperU	18.0 ± 2.4 b	35.8 ± 3.8 a
PCU	29.1 ± 2.4 a	34.5 ± 1.8 a
LSD ($P \leq 0.05$)[¶]	7.7	11.3

[†] NBPT, N-(n-butyl) thiophosphoric tiramide; NP, nitrapyrin; PCU, polymer coated urea.

[‡] Values (means ± standard error, n=4) followed by different lowercase letters in the same column within each soil texture differ significantly ($P \leq 0.05$).

[¶] Least significant difference (LSD) values provided for 0.05 level of significance.

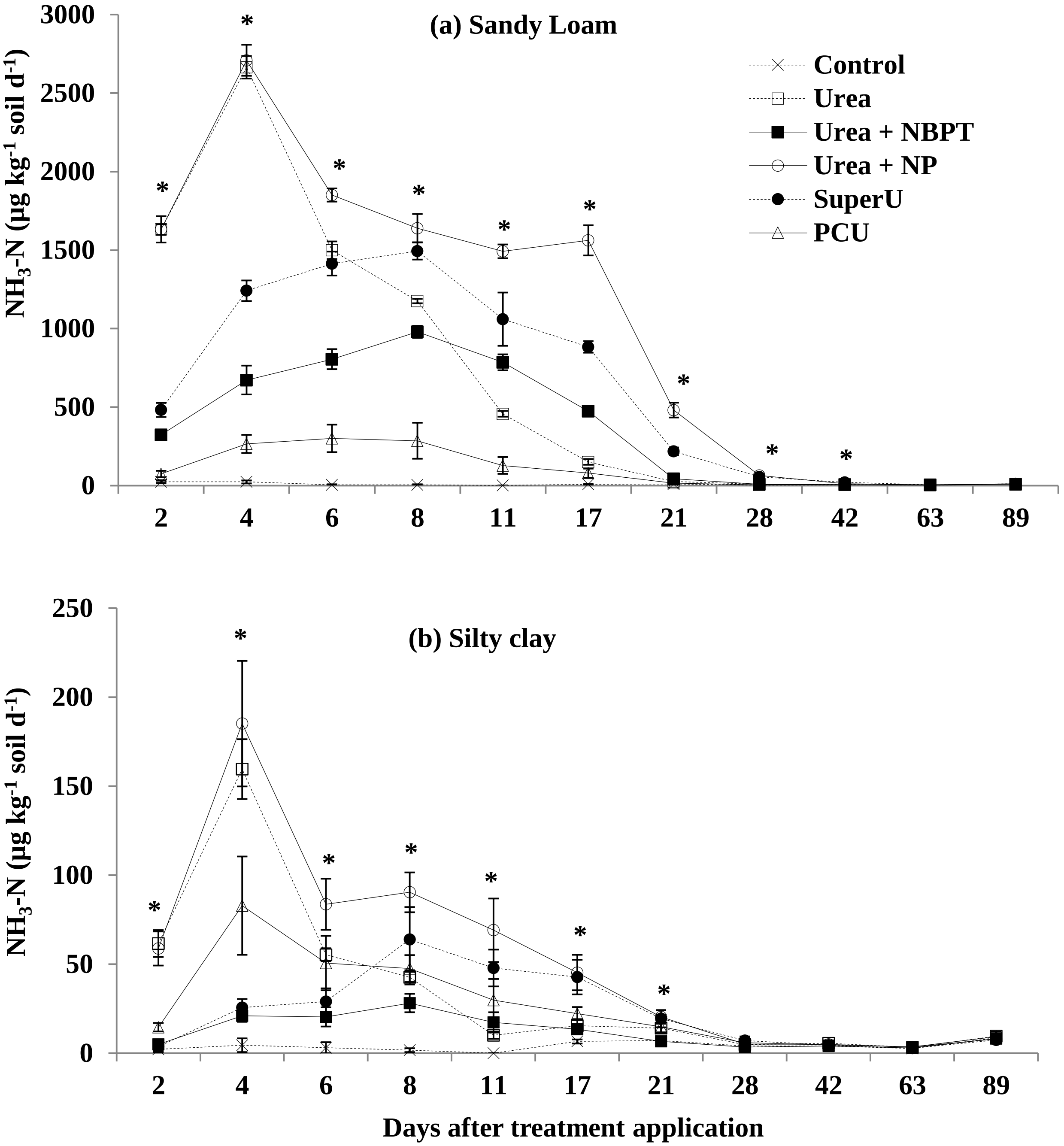

Figure 18. Ammonia (NH_3-N) volatilization from various surface applied N fertilizers on (a) Sandy loam and (b) Silty clay soils over 89 d of incubation. Error bars are standard errors (n=4). *Indicate significant ($P \leq 0.05$) treatment differences at the day. Please note the large differences in y-axis scaling.

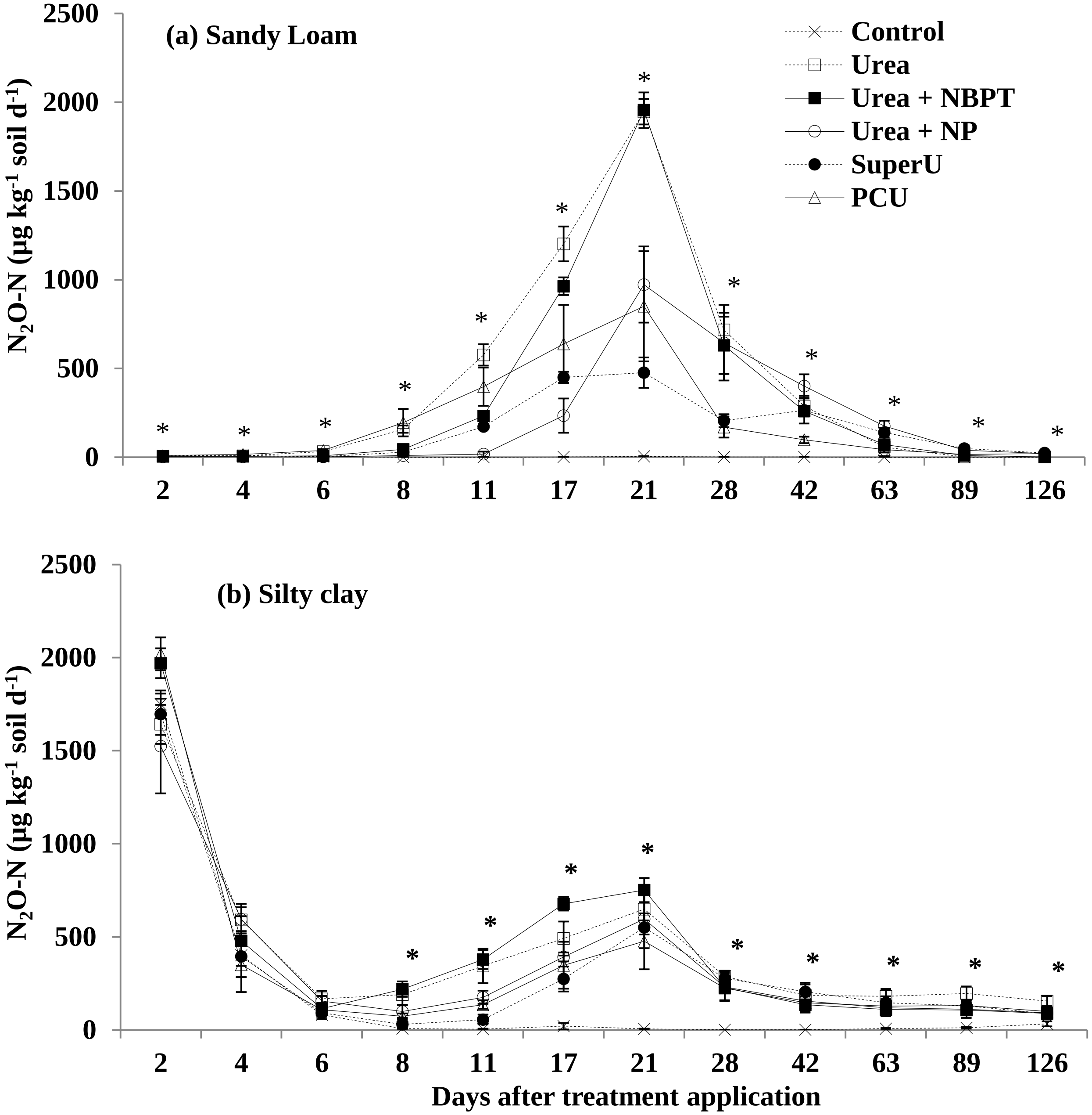

Figure 19. Soil nitrous oxide (N_2O-N) emissions from various surface amended N fertilizers on (a) Sandy loam and (b) Silty clay soils over 126 d of incubation. Error bars are standard errors (n=4). *Indicate significant ($P \leq 0.05$) treatment differences at the day.

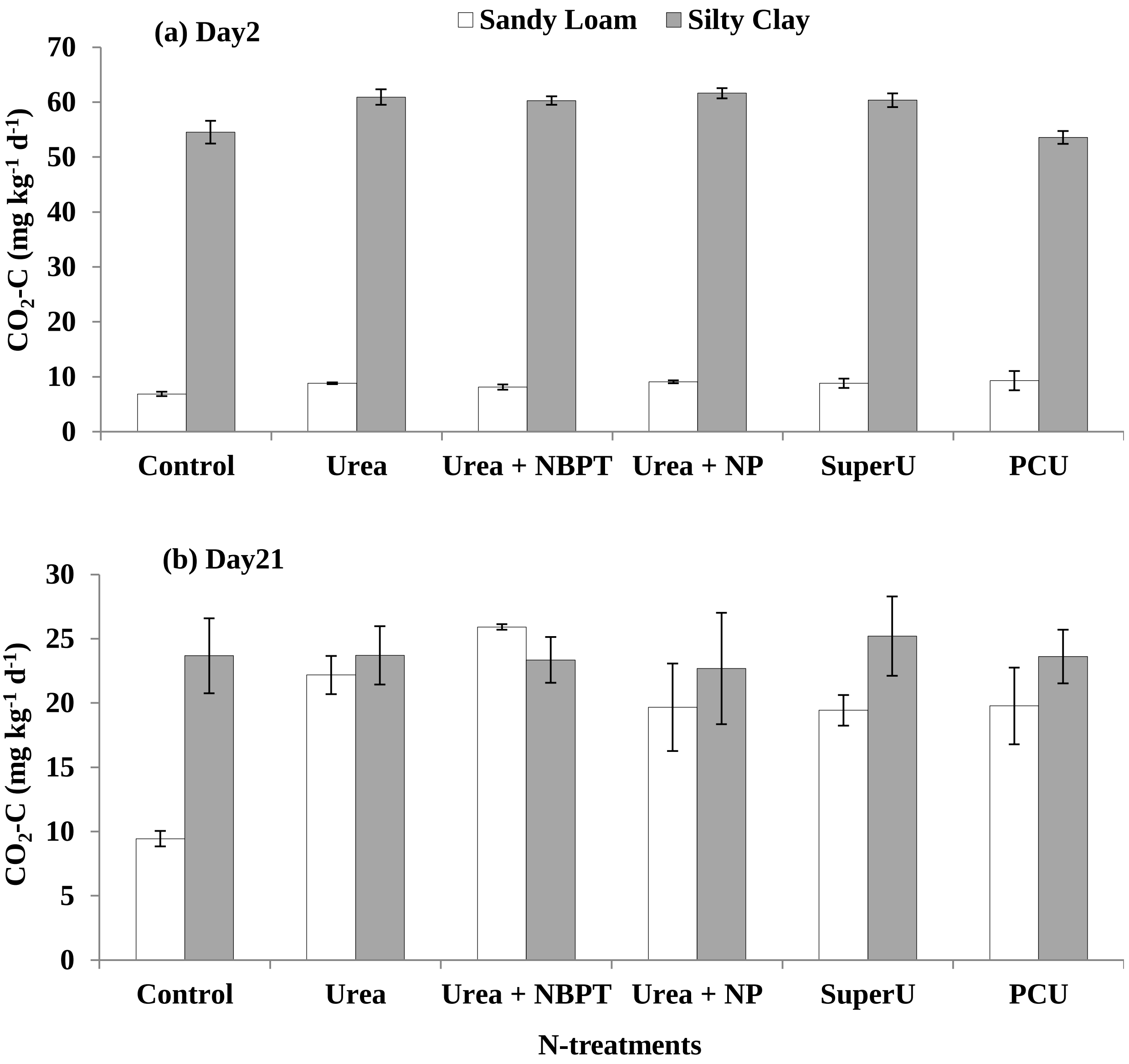

Figure 20. Soil carbon dioxide (CO_2-C) fluxes measured from sandy loam and silty clay soils on (a) day2, and (b) day21 following the application of N fertilizers. Error bars are standard errors (n=4).

SUMMARY AND GENERAL CONCLUSIONS

The field research provided an opportunity to evaluate the effectiveness of subsurface (tile) drainage and N fertilizer management across four crop (corn, spring wheat, sugarbeet, and soybean) production during two growing seasons (2012 and 2013) in a high clay containing poorly drained Fargo silty clay soil in the Red River Valley of North Dakota. Yields of the crops were primarily dictated by the growing season climatic conditions, particularly precipitation. The 2012 growing season was excessively dry compared to the normal years. Consequently, water table depth did not reach the level to cause any flow in the drainage tile, and therefore, the drainage effect was not considered and only N management effect on crop and soil parameters were compared for this growing season. In sharp contrast, the early 2013 growing season was wet, with more than 50% of the total growing season precipitation (596 mm, May-October) already received by the end of June. High precipitation received during the early growing period allowed the drainage tiles to move water to the ditch only for four events during this period. However, the mid-growing season was excessively dry, and the precipitation that occurred in the subsequent months was not sufficient to cause any flow in the drainage tile throughout the rest of the season. As a result, within the scope of these two growing seasons, subsurface drainage showed no improvement in yields in any crops studied. Prolong period of soil saturation due to poor internal drainage has typically been the greatest limiting factor affecting crop yields in this soil. And, contrary to the norm, soil water deficit was likely the most limiting factor affecting crop yields over the two study years, due to abnormally dry conditions experienced during the growing seasons. In spite of dry growing periods, the crop productivity did vary slightly with N fertilizer management, particularly in 2013, with corn and wheat.

In 2013, applying 134 kg N ha^{-1} from urea either at planting, with and without the addition of nitrification inhibitor Nitrapyrin, or applying the same rate in two equal split doses (half at planting and half at V6 corn growth stage) improved corn grain yields on an average by 2.28 Mg ha^{-1} over unfertilized control, which had an average grain yield of 5.99 Mg ha^{-1}. However, the fertilized N treatments were not different among each other. Similar, results were observed with wheat, as well, in 2013. The wheat grain yields increased by 0.73, 0.70, and 0.75 Mg ha^{-1} with the urea application rates of 112 kg N ha^{-1}, 112 kg N ha^{-1} plus Nitrapyrin, and 202 kg N ha^{-1}, respectively over the unfertilized control, which yielded 3.32 Mg ha^{-1} on average. These results indicate the necessity of N fertilization, regardless of source, to increase productivity of corn and wheat crops. However, lack of response of crop yields among N fertilizer management (source, rate and application time) was likely due to a combination of factors such as soil water deficit during mid-growing season, and inherent soil N mineralization along with high residual soil N. Due to such factors, crop yields in any crops in 2012 as well as in sugarbeet and soybean in 2013 were irresponsive to any N fertilizer management.

Management of N application influenced soil N availability in 2012, and the effect of N management on N availability varied slightly with drainage in 2013. For instance, in 2012, applying higher N-rate (180 kg N ha^{-1}) than recommended N-rate (146 kg N ha^{-1}), in sugarbeet, increased the soil NO_3^- levels during mid-growing season. Applying urea at the same rate, but with Nitrapyrin, was not different than either recommended or higher N-rate. Similarly, in soybean, applying higher N-rate (39 kg ha^{-1}) with Nitrapyrin significantly increased soil NO_3^- level compared to lower N-rate (26 kg ha^{-1}) with or without Nitrapyrin during mid 2012 growing season. In 2013 corn mid-growing season, Nitrapyrin treated urea accumulated more soil NH_4^+ level and delayed NO_3^- buildup compared to untreated urea at the similar N-rate, particularly under drained condition. And, higher urea application rate (202 kg N ha^{-1}) than recommended (146 kg N ha-1) in wheat build up soil NO_3^- level during 2013 mid-growing season under both drainage conditions. Although soil N availabilities varied with N management and/or drainage, crop yields did not differ among N-fertilizer management. Therefore, use of recommended rates of N fertilizer along with nitrification inhibitor Nitrapyrin may be a viable N management strategy, considering the additional cost of adding N fertilizer and potential N losses in this soil. In fact, applying additional N was usually associated with greater N_2O emission and NH_3 volatilization losses measured during 2012 and 2013 growing seasons, respectively. However, NH_3 volatilization were limited to up to 1.7% of applied N. Soil incorporation of surface applied N fertilizers manually and/or irrigation seems to be a viable option for reducing N loss associated with NH_3 volatilization in this soil.

Adoption of subsurface drainage practice has been increasing since last 15 years in the RRV, triggered by the recent wet climatic cycles, and preponderance of high clay and soluble salts within this region. Therefore, overall, the research results may provide important information to growers considering suitable N management and use of subsurface drainage systems within this region. However, subsurface drainage effect on crop yield and N dynamics were limited within the scope of two growing seasons, and therefore a long-term research is deemed required.

In order to further determine the control mechanism of soil water, N management, and soil texture on N losses (N_2O emission and NH_3 volatilization); two separate experiments were conducted under controlled condition in the laboratory. The results from the first experiment indicated an increased potential of denitrification loss of urea as N_2O above 60% soil water holding capacity in silty clay soils. Preponderance of high clay containing poorly drained soils, as such found within the RRV, are therefore prone to denitrification loss of N_2O upon soil saturation due to internal poor drainage. Efficient N fertilizer management for reducing N_2O emissions include optimization of urea-N rates, usage of nitrification inhibitors (such as Nitrapyrin), and avoiding N application at the times of excessive rainfall, irrigation, or spring thaw events.

The second laboratory experiment demonstrated that soil texture and N-additives exert a strong influence on volatilization and denitrification losses. The urease inhibitor NBPT could reduce NH_3 volatilization losses associated with surface-applied urea in both fine-textured silty clay and coarse-textured sandy loam soils. Applying nitrification inhibitor Nitrapyrin and SuperU (urea stabilized with urease inhibitor NBPT and nitrification inhibitor Dicyandiamide) may increase NH_3 volatilization losses. However, Nitrapyrin and SuperU seem favorable in reducing N_2O emissions in sandy loam, low organic matter soils. Application of the slow-release polymer coated urea fertilizer would be the most effective strategy to control both NH_3 volatilization and N_2O emissions, particularly in sandy loam soils. The potential of urea-N stabilizers and slow release fertilizers may be restricted in soils, containing high organic matter content. Therefore, depending upon soil conditions, selection of suitable N-source can be a viable management practice for reducing NH_3 and/or N_2O emissions.

Denitrification and volatilization loss of applied urea-N is both agronomic and environmental concerns. Therefore, the findings from the laboratory studies have important implications for the development of N-management strategies for reducing N_2O emissions and NH_3 volatilization within the RRV region. In addition, the research results may assist public agencies when devising estimates of N_2O production and NH_3 volatilization as a consequence of N fertilizer management within the RRV.