NITROGEN MANAGEMENT STRATEGIES TO IMPROVE CORN GROWTH AND REDUCE SOIL GREENHOUSE GAS EMISSIONS FROM CLAYPAN SOILS

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by

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ABSTRACT

Adoption of nitrogen (N) management strategies to minimize gaseous N loss from agriculture while maintaining high yield production is increasingly important for an exponentially growing population. Agricultural management on poorly-drained claypan soils in the Midwestern U.S. make corn (*Zea mays* L.) production even more challenging due to the subsoil's low permeability, which may result in wetter soil conditions and relatively larger amounts of soil N_2O emissions during the growing season. The objective of this study was to determine the effects of urea fertilizer placement with and without the addition of a nitrification inhibitor (NI) on corn yield, N use efficiency (NUE), and cumulative soil N_2O emissions on a Northeastern Missouri claypan soil. The fertilizer strategies utilized in this study consisted of deep-banded urea (DB) or urea plus nitrapyrin [2-chloro-6-(trichloromethyl) pyridine] (DB+NI) at a depth of 20 cm compared to urea broadcast surface applied (SA) or incorporated to a depth of 8 cm (IA). The addition of a NI with deep-banded urea resulted in 27% greater apparent N recovery efficiency than all other N treatments. Additionally, DB+NI had 54 and 55% lower cumulative soil N_2O emissions than IA and SA treatments in the two combined growing seasons. These results suggest that deep placement of urea with or without nitrapyrin is an effective management strategy for increasing corn yield and reducing N loss on a claypan soil.

CHAPTER 1

LITERATURE REVIEW

Agriculture's Impact on World Hunger and Its Environmental Implications

One of the greatest challenges facing humanity today is to feed a rapidly growing world human population. World hunger is a rising global challenge that is creating a demand for higher and efficient food production. The total world human population is expected to reach 9.2 billion by 2050 (Zilberman, 2013), which is nearly an increase of 2.3 billion people from the world's population in 2009. Global food production will need to increase by 70% and nearly to 100% in developing countries to cope with the increase in world population by 2050 (FAO, 2011).

Over the past half century, increased production of reactive nitrogen (N) fertilizers has increased crop yields to provide sufficient food for most of the global population (Smil, 2001). Fertilizer for crop production is responsible for the manufacturing of more reactive N than all terrestrial natural processes (Rockström et al., 2009). This contributes to an average of approximately 100 Tg year^{-1} of reactive N fertilizer spread on agricultural fields (Fields, 2004). The application of N fertilizers for row-crop production is essential to achieve crop yields that will help meet the demand for food as world population grows. However, as N fertilizer inputs increase, more reactive N is released into the environment, negatively affecting soils, ecosystems, and climate via nitrous oxide (N_2O), a major greenhouse and ozone depleting gas (Schlesinger, 2009).

Increased use of synthetic N based fertilizers on agricultural soils has caused agriculture to be the largest source of N_2O emissions in the U.S., accounting for about 75% of total U.S. N_2O emissions in 2015 (USEPA, 2017). Greenhouse gas emissions

(GHG) from agriculture have increased by about 8% since 1990 (USEPA, 2017). Future global N_2O emissions are projected to increase 35 to 60% by 2030 due largely to the projected increase in N fertilizer use and animal production (FAO, 2003). While carbon dioxide (CO_2) and methane (CH_4) contribute to a majority of GHG emissions, N_2O is of concern because it has a global warming potential 298 times greater than CO_2 and 12 times greater than CH_4 (Forster et al., 2007). Nitrous oxide is a chemically stable, persistent GHG that has a residence time of 120 years before being removed by a sink or destroyed, and it also has the potential to decrease the stratospheric ozone layer (USEPA, 2011). The presence of N_2O in the atmosphere is able to come into contact with ultraviolet light, which in turn produces nitric oxide (NO), which allows NO to act as a catalyst in the breakdown of ozone (Fields, 2004). Therefore, mitigating agricultural soil N_2O emissions is critical to minimize the effects of climate change and ozone depletion.

Adoption of management techniques to limit soil N_2O emissions from agriculture while maintaining high yield production is increasingly important for a growing population. Efficient use of N may become more difficult to manage due to climate change causing more extreme weather events, such as higher intensity rainfalls and severe droughts (Rosenzweig et al., 2002). One way for mitigation of soil N_2O emissions would be to reduce the amount of N fertilizer applied to agriculture fields. However, this practice may lead to potential food shortages because crop yields would possibly be lower due to N deficiency (Smil, 2001). A more realistic approach is to continue to apply N fertilizer, but implement more efficient N management practices that still achieve high crop yields while minimizing soil N_2O emissions (Robertson and Vitousek, 2009; Drury et al., 2012). In order to be successful, research focused on developing N management strategies that work with soil and environmental conditions to manage biological N transformations and increase plant N uptake needs to be conducted. Research will help achieve the goal of sustainable development: end hunger, achieve food security and improve nutrition and promote sustainable agriculture by 2030 (United Nations, 2015). Nitrogen management strategies for sustainable agriculture is an integral part of the 4R Nutrient Stewardship program, focusing on the four major fertilizer management factors: right rate, right source, right placement, and right timing (Bruulsema et al., 2009).

Biological Nitrogen Transformations Effect on Nitrogen Loss in Row Crop Production

Nitrogen is an essential nutrient for survival of all living organisms since it is a necessary component of important compounds, such as proteins, DNA, and chlorophyll. Nitrogen can take nine forms in terrestrial ecosystems based on different oxidative states (Robertson and Vitousek, 2009). Although abundant in the atmosphere, making up 78% as nitrogen gas (N_2), it is inaccessible to most organisms due to the strength of the triple bond between N atoms. It requires a large amount of energy and kinetics to break this bond between the N atoms into a plant useable form. Nitrogen fixation is carried out only by a select group of microbes in the soil and can also be achieved through abiotic processes, such as used the industrial production of N fertilizer, or by lightning. The development of the Haber-Bosch process, a high temperature and energy-intensive chemical reaction used to industrially synthesize plant-available N from the air, revolutionized agriculture by the ability to mass-produce synthetic N fertilizer (Erisman et al., 2008). The process obtains N from the atmospheric N pool and combines N_2 with hydrogen gas (H_2) to form ammonia (NH_3). Hence, anhydrous ammonia, urea, and other commercial N fertilizers do not need to rely on biological N fixation to transform N into a reactive form. Once applied to the soil, synthetic N fertilizers will continue to cycle through multiple processes, which are commonly mediated by soil microbes. Microbes in the soil influence rates of N transformations by producing enzymes which lower the activation energy required to cycle N. These microbial N transformations include urea hydrolysis, nitrification, and denitrification, which are dependent on factors such as soil temperature, soil water content, soil organic matter (SOM), and microbial diversity and activity (Shi et al., 2004).

Urea Hydrolysis

Urea hydrolysis is the biochemical conversion of synthetic organic N (urea), in the presence of urease enzymes (urea), to gaseous ammonia (NH_3).

$$(NH_2)_2CO + 2H_2O \rightarrow (NH_4)_2CO_3 \tag{1}$$

$$(NH_4)_2CO_3 + 2H^+ \rightarrow 2NH_4^+ + CO_2 + H_2O \tag{2}$$

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O \tag{3}$$

The urease enzyme is located in active microbial cells and is able to thrive in the soil environment after mortality of the cells (Krajewska, 2009). The rate of activity for urea to hydrolyze is dependent upon many factors including the combined amount of urease enzymes and soil conditions. Soil conditions that promote urease enzyme activity will also result in higher rates of urea hydrolysis. Previous studies show increased soil urease activity with high clay content, organic matter, and urea content in the soil (Yadev et al., 1986; Wali et al., 2003; Sommer et al., 2004). Aerobic soil conditions with increasing temperatures, a neutral pH, and water content above the wilting point had the highest rates of microbial urease activity (Fisher and Parks, 1958). Soil urease activity can be depressed under flooded soil conditions (Wali et al., 2003), high soil pH (Gould et al., 1986), and low soil temperature (Sommer et al., 2004). For a silt loam soil, optimum pH for urease activity was measured to be 6 to 8, while other studies on different soil types found no relationship between pH and urease activity (Zantua et al., 1977; Kumar and Wagenet, 1984). Urease is associated with clay soil properties and humus, stabilizing the urease enzyme for long periods (Borghetti et al., 2003; Renella et al., 2007). The rate of urease activity increases with plant residue age and soil organic matter in a clay soil, although this may be due to higher cation exchange capacity associated with clay soils (Kumar and Wagenet, 1984; Hasan, 2000).

Ammonia Volatilization

Ammonia volatilization is a natural byproduct from hydrolysis of urea, but all fertilizers that contain or produce ammonium (NH_4^+) are subject to loss through volatilization. The rate of NH_3 volatilization depends on the rate of urea hydrolysis, environmental conditions, and soil properties. The amount of $NH_{3\ (g)}$ volatilized is mainly influenced by the concentration of total [NH_3] in the soil solution (Sommer et al., 2004). During the urea hydrolysis, the release of OH^- into soil solution has the potential to raise the pH of the soil surrounding the fertilizer granules. This process favors the conversion of N to $NH_{3\ (g)}$ and consequently, volatilization. Thus, the most significant parameter influencing NH_3 volatilization from urea application is soil pH due to its effect on the ratio of NH_3 / NH_4^+ end product (Sommer et al., 2004):

$$NH_4^+ \leftrightarrow NH_3 + H^+ \text{ (pKa 9.49)} \tag{4}$$

Generally, NH_3 volatilization increases with increasing soil pH (Sharpe and Harper, 1995; Sommer and Ersboll, 1994). Little NH_3 volatilization has been shown to occur if the pH of the soil is less than 7 (Sommer et al., 2004). Fertilizers containing NH_4^+ (i.e. ammonium nitrate) initially form an acidic solution (pH 4.5 – 5.5) after they dissolve in the soil, but these N fertilizers rarely lose significant amounts of NH_3 through volatilization (Holcomb et al., 2011).

Since NH_3 volatilization is a microbially-meditated process, soil conditions can influence the amount of NH_3 that is volatilized, including soil temperature, moisture, and organic matter. Dry soil conditions can slow down microbial activity and NH_3 volatilization, while warm and moist soil conditions have a higher potential for NH_3 loss following application (Cantarella et al., 2008). An increase in soil temperature from 7°C to 32°C corresponded to an increase in NH_3 volatilization (Ernst and Massey, 1960). These factors affect the dynamics of total [NH_3] concentration and its subsequent depletion through nitrification (Malhi and McGill, 1982; Sommer et al., 2004).

Nitrification

Nitrification is the aerobic oxidation of NH_3 or NH_4^+ to nitrite (NO_2^-) and NO_3^-. Chemolithoautotrophic bacteria (*Nitrosomonas* and *Nitrobacter*) perform the two-step microbial reaction in the soil. In the first step of nitrification, ammonia-oxidizing bacteria (AOB) and ammonium-oxidizing Archaea (AOA) transform NH_3 to NO_2^- (Prosser and Nicol, 2008).

$$NH_3 + O_2 \rightarrow NO_2^- + 3H^+ + 2e^- \tag{5}$$

In the second step, nitrite-oxidizing bacteria oxidize NO_2^- to NO_3^-.

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^- \tag{6}$$

Nitrosomonas and *Nitrobacter* bacteria accomplish nitrification by building organic molecules using energy obtained from inorganic sources (NH_3 and NO_2^-). Ammonium oxidation is performed by the enzyme ammonium monooxygenase encoded in *amo*-genes, present in AOB and AOA. Oxidation of nitrite is catalyzed by the enzyme hydroxylamine oxidoreductase and is further oxidized to nitrate by the enzyme nitrite oxidoreductase (Prosser and Nicol, 2008).

Nitrification requires oxidized soil conditions and microbial enzymes, with the rate of nitrification related to the concentration of NH_3 or NH_4^+ in the soil. Thus, soil pH and temperature affect nitrification in soils (Anderson and Boswell, 1964). Additionally, nitrification has been shown to be dependent upon soil water content and oxygen (O_2) levels (Schmidt, 1982). Optimal soil conditions for nitrification to occur are at soil temperatures of 30-35°C, oxygen levels in the soil of 20%, and soil moisture content near field capacity (Sahrawat, 2008).

The process of nitrification transforms the most reduced form of soil N, NH_3, into the most oxidized form of soil N, NO_3^-. The two inorganic forms are often the controlling factor for nitrification in soil environments. Although NH_4^+ (or NH_3) and NO_3^- are plant available forms of N, NO_3^- is more mobile due to its negative anionic charge and solubility in water. Nitrate has a reduced potential for adsorption to negatively charged soil particles, such as clay textured soils and SOM. Positively charged ammonia ion particles (NH_4^+) are retained in negatively charged soil matrices and are less vulnerable to leaching into groundwater and loss through surface water. Nitrate leaching from global agriculture production was estimated to be about 19% of total N applied (Lin et al., 2001). Claypan soils are poorly-drained and this limits vertical movement of NO_3^-, but potentially results in greater N loss through soil N_2O emissions by denitrification.

Denitrification

Denitrification is the multiple step biochemical reduction of NO_3^- to $N_{2\ (g)}$ under anaerobic conditions. Denitrification is the only point in the N cycle where fixed N reenters the atmosphere as N_2. The process occurs when NO_3^- is used as an alternative terminal electron acceptor for O_2 to gain energy during respiration under conditions of oxygen limitation (Knowles, 1982). Oxygen depletion occurs in waterlogged soil conditions where gas diffuses 10,000 times slower in water compared to air (Geigenberger, 2003). Denitrification loss and subsequent release of N_2O is typically greater with increased soil moisture and soil temperature (Sexstone et al., 1985). Generally, soils containing 60% of water filled pore space begin to undergo denitrification (Groffman and Tiedje, 1988). Complete reduction of NO_3^- to N_2 starts with NO_3^- or NO_2^- as the initial substrate and yields N_2O and N_2.

$$2NO_3^- \rightarrow 2NO_2^- \rightarrow 2NO \rightarrow N_2O_{(g)} \rightarrow N_{2(g)} \tag{4}$$

The first step in denitrification is the reduction of NO_3^-, which is catalyzed by through nitrate reductase (NAR) (van Spanning et al., 2007). Next, NO_2^- is reduced to nitric oxide (NO) and is catalyzed by two different types of nitrite reductases (NIR). One is a metalloprotein containing copper and the other is heme protein that contains c- and d-type cytochromes (Ferguson et al., 2007). Nitric oxide is further reduced to N_2O by the enzyme nitric oxide reductase (NOR), which N_2O is then reduced to $N_{2\ (g)}$ by nitrous oxide reductase (NOS) during the last step of denitrification (van Spanning et al., 2007).

Denitrification is a sequential process and substrate dependent. When a substrate is lacking (i.e., soil NO_3^-), denitrification can experience delays before the next reduction step (Roberston and Groffman, 2015). Reduction steps of denitrification may undergo lag times that persist for multiple hours and can cause N_2O to be released into the atmosphere as a byproduct (Robertson and Groffman, 2015). Enzymes degrade at different rates and respond to different environmental conditions. Denitrification is carried out by a broad assortment of microorganisms belonging mostly to the prokaryotic families (Philippot, 2005). Some microorganisms possess the whole set of enzymes and are capable of completing the entire denitrification process, whereas others do not have the genes capable for a full denitrification pathway (Zumft, 1997). Consequently, N_2O is potentially released during denitrification. Nitrous oxide formation is a required intermediate step for denitrification and is a potential endpoint of the process (Anderson and Levine, 1986).

In addition to soil water content, temperature, and O_2, denitrification is also regulated by the amount of available carbon and NO_3^- in the soil. The oxidation of carbon is source that can serve as an electron donor for denitrifiers that ultimately reduce NO_3^- so ATP can be synthesized (Mahne and Tiedje, 1995). Nitrate is important because it serves as the main electron accepter when conditions are O_2-limited. The amount of NO_3^- in the soil is dependent upon fertilizer input, rainfall, and preliminary N transformations including nitrification. Poorly-drained claypan soils have persistent saturated conditions in wet growing seasons so NO_3^- loss becomes even more of a limiting factor. In wet soil conditions, denitrification occurs closer to the soil surface where there is sufficient O_2 for nitrification that allows nitrifiers to oxidize NH_4^+ to NO_3^- using O_2 as electron acceptor (Robertson and Groffman, 2015). This is present in urea-based fertilizers because urea undergoes urea hydrolysis and nitrification, which is followed by the bacterial oxidation into NO_3^-.

Soil pH has also been observed to affect denitrification rates and the N_2O/N_2 ratio. Optimal soil pH is 7 to 8 for denitrification to occur (Simak and Cooper, 2002). Similarly, Bergsma et al. (2002) observed that a soil pH above 6 lowers the proportion of N_2O/N_2, resulting in a rapid and complete reaction of denitrification. Soil pH values below 6 and above 8.5 have been shown to have a greater N_2O/N_2 ratio (Simak and Cooper, 2002).

Vulnerability of Missouri Claypan Soils to N Loss and Implications of Rainfall Distribution on N Transformations

Properties of Claypan Soils

Claypan soils are characterized by a subsoil layer that is located 20 to 40 cm below the soil surface and has at least a 100% higher clay content than the horizon directly above it (Myers et al., 2007). A claypan soil has a dense, compact layer in the subsoil that has the potential to create saturated soil conditions that negatively affect crop production. Restrictive clay properties of the subsoil reduce the flow of water, which creates a poorly drained environment (Jung et al., 2006). Claypan soils are prevalent in the Midwestern, United States, accounting for an area of about 4 million hectares (Anderson et al., 1990). This area includes parts of Missouri, Kansas, and Illinois where claypan soils dominate the subsoil making conditions difficult for corn production. The low permeability of claypan soils makes it susceptible to waterlogged conditions following a rainfall event (Kaur et al., 2017). Waterlogged conditions in these soils can subsequently create ideal conditions N loss via denitrification (Zurweller et al., 2015). The environmental and climatic conditions in Missouri causes a high potential for denitrification loss due to high air temperatures and extended periods of saturated soils

(Nash et al., 2015). This is common early in the growing season when plant N uptake is low and the rate of evapotranspiration is exceeded by rainfall. Saturated soil conditions reduce the amount of NO_3^- leaching, but it can potentially result in higher soil surface N_2O emissions. Nash et al. (2012) observed 2 to 4% loss of applied fertilizer N as N_2O gas from a claypan soil. Applied N fertilizer is also lost in a claypan soil through runoff and other forms of N gas emissions (i.e., ammonia volatilization), but the relative N loss among different N processes varies due to the distribution of rainfall and other management and environmental factors.

Rainfall Distribution's Impact on Nitrogen Use Efficiency

The Midwest region of the United States can experience high intensity rainfall events that reduce corn production. It is estimated that the Corn Belt region of the Midwest averages $600 million per year of possible crop production loss due to excessive soil moisture from extreme rainfall events and could double by the year 2030 (Rosenzweig et al., 2002). Corn is often susceptible to the consequences of high soil saturation from extreme rainfall events particularly early in the growing season. Extreme precipitation events are expected to increase during the months of March to May, putting corn production at even a greater risk (Rosenzweig et al., 2002; Patricola et al., 2012). Additionally, air temperature is expected to increase by 3% by the year 2050 (Lobell, 2007).

Claypan soils in Missouri are especially vulnerable to N loss depending on the distribution and amount of rainfall. Excessive soil moisture can lead to environmental N loss, which in turn affects crop production. The majority of environmental N loss occurs through ammonia volatilization, denitrification, and lateral movement of N in the soil

(Wilkinson et al., 2000). However, the claypan layer's low water permeability limits vertical drainage in the subsoil and the potential for NO_3^- leaching. Urea-based fertilizers must first be converted to NO_3^- through urea hydrolysis and nitrification before denitrification N loss occurs. Therefore, soil microbial N transformations and ensuing N loss can be affected by the magnitude and timing of soil wetting and drying cycles. Extended soil wetting and drying cycles enhance aerobic conditions that are favorable for nitrification and anaerobic conditions that are required for denitrification to occur (Alukah et al., 1991). When an aerobic soil becomes anaerobic, there are changes in the activities of denitrifying reductases (Smith and Tiedje, 1979). Nitrous oxide reductase availability is unstable in dry soil conditions and cannot be produced by denitrifiers until saturated and low O_2 soil conditions exist (Bergsma et al., 2002). Rainfall accumulating on a dry soil will result in an increase in the molar fraction of N_2O/N_2 compared to the same soil when it is wet (Groffman and Tiedje, 1988). The proportion of N_2O/N_2 is greatest immediately after a heavy rainfall where the soil was previously dry due to the absence of NOS in dry soils (Bergsma et al., 2002). After one to two days, N_2 replaces N_2O as the major end product because NOS increases (Firestone and Tiedje, 1979; Smith and Tiedje, 1979). The magnitude and timing of rainfall can determine denitrification and NOS activity, which greatly affects N loss as N_2 or N_2O.

Leaching and runoff are two other N loss mechanisms that reduce N use efficiency. Both NO_3^- leaching and runoff depend on the amount and timing of rainfall events. Rainfall influences soil water content and substantial N loss may occur when soil water content is high. Nitrate or urea forms of N fertilizer can move vertically through the soil and is greatly enhanced by rainfall. Rainfall prior to surface application of urea fertilizers may positively impact crop production because it reduces the potential for volatilization that typically occurs on the soil surface (Jantalia et al., 2012). Both urea and NO_3^- are water-soluble and will move through the soil (Magdoff, 1991). Intense water movement can cause N fertilizers to leach out of the rooting zone; therefore, N is unavailable for plant uptake and could ultimately reach groundwater sources (Drury et al., 1996). Cation exchange sites mostly hold ammonium forms of N fertilizers in soil organic matter or clay-textured soils and, therefore, the ammonium is lost subject to leaching loss. Flooded soil conditions from heavy rainfall events can move N fertilizers laterally on the soil surface and result in substantial N loss through runoff (Nelson et al., 2009). Most N fertilizers rely on gentle amounts of rain after application to move the N in the soil for plant uptake. However, too much rainfall can cause N loss and decrease crop production if N fertilizer is not carefully applied.

Agricultural Management Factors Affecting Soil Nitrous Oxide Emissions

Nitrogen Fertilizer Placement

Nitrogen fertilizer placement methods can impact soil N loss through N_2O emissions. Placement of N fertilizer and its impact on soil N_2O emissions differs as to the location of the fertilizer placement and the method used for the placement (Nash et al., 2012). Placement of fertilizer can differentiate in soil location such as surface applied or at various depths in the soil. The placement of N fertilizer can be broadcasted across the field or banded in concentrated zones. The main difference between broadcasting and banding fertilizers is the amount of surface area covered with broadcasting fertilizer. Broadcast application of N fertilizer results in more uniform surface coverage of the N applied, but banding N fertilizer increases the potential for plant roots, especially early in the growing season, to utilize the applied N. Corn root access to available N in the growing season can also depend on placement depth of banded fertilizer (Johnson et al., 2016). Research has shown different results in cumulative and daily soil N_2O emissions comparing broadcasted compared to banded N fertilizer. Moraghan et al. (1984) observed a 6% decrease in N loss with banded urea fertilizer compared to surface-applied. Wetselaar et al. (1972) observed that banding N fertilizer reduced soil N_2O emissions compared to other treatments. Hultgreen and Leduc (2003) reported 51 to 65% greater emissions of N_2O from broadcasting over mid-row placement of urea. One study suggests that banding N fertilizer within the soil profile can reduce the rates of nitrification and denitrification, thereby lowering the total amount of N fertilizer lost as N_2O (Grant et al., 2010).

Placement of N fertilizer in bands may be applied to the soil surface or into the soil at different depths ranging from shallow (2 cm) to deep (10-20 cm). Drury et al. (2006) showed less soil N_2O emissions when banding N fertilizer at 2 cm compared to 10 cm. Nash et al. (2012) reported a decrease in soil N_2O emissions with urea banded at 20 cm compared to when it was surface-applied. Khalil et al. (2009) found cumulative soil N_2O emissions to decrease 35 and 77% with a urea placement depth of 5 and 7.5 cm, respectively. Gao et al. (2015) found that double midrow-banding urea reduced soil N_2O emissions compared to broadcast-incorporated (2.5 cm) when soil conditions were conducive for emissions (i.e., high soil moisture and temperature).

Application of N fertilizers deep in the soil profile may have reduced soil temperature and SOM levels compared to surface applications. Deep placement results in lower microbial activity and potentially lower soil N_2O emissions (Grant et al., 2010).

However, results of banding N fertilizer to reduce soil N_2O emissions are not conclusive. Other studies did not find any advantage of banding over broadcasting N fertilizer (Fox et al., 1986; Raun et al., 1989). Venterea et al. (2010) suggested that deep banding can increase soil N_2O emissions due to higher soil NO_2^- with this application method. Engel et al. (2010) observed broadcasting urea on the soil surface has less N_2O emissions than banding urea. Deep placement of urea in a concentrated band has shown to increase soil pH and reduce the rate of nitrification causing an increase in soil NO_2^- levels and N_2O emissions (Venterea et al., 2012; Tao et al., 2015). Surface applied urea has a greater potential for loss to the air as NH_3 compared to placement within the soil profile. Consequently, deep N fertilizer placement can result in more loss as N_2O compared to when the fertilizer is surface-applied when more loss may occur as NH_3.

Overall, deep placement of N may reduce soil N_2O emissions but site-specific factors need to be considered for agricultural management decisions. Different environmental and soil conditions can result in microbial N transformations impacting soil N_2O emission. The diverse research results that are found in the literature reinforce the need for a continued analysis of the impact on N fertilizer placement and soil N_2O emissions in order to improve management objectives.

Nitrification Inhibitors

Urea is the dominant fertilizer N source consumed globally, representing 57% of total fertilizer N consumption (Bierman et al., 2011). The use of urea as an N source for corn production can contribute to soil N_2O emissions. Reducing the amount of urea and overall N fertilizer inputs for agriculture is not a practical solution to mitigate soil N_2O

emissions because it will probably lower crop production. A decrease in crop yields puts global food security at risk even though it has potential to decrease soil N_2O emissions.

Many researchers have demonstrated that incorporating urea fertilizer with nitrification inhibitors (NIs) can mitigate soil N_2O emissions (Abalos et al., 2014; Halvorson et al., 2014; Yang et al., 2016). Nitrification inhibitors function by directly limiting the rate of NH_4^+ oxidation into NO_2^- during nitrification, and subsequently decrease the substrate (NO_3^-) concentration for denitrification (Zerulla et al., 2001). The conversion of NH_4^+ to NO_3^- is usually blocked by ammonia monooxygenase, an enzyme produced by *Nitrosomonas* bacteria, permitting a readily available N form to plants (NH_4^+) that is stable in the soil and reducing N loss to denitrification and leaching. Several studies show NIs to be effective in reducing soil N_2O emissions. Misselbrook et al. (2014) observed a mean reduction of 69% N_2O emissions with urea combined with a NI. Bronson and Mosier (1993) reported that NIs applied with N fertilizer decreased soil N_2O emissions by 43 to 71% over the growing season. McCarty et al. (1990) showed a decrease in nitrification by 85% and 65% after a period of 14 and 28 days, respectively. Another study observed a reduction of 81 to 83% of N_2O emissions when urea was combined with a NI with no effect due to fertilizer rate (Khalil et al., 2009). However, one study reported NIs reduced N_2O emissions by 20 to 60% over cropping phases but soil N_2O emissions increased after harvest (Scheer et al., 2017).

Nitrapyrin (2-chloro-6-(trichloromethyl)-pyridine, trade name N-serve or Instinct) is the commonly used NI in the US (Wolt, 2004). Nitrapyrin has shown to be effective in environments to inhibit nitrification and reduce soil N_2O emissions in many studies (Burzaco, et al., 2013; Vyn and Omonode, 2013). Compared to urea alone, one study observed urea with the addition of nitrapyrin to be more effective in controlling the nitrification process and retaining more NH_4^+-N in the soil (Liu et al., 2017). A meta-analysis covering 13 site-years of research where corn was the primary crop showed a 51% reduction in soil N_2O emissions when using nitrapyrin (Wolt, 2004). Performance of NIs was best established for corn production because corn requires a high amount of N and is frequently grown on soils with high N loss potential (i.e., claypan soils).

The overall effectiveness of nitrapyrin and other NIs can depend on a number of environmental factors. Generally, the effectiveness of nitrapyrin can be linked to soil temperature. High soil temperatures can initiate microbial activity and N loss through volatilization (Slangen and Kerkhoff, 1984). However, nitrapyrin has been shown to be effective at temperatures as high as 35 °C (Ali et al., 2008). Nitrapyrin also shows a high potential to sorb to soil organic matter (Touchton et al., 1979; Wolt 2000). Soil organic matter can provide an energy source to microorganisms, which degrade nitrapyrin, thus preventing the ability for nitrapyin to inhibit nitrification (Goring, 1962). The effectiveness of NIs can be improved through crop management decisions (i.e., crop residue control), but it is often difficult to control because of complex interactions among soil and environmental factors (i.e., rainfall). Continued research on NIs combined with fertilizer sources on different soil types needs to be conducted to have an appropriate understanding effectiveness of NIs.

Alternative Management Factors Effect on Corn Yield

Timing and Rate of Nitrogen Application

Methods of N fertilizer application can vary on timing and the amount of N that is applied for corn production. Proper timing and distribution of N fertilizer application can result in increased yields, increased plant N uptake, and reduced N loss to the environment. In general, reducing the amount of N fertilizer will lower crop yields so it is not a common management decision to utilize this method unless the N fertilizer source that is used has higher N use efficiency. Ideally, the amount of N fertilizer that is applied to agricultural crops should be removed in crop harvest. However, crop N use is regularly inefficient and only about 50% of added N fertilizer is removed in annual grain crop harvest (Robertson, 1997).

Synchronizing N fertilizer application and soil N availability with the patterns of crop N uptake over a growing season may optimize N use efficiency. Crop N uptake is usually low at the beginning of the season, high during the growing stages, and low again at crop maturity. An optimal single N application timing for corn is common in the spring when planting takes place over the fall because less N loss may occur in the time between application and plant N uptake. If N is applied too early before the plants needs it, then a significant amount of N may be lost before the crop takes it up through leaching, volatilization, and denitrification (Balkcom et al., 2003).

In theory, split application of N should result in increased N efficiency and reduced N loss, but literature supporting this concept is inconclusive (Binder et al., 2000; Walsh et al., 2012). Research has historically focused on of the differences between spring and fall N application on corn growth. Pearson et al. (1961) observed spring-applied N to be twice as effective in producing corn as fall-applied N in Alabama, Georgia, and Mississippi. A study in Illinois found spring N application of ammonium nitrate produced higher corn yield than fall N application (Welch et al., 1971). A five-year study on a clay loam soil in Minnesota averaged 8% lower corn yields for fall N application of ammonium sulfate compared to spring N application (Randall and Mulla, 2001). The same study observed less N loss as NO_3^- for spring treatments compared to fall treatments. Another study on a clay soil compared spring and fall N application using ammonium nitrate, urea, and anhydrous ammonia fertilizer sources and found corn grain yields to be 0.37 to 2.6 Mg ha^{-1} higher in all spring applications (Stevenson and Baldwin, 1969). Although, significant increases in corn yield do not occur every season, fall applications of N had significantly lower yields when averaged over multiple seasons (Randall et al., 2003)

Weather has a major influence on plant N uptake and N loss, causing crop productivity to be unpredictable. Spring conditions in Missouri are often associated with heavy and intense rainfalls making spring N application inefficient for crop productivity. Fall is typically drier than spring and offers more flexibility to perform field operations. Spring field operations have little margin of opportunity because planting and fertilizer applications typically occur simultaneously and must be performed in a short time period, otherwise farmers can face economic losses (Scharf et al., 2002). Wet field conditions associated with wet springs can delay field operations and impact crop yields. However, fall application is seldom superior to spring application. The dry and cold period associated with fall application is beneficial because most nitrifying microorganisms are inactive below 10 °C and which allows a better chance for N to be present in the soil for plant uptake next year (Sabey et al., 1956).

Nitrogen Fertilizer Placement

In order to maximize yields and reduce N loss through optimal N placement, sufficient amounts of plant available N should be produced through chemical and microbial N transformations in the soil. Placement strategies, such as broadcasting uniformly over the soil surface or banding shallow or deep in the soil profile, can influence soil microbial activity, chemical reactions, and N loss potential. Placing N fertilizer in the soil profile and near the zone of root uptake may increase plant N uptake and nitrogen use efficiency (CAST, 2004). Placement options can be limited by N fertilizer source (i.e., injected anhydrous ammonia) and combining placement with source is an appropriate method to compare specific treatments on corn yields. Touchton and Hargrove (1982) determined that surface broadcast application of UAN was reported to produce less grain yield and N uptake compared with surface or incorporated band placement in corn. Conversely, UAN applied in a deep band was found to increase yields (Halvorson et al., 2006). A study in a poorly-drained claypan soil found that deep banded urea had at least 10% higher yields compared to surface applied and shallow banded (Johnson et al., 2016). Additionally, Nash et al. (2013) indicated that strip-till, deep banding urea notably enhanced corn yields 1.57 to 5.4 Mg ha^{-1} compared to a no-till, surface broadcast application. Anhydrous ammonia injected into the soil increased corn yields compared to broadcast incorporated applications of urea (Noellsch et al., 2009). These results may be linked to a decline in microbial activity involving N transformations (i.e., urea hydrolysis, ammonia volatilization, nitrification, and denitrification) leading to greater N uptake by the plant.

Some researchers found no difference in corn yields comparing surface broadcast and banding N fertilizer treatments. Raun et al. (1989) showed no differences in corn grain yields when comparing surface-applied urea and deep-placed anhydrous ammonia. Additionally, Fox et al. (1986) did not find an advantage with band placing N fertilizer compared to surface broadcast. Although deep band placement of N fertilizer may conserve N, there might be spatial and temporal shortages of N after deep band application because N may be spatially separated from roots or may not be in a plant-available N form at the appropriate time (Shapiro et al., 2016). In addition, high rates and concentration of N within close proximity of the seed row may increase the potential for salt toxicity (Gerwing et al., 1996) and possibly resulting in lower crop yields.

Conventional and Enhanced Efficiency Nitrogen Fertilizers

Nitrogen fertilizer is extremely important for crop production and many N sources are available for use in the marketplace. Urea, urea-ammonium nitrate, and anhydrous ammonia are all traditional N fertilizers used for corn production (Millar et al., 2010). Increases in corn yield production are not necessarily determined by selection of these conventional fertilizers, but is largely dependent on the ability to provide plant available forms of N (NH_4^+ and NO_3^-) in sufficient concentrations in synchrony with plant N demand. The amount of N available for plant uptake over a growing season depends on several factors including soil conditions, application timing, and N placement. Furthermore, these factors are influenced by regional climate and site-specific weather patterns which can significantly affect microbial N transformations and the ensuing forms of plant available N.

Urea is the most popular source of N fertilizer in the world and accounts for the majority of fertilizer sales due to its relatively high N content (46%), ease of handling, and reasonable price (Bouwman et al., 2002). Urea is synthesized from ammonia and carbon dioxide making it the only primary N product chemically classified as organic. Urea is commonly applied as a solid granule, but it can also be formulated with other chemicals to make liquid N fertilizer products or other forms. Urea-ammonium nitrate (UAN) is liquid N product that contains 28 to 32% N and is often sprayed on the surface or injected below the soil surface. Urea is very soluble in water making it susceptible to weather conditions that cause N loss. Saturated soil conditions triggered by intense rainfalls make it easy for urea to be leached laterally and vertically through the soil profile. However, concerns over urea-based fertilizers are centered on its susceptibility to gaseous N loss due to its solubility (Drury et al., 2009; Nash et al., 2012). The magnitude of ammonia volatilization from soil depends on a number of environmental factors and management practices. Management decisions should focus on maximizing efficiency by controlling the rate of urea hydrolysis to limit NH_3 volatilization. Surface application of urea is one management practice that increases the amount of NH_3 lost to the atmosphere (Sommer et al., 2004). Incorporating urea at a shallow depth in the soil can reduce the rate of urea hydrolysis and N loss as NH_3. Surface-applied urea typically relies on rainfall after application to incorporate urea in the soil. Urease enzymes are largely present on crop residue on the soil surface so it is critical to incorporate urea into areas with little microbial activity occurring. Urea-ammonium nitrate is subject to the same reactions as urea fertilizer, but the potential for volatilization is theoretically less because urea makes up only half of the material in UAN.

Anhydrous ammonia (AA) is another N fertilizer product that is popular for corn production. This source is often the least expensive of N products and has the highest percent N by weight (82%) compared to other N sources. Although relatively cheap as a product, risks of handling and field application of anhydrous ammonia can be a drawback. Anhydrous ammonia must be stored as a pressurized liquid until application when it turns into a gas. This requires special application equipment and safe-handling procedures because it must be injected into the soil. Humans and other living organisms are at risk in the event the gas escapes into the air. When AA is released into the soil, it readily combines with water in the soil to form ammonium ions. The ammonium ions tend to remain in the soil for longer time periods compared to other sources of ammonium (i.e., UAN). Loss of AA as NH_3 at the time of application is dependent on the moisture content of the soil, soil texture, amount of organic matter, and depth of application (Sommer and Christensen, 1992; Hanna et al., 2005). Increasing retention time and minimizing loss of NH_3 in the soil can be linked to increasing plant N uptake and corn yields. Many studies have reported increases in corn yields using AA application compared to other N fertilizer treatments. Stehouwer and Johnson (1990) performed an eight-year study in Ohio where they observed AA to produce higher corn yields and percent ear-leaf N than urea treatments. Noellsch et al. (2009) found AA increased corn grain yields and N uptake over urea treatments on a claypan soil. In order to improve effectiveness of N fertilizer treatments, timing of application must be considered with different N sources.

Enhanced efficiency products are intended to minimize N loss and potentially improve the synchrony of inorganic N sources in the soil and plant N demand. Nitrification inhibitors (NIs) are a type of enhanced efficiency product that is commonly applied with N fertilizers to potentially increase grain yield and improve NUE. Nitrification inhibitors act on *Nitrosomonas* bacteria to slow the conversion of NH_4^+ to NO_2^-. Nitrification inhibitors are chemical compounds that restrict, delay or slow down the nitrification process, thereby reducing losses of nitrate before plants satisfy their N fertilizer needs (Zerulla et al., 2001). Previous literature shows NIs to reduce soil N_2O emissions, but NIs also can significantly increase corn yields and NUE. Gagnon et al. (2012) reported increases in grain yield from 0.3 to 0.6 Mg ha^{-1} using a NI in comparison to conventional urea in wet years, but no significant increase with NI during a dry year. Hendrickson et al. (1978) found that following a fall application of anhydrous ammonia, 53% of the recoverable N was ammonium-N with nitrapyrin compared to 11% ammonium-N without nitrapyrin. Studies show differences in crop yields when N source is applied at pre-plant or fall applications with and without the use of a nitrification inhibitor. Fall application of AA with nitrapyrin increased corn grain yields over fall applied AA without a nitrification inhibitor (Stehouwer and Johnson, 1990). Another study by Randall et al. (2008) conducted in Minnesota over seven years concluded fall application of AA combined with nitrapyrin had 0.94 Mg ha^{-1} more corn yield than fall applied AA alone and 1.7 Mg ha^{-1} more for spring applied AA compared to fall applied AA. Ferguson et al. (2009) showed no increase in corn grain yield when utilizing UAN with nitrapyrin compared to other urea treatments, but their results were affected by heavy rainfall that occurred during the growing season. Nitrification inhibitors can be inconsistent due to variability that leads to leaching, volatilization, and denitrification losses in different soils.

A recently developed enhanced efficiency N additive is the slow release liquid fertilizer called Nitamin Nfusion (NF) (Koch Agronomic Services, Wichita, Kansas). The product is 22% N with 94% in the slowly available form of urea polymers including methylene urea and triazine and the remaining 6% as urea. Nitamin Nfusion can be converted to plant available forms by soil microbes over a period of 60 to 90 days. The product is completely water-soluble and can be blended with UAN, liquid urea, and other solutions at different ratios allowing for flexibility. Several slow-and controlled-release N fertilizers have been observed to minimize N losses and improve the synchronization of N release and plant demand (Nash et al., 2013; Halvorson and Bartolo, 2014; Sistani et al., 2014). There is a lack of research studies that have investigated the effects of Nitamin Nfusion on corn grain yield. In a study by Shapiro et al. (2016), mixing NF at a 30:70 ratio (% N basis) with UAN increased corn grain yields 4% and N uptake 7% compared to broadcast UAN. Generally, research has shown enhanced efficiency N products to be effective; however, enhanced efficiency N products do not always produce higher yields and their effectiveness depends on plant N demand, soil conditions, and weather.

Research Objectives

1. Determine the effectiveness of different N fertilizer placement practices including deep banding urea or urea plus a nitrification inhibitor on corn yields and N use efficiency in a poorly-drained claypan soil.
2. Assess the differences in cumulative soil nitrous oxide gas emissions with deep banding and other N fertilizer placement strategies.
3. Determine the effect of two timings (spring and fall), five source-placements, and three rates of enhanced efficiency liquid N source applied on corn response.

Hypotheses

i. Deep-banded urea fertilizer with a NI will reduce cumulative soil GHG emissions compared to other treatments.

ii. Deep banding urea fertilizer with a NI will increase corn production.

iii. Deep-banded UAN with Nitamin Nfusion will increase corn grain yield compared to other treatments, regardless of N timing.

Arrangement of the Thesis

This thesis contains three research chapters which have been organized in a standard research journal format. All chapters provide corn production results of field experiments conducted at the Greenley Memorial Research Center near Novelty, MO. Chapter two also includes soil greenhouse gas emissions (N_2O and CO_2) data collected from a portion of the corn production experiment described in chapter three. Chapter four discusses alternative N management placement, and timing strategies to increase corn production. A final concluding chapter is added to provide overall conclusions of the thesis research.

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CHAPTER 2

FERTILIZER PLACEMENT EFFECTS ON SOIL NITROUS OXIDE EMISSIONS IN A CLAYPAN SOIL

ABSTRACT

Adoption of nitrogen (N) management strategies to minimize soil N_2O emissions from agriculture while maintaining high yield production is increasingly important for an growing population. Agricultural management on poorly-drained claypan soils in the Midwestern U.S. make corn (*Zea mays* L.) production even more challenging due to the subsoil's low permeability, which may result in wetter soil conditions and relatively large amounts of soil N_2O emissions during the growing season. The objective of this study was to determine the effects of urea fertilizer placement with and without the inclusion of a nitrification inhibitor (NI) on daily and cumulative soil N_2O emissions, and the amount of N_2O release per unit of grain produced. Treatments included urea deep banded at a depth of 20 cm (DB), urea deep banded at 20 cm plus nitrapyrin (2-chloro-6-(trichloromethyl) pyridine) at 0.51 kg a.i. ha^{-1} (Instinct II®, Dow AgroSciences, Indianapolis, IN) (DB+NI), urea incorporated after a surface broadcast application at a depth of approximately 8 cm (IA), urea broadcast surface applied after incorporation (SA), and a non-fertilized control (NC). Fertilized treatments were applied at 202 kg N ha^{-1} during both growing seasons (2016 and 2017). Soil N_2O emissions generally lower (<50 g N_2O-N ha^{-1} d^{-1}) during the first three weeks after N fertilization and latter parts of the growing season in 2016 and 2017. When averaged across the 2016 and 2017 growing seasons, all fertilized treatments had significantly ($P < 0.05$) greater (2.33 to 5.60 kg N_2O-N ha^{-1}) cumulative soil N_2O emissions than the non-fertilized control. Deep-banded

urea with nitrapyrin had 54 and 55% lower cumulative soil N_2O emissions than IA and SA treatments, respectively. High precipitation, soil temperature, and soil water content during the early and mid-growing season can be associated with soil N_2O peaks in fertilized treatments. Deep-banded urea with a NI had similar soil N_2O emissions per Mg of grain produced compared to NTC in 2017. These results suggest that deep-banded urea with or without a NI is an effective management strategy for reducing cumulative soil N_2O emissions over the growing season.

INTRODUCTION

Greenhouse gas emissions from agriculture have increased about 8% since 1990 (USEPA, 2017). While carbon dioxide (CO_2) and methane (CH_4) have contributed to a majority of GHG emissions, N_2O is of concern because it has a global warming potential 298 times higher than carbon dioxide (CO_2) and 12 times greater than methane (CH_4) (Forster et al., 2007). Increased use of synthetic N based fertilizers on agricultural soils has caused agriculture to be the largest source of N_2O emissions in the U.S., accounting for about 75% of total U.S. N_2O emissions in 2015 (USEPA, 2017). Future global N_2O emissions are projected to increase 35 to 60% by 2030 due largely to the projected increase in N fertilizer use and animal production (FAO, 2003). Nitrous oxide is a chemically stable and persistent stratospheric ozone depleting gas that has a residence time of 120 years before being removed by a sink or destroyed (USEPA, 2017). Thus, adopting management techniques to minimize soil N_2O emissions from agriculture while maintaining high yield production is increasingly important for a growing population.

Efficient use of N may become more difficult to manage due to climate change causing more extreme weather events, such as higher intensity precipitation, and severe droughts (Rosenzweig et al., 2002). Claypan soils can make crop production far more challenging because of their poorly drained properties that make the soil susceptible for N_2O loss (Nash et al., 2012). Claypan soils are characterized by a subsoil layer that is located 20 to 40 cm below the soil surface and at least 100% higher clay content than the horizon directly above it (Myers et al., 2007). Claypan soils encompass an area of approximately 4 million ha across the Midwestern U.S. (Anderson et al., 1990). These poorly drained soils can have potentially long periods of saturation in the rooting zone that negatively affect crop production and increase N loss through runoff, leaching, and denitrification (Blevins et al., 1996; Drury et al., 2009).

Research has shown that incorporating N fertilizer in deep uniform bands within in the rooting zone rather than broadcasting on the soil surface may reduce gaseous N losses, increase plant N uptake, and increase yields (Malhi et al., 2001; CAST, 2004). Research on a poorly drained claypan soil has showed that deep banded placement of N fertilizer to a depth of 20 cm in a strip tillage system reduced soil N_2O emissions from 0.25 to 1.09 kg N_2O-N ha^{-1} and increased corn yields 8% compared to surface broadcast N application (Nash et al., 2012). Touchton and Hargrove (1982) determined that a surface broadcast application of UAN produced less corn yield and greater N_2O emissions than incorporated band placement in corn. However, deep N fertilizer placement does not always reduce soil N_2O emissions, and may cause spatial and temporal N shortages in the soil (Raun et al., 1989; Shapiro et al., 2016)

Several enhanced efficiency fertilizers products (e.g., controlled release fertilizers and nitrification or urease inhibitors) have been observed to improve the synchronization of N release and minimize soil N_2O emissions during the growing season (Nash et al., 2012; Halvorson and Bartolo, 2014; Sistani et al., 2014). Nitrification inhibitors function by directly limiting the rate of NH_4^+ oxidation into NO_2^- during nitrification, and subsequently decrease the substrate (NO_3^-) concentration available for denitrification (Zerulla et al., 2001). Misselbrook et al. (2014) assessed urea fertilizer combined with a NI reduced soil N_2O emissions by 69%. Khalil et al. (2009) observed a reduction of 81 to 83% of N_2O emissions when urea is combined with a NI, regardless of N rate. A meta-analysis covering 13 site-years of corn showed a 51% reduction in soil N_2O emissions for treatments using the nitrification inhibitor nitrapyrin [2-chloro-6-(trichloromethyl)-pyridine] (Wolt, 2004). Burzaco et al. (2013) observed nitrapyrin combined with urea-ammonium nitrate (UAN) reduced yield-scaled N_2O emission by 22% than UAN without nitrapyrin. In Indiana, nitrapyrin with a sidedress N application had a 35% reduction in soil N_2O emissions (Omonode and Vyn, 2013).

Despite numerous studies finding reductions in soil N_2O emissions from enhanced efficiency fertilizers, there are several soil and climatic factors that affect the primary processes involved in N_2O production. Air and soil temperature was correlated with soil N_2O emissions, but it was at a non-linear rate (Smith et al., 2003). Soil moisture, expressed as either soil water content or water-filled pore space (WFPS), is another primary controlling factor that influences denitrification and subsequent N_2O emissions (Linn and Doran, 1984). Other soil factors affecting soil N_2O emissions include soil pH (Van den Heuvel et al., 2011) and soil available carbon (Drury et al., 1991).

Minimal research has been conducted to observe the effects of N fertilizer placement including deep banding urea with or without nitrapyrin in a poorly-drained claypan soil. However, deep banding urea with nitrapyrin may be an effective practice to reduce soil N_2O emissions in poorly-drained claypan soils. The objectives of this study were to determine the effects of urea fertilizer placement including deep banding urea with and without an NI in a poorly-drained claypan soil on daily and cumulative soil N_2O emissions and the amount of N_2O released per grain yield.

MATERIALS AND METHODS

This research was conducted in 2016 and 2017 at the University of Missouri Greenley Memorial Research Center (40°1’17” N, 92°11’24.9” W) in Northeast Missouri on a poorly-drained Putnam silt loam (fine, smectitic, mesic Vertic Albaqualfs). The claypan subsurface layer at this research location was as shallow as 31 cm and as deep as 50 cm (personal observation). Daily precipitation data were obtained from an automated weather station located on-site. The initial soil properties for each year (Table 2.1) were determined from analysis of soil samples taken at a 0-15 cm depth from the non-treated control plots in all replicates. Samples were taken using a stainless steel push probe with five subsamples plot^{-1}. All soil samples were air-dried and ground to pass through a 2 mm sieve. Initial soil samples were analyzed by the University of Missouri Soil and Plant Testing Laboratory (Columbia, MO) using standard soil testing protocols (Nathan et al., 2006).

Two different field locations at the Greenley Memorial Research Center were used for the 2016 and 2017 experiments. DeKalb 61-88 was planted following soybean (*Glycine max* L.) the previous year. Plots were 3 by 61 m. Corn was planted using a John Deere 7000 planter (Deere and Co, Moline, IL) with a 76 cm row spacing at 79,000 seeds ha^{-1} in 2016 and 82,000 seeds ha^{-1} in 2017. The experimental design was a randomized complete block with five replications of five treatments. Treatments consisted of a non-fertilized control (NC), and four N treatments at 202 kg N ha^{-1} applied at different depth-placements. Treatments included urea deep banded at 20 cm (DB), urea deep banded at 20 cm plus nitrapyrin (2-chloro-6-(trichloromethyl) pyridine) at 0.51 kg a.i. ha^{-1} (Instinct II®, Dow AgroSciences, Indianapolis, IN) (DB+NI), urea incorporated after a surface broadcast application at a depth of approximately 8 cm (IA), and urea broadcast surface applied after incorporation (SA). Planting and harvest dates as well as other management practices are listed in Table 2.2.

The urea deep-banded treatments were applied using a custom designed strip-till conservation C-jet unit (Lanpher, 2002). The DB and DB+NI treatments were banded below the planted row in 76 cm wide spacings. Fertilizer for deep-banded treatments was released using a Montag dry fertilizer air delivery system (Montag Manufacturing, Inc., Emmetsburg, IA). After the banded fertilizer application, the soil was surface tilled with a field cultivator (John Deere 1000, Moline, IL) to remove the potential effects of strip tillage on crop response. The SA treatment was applied after the field cultivator operation.

In-field measurements of soil N_2O flux were measured following the USDA-ARS GRACEnet chamber-based trace gas flux measurement protocol (Parkin and Venterea, 2010). A static ring chamber design was employed in the soil and chambers were constructed out of PVC pipe with detachable rubber PVC pipe caps. The PVC pipes were 22 cm high and had a diameter of 20 cm. Caps for the PVC chambers were fitted with a gas sampling port (Swaglok, bulkhead connector with a septa plug) and a vent port attached to an aluminum tube that was 10 cm in length with a 0.64 cm diameter designed for pressure stabilization while capped on the chambers.

Chambers were placed 8 cm in the soil with 14 cm of chamber remaining above the soil surface for a total volume of 5000 cm^3. The chambers were placed in the field a week after N fertilizer application and planting. Chambers were removed from the field a week before harvest. In plots containing deep placed banded urea with and without a nitrification inhibitor, two chambers were utilized to take N_2O measurements. There was one chamber directly above the band and planted row and one chamber in the center between the rows. Based on the relative proportion of the plot areas, it was estimated that the chamber over the row represented 33.3% of the N_2O flux and measurements from the chamber in between the rows represented 66.6% of the N_2O flux. A similar calculation for determining soil N_2O flux was utilized in other research measuring soil N_2O flux with deep-banded N fertilizer treatments (Nash et al., 2012).

Nitrous oxide gas samples were collected at t_0 (0 min), t_1 (30 min), and t_2 (60 min) after the chambers were capped. An ambient air sample was taken for each replication representing t_0. Gas samples were taken with a 20 mL syringe and injected into 5 mL vacuumed glass serum vials (Wheaton Science Products, Millville, New Jersey), which over pressurized the sampling vials as recommended in the GRACEnet protocol (Parkins and Venterea, 2010). Nitrous Oxide gas samples were analyzed using a gas chromatograph (GC) (Shimadzu, Kyoto, Japan) equipped with a ^{63}Ni electron capture device (ECD). Depending on the linearity of time vs. concentration N_2O flux data, either the algorithm by Hutchinson and Mosier (1981) or linear regression was utilized for calculating soil N_2O flux. The Hutchinson and Mosier algorithm was utilized for curvi-linear data and linear regression when appropriate (Parkin and Venterea, 2010). This data were used to calculate cumulative N_2O emissions over the growing season for the 2016 and 2017 growing season by linear interpolation and numerical integration using the trapezoid rule. The emission factor (EF) of N fertilizer-induced soil emissions was calculated using:

$$AE = \left(\frac{Cumulative\ emissions\ (Treatment) - cumulative\ emissions (Control)}{Nitrogen\ rate\ of fertilized\ treatment}\right) \text{ x } 100 = \%$$

In addition to N_2O gas sampling, soil samples were taken with a push probe 15 cm deep on each gas sampling date. The composite sample consisted of five subsamples for each plot and were retrieved from near each of the chambers at the time of sampling. The samples were analyzed for soil gravimetric water content and soil temperature in the plot of each replication. Soil temperature was measured using an Oakton Temp 10 thermocouple (Vernon Hills, Illinois).

Analysis of variance was performed using the SAS v9.4 statistical program (SAS Institute, 2015) and PROC GLM to determine the significant effects of treatment and year on cumulative soil N_2O emissions as well as N_2O emitted per Mg^{-1} of corn grain yield. Fisher's Least Significant Difference (LSD) at $P \leq 0.05$ was used to separate means and examine significant treatment and year effects.

RESULTS AND DISCUSSION

Weather and Soil Conditions

Cumulative precipitation for 2016 and 2017 were 562 mm and 508 m, respectively (Figure 2.1). The average ten-year precipitation amount from 2000 to 2009 during the growing season (from April through September) was 655 mm (University of Missouri Extension, 2017). Both seasons fell below the ten-year average by 14% in 2016 and 22% in 2017. Although total rainfall in the 2017 growing season was lower than 2016, early growing season rainfall was higher in 2017 compared to 2016. There was 126 mm of rainfall that occurred during the first three weeks of the growing season in 2017 compared to 49 mm in 2016. In 2017, cumulative rainfall in June was 122 mm higher than 2016 and was 35 mm higher than the ten-year average (125 mm). Cumulative rainfall in July was lower in 2017 (23 mm) compared to 2016 (116 mm). Cumulative rainfall in August for both years exceeded the ten-year average by 85 mm (70%) in 2016 and 22 mm (18%) in 2017.

The average air temperature in the 2016 and 2017 growing season was 20.2°C and 19.6°C, respectively (Figure 2.2). The average ten-year air temperature from 2000 to 2009 was 19.7°C over the growing season (University of Missouri Extension, 2017). In 2016, average air temperature was 5.5°C higher during the first two weeks of the growing season compared to the first two weeks of the growing season in 2017.

Soil gravimetric water content (Figure 2.3) and soil temperature (Figure 2.4) at a depth of 15 cm showed minimal differences between N treatments during field measurements of N_2O flux. Air and soil temperature over the 2016 and 2017 growing season during field measurements were similar. Higher precipitation in the early and mid-growing season of 2017 generally resulted in higher soil water content. In 2016, low precipitation in June resulted in low soil water content. Generally, lower total precipitation throughout the early growing season of 2016 resulted in less defined wetting and drying cycles compared to 2017. Higher total precipitation in July and August generally resulted in more extreme fluctuations of soil water content in 2016.

Daily Soil Nitrous Oxide Flux

Temporal variation in soil N_2O emissions followed similar trends in 2016 and 2017 (Figure 2.5). Soil N_2O emissions generally remained lower (<50 g N_2O-N ha^{-1} d^{-1})

during the first three weeks after N fertilization and latter parts of the growing season in 2016 and 2017. The first 3 weeks after fertilizer application in 2016 were characterized by low cumulative rainfall (<48 mm) and the following next 4-week period (5 May to 1 June) had a total of 108 mm (Figure 2.1). During this 4-week period, several soil N_2O peaks were observed in the treatments. The highest soil N_2O flux rate occurred on 26 May in the IA treatment (324 g N_2O-N ha^{-1}) in 2016. The IA treatment consistently had higher emissions during the early growing season. Soil N_2O flux rate in the SA treatment was generally lower than the IA treatment in the early part of the growing season and did not exceed the IA treatment flux rate until 1 June. In contrast, low soil N_2O flux rates were observed in the DB+NI treatment for a majority of the growing season up until the late part of the growing season in 2016. Soil N_2O flux rate in the DB+NI treatment was highest on 6 August, which totaled 91 g N_2O-N ha^{-1}. Late growing season flux observed in the DB+NI treatment suggested nitrapyrin kept soil NO_3^- concentrations or greater plant uptake occured during the early and mid-growing season, which decreased the concentration of NO_3^- substrate utilized for denitrification (Wolt, 2004; Liu et al., 2017),

Similar to 2016, soil N_2O flux rates in 2017 were highest during the middle parts of the growing season and remained lower during the middle and late growing season in 2017 (Figure 2.5). The highest soil N_2O flux rate during the growing season in 2017 occurred on 22 May in the SA treatment (319 g N_2O-N ha^{-1} da^{-1}). The highest N_2O flux rate for DB treatment (187 g N_2O-N ha^{-1}) also occurred on 22 May. Soil N_2O flux rate for the IA treatment was highest on 25 May (236 g N_2O-N ha^{-1} d^{-1}) and was 30 g N_2O-N ha^{-1} higher than the SA treatment. The second highest soil N_2O flux rate for the SA treatment occurred on 15 June (204 g N_2O-N ha^{-1} d^{-1}). The highest soil N_2O flux rate for the

DB+NI treatment in 2017 occurred on 30 June (106 g N_2O-N ha^{-1} d^{-1}). Emissions for all treatments were generally low (<80 g N_2O-N ha^{-1} d^{-1}) for the remainder of the growing season.

The peak in soil N_2O emissions that occurred on 15 June was in response to the precipitation event that occurred on 14 June (35 mm) after an 18-day period of no precipitation (Figure 2.1). High soil water content (~0.25 g g^{-1}) following the precipitation event coupled by a high soil temperature (~25 °C) could have initiated substantial microbial activity and N_2O production (Smith et al., 2003; Bateman and Baggs, 2005). Rainfall activity after the 18-day dry period (27 May to 13 June) may have further enhanced soil N_2O production because of the 18-day dry period in 2017 and the effect of wetting and drying cycles which are found to stimulate activity of nitrifying and denitrifying microbial populations in the soil (Hu et al., 2015). The soil N_2O emission peak detected in the first 24 h after precipitation is consistent with several previous studies where dry soil was rewetted (Norton et al., 2008; Beare et al., 2009; Guo et al., 2010). The greater degree of drying before rewetting of the soil has been linked to higher substrate (NO_3^-) concentrations and microbial pools of C in the soil (Davidson, 1992; Williams and Xia, 2009).

Cumulative Soil Nitrous Oxide Emissions

Cumulative soil N_2O emissions in fertilized treatments over the 2016 growing season ranged from 3.83 kg N_2O-N ha^{-1} in the DB+NI treatment to 7.76 kg N_2O-N ha^{-1} in the IA treatment (Figure 2.6). In 2017, cumulative soil N_2O emissions in the fertilized treatments ranged from 3.95 kg N_2O-N ha^{-1} in the DB+NI treatment to 8.43 kg N_2O-N ha^{-1} (Figure 2.6). Total soil N_2O emissions for fertilized treatments were higher than the total soil N_2O emissions of 2 to 3 kg N_2O-N ha^{-1} generally found in studies with controlled irrigation in dry climates (Venterea et al., 2010; Halvorson and Bartolo, 2014), further indicating the susceptibility of high N_2O emissions of poorly-drained claypan soils.

When averaged across the 2016 and 2017 growing seasons, cumulative soil N_2O emissions were significantly different ($P < 0.05$) among treatments (Table 2.3). All fertilized treatments had 2.33 to 5.60 kg N_2O-N ha^{-1} greater cumulative soil N_2O emissions than the non-fertilized control (Table 2.4). The IA and SA treatments had 2.09 to 3.27 kg N_2O-N ha^{-1} higher soil N_2O emissions than deep banding urea with or without a NI. No significant differences were observed between DB and DB+NI treatments. Although cumulative soil N_2O emissions were combined over years, data on the average cumulative N_2O emissions were reported separately for 2016 and 2017 (Figure 2.6).

The seasonal pattern of soil N_2O emissions observed is consistent with previous research in the Midwestern CornBelt region (Nash et al., 2012; Parkin and Hatfield, 2014; Fernandez et al., 2015). The rapid rise in cumulative soil N_2O emissions for IA and SA treatments shortly after N fertilizer application in 2016 and 2017 (Figure 2.6) may suggest that urea hydrolysis was rapid for both N management strategies, with the IA treatment's emissions sooner than SA in 2016. Nitrous oxide emissions for SA may have been more rapid in 2017 because of potentially greater amounts of N loss occurring via NH_3 volatilization in 2016; however, N fertilizer loss as NH_3-N can be reduced if fertilizer is banded or injected into the soil (Tomar and Soper, 1981). The majority of N loss from NH_3 volatilization urea sources typically occurs within the first two to three week period when urea is not properly incorporated by rain, irrigation, or tillage and when exposed to warm spring temperatures (Al-Kanani and MacKenzie, 1992). Field conditions in the first two weeks after N application in 2016 had a relatively warm air temperature (16.2°C) and low cumulative precipitation (26 mm) compared to 2017, indicating that site conditions may have been more susceptible to N loss via NH_3 volatilization. Differences in soil N_2O emissions for the IA and SA treatments were minimal in 2017 during the early part of the growing season, but occurred more rapidly compared to 2016, which could be due to higher total rainfall in the early part of the growing season.

Previous studies showed higher soil N_2O emissions following the application of N fertilizers in the spring and were all linked to early season rainfall (Glenn et al., 2012; Gao et al., 2013). Increases in soil N_2O flux also occurred after precipitation events in July and August of each year (Figure 2.3). Higher soil gravimetric water content was associated with soil N_2O peaks in 2016 and 2017, suggesting gaseous diffusion was restricted and O_2 concentration in the soil was low, which stimulated denitrification (Asgedom et al., 2014). The slow decline in soil water content in the mid-growing season months may have extended anaerobic respiration due to the poorly drained properties of the claypan soil (Zurweller et al., 2015). However, it is difficult to conclude reasons for peak soil N_2O emissions because of the naturally high variability of drainage in claypan soils (Nash et al., 2012).

Deep banding urea with nitrapyrin resulted in the lowest soil N_2O emissions in fertilized treatments in both 2016 and 2017 (Table 2.4). Compared with the SA and IA treatments, application of deep-banded urea with nitrapyrin reduced cumulative soil N_2O emissions by 45 and 46% in the two combined years. The effect of nitrapyrin in this study resulted in emissions reductions that were greater than the calculated nitrapyrin average reduction of 39% reduction as showed in one meta-analysis (Akiyama et al., 2010). Similarly, Omonode and Vyn (2013) found the banded nitrapyrin with UAN had a 44% reduction in soil N_2O emissions compared to sidedress-applied UAN. An irrigated corn study in Colorado found stabilized urea with urease and nitrification inhibitors (SuperU) had a 35% reduction in soil N_2O emissions and lower soil NO_3 levels than conventional urea during the 2-month period following N application (Halvorson and DelGrosso, 2012). The DB+NI treatment showed peaks in the late growing season in both 2016 and 2017 (Figure 2.5). The potential for NIs for reducing soil N_2O emissions is based on the premise of reducing the rate of NH_4^+ oxidation during nitrification, and subsequently decreasing the NO_3^- concentration for denitrification, resulting in potentially less N_2O production. However, results in our study showed deep-banded urea without a NI was equally as effective in reducing soil N_2O emissions as including nitrapyrin with deep-banded urea when combined over years.

Emission Factor and Nitrous Oxide Emitted Mg^{-1} Grain Yield

There were significant differences in emission factors among treatments in the combined growing seasons (Table 2.3). The IA and SA treatments had an EF (2.7 to 2.8%) that was higher than DB and DB+NI (Table 2.4). Deep-banded urea with nitrapyrin had the lowest EF (1.2%), but it was not significantly different than DB alone (1.7%). This shows that N treatments were slightly above the default factor of 1% estimated for annual application of N fertilizer by the IPCC (Pachauri and IPCC, 2008). However, EF values are shown to be variable and are largely influenced by N fertilizer's effect on soil pH and soil carbon availability (Decock, 2014; Shcherbak et al., 2014).

A significant ($P < 0.05$) year by treatment interaction was detected for N_2O emissions emitted Mg^{-1} corn grain produced (Table 2.3). In 2016, IA and SA had higher (0.29 to 0.33 kg N_2O-N Mg grain^{-1}) amounts of N_2O emitted per Mg of grain produced than DB and DB+NI (Table 2.4). This was similar to Nash et al. (2012) in which strip-till/deep-banded urea reduced amounts of soil N_2O emitted Mg^{-1} of grain on a claypan soil compared to no/till surface-applied urea. The DB and DB+NI treatments had 0.16 to 0.17 kg N_2O-N Mg grain^{-1} higher than the non-fertilized control in 2016. In contrast, the DB+NI treatment in 2017 was not significantly different than the non-fertilized control and was lower than DB, IA, SA treatments. The IA and SA treatments were 0.17 and 0.13 kg N_2O-N Mg-grain^{-1} lower in 2017 compared to 2016, possibly due to rainfall differences in the early and middle parts of the growing season.

Emissions were generally similar between area- and yield-scaled data (Table 2.4). Corn grain yields in 2016 were generally lower compared to treatments in 2017. Not only was this due to greater gaseous N loss, but could also be due to below average June rainfall in 2016 during the late vegetative growth stages of corn (Abendroth et al., 2011), which may have had the greatest impact on corn grain yields (Rhoads and Bennett, 1990; Shaw, 1988). Excluding the non-fertilized control, corn grain yields were highest for the DB+NI treatment in 2016 and 2017, indicating potentially improved N uptake and nitrogen use efficiency (see Chapter 3).

CONCLUSIONS

During both years of this research, significant reductions in cumulative soil N_2O emissions were observed under deep-banded placement of urea with or without the addition of a NI. Additionally, deep-banding urea with or without a NI had a 1.0 to 1.6%

lower emission factor compared to the IA and SA treatments. Deep-banding urea with nitrapyrin may be more effective in low precipitation growing seasons with high overall grain yields since cumulative precipitation was below the ten-year average in both the 2016 and 2017 growing seasons. Although early and mid-growing season precipitation differences had no negative effect on DB+NI, precipitation influenced soil N_2O emissions in the DB, IA, and SA treatments. The year by treatment interaction for soil N_2O-N emitted Mg^{-1} of grain produced was the result of DB+NI being greater than or equal to NC and DB in 2016, but equal to NC and lower than DB in 2017. Therefore, crop management decisions should consider applying a NI with deep-banded urea on poorly-drained soils to overcome the potential of higher growing season soil N_2O emissions. Further research is necessary under varying climatic and soil conditions to confirm under what conditions deep banding is effective in lowering cumulative soil N_2O emissions in conjunction with improvements in crop production.

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Table 2.1. Initial soil properties evaluated at a 0-15 cm depth in 2016 and 2017.

Soil properties[†]	2016	2017
pH (0.01 M $CaCl_2$)	6.9 ± 0.1[‡]	5.6 ± 0.3
Neut. Acidity ($cmol_c$ kg^{-1})	0.1 ± 0.2	2.5 ± 1.7
Organic Matter (g kg^{-1})	29 ± 3	24 ± 1
P Bray I (kg ha^{-1})	88.5 ± 20	69.9 ± 13
Exch. Ca (kg ha^{-1})¶	4713 ± 446	4247 ± 286
Exch. Mg (kg ha^{-1})	371 ± 30	417 ± 30
Exch. K (kg ha^{-1})	346 ± 33	304 ± 29
CEC ($cmol_c$ kg^{-1})	12.4 ± 1.0	13.9 ± 1.3

[†]Abbreviations: Neut. Acidity, Neutralizable Acidity; Bray I P, Bray-1 Phosphorus; Exch. Ca, Exchangeable Calcium; Exch Mg, Exchangeable Magnesium; Exch. K, Exchangeable Potassium; CEC, Cation Exchange Capacity.

[‡]Standard deviation

¶Ca, Mg, and K were exchangeable with 1M NH_4AO_c

Table 2.2. Field management information in 2016 and 2017.

Field information†	2016	2017
Planting date	13 Apr.	21 Apr.
Harvest date	22 Sep.	22 Sep.
Maintenance fertilizer date	15 Feb.	6 Mar.
Rate (N-P_2O_5-K_2O kg ha^{-1})	32-161-284	32-161-284
Source(s)‡	MAP and potassium chloride	MAP and potassium chloride
N placement date	13 Apr.	21 Apr.
Crop protection management		
Burndown	14 Apr.	NA
	Glyphosate (1.14 kg a.i. ha^{-1}) + DAS (0.02 kg ha^{-1})	
Postemergence	25 Apr.	9 May
	Acetochlor (2.3 kg a.i. ha^{-1}) + atrazine (1.7 kg a.i. ha^{-1})	*S*-metolachlor (1.33 kg a.i. ha^{-1}) + atrazine (1.3 kg a.i. ha^{-1}) + mesotrione (0.17 kg a.i. ha^{-1}) + glyphosate (0.04 kg a.i. ha^{-1}) + DAS (0.02 kg ha^{-1}) + NIS (0.25% v/v) + lambda-cyhalothrin (0.03 kg a.i. ha^{-1})
Late postemergence	18 June	NA
	Glyphosate (1.05 kg a.i. ha^{-1}) + topramezone (0.01 kg a.i. ha^{-1}) + COC (2.34 L ha^{-1}) + DAS (0.02 kg ha^{-1})	

†Abbreviations: COC, crop oil concentrate; DAS, diammonium sulfate; MAP, monoammonium phosphate; NA, not applied; NIS, non-ionic surfactant

‡Chemical names: acetochlor, (2-chloro-2’-methyl-6’ethyl-N-ethoxymethylacetanilide); atrazine, [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine], glyphosate, N-(phosphonomethyl) glycine; lambda-cyhalothrin; mesotrione [2-4-(methylsulfonyl)-2-nitrobenzoyl-1,3-cyclohexanedione]; *S*-metolachlor, 2-Chloro-N-(2-ethyl-6-methylphenyl)-N-[(1S)-2-methoxy-1-methylethyl1] acetamide; topramezone, [3-(4,5-dihydro-3-isoxazolyl)-2-methyl-4-(methylsulfonyl) phenyl] (5-hydroxy-1-methyl-1H-pyrazol-4-yl) methanone.

Table 2.3. ANOVA table of cumulative growing season soil N_2O emissions, emission factor, and N_2O-N emitted per grain yield produced.

Source	Degrees of freedom	Cumulative N_2O emissions	Emission factor	N_2O Mg^{-1} grain
		Pr > F	Pr > F	Pr > F
Year	1	0.4483	0.1815	0.1161
Year (rep)	8	0.2276	0.3324	0.1453
N treatment	4	<.0001	<.0001	<.0001
Year x N treatment	4	0.2045	0.2189	0.0252

Table 2.4. Cumulative growing season soil N_2O emissions, emission factor, and N_2O-N emitted per yield produced. Data were combined over years in the absence of a significant interaction.

N treatment	Cumulative emissions	Emission factor	N_2O Mg^{-1} grain 2016	2017
	kg N_2O-N ha^{-1}	%	kg N_2O-N Mg^{-1} grain	
NC†	1.56c	-	0.14c	0.21b
DB	4.96b	1.7b	0.32b	0.38a
DB+NI	3.89b	1.2b	0.30b	0.25b
IA	7.16a	2.8a	0.63a	0.46a
SA	7.05a	2.7a	0.61a	0.48a
$LSD_{(0.05)}$‡	1.15	0.6	--------- 0.12 ---------	

†Abbreviations: DB, urea deep-banded; DB+NI, urea deep-banded plus nitrapyrin; IA, urea incorporated after surface broadcast application; NC, non-fertilized control; SA, urea surface-applied.

‡Fisher's least significant difference at $P \leq 0.05$.

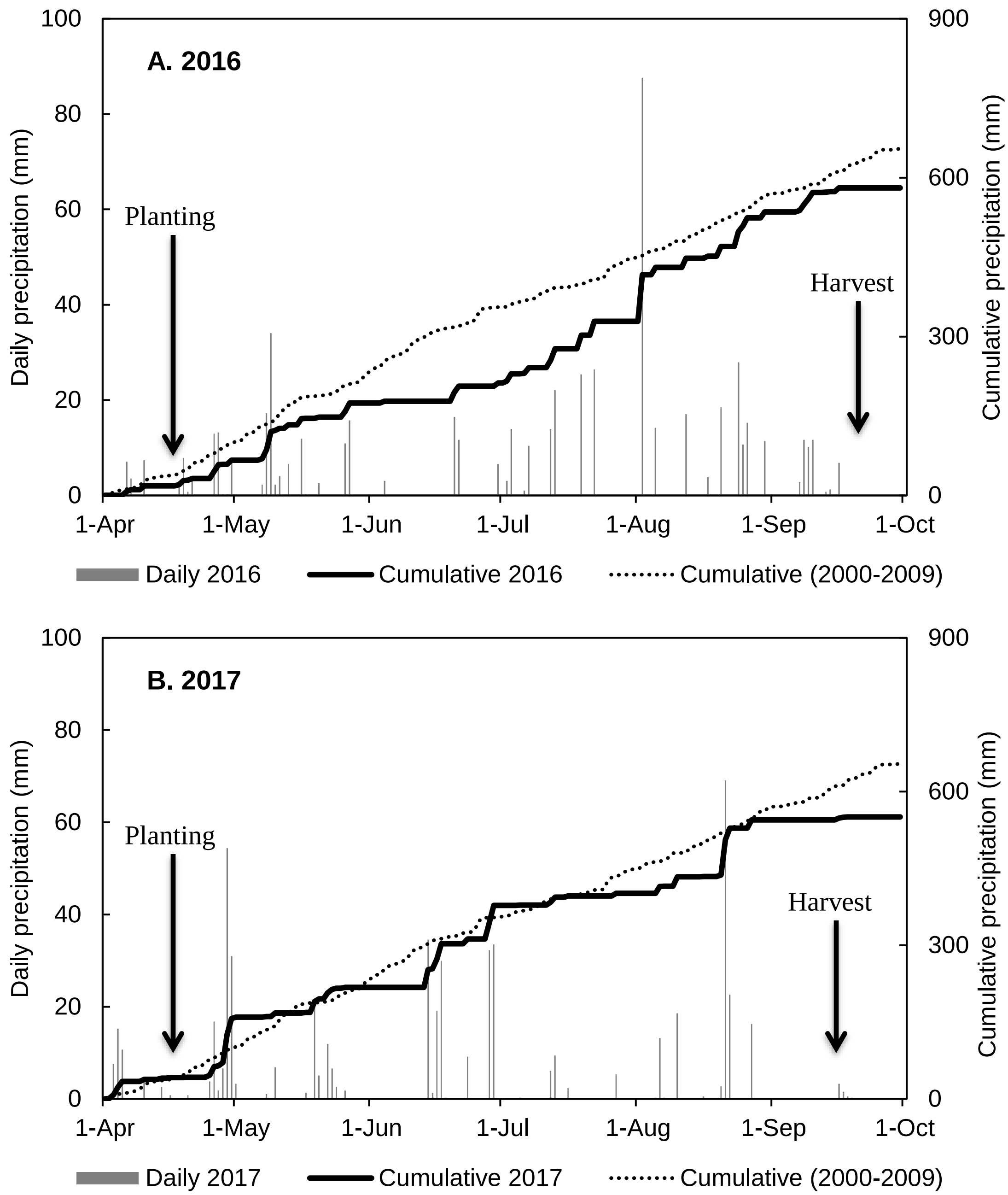

Figure 2.1. Precipitation history and timing of crop management practices for A) 2016 and B) 2017.

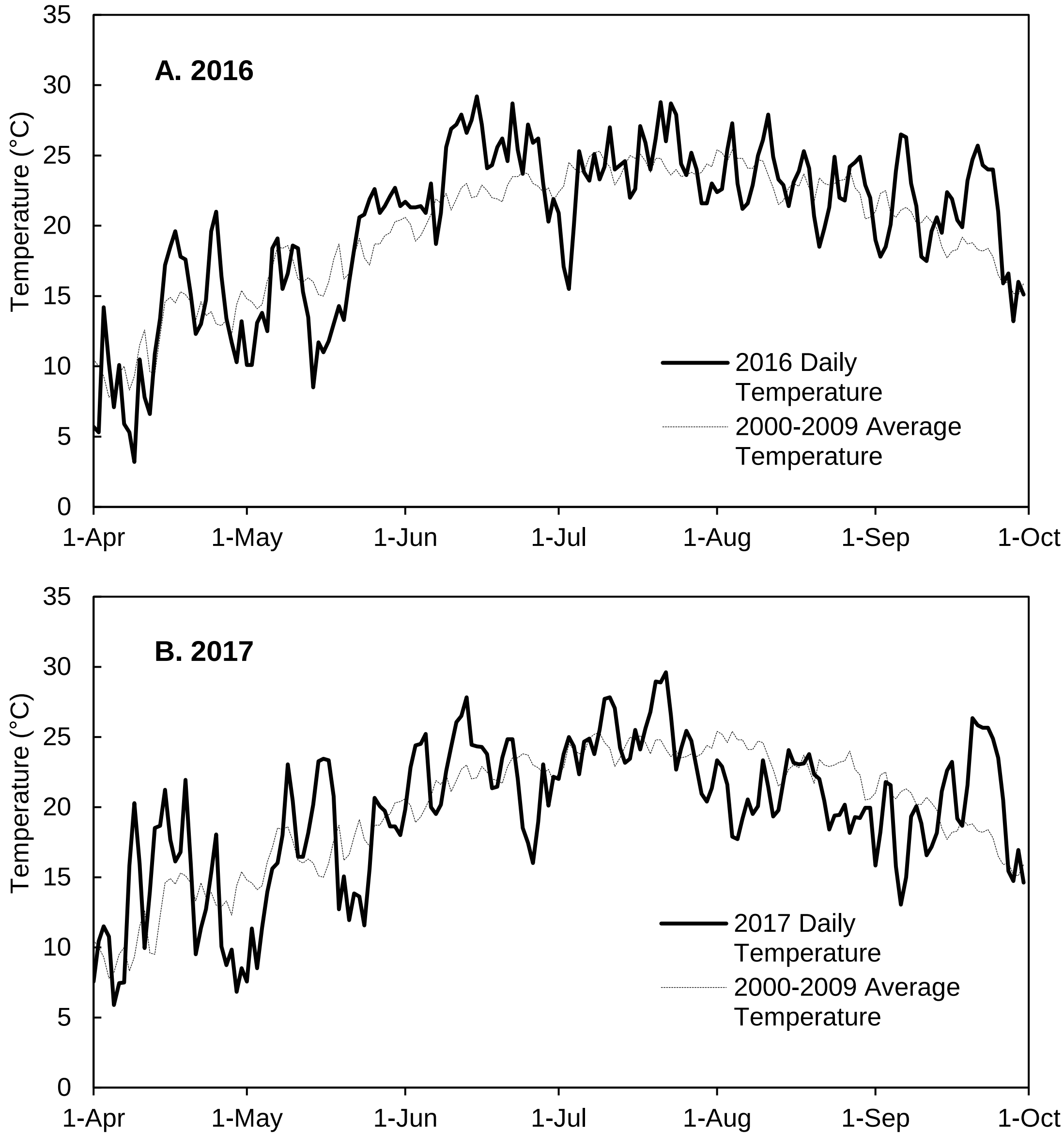

Figure 2.2. Daily average air temperature (°C) during the growing season in A) 2016 and B) 2017.

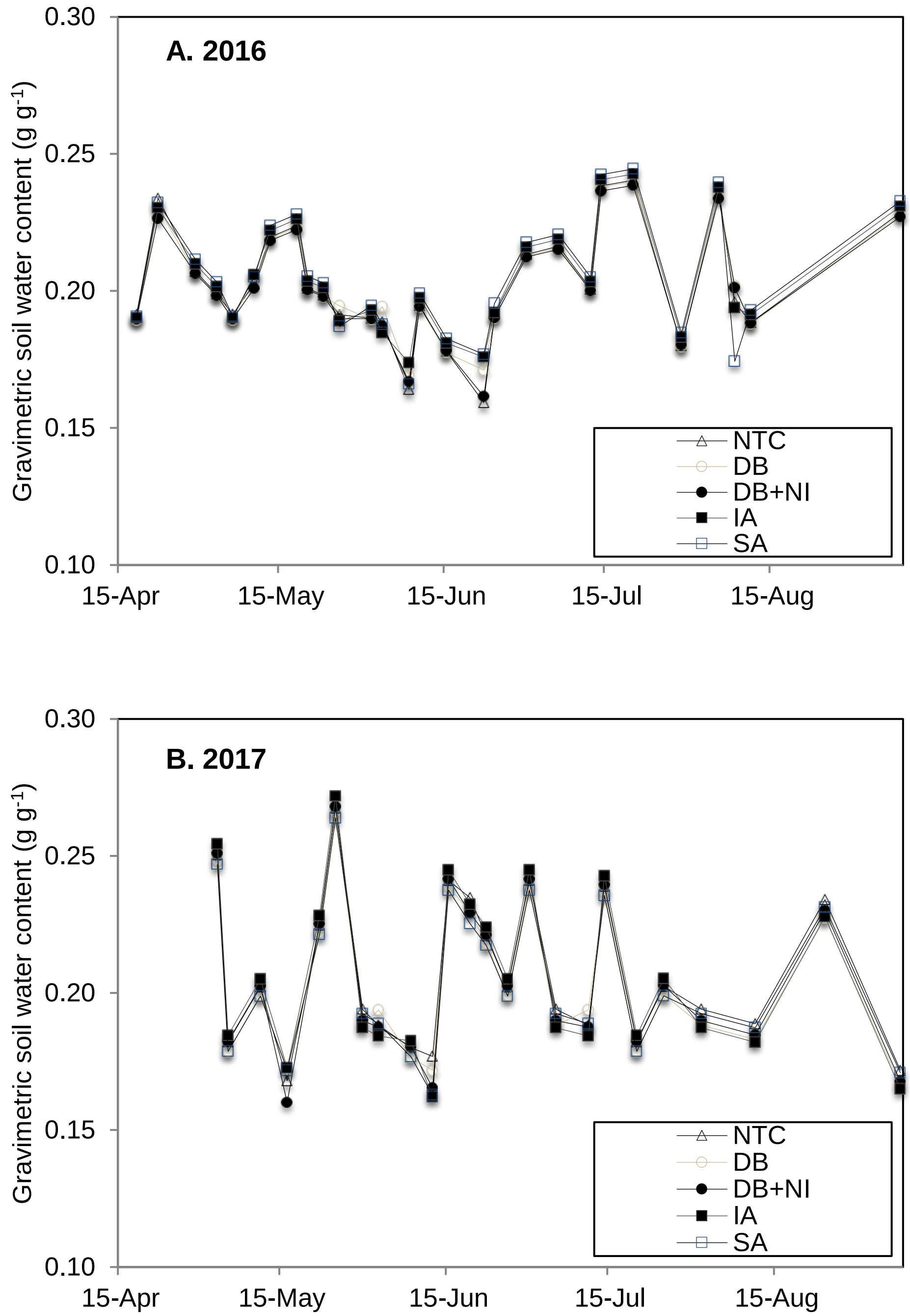

Figure 2.3. Gravimetric soil water content at a depth of 15 cm in the planted row for different nitrogen fertilizer placement treatments on selected gas sampling dates in A) 2016 and B) 2017.

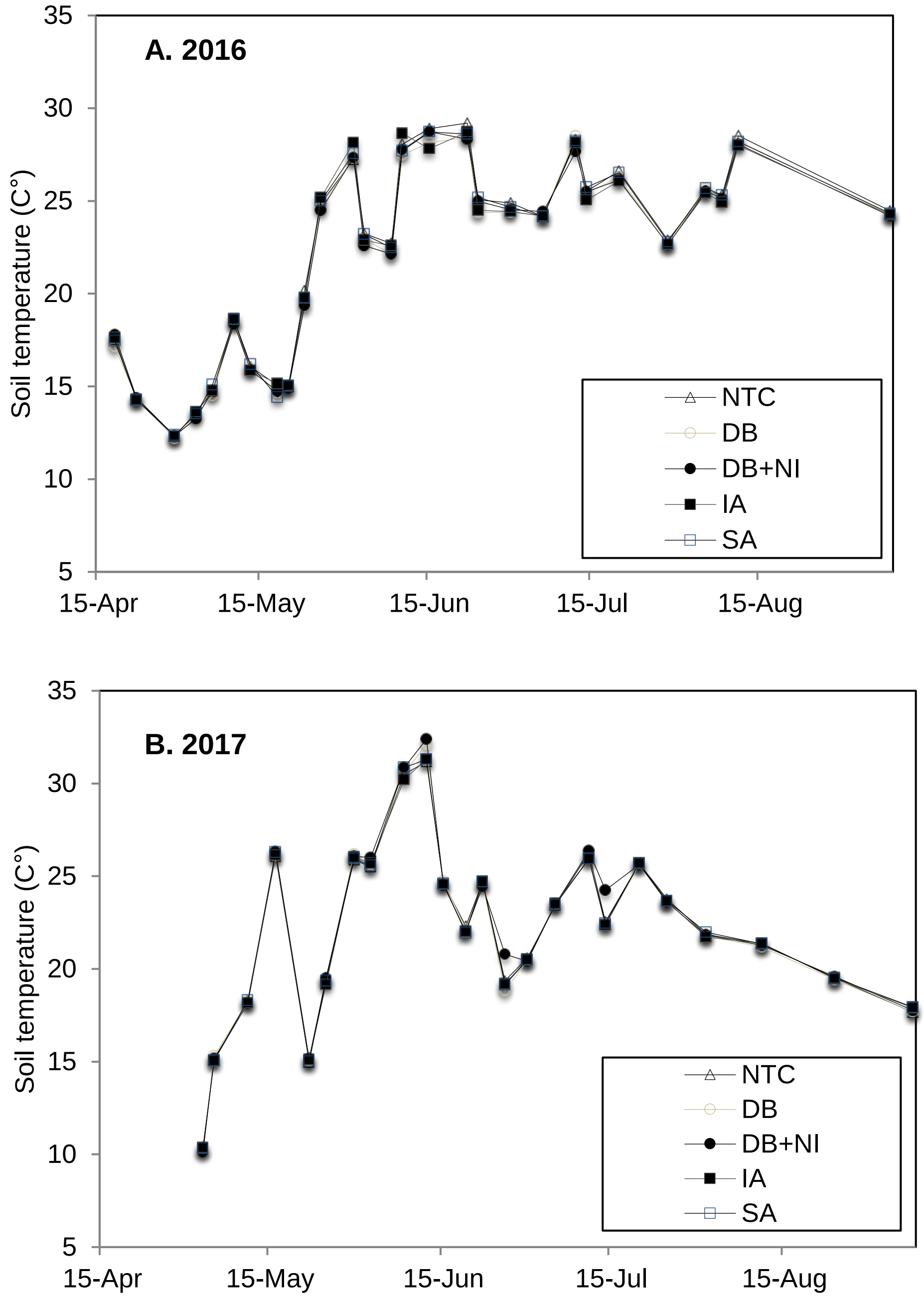

Figure 2.4. Soil temperature (°C) in the planted row with nitrogen treatments on selected gas sampling dates in A) 2016 and B) 2017.

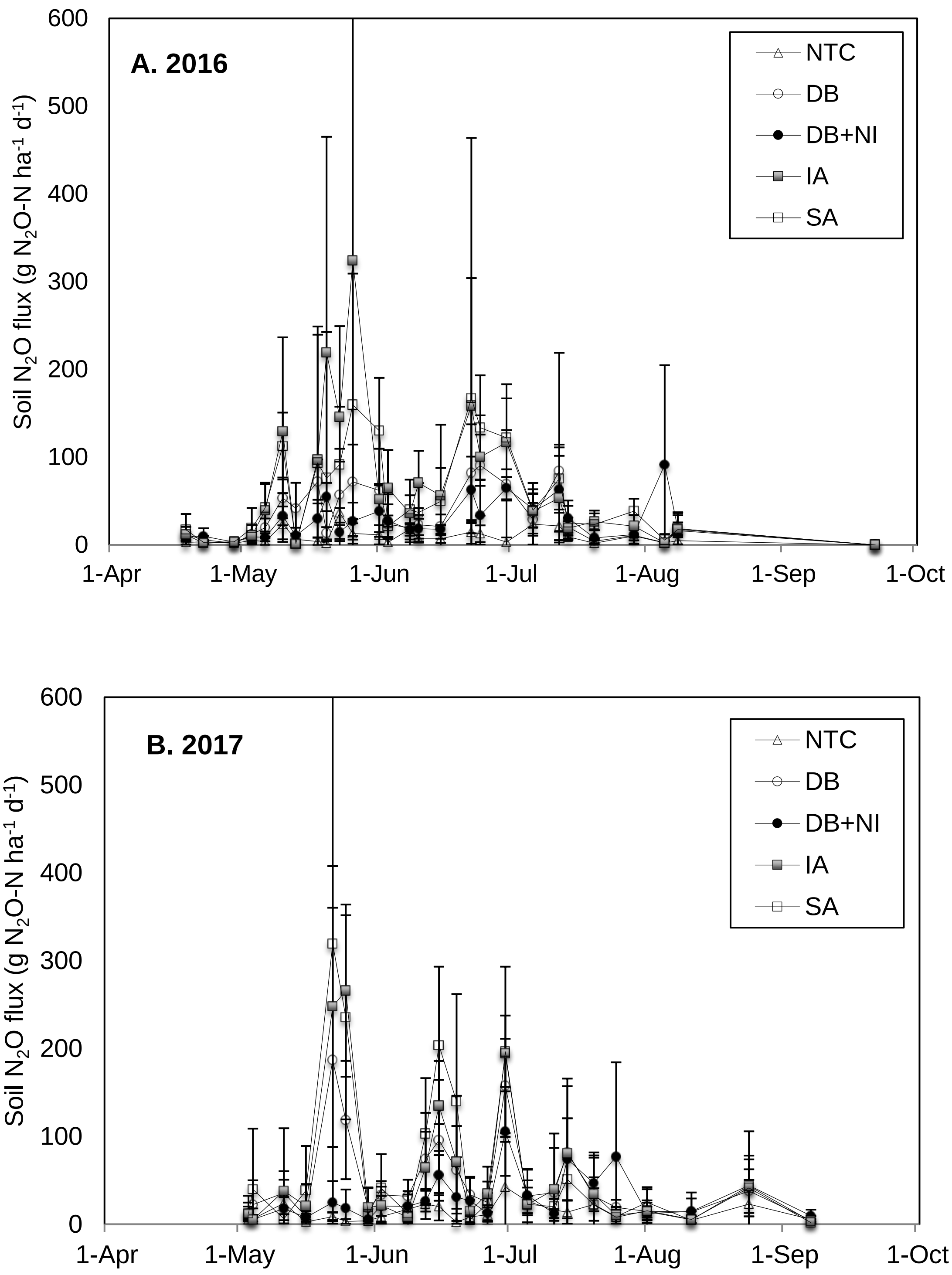

Figure 2.5. Nitrogen placement effect on soil N_2O flux over the growing season with standard deviations in A) 2016 and B) 2017.

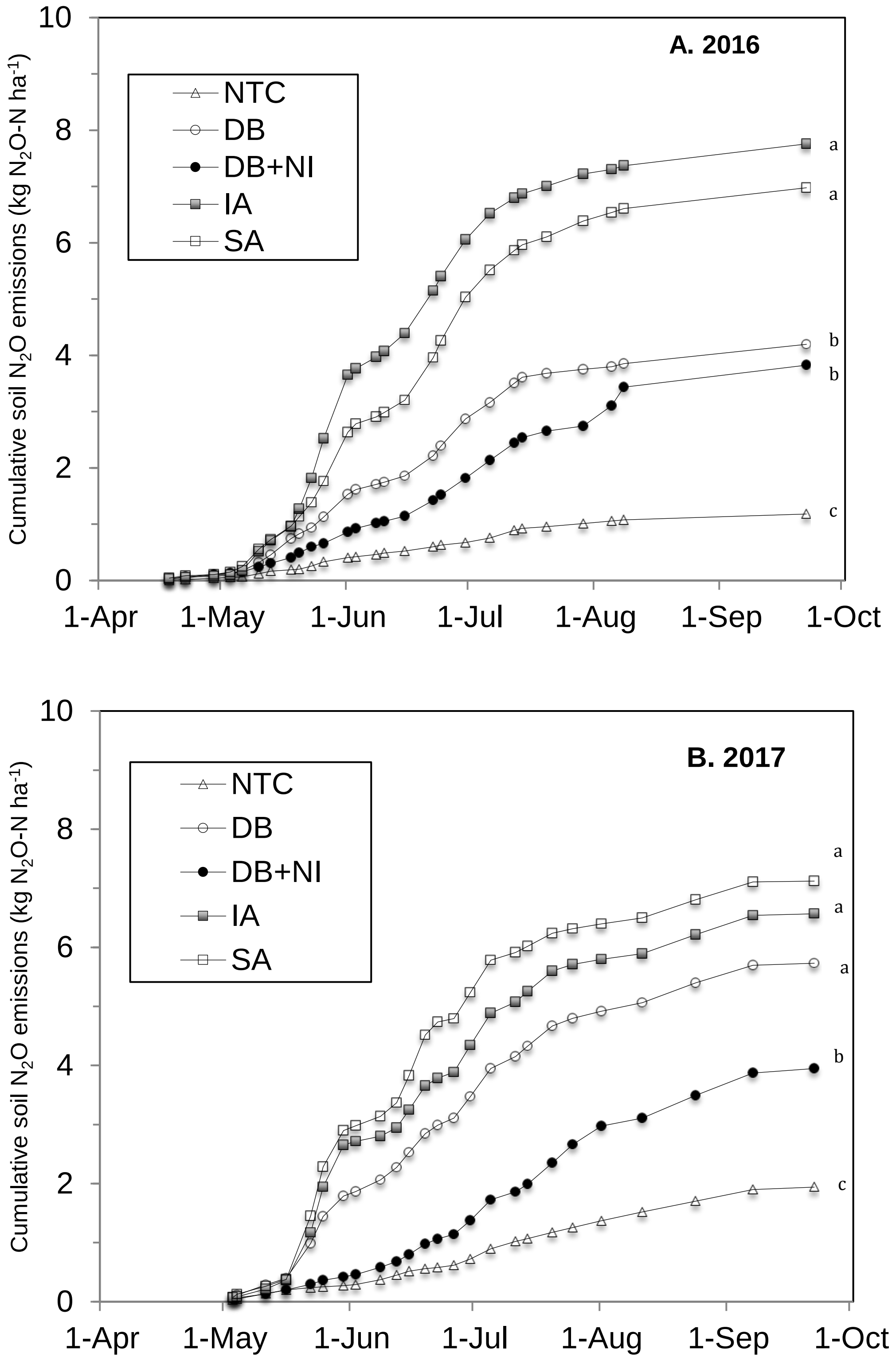

Figure 2.6. Nitrogen fertilizer placement treatment effects on the cumulative soil N_2O emissions over the growing season in A) 2016 and B) 2017. Letters over lines indicate differences among treatments within a given year using Fisher's Protected LSD ($P < 0.05$).

CHAPTER 3

FERTILIZER PLACEMENT AFFECTS CORN AND NITROGEN USE EFFICIENCY IN A CLAYPAN SOIL

ABSTRACT

Nitrogen (N) fertilizer applications to increase N use efficiency (NUE) can include N fertilizer placements strategies, such as broadcasting uniformly over the soil surface or deep banding N fertilizer in the subsoil profile near the root zone; however, minimal research has focused on poorly-drained claypan soils which are prone to saturated conditions which cause N loss. The objective of this research was to determine the effectiveness of urea fertilizer placement practices with and without a NI on corn (*Zea mays*. L) yields and NUE. This study was conducted in Northeastern Missouri at the University of Missouri-Greenley Memorial Research Center on a poorly drained claypan soil starting in 2016 and 2017. The N fertilizer strategies consisted of five replications of deep-banded urea (DB) or urea plus a nitrification inhibitor (DB+NI) at a depth of 20 cm compared to urea broadcast surface applied (SA) or incorporated to a depth of 8 cm (IA). Corn grain yields were significantly higher in 2017 compared to 2016 because of low cumulative rainfall during the middle parts of the growing season. Deep-banded urea with or without nitrapyrin resulted in higher grain and silage yields than NC, IA, and SA treatments in 2016 and 2017. Applying a NI with deep-banded urea had an increase of 4.14 to 4.77 Mg ha^{-1} in silage yield over the SA and DB treatments in 2016, respectively. Additionally, DB+NI had 21 and 26.8% greater N uptake and apparent N recovery efficiency than other N placement treatments, respectively. The addition of nitrapyrin with deep-banded urea was a reliable strategy for increasing corn yields and improving NUE on a poorly-drained claypan soil.

INTRODUCTION

The application of N fertilizers for corn production is essential to achieve crop yields that will help meet the demand for food as world population grows. As N fertilizer rates increase, lower N use efficiency (NUE) may occur and result in more reactive N released into the environment (Peng et al., 2006; Karim et al., 2013). In order to maximize yields and minimize N loss, adequate amounts of N should be applied to satisfy plant N needs. Nitrogen fertilizer management strategies to increase NUE and corn production include the use of different N fertilizer sources (Snyder et al., 2009), timing of fertilizer application (Randall et al., 2003), and the fertilizer placement in soil (Halvorson et al., 2010).

Claypan soils have a high potential for N loss due to their fine textured properties. Claypan soils are characterized by a subsoil layer that is located 20 to 40 cm below the soil surface and at least 100% higher clay content than the horizon directly above it (Myers et al., 2007). These soils encompass an area of approximately 4 million ha across the Midwestern U.S. (Anderson et al., 1990). These poorly drained soils can have long periods of saturation in the rooting zone that negatively affect crop production and increase N loss through runoff, leaching, and denitrification (Blevins et al., 1996; Drury et al., 2009). The magnitude and length of each wetting or drying period can significantly affect N transformation and ensuing N loss. Denitrification is the primary N loss mechanism in poorly drained claypan soils and can reduce the amount of N available for plant uptake (Nash et al., 2013).

Deep-banding N fertilizer is the placement of N fertilizer in the rooting zone, allowing for greater plant N uptake and nitrogen use efficiency (CAST, 2004). Research on a poorly drained claypan soil has indicated that deep banding N fertilizer to a depth of 20 cm increased corn yields 8% compared to a broadcast surface application (Nash et al., 2013). This study also indicated that strip-till, deep banding urea notably increased corn yields 1.57 to 5.39 Mg ha^{-1} compared to a no-till, surface broadcast application. Touchton and Hargrove (1982) determined that a surface broadcast application of UAN was reported to produce less grain yield, silage yield, and N uptake than incorporated band placement in corn. Similarly, N applied in a deep band had 400 kg ha^{-1} greater corn yield compared to surface N application (Riedell et al., 2000).

Enhanced efficiency N fertilizer products are intended to minimize N loss and potentially improve the synchrony of inorganic N sources in the soil with plant N demand. Nitrification inhibitors (NI) are a type of enhanced efficiency product that is commonly applied with N fertilizers to potentially increase grain yield and NUE. Nitrification inhibitors are chemical compounds that restrict, delay or slow down the nitrification process, thereby reducing nitrate loss before plants satisfy their N needs (Zerulla et al., 2001). Burzaco et al. (2013) observed reduced nitrification rates and found 22% lower yield-scaled N_2O emissions in urea-ammonium nitrate treatments with the addition of nitrapyrin than without nitrapyrin. Hendrickson et al. (1978) found that following a fall application of anhydrous ammonia, 53% of the recoverable N was ammonium-N with nitrapyrin compared to 11% ammonium-N without nitrapyrin. Reducing the nitrification rate can increase the amount of N in the ammonium form, which can prevent N loss through processes such as nitrate leaching and denitrification. Delaying nitrification may increase plant availability since ammonium is a plant available form of N (Zerulla et al., 2001). The objectives of this research were to determine the effectiveness of different N fertilizer placement practices including deep banding urea or urea plus nitrapyrin on corn grain yield and N use efficiency on a poorly drained claypan soil.

METHODS AND MATERIALS

This research was conducted in 2016 and 2017 at the University of Missouri Greenley Memorial Research Center (40°1'17" N, 92°11'24.9" W) in Northeast Missouri on a poorly-drained Putnam silt loam (fine, smectitic, mesic Vertic Albaqualfs). The claypan subsurface layer at this research location was as shallow as 30 cm and as deep as 50 cm (personal observation). Daily precipitation data were obtained from an automated weather station located on-site. The initial soil properties for each year (Table 3.1) were determined from analysis of soil samples taken at 0-15 cm depths from the non-treated control plots in all replicates. Samples were taken using a stainless steel push probe with four subsamples per plot and were air-dried and ground to pass through a 2 mm sieve. The initial soil samples were analyzed by the University of Missouri Soil and Plant Testing Laboratory (Columbia, MO) using standard soil testing procedures (Nathan et al., 2006).

Two different field locations at the Greenley Memorial Research Center were used for the 2016 and 2017 field trials. DeKalb 61-88 was planted following soybean (*Glycine max* L.) the previous year. Plots were 3 by 61 m. Corn was planted using a John Deere 7000 planter (Deere and Co, Moline, IL) with a 76 cm row spacing at 79,000 seeds ha^{-1} in 2016 and 82,000 seeds ha^{-1} in 2017. The experimental design was a randomized complete block with five replications of five treatments, containing a non-fertilized control (NC) and four N treatments applied at 202 kg N ha^{-1} applied at different depth-placements. Nitrogen treatments included urea deep banded at a depth of 20 cm (DB), urea deep banded at 20 cm plus nitrapyrin (2-chloro-6-(trichloromethyl) pyridine) at 0.51 kg a.i. ha^{-1} (Instinct II®, Dow AgroSciences, Indianapolis, IN) (DB+NI), urea incorporated after a surface broadcast application at a depth of approximately 8 cm (IA), and urea surface broadcast applied after incorporation (SA). Planting and harvest dates as well as other management practices are listed in Table 3.2.

The urea deep-banded treatments were applied using a custom designed strip-till conservation C-jet unit (Lanpher, 2002). The DB and DB+NI treatments were banded below the planted row in 76 cm wide spacings. The deep-banded fertilizer was released using a Montag dry fertilizer air delivery system (Montag Manufacturing, Inc., Emmetsburg, IA). Immediately following banded fertilizer application, the soil surface was tilled with a field cultivator (John Deere 1000, Moline, IL) to remove the potential effects of strip tillage on crop response. The SA treatment was applied after tillage with the field cultivator.

Daily precipitation and air temperature data for each growing season were collected from an automated weather station maintained by the University of Missouri at the Greenley Memorial Research Center. Leaf chlorophyll (SPAD) measurements (Minolta SPAD-502, Konica Minolta Optics, Inc. Tokyo, Japan) were recorded from the ear leaf ear of 10 plants $plot^{-1}$ at the VT growth stage (Abendroth et al., 2011) and were averaged. Stand counts were measured in the middle two corn rows of each plot at row length of 15.2 m.

Corn silage was harvested at physiological maturity by cutting plants from 3.1 m of one row and weighing the total above ground plant biomass. Subsamples were collected to determine silage moisture to calculate silage yield on a dry weight basis and to conduct tissue N analysis. Silage samples were dried at 70° C and ground using a Wiley-Mill (Swedesboro, NJ) to pass through a sieve with 1 mm openings. Tissue N was analyzed using the combustion method with a total carbon-nitrogen analyzer (LECO Corp., Township, MI). Tissue N concentration and plant biomass were used to calculate N uptake and subsequently the apparent N recovery efficiency (RE) in the silage (Dobermann, 2007). The apparent N recovery efficiency is an indicator of the potential for nutrient loss and was calculated using the equation:

$$RE = \left(\frac{N\ Uptake\ (Treatment) - N\ Uptake\ (Control)}{Quantity\ of\ N\ applied}\right) \text{ x } 100 = \%$$

Corn grain was harvested in the center two rows in each plot using a combine (Wintersteiger, Salt Lake City, UT). Grain yield was also used to assess the impact of applied nutrients on agronomic efficiency (AE) (Dobermann, 2007) using the equation:

$$AE = \left(\frac{Yield\ (Treatment) - Yield\ (Control)}{Quantity\ of\ N\ applied}\right) \text{ x } 100 = \%$$

Corn test weight and grain moisture was measured (Harvest Master, Logan, UT) following harvest. All grain yields were adjusted to 150 g kg^{-1} moisture prior to analysis. Grain samples were collected from each plot for analysis of starch, oil, and protein concentration (Foss Infratec 1241, Eden Prairie, MN).

Analysis of variance (ANOVA) was performed using PROC GLM on grain yields, grain moisture, N uptake, and AE, using the statistical analysis software (SAS) (SAS Institute, 2014). Data were combined over years in the absence of a significant interaction between treatment and year. Fischer’s Protected LSD at $P \leq 0.05$ was used to separate means and determine significant differences among means.

RESULTS AND DISCUSSION

Weather Conditions

Cumulative rainfall amounts for the 2016 and 2017 growing seasons were 562 mm and 508 m, respectively (Figure 3.1 A&B). The average ten-year precipitation amount from 2000 to 2009 during the growing season (from April through September) was 655 mm (University of Missouri Extension, 2017). The cumulative rainfall in the growing season of 2016 was 14% lower than the ten-year average. In 2017, cumulative rainfall in the growing season was 22% lower than the ten-year average. Although total rainfall was much lower in 2017, early growing season months (April and May) experienced 25% greater cumulative rainfall compared to 2016. The two years were drastically different in June rainfall with only 38 mm in 2016 compared to 160 mm in 2017. Rainfall in June 2017 was above the ten-year June average of 125 mm, and June 2016 had 87 mm less rainfall than the ten-year June average. The majority of the rainfall in 2016 occurred late in the growing season with 116 mm in July and 207 mm in August. The average air temperature in the 2016 and 2017 growing season was 20.2 °C and 19.6 °C, respectively (Figure 3.2 A&B). The average ten-year air temperature from 2000 to 2009 was 19.7 °C over the growing season (University of Missouri Extension, 2017). In 2016, average air temperature was 5.5 °C higher during the first two weeks of the growing season compared to the first two weeks of the growing season in 2017. In the Midwest US Corn Belt, corn is more sensitive to water stress during the summer months when corn is at the V12 to denting stages (Abendroth et al., 2011; Wang et al., 2016;). Heat stress during these critical growth periods contributes to drought stress through increasing vapor pressure deficit, which ultimately increases the demand for soil water due to high evapotranspiration rates (Lobell, 2014). Differences in rainfall distribution and air temperature during the mid-growing season months may account for the greatest corn production differences among the two years.

Plant Population

Analysis of variance of plant populations showed the interaction of N placement by year was significant ($P < 0.05$) (Table 3.3). Corn plant populations in 2016 were significantly greater in DB, DB+NI, IA, and NC treatments compared to 2017, but there was no significant difference among treatments in 2016 (Table 3.4). Surface applied urea had 83,500 plants ha^{-1} and was significantly lower than all other N placements in 2016, which could be due to a combination of high early season air temperatures and distribution of rainfall that caused greater N loss with a surface application (Riedell et al., 2000). In 2017, DB and DB+NI had 6900 plants ha^{-1} (8%) less than SA. There was no difference in plant population between NC, IA, and SA treatments in 2017. Plant population differences in 2017 were unexpected because of grain yield results. This suggests a high probability for poor initial seed germination and stand establishment due to more intense rainfalls in the first 21 days after planting following spring strip tillage in 2017. Nevertheless, corn plant populations in 2016 and 2017 were much higher than the average plant population of 56,000 plants ha^{-1} that farmers have utilized to optimize profit in North America (Williams II, 2012).

SPAD Meter

Corn chlorophyll meter readings (SPAD units) were combined over years due to the absence of a significant interaction between N treatments and years (Table 3.3). Mean chlorophyll readings were not significantly different between DB, DB+NI, and SA placements. Deep-banded urea plus nitrapyrin had the highest chlorophyll meter readings (Table 3.4). This indicates that nitrapyrin combined with deep placement of urea may have reduced N loss. Chlorophyll meter readings have been used as an indirect measurement of corn tissue N concentration and can be correlated to grain yield response (Ntamatungiro et al., 1999).

Corn Grain and Silage Yields

Corn grain yields due to the treatments varied between 2016 and 2017 (Table 3.3). Corn grain yields were significantly greater in 2017 compared to 2016, ranging from 9.61 Mg ha^{-1} in the NC to 15.52 Mg ha^{-1} in the DB+NI treatment (Table 3.5). All N treatments increased yield 2.98 and 4.7 Mg ha^{-1} compared to the NC treatment in 2016 and 2017, respectively. In 2016, corn grain yields ranged from 8.31 to 13.3 Mg ha^{-1}. There was no significant difference between DB and DB+NI in 2016 or 2017. However, both treatments produced significantly higher grain yields than SA in 2016 and also produced higher grain yields than IA in 2017. In 2016, the addition of a NI to deep-banded urea provided a 3% increase in grain yield compared to deep-banded urea alone, but it was not significantly different. Schwab and Murdock (2009) observed 1.3 Mg ha^{-1} higher grain yields with surface broadcast application of urea with a NI compared to urea alone. Furthermore, a seven-year study in Minnesota found an average increase of 1.0 Mg ha^{-1} in corn grain yield when combining deep placed anhydrous ammonia with nitrapyrin compared to anhydrous ammonia alone (Randall et al., 2008). The IA treatment produced significantly higher grain yield (10%) than SA in 2016. This was similar to a study by Touchton and Hargrove (1982) where they observed surface broadcast application of UAN had 3.5 Mg ha^{-1} less corn grain yield than incorporated band placement of UAN.

In 2017, deep-banded urea with or without a NI had significantly higher grain yield than IA, but there were no significant differences among DB, DB+NI, and SA (Table 3.5). The IA treatment produced 14.31 Mg ha^{-1} of grain yield in 2017 and was not different than SA (14.83 Mg ha^{-1}). Placing urea deep in a band with or without a NI resulted in an increase in grain yield by at least 6% compared to IA in 2017. This was similar to research where banding N fertilizer increased corn grain yield 11% compared to broadcast N application (Lehsrch et al., 2000). These results were further supported by Johnson et al. (2016) who observed that deep banding urea had 10% higher corn grain yields than surface broadcast and shallow placement of urea. Surface broadcast urea had significantly lower corn grain yield (11.29 Mg ha^{-1}) than IA in 2016, but it was similar to IA in 2017. These results imply that higher than average air temperatures and lower than average rainfall shortly after N application (15 April to 30 April) in 2016 may have caused significant N loss to the atmosphere. Urea fertilizer is prone to atmospheric N loss via ammonia volatilization duirng warm spring temperatures (> 50°C) and when N is left on the soil surface (Keller and Mengel, 1986). Our results are consistent with a previous study by Tomar and Soper (1981) which observed reduced atmospheric N loss in treatments that were banded or injected into the subsoil compared to surface N application. Surface placement of N fertilizer was most effective if there was a rain following application so that N is incorporated in the root zone and is not exposed to the atmosphere (Al-Kanai and MacKenzie, 1992). Our results suggest that SA was left on the soil surface and not properly incorporated into the subsoil because of relatively low rainfall shortly after N application in 2016. Conversely, higher than average rainfall and lower than average air temperature shortly after planting in 2017 potentially had minimal atmospheric N loss via volatilization. However, wet soil conditions from early growing season rainfall in 2017 may have caused anoxic soil conditions for anaerobic respiration from microorganisms, subsequently increasing N loss through denitrification (Thauer et al. 1977).

Cumulative precipitation was similar in the two growing seasons, but the distribution of rainfall can more likely explain the influence year and N placement had on grain yield. Corn yield is most susceptible to water stress during the late vegetative and early reproductive stages, with about 3.2 to 6.8% yield loss per day of stress possibly occuring during these corn growth stages (Rhoads and Bennett, 1990; Shaw, 1988). Tasseling (VT) and pollination (R1) occurs after the accumulation of approximately 1135 GDUs, which typically begins 9 or 10 weeks after corn emergence (Neild and Newman 1990). In both years, corn emergence was observed within the same week of planting (mid-April) and VT was detected in early July. This pattern suggests that corn grain yields for all N treatments in 2016 were lower compared to 2017 because of lower than average cumulative rainfall in June 2016. Cumulative rainfall in July was relatively lower in 2017, but June rainfall was higher than the ten-year average by 35 mm. Corn requires at least 180 mm of water from VT through R4 growth stages for normal development to occur (Rhoads and Bennett, 1990; Shaw, 1988). Cumulative rainfall in June and July was 183 mm in 2017, while the same period in 2016 had 154 mm and was most likely not sufficient for corn development during the late vegetative and early reproductive stages. This was similar to the results of a multi-year study by Gagnon et al. (2012) in which they observed a 0.3 to 0.6 Mg ha^{-1} increase in corn grain yield in urea plus a NI treatments when there was relatively more rainfall in June compared to no significant increase in grain yield among treatments when June conditions were dry.

There was also an interaction between year and treatment ($P < 0.05$) for silage yield (Table 3.3). Applying a NI to deep-banded urea was the only N fertilizer placement method that consistently produced the highest silage yield in both years (Table 3.6). Other treatments showed an increase in silage yield in 2017 and this response appeared to be affected by rainfall distribution over the growing season during the two years. Lack of rainfall early in the growing season and after VT potentially affected silage yields for N placement treatments in 2016.

In 2016, silage yield ranged from 14.86 to 23.28 Mg ha^{-1} (Table 3.6). All N treatments increased silage yield compared to the NC. Silage yield of the DB treatment was 23.28 Mg ha^{-1}, and was significantly greater than all other N placement treatments in 2016. Deep-banded urea with a NI increased silage yield 21% compared to SA and 38% to IA. In 2017, corn silage yield for the NC was similar to all N treatments except DB+NI.

Silage N Concentration, N Uptake, and NUE

Nitrogen concentration, N uptake, and apparent N recovery efficiency in silage tissue were combined over years since there was no significant interaction (Table 3.3). Nitrogen concentration in the corn silage tissue ranged from 7.7 g kg^{-1} in the NC to 11.3 g kg^{-1} in the DDB+NI treatment (Table 3.6). All treatments increased N concentration in the silage compared to the NC. There was no statistical difference between DB, DB+NI, IA, and SA placement treatments. Similarly, Johnson et al. (2016) observed minimal differences in corn silage N concentrations between surface broadcast N fertilizer and deep-banded N fertilizer.

Total N uptake with deep-banded urea plus nitrapyrin had the greatest N uptake (262.3 kg N ha^{-1}) when combined over years (Table 3.6). All N placement treatments had 70.3 to 130.8 kg N ha^{-1} greater N uptake than the NC. There was no difference between DB, IA, and SA placement treatments. The addition of nitrapyrin with deep-banded urea resulted in 45.8 kg N ha^{-1} (21%) and 48.4 kg N ha^{-1} (23%) greater N uptake compared to DB and SA, respectively. These findings are similar to that of Randall et al. (2003) in which they observed the addition of nitrapyrin to anhydrous ammonia increased N uptake 23% compared to anhydrous ammonia alone. In addition, Lehrsch et al. (2000) observed N uptake in banded treatments were 6% higher compared to surface broadcasted treatments. These results are counter to Johnson et al. (2016), in which they observed significantly higher N uptake with surface broadcast application of urea compared to deep-banded urea with or without a NI. Generally, N treatments that had low N uptake in corn silage were shown to have low silage yield in 2016 and 2017 (Table 3.6), thus suggesting N uptake in the silage to be a good indicator for potential silage yields. These findings are similar to that of Ciampitti and Vyn (2011) in which they observed a significant correlation between grain yield and N uptake.

Apparent N recovery efficiency for DB+NI showed 76.5% efficiency and was significantly higher than all other treatments (Table 3.6). The addition of nitrapyrin with deep-banded urea had 26.8% higher N recovery efficiency than urea deep-banded without nitrapyrin. Correspondingly, corn silage yield and N uptake in the DB+NI treatment were significantly greater than other N treatments, which in combination with greater plant N concentration had higher apparent N recovery efficiency. The apparent N recovery efficiency for the DB, IA and SA treatments were similar. The relatively low response in apparent N recovery efficiency for DB, IA, and SA may have occurred because of the influence of rainfall and temperature on N cycling in soils (Brzostek et al., 2012), and also the effects of the claypan soil, which are susceptible to N loss via denitrification (Nash et al., 2013). In our study, early season rainfall in 2017 potentially caused a long period of saturated and anoxic soil conditions in the deep subsoil and resulted in significant denitrification loss of urea N from the deep-banded treatments. This explanation is further supported by Halvorson and Del Grosso (2012), in which they observed higher N_2O emissions in subsurface banding polymer-coated urea (PCU) treatments compared to surface-applied PCU. Their result was attributed to observing higher levels of water-filled pore space at deep soil depths in the early growing season.

There was an interaction between N placement and year ($P < 0.05$) for agronomic efficiency in corn grain (Table 3.3). Agronomic efficiency, which evaluates grain yield in relation to N application, showed DB, DB+NI, and IA treatments were significantly higher than the SA treatment in 2016 (Table 3.5). The shallower urea was incorporated in the soil, the lower the agronomic efficiency in 2016. In 2017, DB+NI agronomic efficiency was higher than IA and SA treatments compared to 2016, but there was no significant difference between IA and SA. The agronomic efficiency of DB and DB+NI was 2.1 to 2.8 kg kg-N^{-1} greater than the IA treatment in 2017. Agronomic efficiencies for all placement treatments were significantly higher in 2017 than 2016, which was due to higher overall grain yields in 2017. According to Dobermann (2007), agronomic efficiencies for corn ranged from 10 to 30 kg kg-N^{-1}, where efficiencies below 10 kg kg-

N^{-1} suggest a poorly maintained and imbalanced system. This indicates DB and DB+NI were the most consistent treatments in both 2016 and 2017.

Deep-banded urea with or without a NI had a consistently higher agronomic efficiency than IA and SA treatments in both years. Results from multiple studies suggest incorporating multiple management practices to improve N uptake and NUE. For example, Stehouwer and Johnson (1990) studied the effectiveness of applying anhydrous ammonia with nitrapyrin in the fall and spring. In their study, they observed an increase in ear-leaf N and grain yield with fall-applied anhydrous ammonia with nitrapyrin treatments compared to anhydrous ammonia alone, while nitrapyrin with spring-applied anhydrous ammonia did not increase ear-leaf N or grain yield. Moreover, Takahashi et al. (1991) reported a 22% increase in NUE using top-dress N applications in soybean. Ferguson et al. (2009) recorded dissimilar results where UAN with nitrapyrin was ineffective and did not increase N uptake or corn grain yield. However, this could be explained by heavy rainfall that occurred during the growing season. In general, the addition of a NI to N fertilizer treatments is shown to be effective at improving NUE, but can be highly variable depending on climatic and soil conditions that lead to N loss.

Grain Quality

Corn grain moisture content was averaged over both years due to the absence of a year by treatment interaction (Table 3.3). Corn grain from the non-fertilized control plots contained the lowest moisture content (138 g kg^{-1}), while grain from the DB+NI contained the highest moisture content (161 g kg^{-1}) (Table 3.7). Both deep-banded urea treatments had significantly higher grain moisture than all other treatments, but were not significantly different between either of the deep-banded urea treatments. Grain moisture content for SA and IA treatments were approximately 154 and 149 g kg^{-1}, respectively. Surface-applied urea was 5 to 16 g kg^{-1} greater than IA and NC treatments, and IA was significantly greater than the NC. Corn grain moisture content is affected by multiple factors including N fertilizer type, corn hybrid, climate, and many others (Vetsch and Randall, 2002). All of these factors influence the rate of corn maturation, in which a faster rate typically results in lower relative grain moisture (Beegle et al., 2007). One study observed corn grain moisture to be negatively correlated to NUE using a sidedress N application, but corn response was due to a cool and humid growing season (Biswas and Ma, 2015).

Corn starch concentrations were combined over years due to the absence of a year by treatment interaction (ANOVA not presented). Starch concentrations in corn grain ranged from 723 g kg^{-1} in the DB+NI plots to 737 g kg^{-1} in the NC treatment (Table 3.7). All treatments were significantly lower than the NC treatment by at least 9 g kg^{-1} (1.2%). There was no significant difference in starch concentration in corn grain between DB, DB+NI, and SA; however, DB+NI was significantly lower than the IA treatment by 5 g kg^{-1}.

There was no significant year by treatment interaction for protein concentration in corn grain (Table 3.3). Protein concentration ranged from 66.7 g kg^{-1} in the NC to 87.1 g kg^{-1} in the SA treatment (Table 3.7). The non-fertilized control had a protein concentration that was 24% lower than all other treatments. Deep-banded urea plus nitrapyrin protein concentration was 4.1 g kg^{-1} greater than IA, but there is no significant difference between DB+NI and DB. Surface-applied urea had the highest protein concentration in corn grain with 87.1 g kg^{-1}, but it was only significantly greater than the

IA and NC treatments. The high protein concentration for the SA treatment can be explained by the high N uptake and apparent N recovery since protein content is directly related to N application when N is not limiting (Gauer et al., 1992).

There was an interaction of N placement by year was significant ($P < 0.05$) for oil concentration (Table 3.3). Oil concentration was 2.4 to 7.8 g kg^{-1} lower for all treatments in 2016 compared to 2017. In 2016, SA and IA had 2 to 2.4 g kg^{-1} greater oil concentrations than DB (Table 3.7). In 2017, the non-fertilized control was significantly greater than all placement treatments by 5%. There was no significant difference between SA, IA, DB, and DB+NI treatments in 2017; however, all placement treatments had a significant increase in oil concentration by at least a 6.3% from 2016 to 2017 possibly due to differences in rainfall distribution. There was no significant year by treatment interaction for corn test weight (data not presented). Test weight ranged from 72.05 to 72.75 kg hL^{-1} and was not significant different among treatments (Table 3.7).

CONCLUSIONS

The effectiveness of deep banding N fertilizers with or without a NI and other N fertilizer placement strategies for corn production in a poorly-drained claypan soil was influenced by climatic conditions. All N fertilizer placement treatments were effective in the year that had sufficient rainfall 14 to 21 days after planting and during the mid-growing season when corn was at the late vegetative growth stages. Deep banding urea with or without nitrapyrin was the most effective treatment in both years, regardless of climatic conditions. Placing N fertilizer in closer proximity to the roots may allow for greater plant N uptake and reduction in N loss due to surface runoff and other N loss processes. Surface urea application had lower grain yields in 2016, which had less precipitation during the early part of the growing season. We speculate that this difference in response was due to above average cumulative rainfall in the early parts of the growing season, which was sufficient for corn growth and proper incorporation of surface applied urea into the soil before major N loss through volatilization in 2017. Results of this study suggest that combining nitrapyrin with deep-banded urea in a claypan soil could increase crop production and may be less vulnerable to N loss during the growing season. These results also suggest deep banding urea with nitrapyrin could increase corn NUE, grain, and silage yields in areas experiencing low cumulative rainfall during critical growth stages of development.

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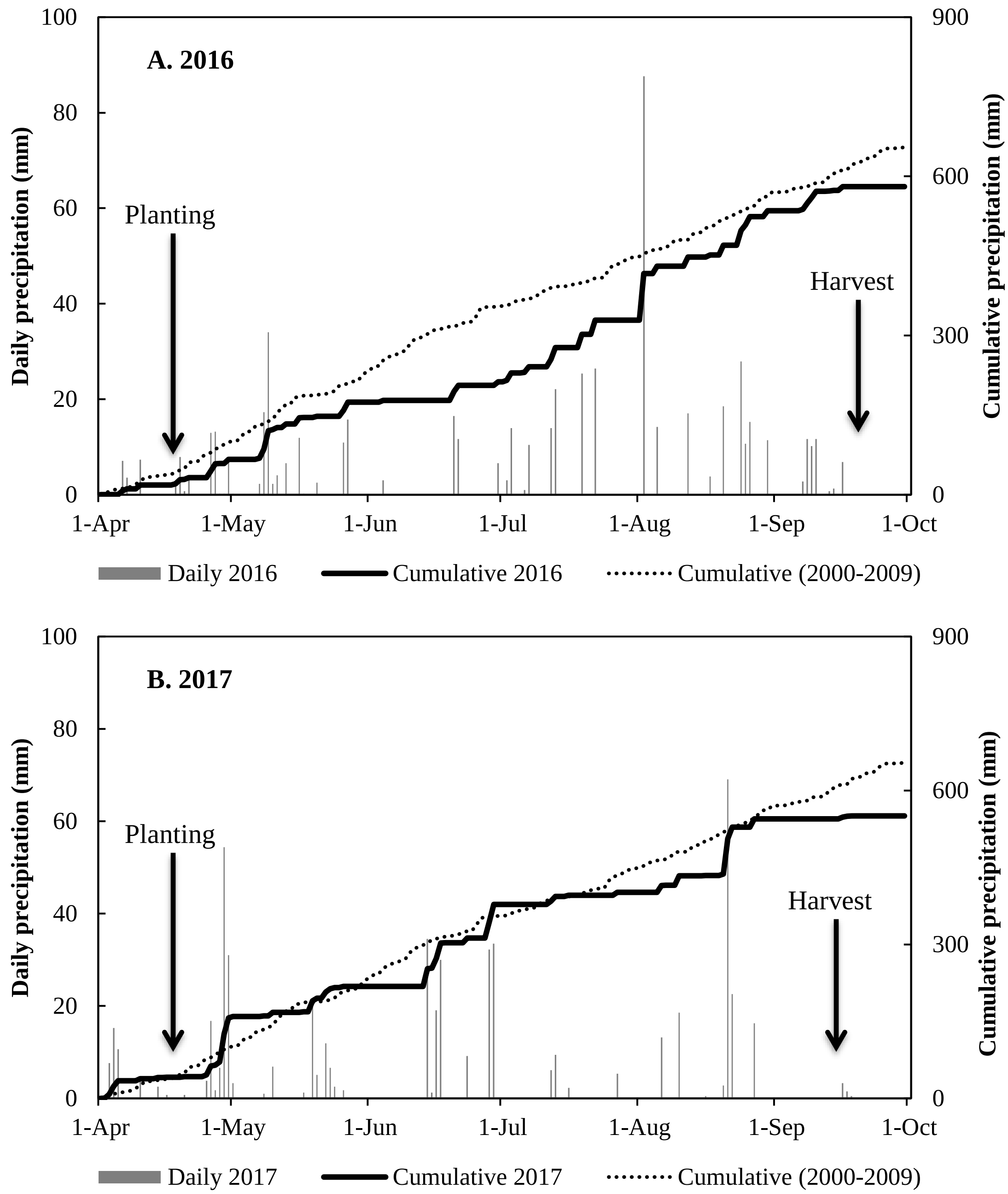

Figure 3.1. Precipitation history and timing of crop management practices for A) 2016 and B) 2017.

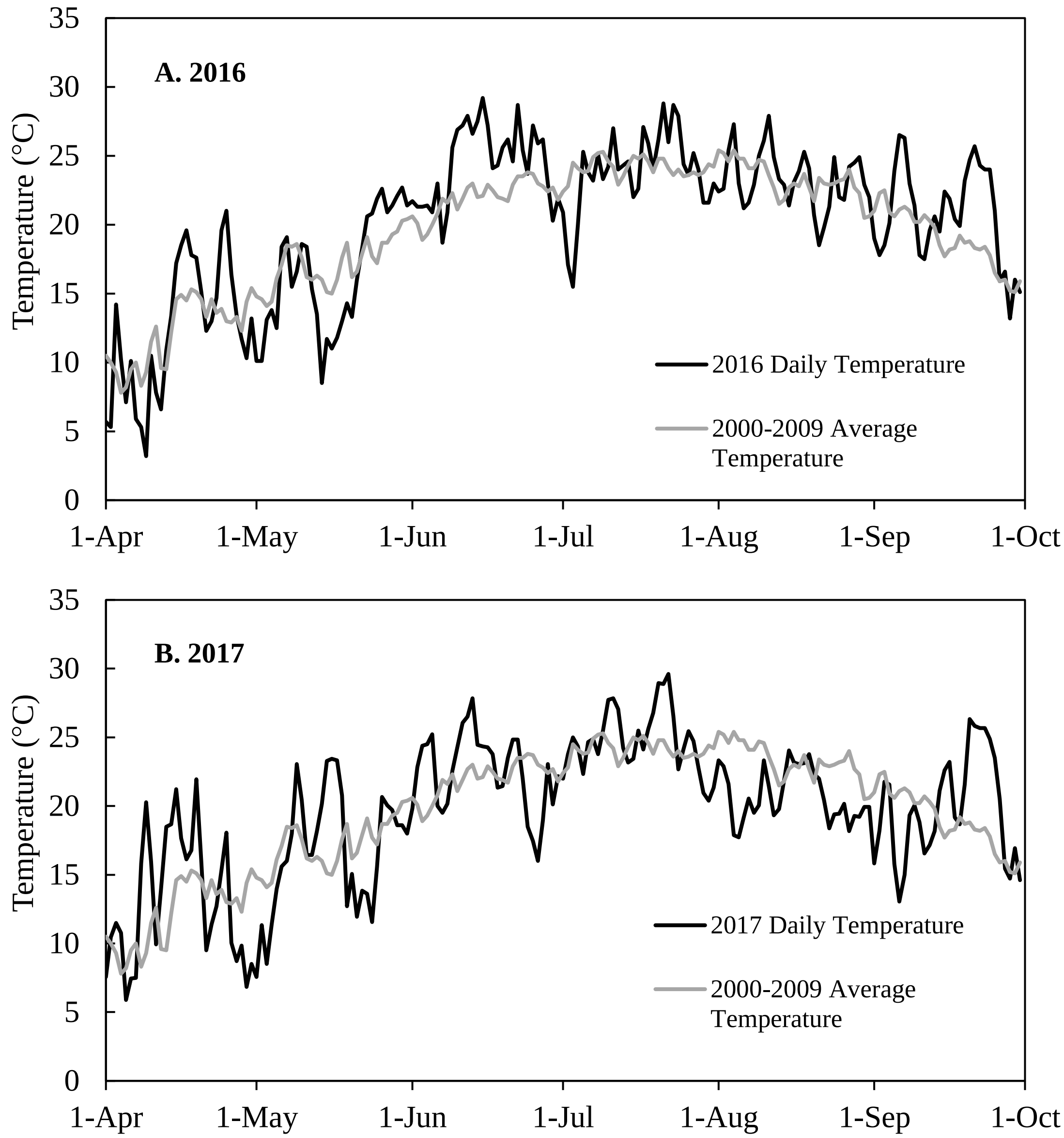

Figure 3.2. Daily average air temperature (°C) for A) 2016 and B) 2017.

Table 3.1. Initial soil properties evaluated at a 0-15 cm depth in 2016 and 2017.

Soil properties†	2016	2017
pH (0.01 M $CaCl_2$)	6.9 ± 0.1‡	5.6 ± 0.3
Neut. Acidity ($cmol_c$ kg^{-1})	0.1 ± 0.2	2.5 ± 1.7
Organic Matter (g kg^{-1})	29 ± 3	24 ± 1
P Bray I (kg ha^{-1})	88.5 ± 20	69.9 ± 13
Exch. Ca (kg ha^{-1})¶	4713 ± 446	4247 ± 286
Exch. Mg (kg ha^{-1})	371 ± 30	417 ± 30
Exch. K (kg ha^{-1})	346 ± 33	304 ± 29
CEC ($cmol_c$ kg^{-1})	12.4 ± 1.0	13.9 ± 1.3

†Abbreviations: Neut. Acidity, Neutralizable Acidity; Bray I P, Bray-1 Phosphorus; Exch. Ca, Exchangeable Calcium; Exch Mg, Exchangeable Magnesium; Exch. K, Exchangeable Potassium; CEC, Cation Exchange Capacity.

‡Standard deviation

¶Ca, Mg, and K were exchangeable with 1M NH_4AO_c

Table 3.2. Field management information in 2016 and 2017.

Field information[†]	2016	2017
Planting date	13 Apr.	21 Apr.
Harvest date	22 Sep.	22 Sep.
Maintenance fertilizer date	15 Feb.	6 Mar.
Rate (N-P_2O_5-K_2O kg ha^{-1})	32-161-284	32-161-284
Source(s)[‡]	MAP and potassium chloride	MAP and potassium chloride
N placement date	13 Apr.	21 Apr.
Crop protection management		
Burndown	14 Apr.	NA
	Glyphosate (1.14 kg a.i. ha^{-1}) + DAS (0.02 kg ha^{-1})	
Postemergence	25 Apr.	9 May
	Acetochlor (2.3 kg a.i. ha^{-1}) + atrazine (1.7 kg a.i. ha^{-1})	*S*-metolachlor (1.33 kg a.i. ha^{-1}) + atrazine (1.3 kg a.i. ha^{-1}) + mesotrione (0.17 kg a.i. ha^{-1}) + glyphosate (0.04 kg a.i. ha^{-1}) + DAS (0.02 kg ha^{-1}) + NIS (0.25% v/v) + lambda-cyhalothrin (0.03 kg a.i. ha^{-1})
Late postemergence	18 June	NA
	Glyphosate (1.05 kg a.i. ha^{-1}) + topramezone (0.01 kg a.i. ha^{-1}) + COC (2.34 L ha^{-1}) + DAS (0.02 kg ha^{-1})	

[†]Abbreviations: COC, crop oil concentrate; DAS, diammonium sulfate; MAP, monoammonium phosphate; NA, not applied; NIS, non-ionic surfactant
[‡]Chemical names: acetochlor, (2-chloro-2'-methyl-6'ethyl-N-ethoxymethylacetanilide); atrazine, [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine], glyphosate, N-(phosphonomethyl) glycine; lambda-cyhalothrin; mesotrione [2-4-(methylsulfonyl)-2-nitrobenzoyl-1,3-cyclohexanedione]; *S*-metolachlor, 2-Chloro-N-(2-ethyl-6-methylphenyl)-N-[(1S)-2-methoxy-1-methylethyl1] acetamide; topramezone, [3-(4,5-dihydro-3-isoxazolyl)-2-methyl-4-(methylsulfonyl) phenyl] (5-hydroxy-1-methyl-1H-pyrazol-4-yl) methanone

Table 3.3. Overall ANOVA of corn parameters evaluated in 2016 and 2017.

Source	df	Grain yield	Silage yield	Pop.	SPAD	N conc.	N uptake	Moisture	Protein	Oil	df	RE	AE
		Pr > F	Pr > F	Pr > F	Pr > F	Pr > F	Pr > F	Pr > F	Pr > F	Pr > F		Pr > F	Pr > F
Yr[†]	1	<.0001	0.0958	<.0001	<.0001	0.3318	0.1346	<.0001	0.7737	<.0001	1	0.1464	<.0001
Yr (rep)	8	0.1284	0.2004	0.4390	0.0089	0.1278	0.1962	0.0489	0.7031	0.7961	8	0.3413	0.0102
Trmt	4	<.0001	<.0001	0.7352	<.0001	<.0001	<.0001	<.0001	<.0001	0.0365	3	0.0080	<.0001
Yr x Trt	4	0.0087	0.0466	0.0034	0.4047	0.3137	0.2081	0.0707	0.2546	0.0365	3	0.0996	0.0014

[†]Abbreviations: AE, agronomic efficiency; Conc, concentration; Pop, population; RE, apparent N recovery efficiency; Trt, treatment; Yr, year.

Table 3.4. Plant population and chlorophyll readings in response to urea placement and inclusion of a nitrification inhibitor. Chlorophyll meter data were combined over years (2016 and 2017) in the absence of a significant interaction.

Treatment	Population 2016	Population 2017	SPAD
	------- No. ha^{-1} -------		
NC[†]	92,100	83,500	47.9
DB	94,100	81,800	58.4
DB+NI	93,900	81,800	59.4
IA	93,400	85,200	56.6
SA	83,500	88,700	57.1
$LSD_{(0.05)}$ [‡]	--------- 6,600 ---------		2.8

[†]Abbreviations: NC, non-treated control; SA, urea surface-applied; IA, urea incorporated after surface broadcast application; DB, urea deep banding; DB+NI, urea deep banding plus nitrapyrin.

[‡]Fisher's least significant difference at $P \leq 0.05$.

Table 3.5. Corn grain yield and agronomic efficiency in response to urea placement and inclusion of a nitrification inhibitor in 2016 and 2017.

	Grain yield		Agronomic efficiency	
Treatment	2016	2017	2016	2017
	----- Mg ha^{-1} -----		--- kg kg-N^{-1} ---	
NC†	8.31	9.61	--	--
DB	13.30	15.21	11.2	12.6
DB+NI	12.90	15.52	10.3	13.3
IA	12.41	14.31	9.2	10.5
SA	11.29	14.83	6.7	11.7
LSD$_{(0.05)}$‡	--------- 0.86 ---------		-------- 1.3 --------	

†Abbreviations: NC, non-treated control; SA, urea surface-applied; IA, urea incorporated after surface broadcast application; DB, urea deep banding; DB+NI, urea deep banding plus nitrapyrin.

‡Fisher's least significant difference at $P \leq 0.05$.

Table 3.6. Silage yield, N concentration, N uptake, and apparent N recovery efficiency in response to urea fertilizer placement when applied at 171 kg N ha^{-1} in 2016 and 2017. Plant N concentration, N uptake and apparent N recovery efficiency were combined over years in the absence of a significant interaction.

	Silage yield				
Treatment	2016	2017	Plant N concentration	N uptake	Apparent N recovery efficiency
	-- Mg ha^{-1} --		g kg^{-1}	kg N ha^{-1}	%
NC†	14.86	18.30	7.7	131.5	--
DB	19.51	19.85	10.9	216.5	49.7
DB+NI	24.28	22.71	11.3	262.3	76.5
IA	17.62	21.90	10.1	201.8	41.1
SA	20.14	19.58	10.8	213.9	48.2
$LSD_{(0.05)}$‡	---- 3.15 ----		1.3	37.5	20.3

†Abbreviations: NC, non-treated control; SA, urea surface-applied; IA, urea incorporated after surface broadcast application; DB, urea deep banding; DB+NI, urea deep banding plus nitrapyrin.

‡Fisher's least significant difference at P ≤ 0.05.

Table 3.7. Corn grain starch, protein, oil, moisture, and test weight in response to urea placement and inclusion of a nitrification inhibitor. Data were combined over years (2016 and 2017) in the absence of a significant interaction.

Treatment	Starch	Protein	Oil		Moisture	Test weight
			2016	2017		
	--------------------------- g kg^{-1}				----------------------------	kg hL^{-1}
NC†	737	66.7	37.0	43.2	138	72.11
SA	725	87.1	37.4	40.8	154	72.75
IA	728	82.5	37.8	40.2	149	72.20
DB	726	86.1	35.4	40.6	161	72.05
DB+NI	723	86.6	36.4	41.2	160	72.55
$LSD_{(0.05)}$	4.0	3.6	----- 1.8 -----		4.0	NS

†Abbreviations: NC, non-treated control; SA, urea surface-applied; IA, urea incorporated after surface broadcast application; DB, urea deep banding; DB+NI, urea deep banding plus nitrapyrin.

‡Fishers least significant difference at $P \leq 0.05$.

CHAPTER 4

ENHANCED EFFICIENCY LIQUID NITROGEN FERTILIZER MANAGEMENT FOR CORN PRODUCTION

ABSTRACT

Improved nitrogen (N) management strategies for corn (*Zea mays* L.) production are necessary to reduce environmental N loss and maintain plant available N in the root zone for greater yield. Claypan soils can intensify the importance of N timing, source, and placement on high yielding corn production due to these soils' relatively poor drainage characteristics, which can contribute to a higher potential for N loss and subsequently lower corn yields. Field research was conducted on corn (*Zea mays* L.) from 2010 to 2013. Treatments included two N application timings (fall and spring) and five N source/placements, which were arranged in a randomized complete block design at two application rates (84 and 168 kg N ha^{-1}). The five N source/placements systems were no-till (NT)/surface broadcast urea ammonium nitrate (UAN) or strip-till (ST)/deep banded UAN, NT/surface broadcast UAN plus Nitamin Nfusion (10% of total N) or ST/deep banded UAN plus Nitamin Nfusion, and ST/deep banded anhydrous ammonia. Results indicated that use of ST/deep banded UAN with a fall N application produced the highest grain yield (8.12 to 9.12 Mg ha^{-1}) at 84 and 168 kg N ha^{-1}, but was less effective with a spring application in 2011. Fall-applied ST/deep banded anhydrous ammonia produced the lowest grain yields (5.97 and 6.8 Mg ha^{-1}) in 2013 at 84 and 168 kg N ha^{-1} Warmer and wetter soil conditions in the early growing season (April and May) of 2013 resulted in relatively higher grain yields with spring application in all N source/placement treatments compared to spring-applied treatments when cooler and drier conditions in 2011. Poor corn growth in 2012 was due to an extreme drought during the growing

season. In 2013, there were limited differences among UAN alone and the addition of Nitamin Nfusion. Thus, climate conditions may have caused N shortages in the soil when N was deep banded applied as UAN or anhydrous ammonia fertilizer because it may be separated from plant roots or may not be converted into NO_3-N at the appropriate growth stage. Farmers may need to consider risk management strategies when using strip tillage since yields were less when N was applied in the spring of 2011 and similar or greater in the spring of 2013 compared to a fall timing.

INTRODUCTION

Nitrogen (N) management is a crucial and challenging component of sustainable corn production on poorly drained claypan soils. Claypan soils are prevalent in the Midwest, accounting for an area of 4 million hectares in parts of Missouri, Kansas, and Illinois (Anderson et al., 1990). Restrictive clay properties of the subsoil reduce the flow of water, which creates a poorly drained environment (Jung et al., 2006). The low hydraulic conductivity of claypan soils makes it is susceptible to waterlogged conditions following rainfall events, which is ideal for loss of N through denitrification. Saturated soil conditions can also reduce infiltration of water and lead to lateral movement of N on the soil surface, resulting in N loss through surface runoff. The poor drainage properties of claypan soils can affect crop management decisions and reduce grain yields (Nelson et al., 2009). Nitrogen management for improving N utilization by crop plants and minimizing N loss is termed as the “4R” strategy within the fertilizer industry (Bruulsema et al., 2009). This management strategy includes applying N at the right time, at the right placement, using the right source, and at the right rate. Nitrogen fertilizer timing, source, placement, or application rate are viewed as controllable factors that can improve corn yields in poorly drained claypan soil. However, unpredictable weather conditions, including distributions of precipitation and temperature, are uncontrollable factors that may cause the greatest impact on N use efficiency and yield.

Use of effective N management practices in corn production systems is a main concern because N is the most important primary nutrient for corn growth and development (Blumenthal et al., 2008). Single application of N fertilizer in the spring at the time of planting or soon after emergence is a commonly utilized N management practices to improve corn growth and development in the Midwest (Sawyer et al., 2006). The consensus among researchers has been that the application of N fertilizer for corn should be applied nearest to the time N is needed by the crop and when N uptake is maximum in order to achieve higher N use efficiency and to reduce N loss (Fox et al., 1986; Olson and Kurtz, 1982; Welch et al., 1971).

Early planting of corn as soon as soils are suitable in the spring is desirable for highest yields and profit because of generally later drier summer months, but the window of opportunity for spring N application has become very narrow due to generally wetter spring conditions (Randall and Schmidt, 1998). Risk of soil compaction and other challenges such as greater N loss with very wet soils can be unfavorable to spring N application. However, fall application of N is at risk because N is applied several months before the crop needs it, thereby increasing the potential for N loss (Dinnes et al., 2002). A five-year study in Minnesota found 36% or more N loss and an 8% reduction in corn grain yields with fall N application compared to a spring N application (Randall and Mulla, 2001). Malhi and Nyborg (1986) found fall N application to have higher NO_3-N losses in surface water and leaching compared to a spring N application. In Iowa, 49 to

64% of N fertilizer applied in the fall was lost from the upper 1.5 m of the soil profile through pathways other than plant uptake (Sanchez and Blackmer, 1988). However, a study in Kansas reported no differences in corn grain yield between a fall and spring pre-plant N application (Stamper, 2009). In some instances, U.S. corn growers prefer to apply N in the fall because labor is often more available, fertilizer prices are cheaper, and weather and soil conditions are more favorable than the spring (Dinnes et al., 2002). Bundy (1986) concluded that fall N application is an acceptable option on clay textured soils if winter temperatures were below < 10°C so that nitrifying bacteria are inactive. However, fall-applied N was 10 to 15% less effective than a spring application even when winter temperatures were below 10°C.

Fertilizer N placement strategies may improve crop yields and N use efficiency in claypan soils. Touchton and Hargrove (1982) determined that a surface broadcast application of UAN produced less corn grain yield and N uptake compared to surface or incorporated band UAN placement. Another study found UAN applied in a deep band significantly increased grain yields compared to surface-applied UAN (Halvorson et al., 2006). Other studies did not observe any advantages of subsurface band placement of UAN over surface broadcast placement (Fox et al., 1986; Raun et al., 1989). Research on a poorly drained claypan soil in Missouri has indicated that combining strip-tillage with deep banding urea had 1.57 to 5.39 Mg ha^{-1} greater corn grain yield than no-till, surface broadcast urea application (Nash et al., 2013). Johnson et al. (2016) observed similar results on a poorly drained claypan soil where deep banding urea had at least 10% higher corn grain yield compared to surface applied and shallow banded urea.

Placing N fertilizer below the soil surface can result in a higher concentration of nutrients within the root zone, which can increase N uptake, and corn yields (CAST, 2004). Surface applied N is commonly used with no-till systems where high-residue levels can promote increased microbial activity near the soil surface, causing more potential for N loss (Riedell et al., 2000). Strip-till is a reduced tillage practice that allows for subsurface placement of N fertilizers within the tilled, planted row. Strip-till has similar benefits as to no-till systems, but strip-till can have an advantage because it increases internal drainage of the seedbed and initiates earlier warming of the soil in the spring due to less surface residue (Randall and Hill, 2000). Benefits from no-till has shown variable yield results and can depend on a number of factors including seasonal weather conditions and management practices including, N fertilizer timing, source, N placement, soil moisture content, soil temperature, and overall seedbed conditions in the spring (Mehdi et al., 1999; Hendrix et al., 2004). However, surface application of N in no-till or reduced tillage systems can be subject to N loss through denitrification and ammonia volatilization if N remains on the surface long enough and is exposed to the atmosphere (Bandel et al., 1980; Al-Kanani and MacKenzie, 1992). In contrast, N loss can be reduced if N is placed below the soil surface (Tomar and Soper, 1981).

Traditional N fertilizers used for corn production consist of dry, liquid, or gas-based sources. Increases in corn yield are not necessarily determined by selection of these traditional N fertilizer sources, but is largely dependent on the ability to provide inorganic, plant available forms of N (NH_4^+ and NO_3^-) in sufficient concentrations in synchrony with plant N demand. Several slow- and controlled-release N fertilizers have been investigated for their potential to increase crop yield by improving the synchronization of plant N demand and N release (Cahill et al., 2010; Halvorson and Bartolo, 2014; Noellsch et al., 2009). The release mechanism of several slow-release fertilizers is affected by the concentration gradient across the polymer or elemental sulfur coated material as a result of capillary action and water diffusion (Shaviv, 2001), but the release rate can depend on soil properties, soil temperature, and microbial activity (Shapiro et al., 2016). Polymer-coated urea (PCU) was found to increase corn yield and plant N uptake by 23 and 48% compared to traditional urea on a poorly drained silt-loam soil in Missouri, respectively (Noellsch et al., 2009). Conversely, Nash et al. (2013) observed no-till/deep banding of PCU at pre-plant to produce 1.91 Mg ha^{-1} greater corn grain yield and less N loss than non-coated urea (NCU). A study on a silty clay loam soil in Arkansas reported PCU had a significant advantage in grain yield (0.77 Mg ha^{-1}) for continuous corn compared to traditional urea (Halvorson and Bartolo, 2014). Other researchers have reported no differences in corn yield and N uptake between enhanced-efficiency N and conventional N fertilizers (Sistani et al., 2014; Venterea et al., 2011). Nitamin Nfusion (NF) is a new slow release liquid enhanced efficiency N fertilizer product that consists of 22% N, of which 94% is slowly available in the form of polymer urea (Phillips et al., 2006). The product is completely water-soluble and can be blended with UAN, liquid urea, and other solutions at different ratios allowing for great flexibility. Shapiro et al. (2016) found surface broadcast UAN with NF and subsurface banding UAN with NF produced 0.21 to 0.59 Mg ha^{-1} higher grain yield than surface broadcast UAN without Nitamin Nfusion on a loamy sand soil at a site in Nebraska, respectively. However, there is a lack of research studies investigating the effects of NF and other N fertilizer solutions on corn production using a combination of different N timing, sources, placements, and rates.

The objective of this study was to determine the effects of two timings (fall vs. spring pre-plant) and five source placements at two different N rates on corn response on a poorly-drained claypan soil.

MATERIALS AND METHODS

A three-year field experiment was conducted from 2011 to 2013 at the University of Missouri's Greenley Memorial Research Center (40°1'17" N, 92°11'24.9" W) on a poorly-drained claypan soil (Putnam silt loam, fine smectitic, mesic Vertic Albaqualfs). The depth to the claypan at this research location was approximately 31 cm (Nash et al., 2011). Experiments were conducted with corn (*Zea mays* L.) on fields that were planted to soybean (*Glycine max* L.) the previous year. The field trial was a two-factor randomized complete block design with four replications. The main plot was N fertilizer application timing (fall and preplant), which was blocked and randomized within each replication. The source/placements included 32% UAN NT/surface broadcast or ST/deep banded, 32% UAN plus Nitamin Nfusion (Koch Agronomic Services, Wichita, KS) at 10% of the total N NT/surface broadcast or ST/deep banded, and anhydrous ammonia deep banded only which were in a factorial arrangement with two application rates (84 and 168 kg N ha^{-1}). Experimental plots were 3 by 23 m. Deep banded N fertilizer was applied to a depth of 20 cm with a custom designed strip-till conservation C-jet (Advance, Missouri) unit (Lanpher, 2002). Nitrogen application dates as well as other crop management information is in Table 4.1. Dekalb 63-84 was planted on 12 April at 76,000 seeds ha^{-1} in 2011, 11 April at 79,000 seeds ha^{-1} in 2012, and 14 May at 81,500 seeds ha^{-1} in 2013. Maintenance fertilizer was only applied in 2012 at 17-80-120 (N-P_2O_5-K_2O) kg ha^{-1} on 12 April. Corn was harvested on 13 Sep 2011, 23 Aug 2012, and 26 Sep 2013.

Stand counts for the two inner rows of each plot were recorded each year over a row length of 15.2 meters. Leaf chlorophyll measurements were recorded in the growing season on the most recent mature ear leaf from the midrib of 10 plants $plot^{--1}$ at VT (Abendroth et al., 2011) using a SPAD 502 Plus chlorophyll meter (Konica Minolta, Hong Kong) and were averaged for a whole plot value. Plant heights and stage of corn development were determined weekly until VT (Abendroth et al., 2011). Corn test weight, grain moisture (Harvest Master, Logan, UT), and grain yields were determined using a plot combine (Wintersteiger, Salt Lake City, UT) that harvested the two center rows in each plot 23 m in length. Grain yields were adjusted to 150 g kg^{-1} moisture prior to analysis. Grain samples were collected from each plot for determination of starch, oil, and protein concentration (Foss 1241 Infratec, Eden Prairie, MN).

An analysis of variance (ANOVA) was performed using the SAS v9.4 statistical program (SAS Institute, 2015). Fischer's Protected LSD at $P \leq 0.05$ was used to separate means and determine significant treatment effects. Data were analyzed for each rate separately to detect differences between enhanced efficiency products compared to standard N treatments.

RESULTS AND DISCUSSION

Weather Conditions

Cumulative rainfall amounts for the 2011, 2012, and 2013 growing season were 527, 239, and 468 mm, respectively (Figure 4.2A-C). The average ten-year precipitation amount from 2000 to 2009 during the growing season (April through September) was 655 mm (University of Missouri Extension, 2017). The cumulative precipitation in the growing season of all three years was at least 25% lower to the ten-year average. The growing season of 2012 experienced very little rainfall, and both the 2011 and 2013 growing season contained 288 and 231 mm more cumulative rainfall than 2012, respectively. The average air temperature in 2011, 2012, and 2013 over the growing season was 20.9, 22.0, and 21.2 °C, respectively (Figure 4.3A-C). The average ten-year air temperature from 2000 to 2009 was 19.7 °C over the growing season (University of Missouri Extension, 2018). All three years of this research were above the average air temperature. Average soil temperature over the growing season from 2000 to 2009 was 19.7 °C. Average soil temperature in 2011 was approximately the same (19.7 °C) as the prior ten season average, while 2012 was slightly higher (20.8 °C) and 2013 slightly lower (19.3 °C) (Table 4.2). Soil temperatures were mostly below 10 °C from November to March in the 2010-2011 and 2012-2013 study years which is ideal to minimize N loss with fall N application (Keeney, 1982).

An assessment of total rainfall, average air temperature, and soil temperature during portions (e.g., fall and spring) of each year's study period may account for differences in the observed corn response due to N management systems among study years. Over the period of fall N application to planting in 2012-2013, total precipitation was 288 and 75 mm greater than in 2010-2011 and 2011-2012, respectively; however, cumulative rainfall in the 2012-2013 period was greater because of a relatively wetter April. Air temperature after fall N application and before planting in 2011, 2012, and 2013 averaged 0.8, 5.2, and 2.5 °C, respectively. Over the period of fall N application to planting in 2011-2012, average soil temperature was 2.4 and 1.6 °C higher than 2010-2011 and 2012-2013, respectively. Cumulative rainfall in April was similar in 2011 and 2012 at 110 and 119 mm, respectively. Planting was delayed until 1 May in 2013 because spring precipitation was 98 mm (99%) higher in April 2013 compared to the ten-year average. Cumulative rainfall in 2013 was 126 and 105 mm higher in the first four weeks after planting than 2011 and 2012, respectively. Cumulative rainfall observed in June was 135 and 100 mm higher in 2011 compared to 2012 and 2013, respectively. In 2011 and 2013, July had similar rainfall (50 and 48 mm) and was greater than July 2012 (19 mm) cumulative rainfall. There were no rainfall events in August 2013, and August 2011 had 48 mm more cumulative rainfall than August 2012. Both 2011 and 2013 had identical average air temperatures in May at 16.5 °C. In 2012, average air temperature was 19.9 °C in May. Average air temperature in June was similar among the three years, ranging from 21.7 to 23.5 °C. Average soil temperature in 2013 was 3.9 °C and 1.2 °C higher over the first four weeks of the growing season than 2011 and 2012, respectively. Omitting 2012, average soil temperature in June and July was higher by 0.5 and 2.3 °C in 2011 compared to 2013. Average soil temperature in the early spring months showed differences over the three study years. In 2012, average soil temperature was 10.2 °C and was 4.7 °C and 8.1 °C higher than 2011 and 2013, respectively. Average soil temperature in April was 2.3 °C and 4 °C higher in 2012 than 2011 and 2013.

Ear Leaf SPAD

An interaction for corn SPAD meter readings between N source placement, timing, and year was found at 84 kg N ha^{-1} (Table 4.3). SPAD readings were generally higher by 4.7 SPAD units in 2011 and 2012 among all N source placements compared to

2013 regardless of N application timing (Table 4.4). Deep banded UAN, deep banded UAN plus Nitamin Nfusion, and anhydrous ammonia had at least 2.5 SPAD units higher than surface broadcast UAN with or without Nitamin Nfusion in 2011 and 2012 regardless of N application timing. SPAD readings for fall and spring-applied deep banded UAN plus Nitamin Nfusion were 8% higher compared to surface broadcast UAN plus Nitamin Nfusion in 2011 and 2012. Applying N in the fall or spring had no significant differences in SPAD within N source placements in 2011 and 2012. In 2013, SPAD meter readings indicated that plants were 22% greener with spring-applied deep banded anhydrous ammonia compared to fall-applied deep banded anhydrous ammonia. Conversely, SPAD readings were 11% greater with spring-applied deep banded UAN plus Nitamin Nfusion compared to fall-applied UAN with Nitamin Nfusion.

Nitrogen applied at 168 kg ha^{-1} had SPAD values with a significant interaction between year and N source placement ($P < 0.05$) (Table 4.6). Similar to N applied at 84 kg ha^{-1}, SPAD readings in 2011 and 2012 were highest (50.7 to 57.3 SPAD units) among all N source placements at 168 kg N ha^{-1} compared to 2013 (Table 4.7). There were no significant differences in SPAD readings in 2011 compared to 2012 among N source placements. Deep banded UAN, deep banded UAN plus Nitamin Nfusion, and deep banded anhydrous ammonia resulted in 0.3 to 6.6 higher SPAD units than surface broadcast UAN or UAN plus Nitamin Nfusion in 2011 and 2012. Although not significantly different in 2012, deep banded UAN without Nitamin Nfusion resulted in the highest SPAD readings in 2011, 2012, and 2013 by 1.1, 1.3, and 1.9 SPAD units, respectively.

SPAD readings may have been more affected in fall-applied treatments due to the distribution and amount of precipitation during the non-growing season months of November through March. For example, 2013 was relatively wet early in the growing season and these conditions may have affected the spring-applied deep banded anhydrous ammonia at 68 kg N ha^{-1} compared to fall-applied. Furthermore, cumulative precipitation in the months after fall N application (November 2012) to planting was the wettest among the three years and potentially caused increased N loss due to leaching and/or denitrification (Vetsch and Randall, 2004). Nevertheless, SPAD readings in 2011 and 2012 were higher in all deep banded treatments. Previous studies indicated that deep banding N lowered the rates of microbial N transformations over surface application, which limited the amount of N that is lost through denitrification and volatilization (Drury et al., 2006; Grant et al., 2010).

Plant Population

Plant populations had an interaction between N source placement and N timing ($P < 0.05$) at 84 kg N ha^{-1} (Table 4.3). Plant populations in the deep banded UAN and deep banded UAN plus Nitamin Nfusion treatments when N was fall-applied at 84 kg N ha^{-1} were 16 and 14% higher than spring-applied N, respectively (Table 4.4). When N was applied at 168 kg N ha^{-1} in the fall, deep banded UAN plus Nitamin Nfusion had plant populations that were 54,250 plants ha^{-1} greater than spring-applied N (Table 4.7).

There was an interaction between N source placement and N timing ($P < 0.05$) at 168 kg N ha^{-1} (Table 4.6). Plant populations were similar among treatments with a fall timing at 168 kg ha^{-1} (Table 4.7). No-till/surface-applied urea with or without Nitamin Nfusions had plant populations that were 11,650 to 16,200 greater than deep banded treatments with spring application. Comparatively, deep banded N with strip-tillage has been shown to improve seedbed conditions more effectively compared to those of no-tillage treatments (Randall and Hill, 2000; Lithourgidis et al., 2005). Hendrix et al. (2004) found no-till on a silt loam soil to have 37% lower plant populations than with strip-till, potentially due no-till having prolonged saturated soil conditions in the row.

Corn Grain Yield

Corn grain yields had a significant three-way interaction ($P < 0.05$) between timing of N application, source placement, and year at 84 kg N ha^{-1} (Table 4.3). In 2011, ST/deep banded UAN had 1.11 to 1.42 Mg ha^{-1} greater corn grain yield than all of the N source/placements with fall N application (Table 4.4). Spring application of ST/deep banded UAN had 4.21 Mg ha^{-1} lower corn grain yields in 2011 compared to fall-applied N. Strip-tillage for corn in the fall can increase grain yield due to more favorable and drier soil conditions, settling of soil in tilled row during winter, and a warmer and drier seedbed conditions by spring (Randall and Hill, 2000). Fall N application for all NT/surface broadcast and ST/deep banded treatments resulted in 0.93 to 4.21 Mg ha^{-1} greater corn grain yields in 2011 compared to spring-applied N. The severe drought in 2012 (NAOO, 2013) resulted in 1.8 Mg ha^{-1} lower corn grain yields compared to 2011 and 2013, regardless of N timing. Corn grain yields were similar among source/placements and timings in 2012. In 2013, ST/deep banded UAN with or without Nitamin Nfusion showed no significant differences in corn grain yield when N was applied in the fall or spring, which was unlike Shapiro et al. (2016), who reported band Nitamin Nfusion (30% of total N) increased grain yield 4% compared to UAN alone at one Nebraska location. Spring application of NT/surface broadcast UAN plus Nitamin Nfusion in 2013 had the highest corn grain yield (7.75 Mg ha^{-1}).

Corn grain yield in 2013 with ST/deep banded anhydrous ammonia was 1.61 Mg ha^{-1} (27%) greater with spring N application compared to fall application. Kyveryga et al. (2004) reported fall-applied anhydrous ammonia in Iowa soils with pH > 7.5 to have faster nitrification rates and more nitrate loss through denitrification during spring rainfall than anhydrous ammonia applied in the spring. These results suggest that there was a significant amount of nitrate loss through denitrification in 2013 because of the relatively wet month of April (194 mm), which ultimately delayed planting to May.

A significant three-way interaction ($P < 0.05$) between timing of N application, source placement, and year was detected for corn grain yield at 168 kg N ha^{-1} (Table 4.6). In 2011, fall-applied NT/surface broadcast UAN with Nitamin Nfusion, ST/deep banded anhydrous ammonia, and ST/deep banded UAN with or without Nitamin Nfusion resulted in 1.18, 2.70, 2.41, and 3.60 Mg ha^{-1} higher corn grain yield than an equivalent spring N application, respectively (Table 4.7). Higher corn grain yields with fall N application were observed in 2011 for both 84 and 168 kg N ha^{-1} were probably due to wet conditions following strip-tillage and planting, which affected stand establishment. The aggressive tillage knife (Lanpher, 2002) used in this experiment was different than other research on strip-till at this location (Nash et al., 2013). Furthermore, corn grain yields in 2011 at 168 kg N ha^{-1} with spring N application of NT/surface broadcast UAN with and without Nitamin Nfusion had at least a 1.02 and 1.75 Mg ha^{-1} higher corn grain yield than all ST/deep banded source placements. This was similar at 84 kg N ha^{-1}, where NT/surface broadcast UAN in the spring with or without Nitamin Nfusion had 0.98 Mg ha^{-1} higher corn grain yields in 2011 than all ST/deep banded source/placements. This indicates that saturated soil conditions from more frequent precipitation events in the early growing season may have limited the growth of corn roots due to poorly drained soils so that roots were unable to absorb the deep banded fertilizer placement, but were able to obtain the surface N fertilizer placement. Another study at the same location concluded that surface-applied urea was relatively more effective for corn production with abundant early season rainfall, which likely incorporated N from the fertilizer into the shallow soil layer and made the N more available for plant uptake (Johnson et al., 2016).

Similar to nitrogen at 84 kg ha^{-1}, corn grain yields were negatively affected by drought conditions in 2012 at 168 kg N ha^{-1} (Table 4.7). There were no statistically significant differences observed between fall and spring N application in 2012 among N source placements at 84 or 168 kg N ha^{-1}.

A consistent increase in corn grain yield in 2013 with a spring application of NT/surface broadcast UAN with Nitamin Nfusion at 168 kg N ha^{-1} had the highest corn grain yield but it was similar among spring or fall applied N source placements. This was likely due to the slow release rate of N in Nitamin Nfusion because gaseous N loss may have been reduced prior to the period of substantial plant N uptake (Nash et al., 2012). The addition of Nitamin Nfusion with NT/surface broadcast UAN was the highest yielding in 2013 with a spring application at 168 kg N ha^{-1}. This suggests that spring-applied Nitamin Nfusion may have conserved N in the soil profile by delaying the conversion to nitrate until after the heavy rainfall period in May, regardless of placement. Shapiro et al. (2016) found similar results where surface broadcast and subsurface banded

UAN with Nitamin Nfusion produced 0.21 to 0.59 Mg ha^{-1} higher grain yields than surface broadcast UAN without Nitamin Nfusion on a loamy sand soil at a site in Nebraska. Although the study did not assess different N timings, the research was still similar because cumulative rainfall was greater in May (252 mm) at this particular Nebraska location compared to other sites in the experiment.

In 2013, ST/deep banded anhydrous ammonia yielded 1.7 Mg ha^{-1} more grain yield when spring-applied compared to fall at 168 kg N ha^{-1}. This suggests that N loss may have occurred through denitrification over the fall, winter, and early spring period. This is similar to a three-year study done in Minnesota that observed an average increase of 0.8 Mg ha^{-1} in corn grain yield with anhydrous ammonia applied in the spring compared to fall application (Vetsch and Randall, 2004). Furthermore, research done on a poorly drained claypan soil reported a 2.0 Mg ha^{-1} reduction in corn grain yield with fall-applied anhydrous ammonia at 140 kg N ha^{-1} compared to a spring application (Nash et al., 2013). Similarly, Welch et al. (1971) found fall application of ammonium nitrate produced less corn grain yield than spring N application in Illinois which may have been due to less soil retention.

Spring and fall application of NT/surface broadcast and ST/deep banded source placements were similar in 2013 at 168 kg N ha^{-1} (Table 4.7). The inconsistent corn grain yields among the three years in this experiment can be attributed to the variations in precipitation that occurred, especially after the spring N application. Rainfall was relatively more frequent after spring N application in 2011 and may have prolonged saturated soil conditions and caused ST/deep banded treatments to be ineffective because of spatial and temporal N shortages in the root zone and the effect of tillage on the soil following prolonged precipitation. Although deep banding placement may conserve N, there may be spatial and temporal N shortages because N may be spatially separated from plant roots throughout significant parts of the growing season (Shapiro et al., 2016). Furthermore, cumulative precipitation was relatively low between fall N application (November 2010) and planting, suggesting minimal N loss may have occurred during the fall, winter, and early spring months, while more N was potentially lost in the months following the spring N application. Fall N application may have retained more NO_3^- and NH_4^+ in the soil by spring in 2011, which means it was more readily available for plant uptake during the early growing season (Malhi and Nyborg, 1986). Vetsch and Randall (2004) observed greater soil NO_3-N concentrations with fall-applied N than spring-applied N, indicating substantial nitrification of fall-applied N occurred by the early growth stages in the spring. High corn grain yields in 2013 with spring N application of ST/deep banded anhydrous ammonia and NT/surface broadcast UAN with or without Nitamin Nfusion may have been due to an increase in microbial activity from warmer soil conditions in May. There was 27 mm of precipitation that occurred on the same day as fall N application (11 November 2012), which may have caused ST/deep banded anhydrous ammonia to lose a significant amount of N due to physical disruption and improper sealing of the injection knives that may have created zones to allow for ammonia movement to reach the soil surface (Overdahl and Rehm, 1990). Implementing different N management practices is always a good option for farmers to increase corn grain yield. One study combined no-till with subsurface UAN or anhydrous ammonia placement and observed higher corn grain yield compared to utilizing a conventional tillage system with the same N application (Mengel et al., 1982). This likely resulted from decreased ammonia volatilization and immobilization commonly associated with surface N application on high residue soil surfaces.

Grain Moisture and Quality

Corn grain moisture concentration had a significant interaction between N source placement and N timing ($P < 0.05$) when averaged across years at 84 kg N ha^{-1} (Table 4.3). Results in corn grain moisture were variable. No-till/surface broadcast UAN and ST/deep banded UAN with and without Nitamin Nfusion had 7, 23 and 45 g kg^{-1} higher corn grain moisture with spring N application than fall N application at 84 kg N ha^{-1}, respectively (Table 4.5). Conversely, NT/surface broadcast UAN plus Nitamin Nfusion and ST/deep banded anhydrous ammonia had 17 and 16 g kg^{-1} higher corn grain moisture with fall N application compared to spring N application at 84 kg N ha^{-1}, respectively. Strip-till/deep banded UAN in the spring had the highest overall corn grain moisture (224 g kg^{-1}) and had a 25% increase in corn grain moisture with spring N application over fall N application at 84 g kg^{-1} (Table 4.5).

At 168 kg N ha^{-1}, corn grain moisture was different among N source placements ($P < 0.05$) regardless of N timing and year (Table 4.6). Strip-till/deep banded UAN plus Nitamin Nfusion (207 g kg^{-1}) and ST/deep banded anhydrous ammonia (215 g kg^{-1}) at 168 kg N ha^{-1} had at least 17 g kg^{-1} greater moisture concentration than all other N source/placements (Table 4.7). No-till/surface broadcast UAN with Nitamin Nfusion at resulted in the lowest grain moisture content (175 g kg^{-1}), but was not lower than NT/surface broadcast UAN (181 g kg^{-1}) or ST/deep banded UAN (190 g kg^{-1}). Corn grain moisture content is affected by several factors including, but not limited to, N fertilizer type, corn hybrid, tillage system, and climate (Wolkowski, 2000; Vetsch and Randall, 2002). All of these factors influence the rate of corn maturation, in which a slower rate generally results in relatively higher grain moisture content (Beegle et al., 2007).

Protein concentration in corn grain had an interaction between N source/placements and year ($P < 0.05$) at 84 kg N ha^{-1} (Table 4.3). Strip-till/deep banded UAN with Nitamin Nfusion in 2013 had lower grain protein concentration (66.1 g kg^{-1}) than all N source placements in the three years (Table 4.5). Overall, grain protein concentration for N source/placements in 2012 ranged from 100.9 to 103.0 g kg^{-1} and was at least 12.8 g kg^{-1} higher than treatments in 2011 and 2013.

Protein concentration in corn grain also had a significant interaction between N source/placements and year ($P < 0.05$) at 168 kg N ha^{-1} (Table 4.6). Protein concentration in corn grain had a similar response in 2011, 2012, and 2012 (Table 4.7). Protein concentration in corn grain was highest for all N source/placements (103.8 to 104.5 g kg^{-1}) in 2012. No-till/surface broadcast UAN had one of the lowest grain protein concentrations (75.9 g kg^{-1}) compared to all N source/placements in the three years of this research, but was similar to ST/deep banded anhydrous ammonia in 2013 and NT/surface broadcast UAN with (77.5 g kg^{-1}) or without Nitamin Nfusion (77.8 g kg^{-1}) in 2011. Grain protein concentration corresponded with SPAD meter leaf readings since both SPAD meter readings and grain protein concentration had similar patterns in 2011, 2012, and 2013. Corn grain protein concentration was also potentially an indicator of N uptake and removal by the plant since protein concentration is usually calculated from grain N concentration.

Corn grain oil concentrations at 84 kg N ha^{-1} were combined over years since there was no significant interaction (Table 4.3). No-till/surface broadcast UAN had the highest grain oil concentration (34.0 g kg^{-1}), but it was similar to the other N source/placement treatments (Table 4.5). Corn grain oil concentrations were different among N source placements at 168 kg N ha^{-1} (Table 4.6). Grain oil concentration was 1.7 and 2 g kg^{-1} higher with strip-till/deep banded anhydrous ammonia than NT/surface broadcast UAN plus Nitamin Nfusion and ST/deep banded UAN, respectively (Table 4.7). Strip-till/deep banded UAN at 168 kg N ha^{-1} had 1.5 to 2.0 g kg^{-1} lower grain oil concentration than NT/surface broadcast UAN, ST/deep banded UAN plus Nitamin Nfusion, and ST/deep banded anhydrous ammonia. Combining N source placements across the three years at 168 kg N ha^{-1} indicated higher grain oil concentration with the fall application (32.7 g kg^{-1}) compared to a spring application (31.7 g kg^{-1}) (Table 4.8).

Early-Season Corn Plant Height

Corn plant heights measured on 1 June and 6 July had significant ($P < 0.05$) differences among N source placements at 84 kg N ha^{-1} (Table 4.9). No-till/surface broadcast UAN with or without Nitamin Nfusion had significantly greater corn plant heights on 1 June than ST/deep banded UAN with or without Nitamin Nfusion at 84 kg N ha^{-1} (Figure 4.3). Similarly, NT/surface broadcast UAN with or without Nitamin Nfusion had greater corn plant heights on 6 July than all ST/deep banded treatments at 84 kg N ha^{-1} (Figure 4.3). Corn plant height measured on 15 June was significantly ($P < 0.05$) different among N timing at 84 kg N ha^{-1} (Table 4.9). Fall N application had a mean corn plant height that was 2.6 cm higher than spring N application at 84 kg N ha^{-1} on 15 June (Figure 4.4). This suggests that corn plant height can be an indicator for slightly greater growth since fall N application had taller plants ha^{-1} at 84 kg N ha^{-1}.

At 168 kg N ha^{-1}, corn plant height measured on 27 May, 8 June, and 15 June was significantly ($P < 0.05$) different due to N source/placements (Table 4.10). No-till/surface broadcast UAN with Nitamin Nfusion (14.2 cm) was 0.4 to 1.6 cm taller than all ST/deep banded treatments on 27 May (Figure 4.5). No-till/surface broadcast UAN also had significantly greater corn plant heights than all ST/deep banded treatments on 8 June and 15 June. Lower early season plant heights for ST/deep banded treatments suggest that plant emergence and growth was delayed in this research. These results are counter to results from a study in Indiana that found lower early season corn plant heights and delayed maturity in treatments with no-till compared to conventional tillage (Griffith et al., 1973). Delayed plant emergence may result from a variety of factors including cooler soil temperatures, higher soil moisture, and high soil residue cover (Vetsch and Randall, 2002), which is typically associated with no-tillage systems. No-tillage systems may have cooler, wetter seedbed conditions (Randall and Hill, 2000) and can have reduced corn plant heights when combined with a surface N application due to greater N loss (Riedell et al., 2000). Corn plant height had significant ($P < 0.05$) differences at 168 kg N ha^{-1} among N timings (fall or spring) on 1 June, 15 June, and 22 June (Table 4.10). Fall N applications had taller plants than spring N treatments (Figure 4.6). This suggests that greater early-season plant heights with fall N application may not always indicate greater plant heights at later corn growth stages when N was applied at a higher rate (168 kg N ha^{-1}). Fall N application generally has larger amounts of NO_3-N available in the spring (Vetsch and Randall, 2004), which suggests that corn readily utilized N at the early growth stages in the spring, and measured early growth and plant vigor.

CONCLUSIONS

Utilizing different N management strategies for corn production can be difficult due to unpredictable year-to-year climate conditions. On claypan soils, corn production is even more challenging due to these soils' relatively poor drainage characteristics, which contribute to a higher potential for N loss and subsequently lower crop yields. Although the data were variable across N timings, N source/placements, and year, this range of climatic conditions can be expected in the U.S. Corn Belt region. Over this three-year study, the application of strip-till deep banded UAN with fall timing, resulted in the highest corn grain yield (8.12 to 9.12 Mg ha^{-1}) at 84 and 168 kg N ha^{-1} in 2011. Thus, climate conditions may have caused spatial and temporal N shortages when N was deep banded applied as UAN or anhydrous ammonia fertilizer because it may be separated from plant roots or may not be converted into NO_3-N at the appropriate growth stage. Spring N application had higher corn grain yields in all N source/placements in 2013 compared to 2011, which may have been due to warmer and wetter soil conditions in May. The low corn grain yield response in 2012 with fall and spring N applications can be attributed to a warmer soil and low rainfall during the growing season, regardless of N rate. Relatively higher SPAD readings in 2012 did not result in higher grain yield due to extreme drought conditions. Fall-applied ST/deep banded anhydrous ammonia had the lowest grain yields (5.97 and 6.8 Mg ha^{-1}) in 2013 at both N rates. The lower grain yield response with fall-applied anhydrous ammonia might be attributed to the later planting date in 2013. Additionally, NT/surface or ST/deep-banded Nitamin Nfusion with UAN had no grain yield increase compared to UAN alone in 2011, 2012, and 2013, regardless of N timing. This study suggests that ST with deep banding UAN or anhydrous ammonia does not always produce higher corn grain yields and might be more at risk for greater N loss under certain climatic conditions.

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Table 4.1. Field management information in 2011, 2012, and 2013.

Field information	2011		2012		2013	
Timing of N application	Fall	Spring	Fall	Spring	Fall	Spring
N application date	11 Nov. 2010	11 Apr.	15 Nov. 2011	11 Apr.	11 Nov. 2012	1 May
Crop protection management						
Burndown[†]	NA[‡]		15 Nov. 2011, Simazine (0.98 kg a.i. ha^{-1}) + glyphosate (1.14 kg a.i. ha^{-1})		11 Nov. 2012, Simazine (0.98 kg a.i. ha^{-1})	
	11 Apr., Glyphosate (0.78 kg a.i. ha^{-1}) + 2,4-D (0.78 L ha^{-1}) + DAS (0.51 L ha^{-1})		NA		14 May, Acetochlor (2.08 kg a.i. ha^{-1}) + atrazine (1.97 kg a.i. ha^{-1})	
Postemergence	13 Apr., Atrazine (1.9 kg a.i. ha^{-1}) + *S*-metolachlor (1.5 kg a.i. ha^{-1})		11 May, Acetochlor (0.97 kg a.i. ha^{-1}) + flumetsulam (0.03 kg a.i. ha^{-1}) + clopyralid (0.1 kg a.i. ha^{-1}) + glyphosate (1.14 kg a.i. ha^{-1})		22 May, Glyphosate 1.13 kg a.i. ha^{-1}) + mesotrione (0.09 kg a.i. ha^{-1}) + NIS (.25% v/v) + UAN (2.34 L ha^{-1}) + lambda-cyhalothrin (0.02 kg a.i. ha^{-1})	
Late postemergence	NA		5 June, Glyphosate (1.14 kg a.i. ha^{-1}) + mesotrione (0.09 kg a.i. ha^{-1}) + AMS (0.02 kg L^{-1}) + COC (2.34 L ha^{-1})		NA	

[†]Chemical names: acetochlor, (2-chloro-2’-methyl-6’ethyl-N-ethoxymethylacetanilide); atrazine, [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine]; clopyralid, 3,6-dichloro-2-pyridinecarboxylic acid, monoethanolamine salt; flumetsulam, N-(2,6-difluorophenyl)-5-methyl-1,2,4-triazolo-[1,5a]pyrimidine-2-sulfonamide; glyphosate, N-(phosphonomethyl) glycine; Lambda-cyhalothrin, [1α(S*),3α(Z)]-(±)-cyano-(3-phenoxyphenyl)methyl-3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate; mesotrione [2-4-(methylsulfonyl)-2-nitrobenzoyl-1,3-cyclohexanedione]; Simazine, 2-chloro-4.6-bis(ethlyamino)-s-triazine; *S*-metolachlor, 2-Chloro-N-(2-ethyl-6-methylphenyl)-N-[(1S)-2-methoxy-1-methylethyl1] acetamide.

[‡]Abbreviations: AA, anhydrous ammonia; a.i., active ingredient; COC, crop oil concentrate; DAS, diammonium sulfate; NA, not applied; NIS, non-ionic surfactant; UAN, 32% urea ammonium nitrate.

Table 4.2. Average monthly soil temperature at 6 cm depth with soybean residue from time of fall N application to corn harvest in each season.

	Soil Temperature (°C)		
Month	2010-2011	2011-2012	2011-2012
Nov.	7.3	7.7	6.7
Dec.	0.8	3.5	3.9
Jan.	-0.3	1.4	0.9
Feb.	0.3	2.5	0.9
Mar.	5.5	10.2	2.1
Apr.	10.7	13	9
May	16.2	19.4	16
Jun.	21.7	22.6	21.2
Jul.	25.8	27	23.5
Aug.	24.6	23.1	28.3
Sep.	19.1	19.2	22

Table 4.3. Two-factor ANOVA table for SPAD, plant population, yield, moisture, test weight, starch, protein, and oil concentration for nitrogen treatments at 84 kg N ha^{-1}.

Source	df	SPAD	Population	Yield	Moisture	Test Weight	Starch	Protein	Oil
		Pr > F	Pr > F	Pr > F	Pr > F	Pr > F	Pr > F	Pr > F	Pr > F
Year†	2	<.0001‡	<.0001	<.0001	0.0604	0.3102	<.0001	<.0001	<.0001
Timing	1	0.5156	<.0001	0.0005	0.1431	0.4947	0.9282	0.8297	0.6760
Year x Timing	2	0.7480	<.0001	<.0001	0.0053	0.4133	0.2750	0.0312	0.6729
SorcPlac†	4	<.0001	<.0001	0.0056	0.0023	0.4348	0.5886	<.0001	0.3492
Year x SorcPlac	8	0.0053	<.0001	0.4450	0.0031	0.2280	0.4634	<.0001	0.9257
SorcPlac x Timing	4	0.6319	0.0187	0.0022	0.0018†	0.8582	0.8722	0.3250	0.5522
Year x SorcPlac x Timing	8	0.0285	0.0698	0.0046	0.4078	0.2404	0.3521	0.1042	0.2024

†Abbreviations: SorcPlac, source/placement.

‡Fisher's Protected Least Significant Difference at $P \leq 0.05$.

Table 4.4. Corn SPAD, plant population, and grain yield response to nitrogen source/placements at 84 kg N ha^{-1}. Data were combined over factors or years in the absence of a significant interaction.

N source placement	SPAD 2011 F	SPAD 2011 S	SPAD 2012 F	SPAD 2012 S	SPAD 2013 F	SPAD 2013 S	Population F	Population S	Grain yield 2011 F	Grain yield 2011 S	Grain yield 2012 F	Grain yield 2012 S	Grain yield 2013 F	Grain yield 2013 S
							---- No. ha^{-1} ----		---------------- Mg ha^{-1} ----------------					
Surface UAN[†]	48.2	44.6	47.9	48.8	39.2	39.3	70,000	67,800	6.91	5.98	2.14	2.30	6.53	7.23
Deep UAN	54.4	53.4	51.3	53.7	44.0	44.0	66,750	56,100	8.12	3.91	1.73	2.11	7.62	7.53
Surface NF	46.8	47.8	48.6	47.8	41.7	42.1	70,400	70,050	6.85	5.70	2.02	2.50	6.82	7.75
Deep NF	52.1	55.3	52.4	53.4	41.8	37.8	68,500	59,150	7.01	4.72	1.33	1.76	7.17	6.70
Deep AA	55.7	55.2	53.8	52.5	37.5	45.8	64,200	60,100	6.70	4.41	1.60	1.70	5.97	7.58
LSD (P=0.05)[‡]	------------------- 4.7 -------------------						---- 8,700 ----		------------------ 0.95 ------------------					

[†]Abbreviations: AA, anhydrous ammonia; F, fall; NF, Nitamin Nfusion; S, spring; UAN, 32% urea ammonium nitrate.
[‡]Fisher's Protected Least Significant Difference at $P \leq 0.05$.

Table 4.5. Corn grain moisture, test weight, starch, protein, and oil concentration response to nitrogen source/placements at 84 kg N ha^{-1}. Data were combined over factors or years win the absence of a significant interaction.

N source	Moisture		Test		Protein			
placement	F	S	weight	Starch	2011	2012	2013	Oil
	---- g kg^{-1} ----		kg hL^{-1}	g kg^{-1}	------------ g kg^{-1} ------------			g kg^{-1}
Surface UAN†	187	194	55.7	741	72.9	100.9	67.9	34.0
Deep UAN	178	223	53.3	738	87.2	103.0	72.0	32.9
Surface NF	190	173	56.1	740	72.0	101.5	70.0	33.9
Deep NF	201	224	54.9	740	84.6	102.3	66.1	33.2
Deep AA	217	201	55.3	738	88.1	102.3	70.0	33.4
LSD (P=0.05)‡	---- 42 ----		NS	NS	------------- 2.1 -------------			NS

†Abbreviations: AA, anhydrous ammonia; F, fall; NF, Nitamin Nfusion; NS, not significant; S, spring; UAN, 32% urea ammonium nitrate.

‡Fisher's Protected Least Significant Difference at $P \leq 0.05$.

Table 4.6. Two-factor ANOVA table for SPAD, plant population, yield, moisture, test weight, starch, protein, and oil concentration for nitrogen treatments at 168 kg N ha^{-1}.

		SPAD	Population	Yield	Moisture	Test weight	Starch	Protein	Oil
Source	df	Pr > F	Pr > F	Pr > F	Pr > F	Pr > F	Pr > F	Pr > F	Pr > F
Year	2	<.0001[‡]	<.0001	<.0001	<.0001	0.0311	<.0001	<.0001	<.0001
Timing	1	0.3242	<.0001	0.0009	0.4513	0.1823	0.3070	0.3167	0.0356
Year x Timing	2	0.1093	<.0001	<.0001	0.1353	0.5255	0.2270	0.1334	0.2038
SorcPlac[†]	4	0.0028	<.0001	0.1721	<.0001	0.2391	0.0701	<.0001	0.0132
Year x SorcPlac	8	0.0054	<.0001	0.0327	0.1372	0.3354	0.4950	<.0001	0.1423
SorcPlac x Timing	4	0.0809	0.0029	0.0873	0.3683	0.4364	0.9079	0.1826	0.2722
Year x SorcPlac x Timing	8	0.4748	0.1815	0.0231	0.3078	0.4866	0.7902	0.1145	0.6455

[†]Abbreviations: SorcPlac, source/placement.

[‡]Fisher's Protected Least Significant Difference at $P \leq 0.05$.

Table 4.7. SPAD, plant population, grain yield, moisture, protein, and oil concentration response to nitrogen source/placements at 168 kg N ha^{-1}.

N Source	SPAD			Population		Grain yield							Protein			
						2011		2012		2013						
Placement	2011	2012	2013	F	S	F	S	F	S	F	S	Moisture	2011	2012	2013	Oil
				--- No. ha^{-1} ---		------------ Mg ha^{-1} ------------						g kg^{-1}	------ g kg^{-1} ------			g kg^{-1}
Surface UAN†	55.6	52.8	45.9	71,100	70,300	8.94	8.11	1.41	1.75	8.08	8.16	181b	77.8	103.8	75.9	32.7
Deep UAN	57.3	56.9	50.7	66,700	57,000	9.12	5.52	1.27	1.35	8.46	8.60	190b	92.5	104.5	88.4	31.1
Surface NF	50.7	53.6	48.8	73,050	70,450	8.56	7.38	1.63	1.79	8.01	8.68	175b	77.5	103.9	84.4	31.4
Deep NF	56.2	55.6	44.7	69,900	54,250	8.47	6.06	1.30	1.78	8.42	8.36	207a	93.8	104.8	83.1	32.6
Deep AA	55.9	55.4	43.8	64,000	58,650	9.06	6.36	1.44	1.71	6.80	8.50	215a	92.0	104.3	79.9	33.1
LSD (P=0.05)‡	------- 5.2 -------			---- 9,800 ----		-------------- 1.03 --------------						16	------- 6.9 -------			1.3

†Abbreviations: AA, anhydrous ammonia; F, fall; NF, Nitamin Nfusion; S, spring; UAN, 32% urea ammonium nitrate.

‡Fisher's Protected Least Significant Difference at $P \leq 0.05$.

Table 4.8. Fall and spring SPAD, moisture, test weight, starch, and oil concentration response to nitrogen sources at 168 kg N ha^{-1}. Data were combined over years and N source/placements.

N Timing	SPAD	Moisture	Test weight	Starch	Oil
		g kg^{-1}	kg hL^{-1}	g kg^{-1}	g kg^{-1}
Fall	52.6	191	68.0	736	32.7
Spring	51.9	196	69.6	737	31.7
LSD (P=0.05)‡	NS†	NS	NS	NS	0.08

†Abbreviations: NS, not significant.

‡Fisher’s Protected Least Significant Difference at $P \leq 0.05$.

Table 4.9. Two-factor ANOVA table for corn plant heights at 84 kg N ha^{-1}.

		27 May	1 June	8 June	15 June	22 June	30 June	6 July
Source	df	Pr > F	Pr > F	Pr > F	Pr > F	Pr > F	Pr > F	Pr > F
Year	2	<.0001[‡]	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001
Timing	1	0.0909	0.2542	0.0502†	0.0080	0.1304	0.4199	0.1464
Year x Timing	2	0.1699	0.1770	0.0843	0.0021	0.0250	0.0054	<.0001
SorcPlac[†]	4	0.0878	0.0060	0.1925	0.1535	0.9851	0.0337	0.2099
Year x SorcPlac	8	0.5414	0.0543	0.1082	0.0937	0.7844	0.0257	0.1137
SorcPlac x Timing	4	0.2358	0.1852	0.3019	0.2454	0.1515	0.2543	0.0973
Year x SorcPlac x Timing	8	0.8873	0.1855	0.5453	0.6266	0.9517	0.9865	0.4783

[†]Abbreviations: SorcPlac, source/placement.

[‡]Fisher’s Protected Least Significant Difference at $P \leq 0.05$.

Table 4.10. Two-factor ANOVA table for corn plant heights at 168 kg N ha^{-1}.

		27 May	1 June	8 June	15 June	22 June	30 June	6 July
Source	df	Pr > F	Pr > F	Pr > F	Pr > F	Pr > F	Pr > F	Pr > F
Year	2	<.0001[‡]	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001
Timing	1	0.0111	0.0001	0.3070	0.0071	0.0224	0.1618	0.1267
Year x Timing	2	0.0010	<.0001	0.1474	0.0030	0.0198	0.0207	<.0001
SorcPlac[†]	4	0.0001	0.0909	0.0113	0.0345	0.3286	0.1776	0.1033
Year x SorcPlac	8	0.0473	0.0759	0.0001	0.1302	0.3409	0.2188	0.0950
SorcPlac x Timing	4	0.4751	0.0007	0.0361	0.1839	0.3107	0.1450	0.2826
Year x SorcPlac x Timing	8	0.3364	0.0495	0.2730	0.5143	0.7584	0.4955	0.7226

[†]Abbreviations: SorcPlac, source placement.

[‡]Fisher's Protected Least Significant Difference at $P \leq 0.05$.

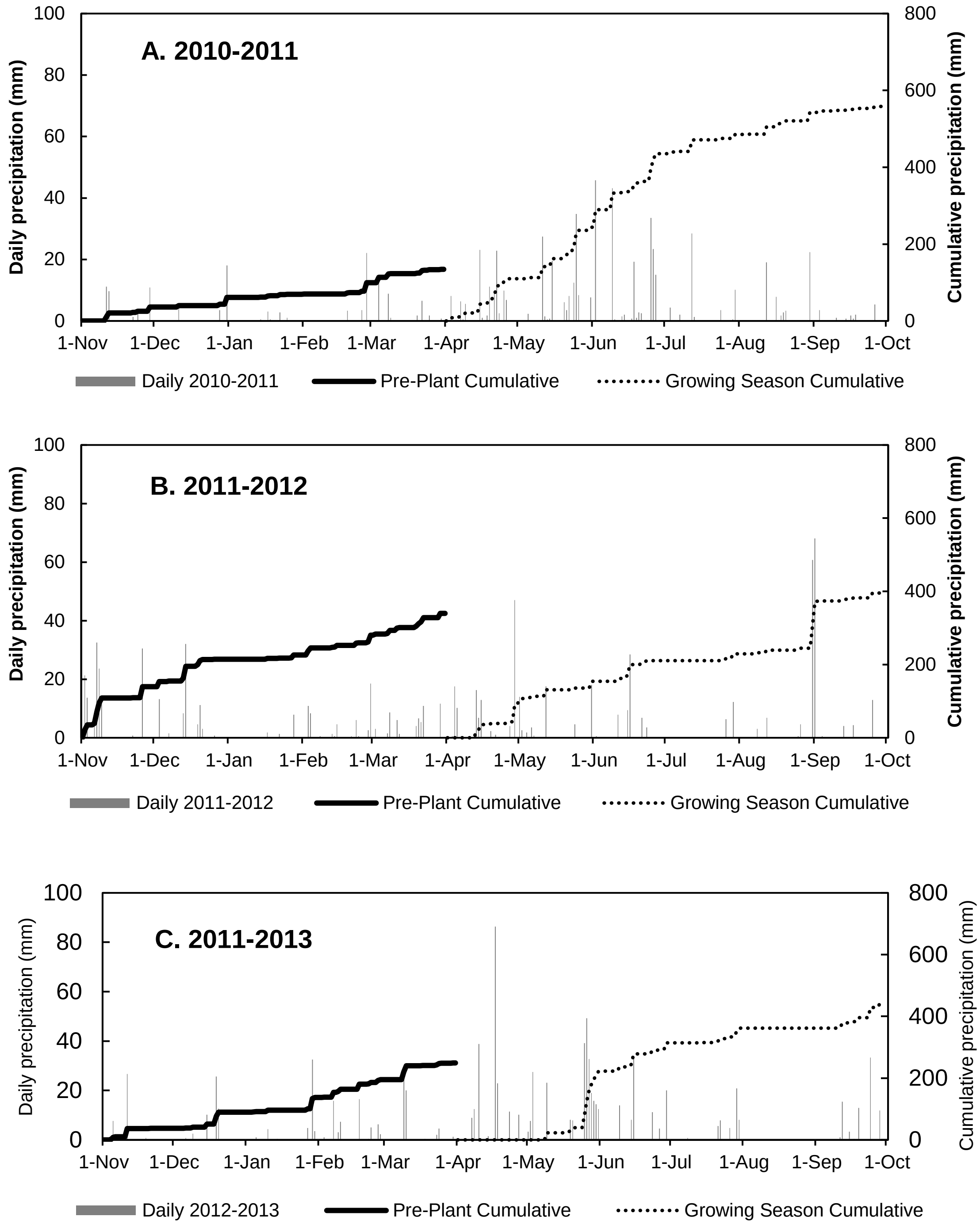


Figure 4.1. Daily and cumulative precipitation history for A) 2010-2011, B) 2011-2012, and C) 2012-2013.

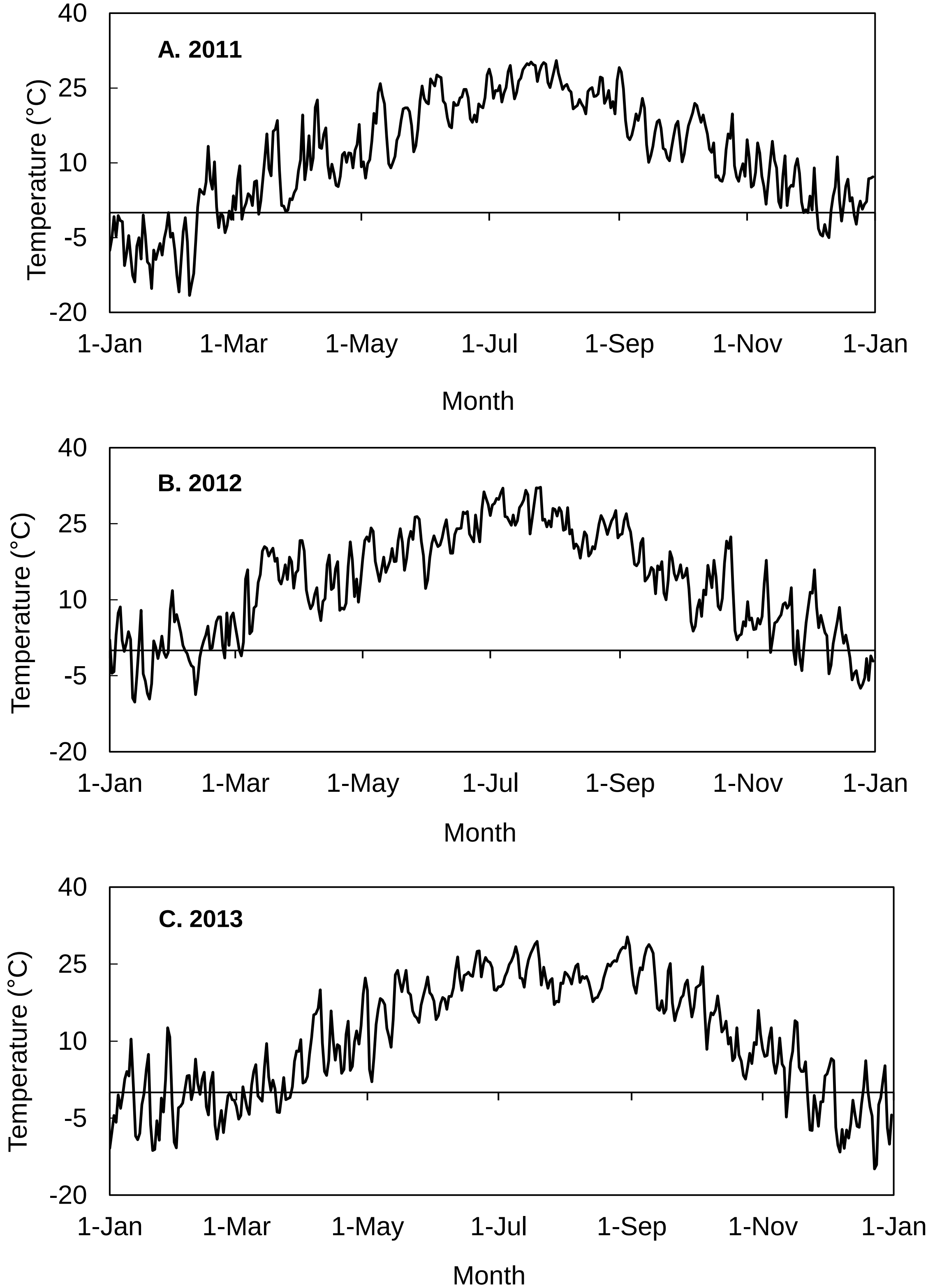


Figure 4.2. Daily average temperature (°C) for A) 2011, B) 2012, and C) 2013.

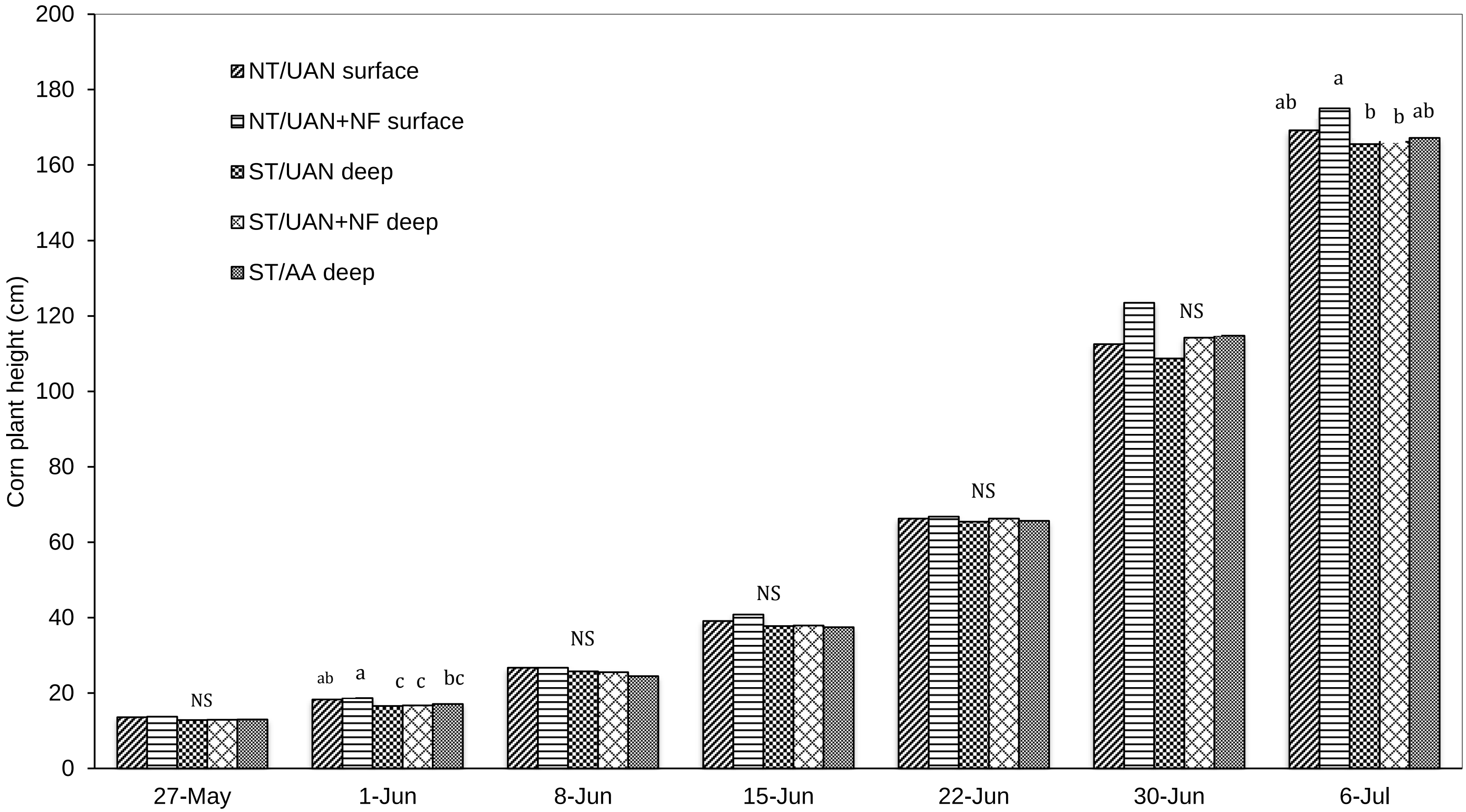


Figure 4.3. Corn plant heights due to N source placements averaged over N timing and years. Plant heights were measured on selected dates before VT at 84 kg N ha^{-1}. Letters over bars indicate differences among treatments within a given measurement date using Fisher's Protected LSD ($P < 0.05$).

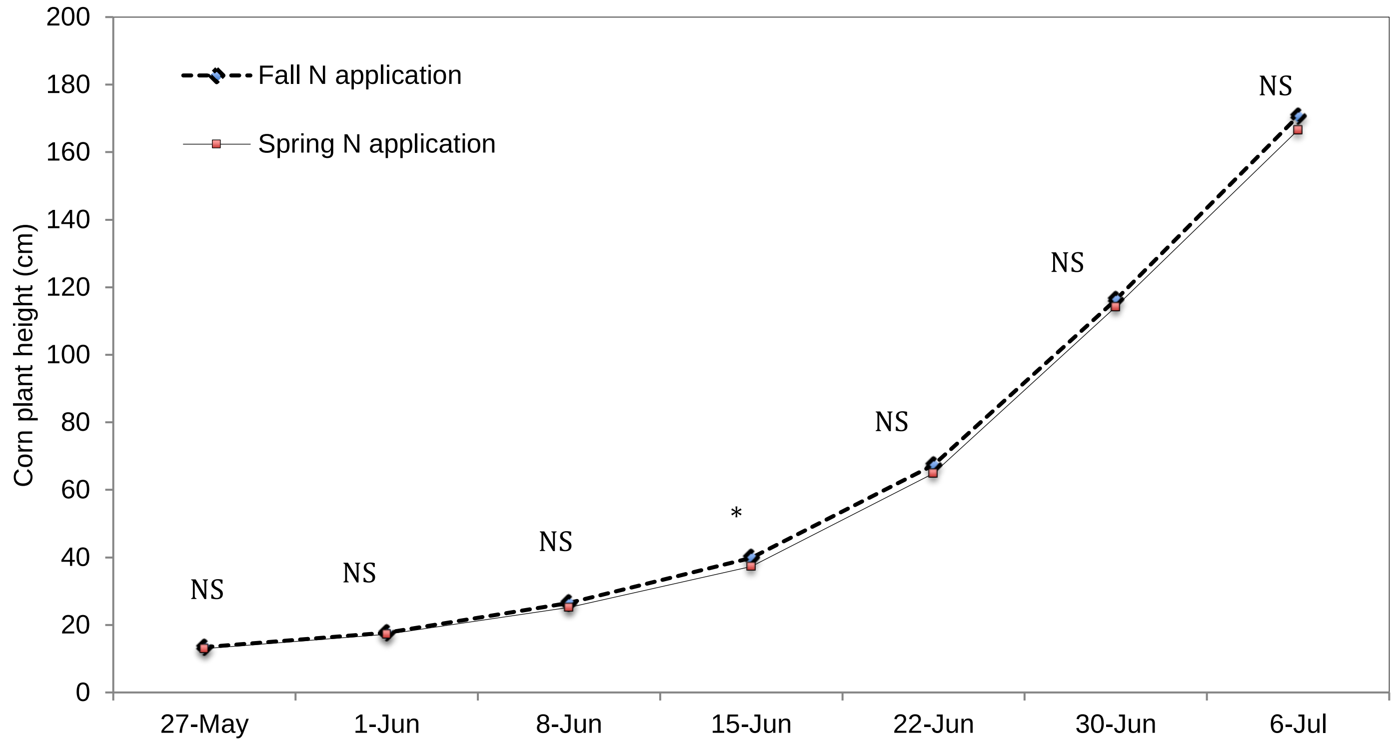


Figure 4.4. Corn plant heights due to N timing averaged over N source placements and years. Plant heights were measured on selected dates before VT at 84 kg N ha^{-1}. Asterisk over lines indicate differences among treatments within a given measurement date using Fisher's Protected LSD ($P < 0.05$).

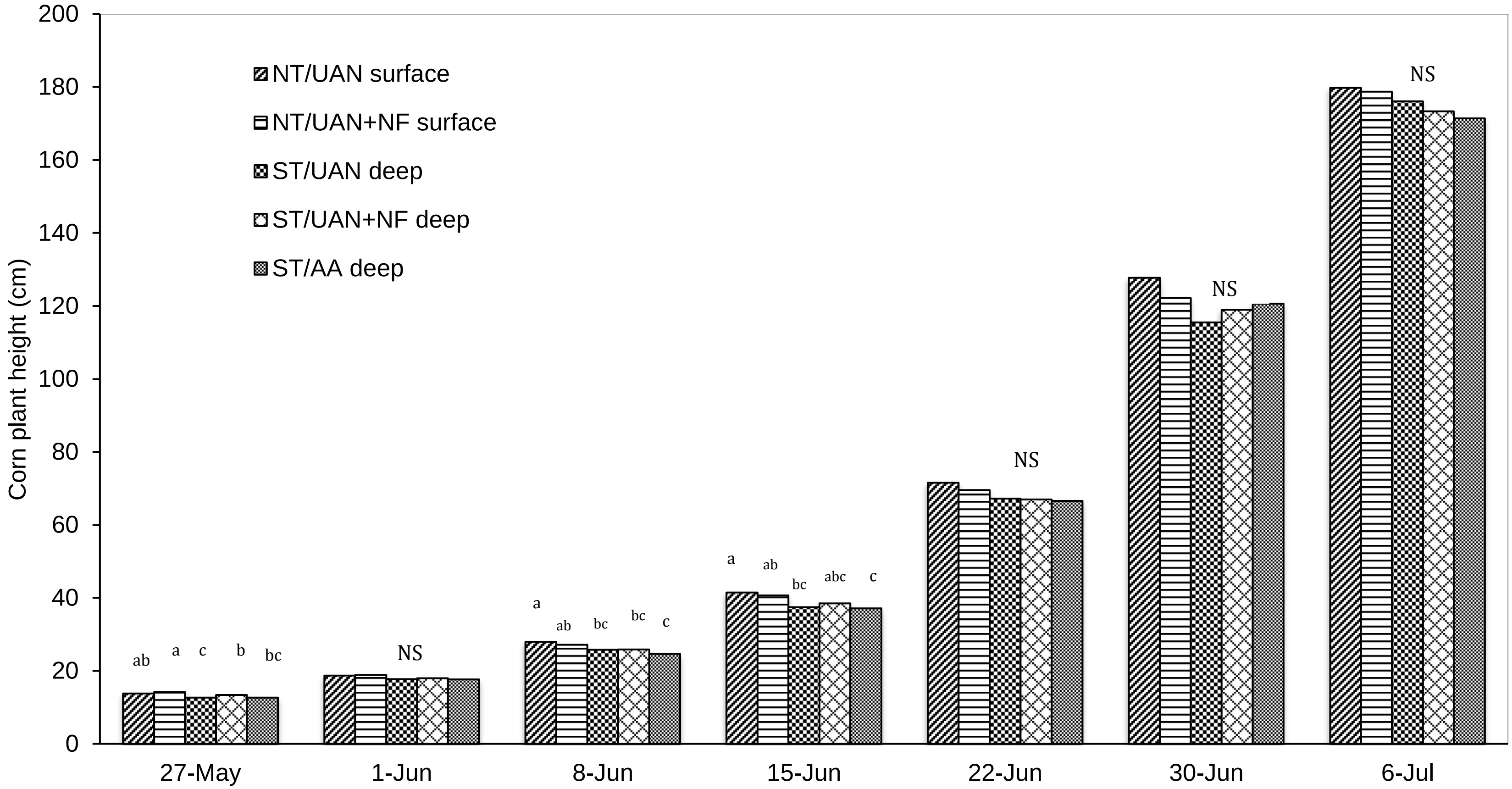


Figure 4.5. Corn plant heights due to N source placements averaged over N timing and years. Plant heights were measured on selected dates before VT at 168 kg N ha^{-1}. Letter over bars indicate differences among treatments within a given measurement date using Fisher's Protected LSD (P < 0.05).

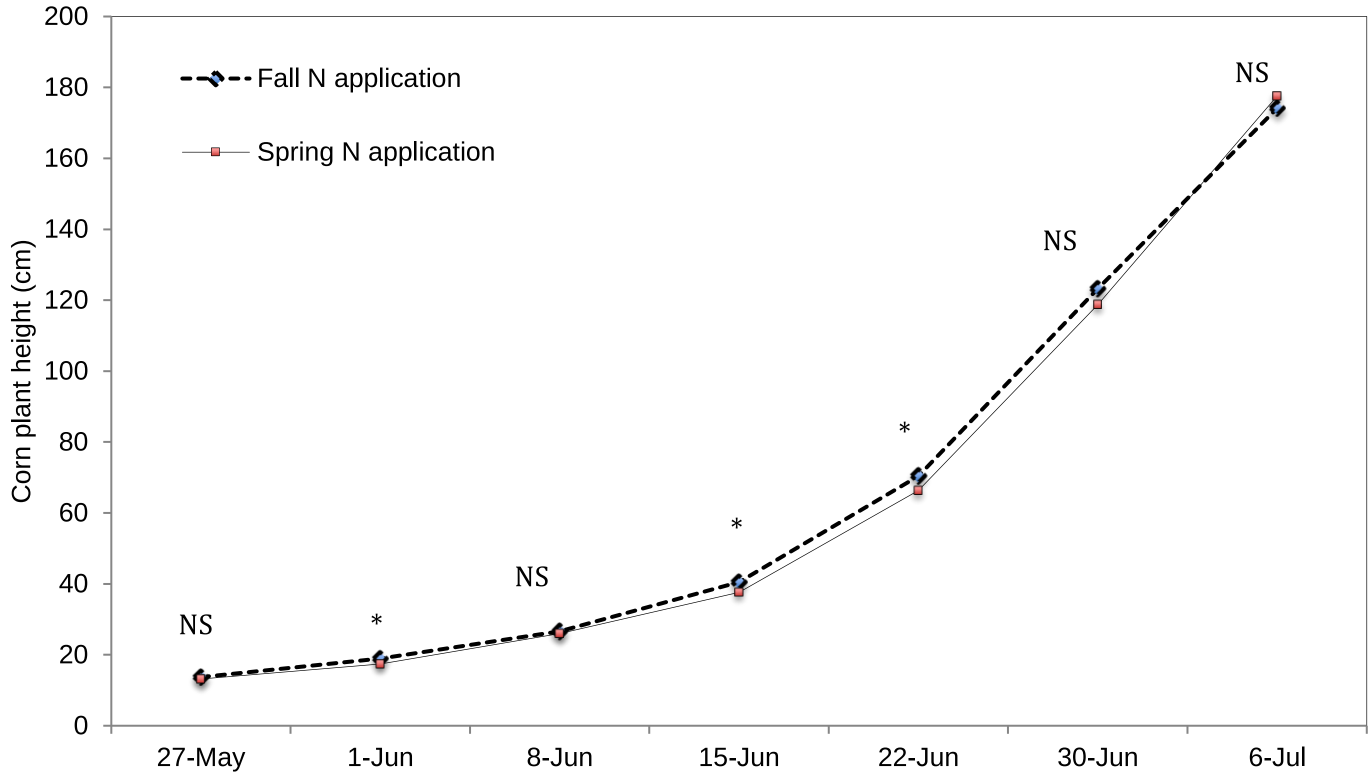


Figure 4.6. Corn plant heights due to N timing averaged over N source placements and years. Plant heights were measured on selected dates before VT at 168 kg N ha^{-1}. Asterisk over lines indicate differences among treatments within a given measurement date using Fisher's Protected LSD ($P < 0.05$).

CHAPTER 5

OVERALL CONCLUSIONS

Utilizing different nitrogen (N) management strategies for efficient corn production can be challenging due to unpredictable year-to-year climate conditions. On claypan soils, corn production is even more difficult due to these soils' relatively poor drainage characteristics, which contributes to a greater potential for gaseous N loss and subsequently lower corn yields. Nitrogen fertilizer timing, source, placement, and rate are viewed as controllable management strategies that can improve corn production on poorly-drained claypan soils. However, unpredictable weather conditions, including distributions of precipitation and temperature, are uncontrollable factors that may cause the greatest impact on N use efficiency (NUE) and yield.

One objective was to evaluate the effectiveness of different N fertilizer placement strategies on reducing cumulative soil N_2O emissions. During both years of this study, significant reductions in cumulative soil N_2O emissions were observed with deep-banded placement of urea with or without the addition of a NI. Cumulative soil N_2O emissions were reduced 30 to 46% with deep-banded urea with or without a NI compared to surface-applied urea and urea incorporated after application treatments. However, soil N_2O emission peaks were observed in the later parts of the growing season with the DB+NI treatment in 2016 and 2017. The potential for NIs for reducing soil N_2O emissions is based on the premise of reducing the rate of nitrification and subsequently decreasing the amount of NO_3^- available for denitrification, resulting in potentially less N_2O production in the soil. Nevertheless, deep-banding urea with a NI was equally as effective as deep-banded urea alone in reducing cumulative soil N_2O emissions.

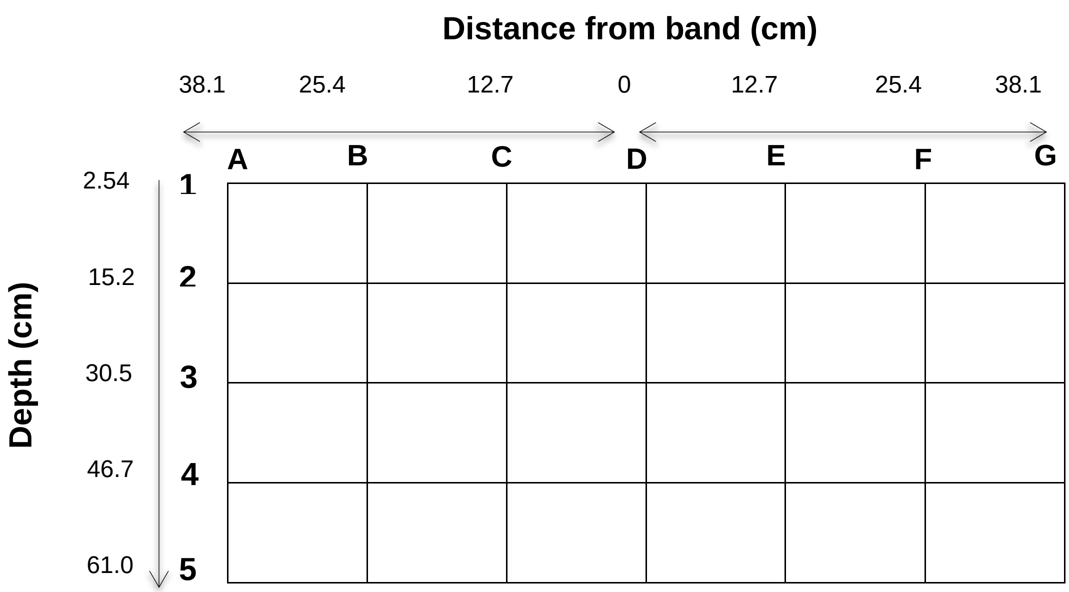
Deep-band placement allows N to be in closer proximity to the corn roots, which may have allowed for greater plant N uptake and reduced N loss. Poorly-drained claypan soils are susceptible to extended periods of saturation following extreme precipitation and may affect corn root growth and nutrient availability during the growing season. Recommendations based on these results should encourage farmers to apply deep-banded N treatments on poorly-drained claypan soils if low rainfall is anticipated during the growing season. Further research is necessary under varying climatic and soil conditions to confirm under what conditions deep banding is effective in lowering cumulative soil N_2O emissions in conjunction with improvements in crop production.

The effectiveness of different N fertilizer placement strategies for increasing corn yield and nitrogen use efficiency (NUE) in a poorly-drained claypan soil was influenced by climatic conditions. Cumulative precipitation was similar in the two growing seasons, but the distribution of precipitation can more likely explain the influence year and N placement had on grain yield. Deep banding urea with or without nitrapyrin was the most effective treatment, increasing grain yields and apparent N recovery efficiency in both years, regardless of climatic conditions. Surface urea application had lower grain yields in 2016, which had less precipitation during the early part of the growing season. Surface applying urea may be recommended if moderate to extreme precipitation is anticipated shortly after N application and planting. Apparent N recovery efficiency for DB+NI was higher than all other treatments and was 26.8% higher than deep-banded urea alone. Results of this two-year study suggest that combining nitrayprin with deep-banded urea in a claypan soil could increase crop yield and NUE, and may be less vulnerable to N loss during the growing season.

The last objective evaluated differences in corn production due to different N source/placements, N application timing (i.e., fall and spring) and rate (84 and 168 kg N ha^{-1}). Corn grain yields were substantially lower in 2012 compared to 2011 and 2013 due to drought conditions. Higher corn grain yields with fall N application compared to spring N application were observed in 2011 at 84 and 168 kg N ha^{-1}. This was likely due to wet conditions following strip-tillage and planting in the spring, which affected stand establishment. Additionally, fall N applications had greater early season plant heights than spring N application, further supporting poor stand establishment occurred after spring application. No-tillage/surface broadcast application of UAN with Nitamin Nfusion resulted in greater plant populations compared to deep placement. However, there was no increase in grain yield with Nitamin Nfusion compared to UAN alone when surface-applied or ST/deep-banded. Farmers may need to consider risk management strategies when using strip-tillage since yields were less with spring application in 2011, and similar or greater than spring application in 2013. Generally, yields with fall N application were similar or greater than spring application for UAN treatments at 84 and 168 kg N ha^{-1}.

APPENDIX A

Diagram showing the soil sampling template used for assessing spatial variation in the soil profile with depth from soil surface and distance from the deep-banded N application.



APPENDIX B

Soil nitrate, ammonium, pH, and gravimetric water content for the non-treated control (NC) treatment at different depths and distances in the soil profile on 17 May 2017.

Soil profile	Rep 1				Rep 2			
coordinates	NO_3-N	NH_4-N	pH	Water content	NO_3-N	NH_4-N	pH	Water content
	mg kg^{-1}	mg kg^{-1}		g g^{-1}	mg kg^{-1}	mg kg^{-1}		g g^{-1}
A1	65.584	15.715	7	0.17	59.8	0.68	7	0.17
B1	84.848	6.088	5.8	0.174	80.9	3.99	6.5	0.171
C1	72.068	7.811	7.5	0.172	63.8	2.08	5.8	0.167
D1	40.422	1.98	6.9	0.165	45.4	4.46	6.8	0.173
E1	58.228	5.228	6.2	0.172	84.7	3.87	6.8	0.171
F1	43.438	3.666	7.1	0.171	57.8	3.12	7.1	0.172
G1	33.854	4.601	5.8	0.17	82.9	15.49	7.6	0.171
A2	11.328	1.741	5.8	0.172	11.6	2.43	6.5	0.174
B2	13.159	1.841	7.4	0.17	21.4	2.68	6.9	0.172
C2	11.809	2.345	6.3	0.166	14.7	2.47	6.2	0.167
D2	17.821	3.233	7.9	0.171	13.2	1.64	5.8	0.171
E2	11.027	1.665	6.6	0.171	20.9	3.4	7.2	0.169
F2	15.843	1.742	8.1	0.168	36.7	1.35	5.5	0.166
G2	15.442	1.125	6.8	0.166	34.9	1.75	6.4	0.169
A3	26.167	3.155	7.8	0.166	5.9	2.37	6.8	0.17
B3	12.278	1.583	7.8	0.171	7.4	1.45	7.2	0.168
C3	15.961	3.336	8	0.17	8.7	1.62	6.3	0.175
D3	29.683	1.197	5.9	0.17	6.9	1.84	7.3	0.166
E3	9.761	0.659	6	0.166	9.8	1.48	5.9	0.172
F3	22.162	2.541	5.8	0.17	10.9	2.02	5.6	0.173
G3	11.307	0.614	5.4	0.174	14	1.25	5.9	0.165
A4	15.883	3.952	5.2	0.175	7.2	4.78	5.3	0.183
B4	31.621	4.876	5.5	0.182	5.6	4.82	5.7	0.173
C4	28.049	3.419	5.8	0.17	6.1	4	5.5	0.176
D4	8.885	2.654	5.1	0.179	5.7	4.45	6	0.175
E4	29.614	2.591	4.9	0.184	6.2	4.06	5.7	0.17
F4	14.515	1.955	4.6	0.178	9.6	3.41	4.4	0.182
G4	9.635	1.733	4.9	0.178	7.6	1.75	6	0.176
A5	30.695	3.865	5.1	0.172	9.7	3.22	5.8	0.171
B5	9.849	2.152	5.4	0.171	7.2	3.35	4.5	0.177
C5	32.872	4.895	4.9	0.176	6.6	5.31	4.6	0.172
D5	81.452	4.162	5.9	0.178	7.3	6.05	4.6	0.172
E5	31.145	3.051	6.2	0.177	6.8	5.06	5.3	0.182
F5	32.877	3.867	6.1	0.172	9.8	5.22	4.7	0.17
G5	25.682	6.025	5.5	0.169	8.6	5.8	5.2	0.173

APPENDIX C

Soil nitrate, ammonium, pH, and gravimetric water content for the deep-banded urea (DB) treatment at different depths and distances in the soil profile on 17 May 2017.

Soil profile	Rep 1				Rep 2			
coordinates	NO_3-N	NH_4-N	pH	Water content	NO_3-N	NH_4-N	pH	Water content
	mg kg^{-1}	mg kg^{-1}		g g^{-1}	mg kg^{-1}	mg kg^{-1}		g g^{-1}
A1	26.4	2.92	6.2	0.172	174.528	11.365	6.9	0.167
B1	62.6	1.67	7.3	0.167	118.428	9.292	6.5	0.165
C1	58.6	11.13	5.8	0.172	69.244	1.666	5.9	0.168
D1	105.8	8.25	7.2	0.169	136.892	3.08	7.1	0.175
E1	63.8	6.8	6.4	0.165	58.016	3.388	7.4	0.172
F1	92.9	4.6	7.3	0.174	86.436	2.024	6.5	0.169
G1	49.4	3.09	6.7	0.169	164.001	2.699	5.5	0.169
A2	16.1	2.11	5.5	0.174	100.116	5.538	6.3	0.166
B2	28.1	2.38	6.5	0.166	67.564	2.698	6.2	0.174
C2	39.3	3.27	5.3	0.171	16.426	1.615	6.3	0.173
D2	26.8	3.15	5.3	0.174	10.603	1.394	7	0.175
E2	25.1	2.48	5.4	0.174	15.921	1.855	5.8	0.168
F2	206.6	9.15	5.5	0.174	12.675	2.793	6.1	0.175
G2	101.6	3.21	6	0.166	44.693	12.293	6.9	0.166
A3	11.7	4.04	6.4	0.172	75.241	2.055	6.8	0.166
B3	13	3.18	5.6	0.167	51.516	3.858	5.7	0.166
C3	11.4	2.26	6.5	0.171	12.046	2.665	7.1	0.174
D3	25.7	3.38	5.1	0.175	12.491	2.595	5.4	0.167
E3	13	2.11	5.6	0.168	20.893	4.123	5.9	0.17
F3	33.9	1.9	6	0.173	7.268	2.713	5.9	0.17
G3	38.5	4.69	5.6	0.175	12.691	0.801	6.5	0.17
A4	7.9	1.67	5.1	0.176	20.584	8.295	5.8	0.178
B4	7.2	3.44	5.1	0.169	12.271	5.223	4.5	0.17
C4	7.9	2.96	4.5	0.184	7.819	3.578	6	0.181
D4	5.9	2.58	5.1	0.178	5.885	3.116	5.9	0.183
E4	8.3	2.48	4.8	0.172	9.441	4.147	4.6	0.169
F4	14.6	4.02	5.4	0.179	8.154	3.078	4.6	0.173
G4	10.4	2.26	4.7	0.181	9.974	4.694	5	0.179
A5	23.4	5.31	5.5	0.174	17.542	3.771	5.6	0.176
B5	9.2	4.26	5.3	0.179	13.925	5.297	4.7	0.177
C5	10.1	4.06	5.6	0.181	5.685	3.788	5.2	0.179
D5	10.4	5.75	5.1	0.175	24.097	4.123	5.6	0.174
E5	25.2	4.94	4.8	0.179	11.022	4.116	5.2	0.177
F5	48.7	2.62	5.2	0.181	12.774	3.261	5.7	0.172
G5	10	5	4.9	0.171	9.489	3.927	6.2	0.175

APPENDIX D

Soil nitrate, ammonium, pH, and gravimetric water content for the deep-banded urea plus nitrapyrin (DB+NI) treatment at different depths and distances in the soil profile on 17 May 2017.

Soil profile	Rep 1				Rep 2			
coordinates	NO_3-N	NH_4-N	pH	Water content	NO_3-N	NH_4-N	pH	Water content
	mg kg^{-1}	mg kg^{-1}		g g^{-1}	mg kg^{-1}	mg kg^{-1}		g g^{-1}
A1	76.992	2.491	5.3	0.173	128.088	8.476	7	0.168
B1	87.672	3.393	5.5	0.166	74.559	8.277	7.2	0.172
C1	48.038	2.768	6	0.17	175.536	5.472	5.4	0.166
D1	51.484	0.772	5.7	0.166	55.401	3.673	6.4	0.166
E1	50.795	1.591	5.9	0.165	128.175	11.699	6.1	0.171
F1	87.136	3.428	5.9	0.168	133.812	20.015	5.5	0.167
G1	74.232	2.946	6.1	0.166	118.578	3.861	6.3	0.167
A2	14.779	0.727	6.9	0.174	347.966	94.973	7.1	0.168
B2	13.126	0.939	5.8	0.175	26.399	2.106	7.3	0.166
C2	11.633	0.745	6.1	0.173	22.296	1.231	6.3	0.172
D2	15.978	0.943	5.5	0.172	42.212	5.489	5.7	0.167
E2	61.341	1.968	6.5	0.174	23.291	0.926	7.3	0.173
F2	75.224	14.156	5.6	0.174	30.537	2.319	7.1	0.173
G2	34.512	1.443	5.4	0.166	91.637	2.656	5.3	0.166
A3	9.076	0.521	6.1	0.167	89.761	1.871	5.9	0.166
B3	17.264	0.432	5.8	0.168	37.672	13.256	5.4	0.166
C3	7.787	0.774	5.2	0.169	49.288	3.581	6.7	0.174
D3	11.711	1.301	5.6	0.175	9.391	2.651	5.1	0.174
E3	10.564	0.651	6.9	0.166	9.343	1.864	5.5	0.173
F3	18.835	2.228	5.8	0.172	9.367	1.273	5.1	0.174
G3	22.267	1.163	5.5	0.173	29.426	0.743	6.1	0.168
A4	13.983	0.651	6.3	0.178	17.507	1.603	5.4	0.17
B4	10.954	1.077	4.6	0.183	50.388	3.274	4.5	0.178
C4	18.526	1.251	4.7	0.176	34.011	3.092	5.9	0.176
D4	7.793	1.202	4.7	0.174	24.832	4.677	4.6	0.175
E4	8.814	1.203	4.6	0.181	43.863	3.942	5	0.177
F4	11.116	0.766	5.4	0.176	37.146	4.344	5.2	0.18
G4	43.577	2.904	4.4	0.183	17.899	3.912	4.4	0.177
A5	30.093	0.591	5.9	0.181	18.166	2.788	5.9	0.169
B5	61.676	4.396	5.5	0.174	66.901	11.756	5	0.183
C5	144.008	20.438	5.3	0.17	27.56	3.902	6	0.177
D5	10.952	2.907	4.8	0.182	54.436	2.862	4.8	0.17
E5	26.125	1.385	5.8	0.181	21.013	2.859	5	0.169
F5	79.264	9.851	4.4	0.173	48.483	3.594	5.7	0.178
G5	141.744	19.111	4.7	0.176	18.76	3.441	5.1	0.18

APPENDIX E

Soil nitrate, ammonium, pH, and gravimetric water content for the urea incorporated after application (IA) treatment at different depths and distances in the soil profile on 17 May 2017.

Soil profile	Rep 1				Rep 2			
coordinates	NO_3-N	NH_4-N	pH	Water content	NO_3-N	NH_4-N	pH	Water content
	mg kg^{-1}	mg kg^{-1}		g g^{-1}	mg kg^{-1}	mg kg^{-1}		g g^{-1}
A1	198.8	8.07	6	0.174	87.2	3.24	6.2	0.167
B1	201.1	7.68	6.8	0.168	200.7	23.58	5.8	0.171
C1	111.5	4.26	5.9	0.171	327.2	41.25	6.9	0.171
D1	170.9	4.03	5.8	0.17	113.5	5.97	6	0.171
E1	133.7	2.21	7.8	0.166	322.4	52.56	6.8	0.169
F1	72.2	2.69	6.9	0.174	250.5	6.43	5.9	0.172
G1	129	3.33	7.7	0.169	193.6	9.72	8	0.169
A2	14.7	1.98	7.3	0.171	14.3	3.27	6.7	0.166
B2	12.4	2.05	7.2	0.17	36.7	2.15	6.3	0.168
C2	15.1	2.19	8.1	0.167	17.4	1.88	7.2	0.167
D2	36.1	2.16	8.1	0.166	30.9	1.02	6.8	0.172
E2	23.6	2.31	6.2	0.17	19	2.1	7.2	0.168
F2	28.3	1.96	6.3	0.167	27	2.26	7.1	0.173
G2	48.3	3.62	6.7	0.166	39.1	3.01	6.8	0.168
A3	8	1.28	6	0.168	15.3	1.19	7.7	0.166
B3	8	1.96	7.8	0.171	10.7	1.83	6.6	0.171
C3	9	3.47	7.3	0.17	9.8	1.25	6	0.172
D3	14.9	1.76	5.9	0.171	12.1	2.66	6.1	0.17
E3	10.3	2.53	6.6	0.166	9.3	2.86	8.1	0.172
F3	10.6	1.52	7.6	0.172	10.8	1.41	7	0.165
G3	12.8	1.8	7.3	0.173	8	1.53	6.5	0.168
A4	12.7	4.36	4.6	0.174	9.3	5.54	6.5	0.181
B4	11.9	3.81	5.4	0.183	12.4	3.64	4.9	0.179
C4	9.7	3.78	4.8	0.174	16.4	5.98	5.8	0.173
D4	13.4	4.16	5.7	0.175	8.7	5.21	4.8	0.183
E4	9.7	5.33	5.3	0.174	8.1	5.05	7.1	0.175
F4	12.4	4.57	4.5	0.183	8.5	4.44	5.5	0.172
G4	11.3	4.6	4.9	0.174	10.1	4.14	5.9	0.174
A5	21.6	4.05	4.8	0.174	10.3	4.43	6.2	0.178
B5	12.3	4.74	5.6	0.174	16.4	5.96	4.9	0.178
C5	13.4	4.66	6	0.17	9.9	5.89	5.6	0.176
D5	14.3	4.7	5.7	0.173	9.1	5.39	4.6	0.171
E5	13.5	4.37	4.4	0.175	13.1	5.89	5.3	0.177
F5	18.7	4.7	5.2	0.177	11.5	5.57	5.8	0.172
G5	17.3	4.51	5.7	0.18	9.3	5.94	5.3	0.18

APPENDIX F

Soil nitrate, ammonium, pH, and gravimetric water content for the non-treated control (NC) treatment at different depths and distances in the soil profile on 10 July 2017.

Soil profile	Rep 1				Rep 2			
coordinates	NO_3-N	NH_4-N	pH	Water content	NO_3-N	NH_4-N	pH	Water content
	mg kg^{-1}	mg kg^{-1}		g g^{-1}	mg kg^{-1}	mg kg^{-1}		g g^{-1}
A1	14.6	3.68	5.6	0.177	25.1	1.39	6.4	0.178
B1	14.3	3.32	6.8	0.177	33	1.19	6.3	0.181
C1	28.1	4.99	6.1	0.172	25.4	2.5	6.4	0.175
D1	21.3	4.57	6.6	0.177	26.5	1.3	5.6	0.177
E1	19	6.17	5.9	0.174	53.5	8.79	7.1	0.181
F1	24.1	4.27	7.4	0.174	30.2	2.47	5.6	0.177
G1	17.3	9.22	6.3	0.181	16.2	4.19	6.6	0.177
A2	9.3	2.49	6.9	0.179	3.6	3.81	6.8	0.179
B2	4.6	3.03	7	0.18	3.1	4.97	6.4	0.177
C2	3.5	6.21	6.3	0.182	5.9	2.19	7.4	0.181
D2	1.1	3.81	6.8	0.177	2.8	3.4	6.5	0.177
E2	0.9	1.76	6	0.182	3.5	3.41	6.9	0.181
F2	1.2	1.39	5.4	0.18	3.5	3.83	6.9	0.173
G2	1.1	1.85	7.1	0.179	5.6	3.32	6.4	0.182
A3	0.4	1.43	5.8	0.172	1.2	3.12	7.1	0.18
B3	0.2	3	7.1	0.176	3.6	1.45	7.1	0.173
C3	0.4	1.57	7	0.171	2.7	1.4	5.5	0.176
D3	0.6	1.28	5.5	0.18	1.5	2.56	7.4	0.183
E3	0.8	1.3	7.3	0.177	1.5	2.52	7.1	0.179
F3	2	5.02	6.8	0.172	1.7	3.04	6.3	0.174
G3	1	2.13	6.8	0.176	2.2	3.41	7.2	0.18
A4	1.6	3.47	5.4	0.179	3.4	2.57	6.9	0.187
B4	1.2	1.37	5.3	0.184	0.4	3.89	5.8	0.178
C4	0.7	2.82	6.5	0.177	0.5	2.64	5.1	0.183
D4	0.6	1.45	5.4	0.181	0.6	2.33	5.1	0.181
E4	0.6	1.86	6	0.176	0.3	2.42	6.6	0.184
F4	6.5	3.46	6.1	0.182	0.4	2.04	6.3	0.183
G4	5	2.48	6.6	0.183	0.5	2.42	6.2	0.177
A5	3.6	2.49	5.2	0.177	3.9	7	5.7	0.181
B5	4.7	3.05	5	0.184	0.6	7.13	5	0.181
C5	1.2	5	6.4	0.186	0.8	9.22	6.7	0.18
D5	1.8	5.08	5.9	0.183	1.1	6.73	5.4	0.179
E5	1.9	5.1	6.1	0.178	0.8	7.45	5.5	0.177
F5	1.9	5.84	5.3	0.179	0.4	6.56	4.7	0.181
G5	1.1	7.27	6.1	0.179	0.4	4.53	5.1	0.186

APPENDIX G

Soil nitrate, ammonium, pH, and gravimetric water content for the deep-banded urea (DB) treatment at different depths and distances in the soil profile on 10 July 2017.

Soil profile	Rep 1				Rep 2			
coordinates	NO_3-N	NH_4-N	pH	Water content	NO_3-N	NH_4-N	pH	Water content
	mg kg^{-1}	mg kg^{-1}		g g^{-1}	mg kg^{-1}	mg kg^{-1}		g g^{-1}
A1	14.9	3.76	5.5	0.178	32.679	3.715	7.4	0.173
B1	13.3	1.97	7.3	0.171	30.581	8.269	7.1	0.176
C1	13.1	2.93	6.8	0.182	35.544	1.661	6.6	0.181
D1	22.8	4.14	6.4	0.174	36.425	1.687	5.7	0.177
E1	34.5	2.83	6.8	0.184	30.207	7.653	7.4	0.175
F1	27.8	3.4	5.5	0.18	31.905	3.305	5.8	0.174
G1	19.1	3	5.6	0.18	26.927	4.334	5.7	0.183
A2	12.4	5.06	6.9	0.176	14.865	5.358	5.8	0.171
B2	15.8	2.7	6.7	0.18	9.942	7.247	5.3	0.173
C2	7.8	3.87	6.7	0.181	11.236	3.501	6.1	0.174
D2	11.1	8.73	6	0.181	5.918	2.611	7	0.172
E2	9.2	3.27	5.7	0.178	5.888	2.614	5.3	0.171
F2	5.7	2.64	7.1	0.182	6.695	2.621	6.9	0.174
G2	7.2	3.79	6.5	0.176	11.831	2.149	5.9	0.182
A3	23.6	2.8	5.3	0.179	11.892	2.518	6.3	0.182
B3	18	2.32	6.6	0.174	27.073	3.398	6.2	0.183
C3	10.6	1.47	6	0.183	29.101	2.015	5.9	0.173
D3	6.5	2.03	6.1	0.183	13.147	3.061	6.2	0.178
E3	5.6	1.92	6.5	0.182	4.881	1.795	6.6	0.179
F3	7.2	2.07	7.3	0.184	3.509	1.473	6.2	0.171
G3	9.6	2.32	7.2	0.177	2.875	1.627	5.5	0.182
A4	29.3	1.59	6.9	0.179	47.628	1.898	6.8	0.176
B4	17.1	1.81	5.5	0.179	50.334	1.756	6.2	0.182
C4	7.2	2.43	6.6	0.181	50.078	2.781	5.4	0.178
D4	5.6	2.14	6.7	0.179	44.587	1.479	5.2	0.176
E4	5.2	1.87	5.6	0.186	15.367	1.673	5.7	0.179
F4	9.7	2.38	6.3	0.186	5.564	1.663	5.4	0.181
G4	8.5	2.31	6.5	0.179	5.402	2.172	5.8	0.182
A5	19.7	6.81	5.7	0.181	46.926	2.344	5.3	0.176
B5	12.6	5.91	5.7	0.175	53.425	4.004	5.9	0.187
C5	8.2	6.16	5.3	0.186	52.135	3.737	5.8	0.187
D5	6.9	6.7	6.8	0.186	30.032	2.411	6.4	0.185
E5	7.2	9.56	5.9	0.183	16.486	2.722	5.2	0.176
F5	7.3	5.82	5.9	0.185	12.171	2.004	5.8	0.182
G5	7.9	5.72	6.7	0.187	6.306	1.742	6.8	0.185

APPENDIX H

Soil nitrate, ammonium, pH, and gravimetric water content for the deep-banded urea plus nitrapyrin (DB+NI) treatment at different depths and distances in the soil profile on 10 July 2017.

Soil profile	Rep 1				Rep 2			
coordinates	NO_3-N	NH_4-N	pH	Water content	NO_3-N	NH_4-N	pH	Water content
	mg kg^{-1}	mg kg^{-1}		g g^{-1}	mg kg^{-1}	mg kg^{-1}		g g^{-1}
A1	18.5	3.12	6.5	0.183	26.887	1.235	6.8	0.177
B1	12.8	5.55	5.5	0.181	18.171	0.298	6.6	0.178
C1	13.1	2.48	7	0.182	29.117	0.752	8.4	0.182
D1	13.4	2.2	6.5	0.177	29.912	1.072	7.6	0.182
E1	17.3	2.09	7.4	0.174	32.195	0.243	6.9	0.174
F1	19.9	2.71	6.1	0.172	36.431	2.023	7.7	0.178
G1	27.1	2.73	7.2	0.174	42.522	0.618	8.8	0.177
A2	11.1	4.02	6.3	0.177	24.256	0.697	6.5	0.172
B2	7.5	2.35	5.6	0.177	8.205	0.882	7.2	0.177
C2	10.4	2.84	5.7	0.178	9.293	1.292	8.2	0.176
D2	19	2.43	7.4	0.176	16.535	0.218	7.1	0.181
E2	6.8	2.3	5.4	0.177	21.522	0.401	7.8	0.171
F2	13.2	6.12	6.4	0.176	19.041	0.419	7.8	0.176
G2	8.1	3.04	6.5	0.173	19.936	0.562	8.7	0.184
A3	9.1	7.01	7.1	0.171	11.378	0.785	7.7	0.183
B3	6.1	4.68	7.1	0.174	6.422	1.481	7.6	0.176
C3	5.2	4.51	5.8	0.176	5.643	0.599	7.9	0.173
D3	3.7	4.08	6.8	0.176	6.122	2.083	6.8	0.171
E3	4.5	4.46	6.8	0.179	10.421	0.935	6.6	0.175
F3	3.5	3.29	5.7	0.172	11.838	0.579	7.2	0.175
G3	3.9	1.92	6.4	0.184	9.187	0.285	6.5	0.183
A4	28.4	2.34	4.4	0.179	7.071	2.177	5.5	0.184
B4	12.3	3.99	6.6	0.187	13.761	1.367	5.7	0.184
C4	6.2	4.41	5.6	0.179	4.499	1.221	4.9	0.176
D4	2.5	3.41	6.6	0.187	4.581	1.961	6.3	0.178
E4	4.7	4.77	4.5	0.182	7.451	3.032	4.8	0.179
F4	3.3	2.67	5.4	0.178	7.531	0.995	4.8	0.188
G4	3.7	3.86	6.2	0.179	4.753	3.071	6.1	0.181
A5	23.8	6.8	5	0.178	8.072	2.421	6.4	0.179
B5	7.3	5.11	4.4	0.18	11.014	2.455	6.5	0.187
C5	5.4	6.85	4.8	0.184	6.467	1.422	5.5	0.185
D5	2.7	5.78	5.1	0.18	11.509	1.354	5.4	0.184
E5	3	6.52	5.4	0.176	9.181	1.157	5.7	0.187
F5	3.8	6.61	4.5	0.184	7.339	1.267	4.9	0.183
G5	4.6	5.57	5.4	0.186	5.204	0.746	5.4	0.187

APPENDIX I

Soil nitrate, ammonium, pH, and gravimetric water content for the urea incorporated after application (IA) treatment at different depths and distances in the soil profile on 10 July 2017.

Soil profile	Rep 1				Rep 2			
coordinates	NO_3-N	NH_4-N	pH	Water content	NO_3-N	NH_4-N	pH	Water content
	mg kg^{-1}	mg kg^{-1}		g g^{-1}	mg kg^{-1}	mg kg^{-1}		g g^{-1}
A1	25.291	2.207	5.6	0.178	15.218	3.984	6.7	0.173
B1	31.418	1.001	5.7	0.183	21.001	0.354	7.3	0.182
C1	24.055	3.262	5.9	0.171	17.238	2.249	8.7	0.171
D1	23.929	3.035	5.8	0.174	26.707	0.647	8.5	0.179
E1	29.761	3.015	6.9	0.174	17.158	0.375	8.7	0.174
F1	27.291	4.271	7.1	0.183	13.578	3.409	7.9	0.18
G1	20.679	5.297	5.8	0.176	28.957	5.861	8.7	0.172
A2	11.198	2.652	6.9	0.182	8.576	2.038	8.2	0.176
B2	9.945	2.212	5.4	0.183	4.291	3.785	8.4	0.179
C2	7.195	2.109	7.1	0.183	7.095	3.083	6.5	0.183
D2	7.062	1.934	6.2	0.172	5.063	2.354	7.9	0.178
E2	4.993	1.751	5.5	0.171	8.681	3.056	7	0.181
F2	3.991	1.826	5.3	0.183	8.368	3.351	6.7	0.176
G2	8.296	2.125	6.1	0.176	7.621	3.682	6.6	0.178
A3	3.093	1.998	6.6	0.18	4.957	3.176	6.6	0.177
B3	3.716	1.605	5.8	0.175	6.236	1.796	7.5	0.182
C3	3.415	1.521	5.9	0.171	7.639	2.672	6.7	0.177
D3	4.941	2.251	5.9	0.182	10.032	4.377	7.7	0.177
E3	2.499	1.518	5.6	0.182	17.928	2.561	7.4	0.179
F3	2.236	1.713	6.4	0.174	12.203	3.282	7.1	0.174
G3	4.228	1.515	5.8	0.173	13.229	1.782	7.6	0.183
A4	2.871	1.928	6.5	0.18	3.717	2.313	5.5	0.18
B4	3.122	1.768	4.7	0.175	4.525	2.277	5.6	0.179
C4	8.948	1.414	6.5	0.181	7.579	2.604	6	0.186
D4	10.153	2.432	6.2	0.176	11.978	1.977	5.3	0.183
E4	4.205	2.156	5.6	0.181	11.223	2.791	5.5	0.176
F4	2.497	2.832	6.5	0.184	12.688	2.888	6.6	0.185
G4	7.632	5.001	6.1	0.186	12.661	3.417	6.4	0.186
A5	2.538	2.686	5.5	0.188	3.367	2.611	5.1	0.178
B5	4.691	5.239	4.4	0.186	3.156	3.066	5.9	0.186
C5	6.119	5.369	6.6	0.176	6.508	1.774	4.4	0.181
D5	5.072	4.295	5.5	0.186	7.446	1.953	6.2	0.18
E5	5.126	5.169	5.6	0.188	9.161	1.888	5.9	0.177
F5	2.509	4.015	6.5	0.188	8.744	2.467	6.1	0.188
G5	3.082	5.319	5.4	0.175	15.882	3.678	6.2	0.18