

N FERTILIZER SOURCE AND PLACEMENT IMPACTS NITROUS OXIDE LOSSES,
GRAIN YIELD AND N USE EFFICIENCY IN NO-TILL CORN

by

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Abstract

Agricultural lands receiving N inputs are considered the primary source of N₂O, a potent greenhouse gas. N fertilizer management has shown variable effects on both N₂O losses and corn grain yield. The objectives of this study were to assess the impact of N source and placement on N₂O emissions, fertilizer-induced emission factor (FIEF), corn grain yield, yield-scaled N₂O emissions (YSNE) and N fertilizer recovery efficiency (NFRE). The experiment was conducted from 2013 through 2014 at the Agronomy North Farm located at Kansas State University, Manhattan, KS. The soil was a moderately well-drained Kennebec silt loam. The treatments were broadcast urea (BC-Urea), broadcast urea ammonium nitrate (UAN) (BC-UAN), broadcast coated urea (BC-CU), surface-band UAN (SB-UAN), subsurface-band UAN (SSB-UAN), subsurface-band UAN + nitrification inhibitor (SSB-UAN+I) and a 0 N control. In 2013, SSB-UAN emitted significantly more N₂O (2.4 kg N₂O-N ha⁻¹), whereas control (0.3 kg ha⁻¹) and BC-UAN (0.6 kg ha⁻¹) emitted the least. In 2014, most treatments emitted between 3.3 and 2.5 kg N₂O-N ha⁻¹. Only SSB-UAN+I (1.03 kg ha⁻¹) and control (0.26 kg ha⁻¹) were significantly lower. The use of a nitrification inhibitor decreased N₂O emissions by 62% and 55% in 2013 and 2014, respectively. BC treatments had cumulative emissions significantly higher in 2014 compared to 2013. Only SSB-UAN+I had a significantly lower FIEF (0.4%), and 2013 FIEF (0.68%) was significantly lower than that of 2014 (1.38%). In 2013, banded treatments had significantly higher grain yields (from 9.1 to 10.5 Mg ha⁻¹), whereas in 2014 fewer differences among N treatments were observed, ranging from 7.2 to 8.6 Mg ha⁻¹. Banded treatments had significantly lower grain yields in 2014 compared to 2013. Only BC-UAN and SSB-UAN+I had significantly lower YSNE, and 2013 had lower YSNE than 2014. In 2013, SSB-UAN had the greatest NFRE, whereas BC treatments had the lowest. In 2014, N treatments did not differ in NFRE. SSB-UAN

and SSB-UAN+I had significantly lower NFRE values in 2014 compared to 2013. Fertilizer source and placement have the potential to mitigate N₂O emissions and promote high yields and NFRE in corn, however, the response is dependent on the rainfall pattern after fertilizer application. The option of banding UAN without any additive promoted higher N₂O losses on a year when precipitation was well distributed, but also enhanced grain yield and NFRE. On the other hand, under the same precipitation conditions, broadcasting N fertilizer promoted lower N₂O losses, grain yield and NFRE, but those were all improved in a wet year. Therefore, the subsurface band placement would be the best option under a normal year, whereas broadcasting fertilizer would be the best option under a wetter year. Further, the use of NI with subsurface band UAN provides the most sustainable option, since the NI decreased N₂O losses compared to UAN alone in both years. Further research should evaluate N source and placement combinations under different environments in order to better understand how they impact crop performance and the negative environmental aspects of N fertilization. It is important to test those treatments under different precipitation scenarios and look for trends that indicate the best N management option at the local level.

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Dedication

I dedicate this work to my parents Maria and Anibal Bastos. You have always believed in me and encouraged me to pursue my dreams, no matter how big or far from home they were.

Chapter 1 - Literature Review

Global Perspective

The world population is estimated to reach 9.6 billion by 2050 (United Nations, Department of Economic and Social Affairs, Population Division, 2013). The increase in population is not proportional to the increase in arable land. In 1961, 1.28 billion hectares (ha) supported a population of about 3 billion people (FAOSTAT, 2014), a ratio of 0.43 ha per person. In 2011, the total arable land increased only to 1.4 billion ha, whereas the population increased to 6.9 billion people (FAOSTAT, 2014), yielding a ratio of 0.2 ha per person. For 2050, about 50% more food will be needed to support 9.6 billion people (Tomlinson, 2011). With that, areas currently under production will be expected to be even more reliant for producing food, which may come at the expense of increasing pressure on natural resources such as soil, water and air. The United States is a major player in the world food security. The country is the main world corn producer and exporter, being responsible for the production of 354 million tons of the grain in 2013 (FAOSTAT, 2014).

In order to cope with the increasing demand for crop products, advancements in genetics, cropping system management and crop protection and nutrition are necessary. It has been estimated N fertilization corresponded to about 50% of the increase in corn yields in the past decades (Cardwell, 1982). In the past, the increased demand for food has been attained greatly by the use of nitrogen (N) fertilizer (Erisman et al., 2008). This holds true for future scenarios of increased production, where N fertilizer use is estimated to increase at the same magnitude as the food demand (i.e. 50%) (Wood et al., 2004).

However, agricultural land receiving N fertilization is the main source of nitrous oxide (N₂O), a potent greenhouse gas (GHG) with about 300x higher global warming potential than

carbon dioxide (CO₂) (Intergovernmental Panel on Climate Change, 2014). Furthermore, N₂O is an important molecule driving ozone layer depletion (Crutzen, 1981). It has been estimated that agricultural activities were responsible for 6.3% of the total GHG (CO₂, CH₄ and N₂O) emissions nationally in 2012 (USEPA, 2014). Nonetheless, the agricultural impact comes mainly from the emission of N₂O from agricultural soil management, totaling 75% of the total U.S. N₂O emissions (USEPA, 2014).

Fertilizer Use

N is one of the most required nutrients by plants, and also one of the most limiting for crop growth and development in both natural and managed systems. The global use of N fertilizer in 2009 was estimated at 115 million tons (FAOSTAT, 2014). Corn is the crop that requires the most N fertilizer inputs, 16.1% of all N applied to crops worldwide in 2010 (Heffer, 2009). In the U.S., corn fields received 5 million tons of N fertilizer in the 2010 growing season, representing 44% of all N fertilizer used in the country (Economic Research Service, 2013).

In the past century, N inputs in croplands have increased substantially. This happened mainly due to the advent of the Haber-Bosch process, which fixes inert dinitrogen (N₂) from the air into reactive forms able to be applied and used by plants, and the increase in efficiency and use of legume crops performing biological N fixation (Robertson and Vitousek, 2009).

N fertilizer is key to improve crop yields and supply enough food to an ever-increasing population. However, it has been well documented that N rates beyond that of optimum crop grain yield cause N₂O emissions to increase, mostly exponentially (Kim et al., 2013). Thus, N fertilizer management becomes an important aspect of crop production, as it is needed to

promote high yields but also is environmentally and economically detrimental if applied in excess.

N₂O Loss Potential

N₂O production and importance

The biggest N pool in nature is atmosphere air, of which about 80% is N₂. However, N₂ is inert, and only certain bacteria species are capable of fixing it and use this N source for metabolic functions. Nonetheless, when N enters the soil, by fertilizer application, for example, it is found in a highly reactive form and prone to many different processes and pathways of loss. To illustrate that, in Fig. 1.1 a urea-based fertilizer is applied to the soil. The first reaction that this type of fertilizer undergoes is the breakdown of urea, performed by urease. This enzyme is found in soil and in plant residues. This enzyme converts urea into ammonia gas (NH₃) and CO₂. If applied on soil surface without incorporation by either tillage or rain, formed urea-derived NH₃ can be lost by a process called volatilization. However, NH₃ is found on an equilibrium reaction with ammonium (NH₄⁺), which is a solid form available for plant uptake. If the reaction equilibrium tends to NH₄⁺ formation, volatilization losses are minimized and N becomes available for plants and microbes in the soil.

N₂O is produced in the soil and is originated mainly from two microbial processes: nitrification and denitrification. The amount of N₂O produced by each process is dependent upon many factors, such as soil oxygen/water status, temperature, pH, organic carbon and mineral N substrate availability, among others.

Nitrification is an aerobic, stepwise reaction where NH₄⁺ is first transformed into nitrite (NO₂⁻) and then into nitrate (NO₃⁻). During these reactions, N₂O may be produced and released

to the atmosphere. Nitrification determines which form of plant usable N will be predominant in the soil. As crops can take up both NH_4^+ and NO_3^- , soil inorganic N as NH_4^+ is preferred. That is because NO_3^- is more prone to losses, since it can be lost by leaching and it also is the main substrate for denitrification (Fig. 1.1). Leaching is the process where the negatively charged NO_3^- is repelled by soil particles and carried down through the soil profile due to the water movement, being deposited in lower layers where plant roots cannot access this N.

Denitrification is an anaerobic stepwise reaction where NO_3^- is progressively transformed into N_2 (i.e. $\text{NO}_3^- - \text{NO}_2^- - \text{NO} - \text{N}_2\text{O} - \text{N}_2$). If denitrification is fully realized, inert N_2 will be the last product and emitted to the atmosphere. However, as many intermediate sub products are also in the gas form (i.e. NO , N_2O), they may be lost from the soil system before being converted to N_2 . The more anoxic the environment (water-filled pore space greater than 80%), the higher the chance of complete denitrification (e.g. N_2 formation and emission, rather than N_2O). N_2O emissions from both processes are highly temporal and spatial variable due to the field variability of the many factors impacting its formation, especially the oxygen/water status. Under aerobic conditions, nitrification predominates and NO_3^- builds up. After a rainfall or irrigation event, the infiltrating water causes the air to be displaced, creating anaerobic sites. If NO_3^- is present in an anaerobic site in the soil, it will most likely undergo denitrification, and N_2O emissions will peak. Nonetheless, N_2O emissions are expected to be highest after N fertilizer application, especially following irrigation or rainfall events, usually up to 30 to 45 days. During this period, denitrification may be the main N_2O source, although before and after it, when N_2O emissions are at background levels, nitrification may be the dominant source (Parkin and Hatfield, 2014).

Nitrogen fertilizer losses as N_2O vary depending on many factors, such as soil type, fertilizer management, tillage practices and climate. Nonetheless, N_2O losses usually represent a small portion of the total applied N fertilizer. A commonly reported variable is the emission factor, which represents the percentage of N_2O -N emitted minus background emissions divided by N application rate. The Intergovernmental Panel on Climate Change (2014) uses an emission factor default value of 1% (i.e. 1% of the applied fertilizer is lost as N_2O). However, many studies have reported emission factors ranging from 0.04% (Maharjan et al., 2014) to 8.15% (Fernández et al., 2014) of the applied fertilizer, although values toward the lower range are more commonly observed.

Due to the small magnitude of this pathway of loss, it is recognized that farmer's management decisions usually do not consider N_2O mitigation, as it generally will not significantly impact the farm budget (Snyder et al., 2014). However, with increasing environmental awareness and fertilizer cost rises, farmers have an interest in management practices that promote better N use efficiency (NUE) and economic return (Ruiz Diaz et al., 2008). NUE is the amount of N on total biomass from a treatment minus that of the 0 N control, divided by the amount of fertilizer applied, expressed as a percentage. One way of promoting higher NUEs is by decreasing overall fertilizer losses (i.e. NH_3 volatilization, NO_3^- leaching, N_2O emissions). Van Groenigen et al. (2010) reported that increases in NUE at modest N rates were highly correlated with decreased N_2O emissions. Therefore, N fertilizer management practices such as N source, placement, rate and time that focus on improved NUE may also promote reduction in one or more pathways of N losses from the soil, including N_2O (Snyder et al., 2009).

N₂O Mitigation Strategies

4 Rs

The fertilizer industry sector came together to create and promote the 4 R's Nutrient Management Stewardship. This initiative is based on the four aspects related to N fertilizer that can be managed in order to improve yields and efficiencies while decreasing losses. Those are the use of the right source, at the right time, at the right place, and at the right rate. The program is aimed to research and promote practices to better utilize N fertilizer tools and apply best management practices at the farmer level.

Extensive research has been done on the impact of each one of the 4Rs on both crop yields and fertilizer losses. The use of the 4Rs is an important management tool in controlling N₂O losses from the soil, and its impact on global warming (Snyder et al., 2009). Nevertheless, there is still a lack of information at the local level about how these factors respond, not only alone but also when interacting among each other (Burzaco et al., 2013). For this literature review, N fertilizer source and placement are the main focus and will be more extensively discussed.

N Fertilizer Sources and Enhanced-Efficiency Fertilizers

There is a range of mineral N fertilizer sources used in agriculture. The main sources utilized nationally are urea, ammonium nitrate (AN), urea-ammonium nitrate (UAN) and anhydrous ammonia (AA). In the U.S., 12 million tons of N-containing fertilizers were applied in 2011 (Economic Research Service, 2013). Furthermore, UAN, urea and AA (10, 5.5 and 4 million tons, respectively) were the most applied sources in 2011 nationwide (Economic Research Service, 2013).

Urea is a solid fertilizer containing about 46% N. Its high N concentration, ease of handling, storing and application makes it one of the most used N fertilizers worldwide. In the U.S., urea represents about 20% of the applied N fertilizer.

Ammonium nitrate is a fertilizer in the solid form, and contains 33-34% N. The use of AN has been banned in several countries due to its potential use as an explosive. Most of the AN utilized is in the liquid form as mixtures with other water-soluble fertilizers.

Urea-ammonium nitrate is a liquid fertilizer originated from the mixture between urea, AN and water. It contains between 28-32% N, and its use represents 24% of the total in the U.S. It has benefits over the solid fertilizers, such as better uniformity of application, compatibility with other chemicals (e.g. herbicides, insecticides) and ease of application through irrigation systems.

Anhydrous ammonia is the only N fertilizer in the gas form. It has the highest N concentration, graded at 82%. Moreover, AA is commonly the most affordable N fertilizer source. This fertilizer is toxic to animals and humans, and only certified personnel should perform its application. Since it is a gas, AA has to be injected into the soil in order to avoid losses to the atmosphere.

All of the fertilizers listed above are soluble, readily available when applied to the soil. This can be an issue since N demand and uptake by plants varies throughout the growing season. If great amounts of fertilizer become available in the soil and plant uptake is not able to fully utilize it, the surplus N will likely undergo losses from the field. The asynchrony between N fertilizer supply and demand may increase the environmental impact, decrease yield potential, and ultimately decrease economical returns from fertilizer application. With this in mind, improved N fertilizer sources have been designed and commercialized in the past decades.

These are called enhanced-efficiency N fertilizers (hereafter referred to as EEF), defined as “fertilizers that reduce loss to the environment and/or increase nutrient availability compared with conventional fertilizers” (Olson-Rutz et al., 2011) .

Enhanced-efficiency N fertilizers can be separated in three distinct categories depending on their mode of action: slow-release N fertilizer (SRNF), controlled-release N fertilizer (CRNF) and stabilized N fertilizer (SNF). Generally, SRNFs are microbial and/or chemically decomposable molecules, such as urea-formaldehyde, which slow N solubility by the need of breakdown processing. However, due to its dependency on chemical/biochemical reactions, SRNF release, pattern and duration are not well predicted. Generally, CRNFs are conventional, highly soluble fertilizers (i.e. urea) that receive an outer coating that controls fertilizer solubility and diffusion to the soil. The most common types of CRNF being currently commercialized are polymer-coated urea (PCU, trade name example ESN®), sulfur-coated urea (SCU) and polymer-sulfur-coated urea (PSCU, trade name example Poly-S®). The release pattern of CRNF is dependent upon coating properties (e.g. material, thickness, permeability) and soil properties (e.g. moisture, temperature). SNFs are conventional fertilizers (e.g. urea, UAN, AA) receiving an enzyme-inhibitor additive. The two most common additive types are nitrification inhibitors (NI) and urease inhibitors (UI). The NI temporarily blocks the first step of nitrification (i.e. the transformation of NH_4^+ to NO_2^-). Thus, inorganic N kept in NH_4^+ form is less prone to denitrification and leaching. Commercial examples of NI are nitrapyrin (2-chloro-6-trichloromethyl-pyridine, trade name example N-Serve® or Instinct®), dicyandiamide (DCD, trade name example Guardian®), and DMPP (3, 4-dimethylpyrazole phosphate, trade name example ENTEC®). The UI temporarily inhibits urease activity, an enzyme present in soil and plant residue responsible for the urea breakdown reaction ($\text{NH}_2\text{COONH}_4 \rightarrow (\text{NH}_2)_2\text{CO} + \text{H}_2\text{O}$).

The most common UI in use is N-(n-butyl) thiophosphoric triamide [NBPT, trade name example SuperU® (SU) - contains urea, DCD and NBPT]. By blocking the urease enzyme, NBPT allows more time for surface-applied urea to be incorporated by rain or irrigation, especially important in cropping systems with large amounts of residue on the soil surface and in conservation tillage systems (i.e. no-till). It can also be found mixed with UAN and DCD (trade name Agrotain®Plus), in which case it prevents only the urea portion of UAN from breakdown into NH_3 , while the DCD inhibits the ammonium part from undergoing nitrification, and the nitrate portion is left unprotected by any of the additives.

Due to the form of N, fertilizer solubility, edaphic and climate characteristics, each fertilizer source is particular to which pathway of loss it is more prone when applied to the environment. Fertilizer-derived N_2O emissions vary widely when different N sources are used. Studies evaluating the three most used conventional N sources (urea, UAN, AA) have shown distinct results. For example, some studies under corn found that UAN emitted less N_2O than urea (Halvorson et al., 2010a; Halvorson and Del Grosso, 2012), whereas others found no difference between the two sources (Venterea et al., 2005; Sistani et al., 2014). Yet, others found inconsistent results across different years. Dell et al. (2014) observed lower emissions with UAN compared to urea in only one out of three years, and Halvorson et al. (2011) had the same conclusion in one out of two years. Fernández et al. (2014) and Burton et al. (2008) found no difference between AA and urea, whereas Thornton et al. (1996) and Venterea et al. (2010) observed higher emissions under AA than those under urea.

Enhanced-efficiency N fertilizers are believed to mitigate N_2O emissions when compared to their conventional counterparts due to the fact that the better synchrony between plant uptake and fertilizer availability decreases NO_3^- buildup in the soil, thus avoiding N_2O

losses (Parkin and Hatfield, 2014). However, variable results can be found in the literature. Studies have observed that the use of UAN with DCD+NBPT has decreased emissions when compared to UAN alone (Halvorson 2010a, 2011, 2012). Others have found no difference (Sistani et al., 2011; Parkin and Hatfield, 2014), whereas others have found UAN with DCD+NBPT to emit more than UAN alone [(Dell et al., 2014) in one out of three years]. Furthermore, Burzaco et al. (2013) found lower emissions with the use of NI when comparing UAN with and without the inhibitor. Studies comparing urea with its EEF counterparts found more consistent results. Many studies have shown that PCU decreased emissions compared to urea (Halvorson et al., 2010a; b, 2011; Drury et al., 2012; Halvorson and Del Grosso, 2012, 2013; Fernández et al., 2014). However, in some of these studies, PCU was better than urea only in a given year, and not during the entire experiment length (2-3 years). In accordance, Nash et al. (2012) did not find a difference in any given year between urea and PCU. In studies where SU was evaluated, many authors have shown that SU decreased N₂O losses compared to urea (Halvorson et al., 2011; Venterea et al., 2011) and to urea and/or PCU (Halvorson et al., 2010a; Halvorson and Del Grosso, 2012, 2013; Maharjan et al., 2014). Nonetheless, Halvorson et al. (2011) did not find differences in N₂O emitted between SU and PCU.

Emissions of N₂O are inherently variable in time and space held everything else constant. When different N sources (including EEFs) are factored in, along with year-to-year climatic variation at the local scale, and differences in soil and management practices at the regional/global scale, it is not surprising that the N₂O response across different years and locations to be inconsistent. This fact only reinforces the importance of research to be performed at the local level. This way crop advisors, extension specialists and farmers can

better understand where and when different N sources and EEFs will have the most positive impact in yields and fertilizer losses.

N Fertilizer Placement

Depending on the form of the fertilizer, equipment availability and soil conditions, specific fertilizer placement should be performed in order to achieve better nutrient use efficiency and decreased fertilizer losses. The different placement options available are broadcast (BC), surface band (SB) and subsurface band (SSB).

Broadcast application can be performed with both solid and liquid sources (e.g. urea, UAN). Nevertheless, its choice should be based on cropping system and soil characteristics. For example, BC application of both untreated urea and UAN should be avoided in high-residue systems (e.g. no-till). That is due to the potential of fertilizer immobilization on the residue and higher chance for NH_3 volatilization. For this reason, BC application is recommended under conventional tillage systems, where the fertilizer is later incorporated to the soil, decreasing the risk of losses.

Surface band application can be used with both solid and liquid fertilizers. If liquid fertilizer is used, the application is characterized by a jet stream on the soil surface as a concentrated band. If liquid fertilizer is to be applied on the soil surface, SB is preferred over BC, especially in no-till. This is due to the fact that with SB there is less contact between fertilizer and crop residue, decreasing immobilization and volatilization.

Subsurface band is used with solid, liquid and gas fertilizer. This practice consistently performs better in regard to yield and nutrient use efficiency when compared to BC and SB

applications. Nevertheless, SSB incurs higher fuel consumption due the increased power demand from the tractor when cutting through the soil.

The literature is scant on studies about N fertilizer placement impacting N₂O losses in corn. Nonetheless, N placement has been reported to affect N₂O emissions. Thornton et al. (1996) suggested that BC urea would emit less N₂O when compared to SSB. In agreement, Halvorson and Del Grosso (2013) found less N₂O emissions from BC urea, PCU and SU application than their SSB counterparts. Engel et al. (2010) observed similar results, with BC urea emitting less N₂O than SSB urea in a canola crop. Nonetheless, Nash et al. (2012) did not see any difference in emissions between BC and SSB PCU and urea in a corn trial. Similarly, Burton et al. (2008) found no difference between BC and SSB urea in 6 site-years of wheat. Halvorson and Del Grosso (2012) concluded that SB applied PCU emitted less N₂O than SSB, in a 2-year corn experiment. Similarly, Drury et al. (2006) observed shallow band placement of UAN to have lower emissions than deep band placement. There seems to be a trend for higher emissions from SSB applied fertilizers when compared to both SB and BC applications. However, differences were not consistent on all years, demonstrating that the intricate relationships between soil, climate and fertilizer management affecting N₂O losses. Hence, more research is needed to evaluate different N management practices in order to identify best management practices at the local level.

Crop Yield and N Use Efficiency

Final grain yield is a reliable crop proxy response to every important management aspect that occurs during the growing season. Not surprisingly, the choice of fertilizer N source (conventional and EEF) and placement and their interactions with other variables will impact

grain production. This could be given by both decreasing fertilizer losses to the environment, meaning that more fertilizer would still be available for plant uptake, and facilitating plant uptake itself through the form the fertilizer present and where it is located in the soil (e.g. near to the plant or leached out of root zone).

Generally, the recovery of the applied N by the crop is in the range of 45% to 65% in research fields and about 40% on farms (Roberts, 2008). It has been hypothesized that under an efficient N fertilizer management, N rates applied could be decreased (Dell et al., 2014; Sistani et al., 2014). This lies on the fact that most N recommendation formulas are based on a NUE of 50%. It means that, when recommending fertilizer application, it is generally assumed that only half of it will be used by the plants, whereas the remaining will be either lost to the environment or stay in the soil. Consequently, if plants make a more efficient use of the fertilizer, less of it would need to be applied.

However, best management practices (BMP), including decreased N rates, that promote higher NUE need to be thoroughly researched in order to not compromise yields. When comparing two fertilizer management practices where the only variable is the rate (e.g. 100 and 200 kg N ha⁻¹), the scenario with the lowest rate usually gives the best NUE. Nevertheless, it would be impractical and unsustainable to strive for lower rates if those would negatively impact grain yield (Snyder et al., 2009).

The use of different N sources, especially EEFs, has been of research interest when striving for improved NUE and grain yields. For example, Halvorson and Bartolo (2014) observed 19% higher NUE when PCU was applied, compared to SU and urea in continuous corn production. Furthermore, Burzaco et al. (2014) found increased NUE from UAN+NI

compared to UAN alone, which contrasts with the results from their meta-analysis showing no NUE difference from UAN with and without NI.

When looking at corn grain yields, the scenario seems more variable. Fernández et al. (2014) observed higher yields under PCU compared to urea in 2 out of three growing seasons. Venterea et al. (2011) found PCU and urea to yield the same, but more than SU. Several authors did not observe grain yield increases from PCU and SU (Halvorson et al., 2010a; b; Sistani et al., 2011; Halvorson and Del Grosso, 2013; Dell et al., 2014) compared to urea. Additionally, a study comparing only PCU and urea did not observe yield improvements (Drury et al., 2012). In contrast, Halvorson et al. (2011) and Halvorson and Del Grosso (2012) observed lower grain yields under SU and PCU when compared to urea. Experiments evaluating UAN found no grain yield differences when adding NI+NBPT (Halvorson et al., 2010a; b; Sistani et al., 2011; Dell et al., 2014) and NI alone (Burzaco et al., 2013). Conversely, UAN resulted in higher grain yield than UAN with NI+NBPT in Colorado (Halvorson et al., 2011; Halvorson and Del Grosso, 2012).

Few studies have evaluated the impact of different N fertilizer placement on corn grain yields and N₂O losses where no confounding factor was present (e.g. N source, tillage system). Halvorson and Del Grosso (2012) observed no grain yield differences between BC and SB applications of urea, PCU and SU in corn. Similarly, Halvorson and Del Grosso (2013) found no difference between BC and SSB PCU. Mengel et al. (1982) found higher grain yields with UAN applied as SSB than BC in 3 site-years, but no difference was observed on 4 site-years in an Indiana corn crop. In agreement, Stecker et al. (1993) found variable results, observing UAN to promote higher corn grain yields under SSB than SB and BC in 3 site-years, SSB to yield the

same as BC but higher than SB in 1 site-year and no difference between the three placement options on the remaining 4 site-years.

Variable responses regarding N source and placement can be found in the literature. In the case of EEFs, the variability in corn grain yield response has been attributed to different rainfall timing, amount and frequency, application method and soil properties (Nelson et al., 2008). EEFs have the potential to decrease losses as N₂O emissions, NH₃ volatilization and NO₃⁻ leaching. However, more studies are needed in order to better understand when and where these fertilizers would perform the best (Motavalli et al., 2008) and promote higher yields to pay off the increased cost of these technologies.

Yield-Scaled N₂O emission

Losses of N₂O have been primarily reported on an area basis, such as kg N₂O-N emitted per ha. While this is informative in regard to the amount of N lost from the system, it lacks information about the production system that gave rise to it. Selecting cropping systems that emit less is important, but reduction in emissions should accompany grain yield maintenance or improvement in order to be considered a sustainable practice.

A production system may emit very little N₂O as a result of low N input, which may come at the expense of lost yield potential. On the other hand, a highly productive system may emit more N₂O on an area basis due to N fertilization, but it has a higher potential for improved productivities. With that in mind, a variable that takes into account both losses and yield is more likely to represent the sustainability of a production system.

Yield-scaled N₂O emission (YSNE) considers the amount of N₂O emitted per unit of yield (e.g. g N₂O emitted per Mg of grain produced). In the past years, many N₂O studies have

reported YSNE as its relevance becomes more evident. Reported YSNE values from corn have ranged from 15 (Halvorson et al., 2011) to 1730 (Fernández et al., 2014) g of N₂O-N per Mg of grain. Most values on the lower range come from control plots, where no N fertilizer was applied, and thus, N₂O emissions were low. In most cases, control plot grain yields are significantly lower when compared to fertilized treatments. However, other studies had the control yielding similarly to the fertilized plots, in which case YSNE was of small magnitude.

The benefits of EEF application compared to their conventional counterparts become more evident when looking at YSNE. Fernández et al. (2014) observed lower YSNE from PCU than urea in 1 out of 3 years in corn. Halvorson and Del Grosso (2013) and Venterea et al. (2011) found lower YSNE from SU compared to urea. Furthermore, Halvorson et al. (2011) and Halvorson and Del Grosso (2012) observed no difference between SU and PCU, but both were lower than urea. Halvorson et al. (2010a) found YSNE values in the order SU < PCU=urea under corn in Colorado. Accordingly, Maharjan et al. (2014) observed lower YSNE under SU than PCU. Sistani et al. (2011) found urea and SU to have the lowest YSNE, followed by PCU. In contrast, Drury et al. (2012) and Nash et al. (2012) did not observe differences between PCU and urea. For UAN, even more consistent results have been observed. Halvorson et al. (2011) found YSNE values for UAN with DCD+NBPT to not differ from UAN with Nfusion (a slow-release N source), but both were lower than UAN alone. In accordance, Halvorson et al. (2010a) and Halvorson and Del Grosso (2012) observed UAN + DCD+NBPT to have lower YSNE when compared to UAN. Furthermore, Burzaco et al. (2013) found UAN+NI to have lower YSNE than UAN.

Enhanced-efficiency fertilizers have shown improved cropping system performance than conventional sources if both losses and yields are taken into account. These are important

features to notice, once a the most appropriate management practice would be the one that decreases losses and their associated environmental impact while securing or improving grain yields in corn.

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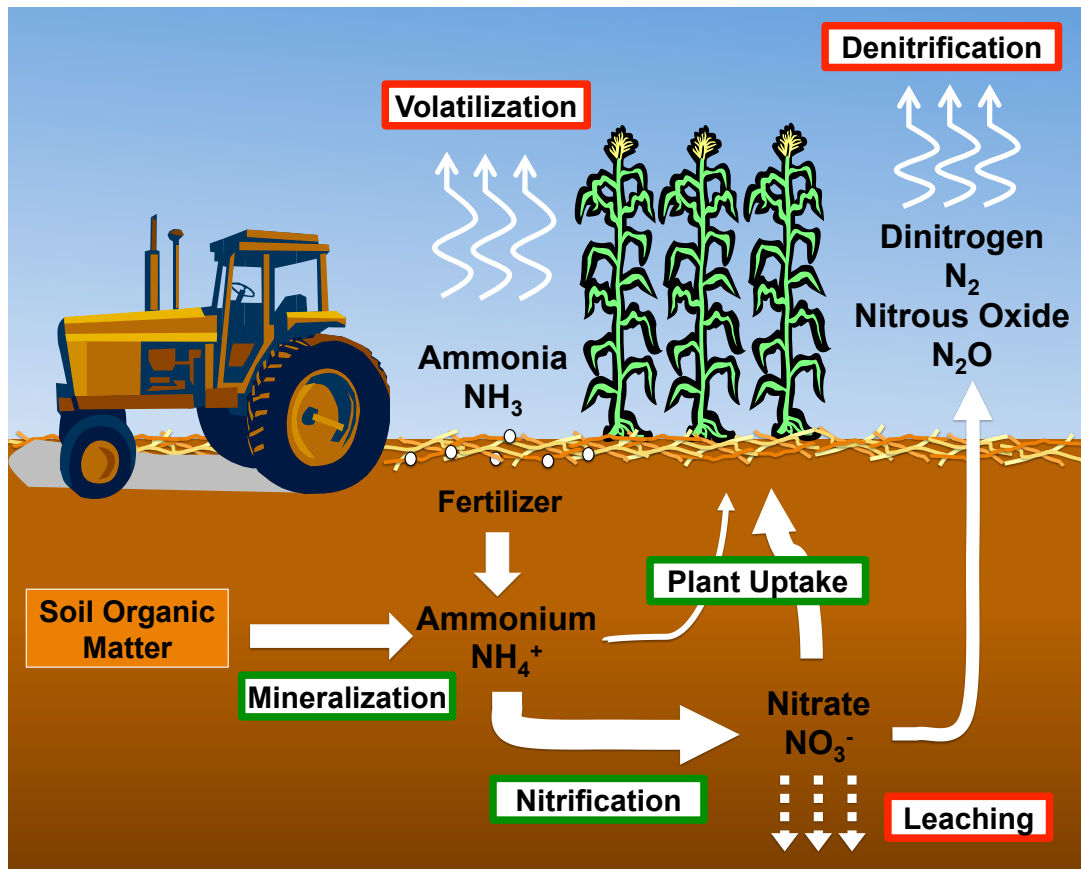


Figure 1.1. Nitrogen Cycle. Red rectangles represent N losses. Green rectangles represent a biological process not directly associated to N losses.

Chapter 2 - N Fertilizer Source and Placement Impacts N₂O

Emissions in No-till Corn

Abstract

Agricultural lands that receive N inputs are considered a primary source of N₂O, a potent greenhouse gas. The objective of this study was to assess the impact of N source and placement on N₂O emissions and fertilizer-induced emission factor (FIEF). The experiment was conducted at the Agronomy North Farm located at Kansas State University, Manhattan, KS. The soil was a moderately well-drained Kennebec silt loam. The treatments were broadcast urea (BC-Urea), broadcast urea ammonium nitrate (UAN) (BC-UAN), broadcast coated urea (BC-CU), surface-band UAN (SB-UAN), subsurface-band UAN (SSB-UAN), subsurface-band UAN + nitrification inhibitor (SSB-UAN+I) and a 0 N control. Treatments were arranged in a randomized complete block design with four replicates. The N₂O emissions were monitored during the 2013 and 2014 growing seasons using static vented chambers. In 2013, SSB-UAN emitted significantly more N₂O (2.4 kg N₂O-N ha⁻¹), whereas the control (0.3 kg ha⁻¹) and BC-UAN (0.6 kg ha⁻¹) treatments emitted the least. In 2014, most treatments emitted 3.3 to 2.5 kg N₂O-N ha⁻¹. Only SSB-UAN+I (0.97 kg ha⁻¹) and the control (0.26 kg ha⁻¹) were significantly lower. The use of nitrification inhibitor decreased N₂O emissions by 62% and 55% in 2013 and 2014, respectively. In 2014, SSB-UAN+I was the only fertilized treatment to emit significantly less than others (1.03 kg N₂O-N ha⁻¹). Overall, 2013 had less N₂O losses than 2014, due to rainfall intensity and timing after fertilizer application. The treatments that behaved statistically differently from one year to the other were BC-Urea (1.63 to 3.37), BC-CU (1.35 to 3.51) and BC-UAN (0.6 to 2.68 kg N₂O-N ha⁻¹ in 2013 and 2014, respectively). Averaged across both

years, only SSB-UAN+I had a significantly lower FIEF (0.4%), while all other treatments did not differ statistically. Averaged across treatments, 2013 FIEF (0.68%) was significantly lower than that of 2014 (1.38%). Fertilizer source and placement management have the potential to mitigate N₂O emissions and FIEF in corn, however, the response varies depends on rainfall pattern after fertilizer application.

Introduction

Nitrogen fertilization is one of the key limiting factors for crop productivity, being responsible for about 50% of the yield increase in the last decades (Cardwell, 1982). However, N applied to croplands is highly reactive and susceptible to losses. The three most important loss pathways are NH₃ volatilization, NO₃⁻ leaching and N₂O emissions. Each loss is associated with specific soil, climate and management practices that may enhance or decrease its potential. For example, regions where precipitation intensity is high and soils are light-textured may be an environment more conducive to NO₃⁻ leaching, whereas if on heavy-textured soils it may be more prone to losses as N₂O emissions. Volatilization as NH₃ is mostly associated with surface-applied, urea-based fertilizers that are not further incorporated. With many factors interacting and controlling N fertilizer dynamics, it becomes important to understand where, when and how these losses occur. That way, it is possible to prepare a fertilizer management plan that makes efficient use of the inputs and decreases losses to the environment.

When comparing these three loss mechanisms, N₂O generally represents the least amount lost, varying from 0.05 (Maharjan et al., 2014) to about 8% (Fernández et al., 2014) of applied fertilizer. Although small in magnitude, N₂O losses are important to quantify and mitigated, as N₂O is one of the main greenhouse gases. It has a global warming potential about

300 times higher than that of CO₂. Furthermore, the main N₂O emitting sector is agricultural fertilized fields, accounting for 75% of all N₂O emitted in the U.S. (USEPA, 2014). Thus, mitigation strategies such as N fertilizer source and placement can be important tools to decrease the overall impact of agriculture on global warming.

Losses as N₂O are impacted by many factors, such as soil pH, C availability, inorganic N and soil oxygen/water status. Furthermore, its formation in soil is associated with two processes: nitrification and denitrification. Nitrification is the main source of N₂O under aerobic conditions, whereas denitrification is the main source under anaerobic conditions, such as after irrigation or precipitation events able to increase soil water content. Nonetheless, denitrification is responsible for the main peak losses, whereas nitrification is associated to background emission losses.

Many studies have quantified N₂O losses associated to N fertilizer source and placement choices in corn cropping fields. For example, some studies under corn found that UAN emitted less than urea (Halvorson et al., 2010a; Halvorson and Del Grosso, 2012), whereas others found no difference between the two sources (Venterea et al., 2005; Sistani et al., 2014). Studies have observed that the use of UAN with dicyandiamide (DCD) + N-(n-butyl) thiophosphoric triamide (NBPT) decreased emissions when compared to UAN alone (Halvorson 2010a, 2011, 2012). Others found no difference (Sistani et al., 2011; Parkin and Hatfield, 2014), whereas others found UAN with DCD+NBPT to emit more than UAN alone [(Dell et al., 2014) in one out of three years]. Furthermore, Burzaco et al. (2013) found lower emissions with the use of nitrification inhibitor (NI) when compared to UAN with and without the inhibitor. Studies comparing urea with its EEF counterparts found more consistent results. Many studies have shown that polymer-coated urea (PCU) decreased emissions compared to urea (Halvorson et al.,

2010a; b, 2011; Drury et al., 2012; Halvorson and Del Grosso, 2012, 2013; Fernández et al., 2014). However, in some of these studies, PCU was better than urea only in a given year, and not during the entire experiment length (2-3 years). In accordance, Nash et al. (2012) did not find a difference in any given year between urea and PCU. In studies where SU was evaluated, many authors have shown that SU decreased N₂O losses compared to urea (Halvorson et al., 2011; Venterea et al., 2011) and to urea and/or PCU (Halvorson et al., 2010a; Halvorson and Del Grosso, 2012, 2013; Maharjan et al., 2014). Halvorson and Del Grosso (2013) found less N₂O emissions from BC urea, PCU and SU application than their SSB counterparts. Engel et al. (2010) observed similar results, with BC urea emitting less N₂O than SSB urea in a canola crop. Nonetheless, Nash et al. (2012) did not measure any difference in emissions between BC and SSB PCU and urea in a corn trial. Similarly, Burton et al. (2008) found no difference between BC and SSB urea in 6 site-years of wheat. Halvorson and Del Grosso (2012) concluded that SB applied PCU emitted less than SSB, in a 2-year corn experiment. Similarly, Drury et al. (2006) observed shallow band placement of UAN to have lower emissions than deep band placement.

Losses as N₂O due to N fertilizer source and placement are highly variable and contrasting results can be found on the literature. Therefore, it is important to understand how these fertilizer management practices respond at the local level. This way, strategies to promote decreased losses and increased input use efficiency can be tailored to a specific region, under a particular soil and climate scenario.

Consequently, the objectives of this study were to evaluate how different N fertilizer sources and placements impact N₂O losses from a no-till continuous corn system. The hypothesis of this study were that i) CU would emit less than urea, ii) UAN with NI would emit

less than UAN alone, iii) subsurface band would emit more than surface band, and iv) surface band would emit more than broadcast.

Materials and Methods

Site Description and Experimental Design

The site was located at the Kansas State University Agronomy North Farm, Manhattan, KS (39°11'30"N, 96°35'30"W). The soil was well-drained Kennebec silt loam (fine-silty, mixed, superactive, mesic Cumulic Hapludolls). Selected soil characteristics can be found in Table 2.1. The region has a 30-year average temperature of 12.9 °C and precipitation of 833 mm yr⁻¹.

The experiment was conducted during the course of two growing seasons (2013 and 2014). Plots were the same for both years. Prior to experiment initiation, the area had been planted to rainfed no-till continuous corn since 2010. Corn was planted on 16 May 2013 (DOY 136) and 15 May 2014 (DOY 136) in 76-cm rows. The average final population was 70,500 and 75,100 plants ha⁻¹ in 2013 and 2014, respectively. Plots were 7.6 m x 6 m, comprising 8 corn rows. Blocks were separated by 3-m alleys. Plots received 2-3 herbicide applications per growing season, and were hand weeded when necessary, to maintain plots weed free during the length of the experiment. The experimental design was a randomized complete-block, with four replicates.

N Fertilizer Source and Placement

Treatments consisted of specific combinations of N source and placement: broadcast urea (BC-Urea), broadcast urea-ammonium nitrate (UAN) (BC-UAN), broadcast coated urea

(BC-CU), surface-band UAN (SB-UAN), subsurface-band UAN (SSB-UAN), subsurface-band UAN + NI (SSB-UAN+I) and a 0 N control. The coated urea used was ESN, and the NI used was Instinct, a form of nitrapyrin. BC-Urea and BC-CU were applied by hand, whereas BC-UAN and SB-UAN were applied with a boom sprayer attach to a tractor. SSB-UAN and SSB-UAN+I were applied with a coulter applicator attached to a tractor, to a depth of about 10 cm, in the row middles, about 38 cm away from the row. SB-UAN boom nozzle spacing was 51 cm. SSB coulter spacing was 76 cm (Fig. 2.1). Fertilizer N was applied at a rate of 168 kg N ha⁻¹, which was considered standard recommendation for the region, at DOY 136 and 137 in 2013 and 2014, respectively.

Nitrous Oxide Measurements and Ancillary Data

Nitrous oxide measurements were performed from April through October. Measurements frequency depended on fertilizer application and rainfall occurrence: two to three times a week right after fertilizer application, one time a week if no rainfall occurred, and once every two weeks 60 days after fertilizer application if no rainfall occurred. After every rainfall, samples were taken the next day and again two to three days after. Soil moisture and temperature at 5 cm depth were measured at the vicinity of the chambers on every gas sampling event. Precipitation values were obtained from a weather station near the plots.

Anchors (0.5 x 0.29 x 0.9 m deep) were made from a 20-gauge stainless steel steam pan, with the bottom part cut out to allow insertion into the soil so the flange was flush with the soil surface. One anchor was installed in between the 5th and 6th corn rows in each plot. Anchors were placed in the middle of the row for BC treatments, and centered on the band for band treatments, with the short side parallel to the corn row. Since anchors encompassed 64% of the in between row spacing, N₂O fluxes from SSB were area-scaled, with the remaining 36% in

between row flux being considered equal to that of the control plot. Anchors were installed 24 hrs prior to the first gas sampling event and were only removed after grain harvest. Chamber tops (0.5 x 0.29 x 0.1 m deep) were made from the same material as the anchors. Chambers were insulated and vented, comprised of a flange where EPDM weather stripping was glued, a gas sampling port, a thermometer and a handle (Fig. 2.2). The sampling port was comprised of rubber septa on one end and a manifold on the other end, out of which four fluorinated ethylene propylene tubing branch out to each quadrant of the chamber, ensuring sample homogeneity.

Samples were taken between 0900 and 1300 h local time. On each sampling date, chamber tops were secured on anchors by the use of binder clips. Gas samples of about 25 mL were collected at 0, 20 and 40 min after deployment using a 30-mL polypropylene syringe and needle. Samples were transferred to 12.5 mL pre-evacuated vials with butyl rubber septa (Labco Ltd.) and analyzed within one week. Sample N₂O concentration was determined using gas chromatography (GC) (Model GC 14A; Shimadzu, Kyoto, Japan) equipped with a ⁶³Ni electron capture detector and a stainless steel column (0.318 cm dia. by 74.5 cm long) with Poropak Q (80-100 mesh, Shimadzu). The instrument was calibrated daily prior to analysis using three levels of analytical-grade standards. Further, the N₂O concentration was calculated by converting the molar mixing ratios determined by the GC to mass per volume concentration by the use of the ideal gas law, air temperature inside the chamber at sampling and anchor area. Flux of N₂O for each chamber was calculated as the slope of the linear regression curve among N₂O concentrations and sampling times. Daily N₂O emissions between sampling dates were calculated by linear interpolation between each sampling date, assuming that flux among days changed linearly. Cumulative area-based N₂O flux was calculated using trapezoidal integration of flux and time. Fertilizer-induced emission factor (FIEF), in %, was calculated as the

difference between the N₂O emission from N treatments and the control plot, divided by the quantity of fertilizer N applied and multiplied by 100.

Soil Inorganic N Sampling and Analysis

Soil samples for NO₃⁻-N determination in 2013 and 2014 were taken in the spring before corn planting, two times during the growing season, and after corn harvest for NO₃⁻-N residual assessment. The preplant and in-season soil samples were taken with 2-cm diameter soil tubes, and post-harvest samples were taken with 4-cm diameter soil tubes.

In 2013, preplant sampling time occurred on 7 April (DOY 97), in-season sampling times occurred on 2 June (DOY 153) and 21 June (DOY 172), and postharvest sampling time occurred on 3 December (DOY 337). Before experiment initiation, sampling time 7 April was performed by taking 10 soil cores from each block, split in the depths 0-5, 5-10 and 10-15 cm, and pooled in a composite sample, as so each block would have 3 composite samples, one for each depth. Samples were taken on a 2-dimensional (2D) fashion (Fig. 2.3), with depth as the vertical vector (0-5, 5-10 and 10-15 cm segments) and location as the horizontal vector (0, 10, 20 and 30 cm). Samples were taken in this manner due to the presence of banded treatments, thus the horizontal variability was of interest. Location 0 was placed on top of the band for the banded treatments, and in the middle position between two corn rows for the BC treatments. One horizontal transect was taken per plot, where each location yielded one soil core that was further split in the three depths already mentioned. Thus, each plot would have a total of 16 samples (3 depths x 4 locations). On sampling time 3 December, samples were taken using a tractor and a Giddings deep soil sampler apparatus (Model GSRTS, Giddings Machine Co., Windsor, Colorado) (Fig. 2.4). Samples were taken to 90 cm depth, in the increments 0-15, 15-

30, 30-45, 45-60 and 60-90 cm. Each plot was sampled three times for NO_3^- -N determination and one time for bulk density determination. Each core x depth sample was bagged individually, for a total of 20 samples per plot.

In 2014, preplant sampling time occurred on 7 May (DOY 127), in-season sampling times occurred on 21 June (DOY 172) and 8 August (DOY 220), and postharvest sampling time occurred on 19 November (DOY 323). Sampling time 7 May was performed before corn planting and fertilizer application with banded treatments being sampled using the same 2D fashion as in-season sampling times of the previous year. However, in 2014 the banded treatments had a total of 3 transects sampled and pooled by depth x location (in 2013, only one transect was taken per plot). Furthermore, BC treatments did not have the location factor. Instead, 10 random sample cores were taken, split in the 0-5, 5-10 and 10-15 cm depth and pooled by depth. Sampling times 21 June and 8 August followed this same scheme (banded treatments sampled on 2D fashion, BC treatments sampled randomly with no location factor). Sampling time 19 November was only analyzed after the completion of this report, thus data concerning this event will not be shown here.

For both years and all sampling times, samples were brought to the lab and stored properly. If analysis could be performed within a week, samples were left in a cooler (4 °C). Otherwise, samples were stored in a freezer (-20 °C) until analysis. Sample inorganic N extraction was performed by weighing moist soil and adding 1 M KCl (1:4 ratio) to an erlenmeyer flask and shaking for 1h. After decanting, supernatant was poured on Whatman no. 42 paper filter and the collected portion was analyzed for NO_3^- -N using a continuous flow analyzer colorimetric analyzer (Lachat Instruments). Soil moisture was determined by weighing 10 g soil and drying at 105 °C until constant weight was obtained. Soil NO_3^- -N concentration

($\mu\text{g NO}_3^- \text{-N g}^{-1}$ soil) was calculated using the extract $\text{NO}_3^- \text{-N}$ concentration, soil moisture, KCl volume and moist soil mass used for extraction.

Data Analysis and Statistics

Cumulative N_2O flux and FIEF response variables were analyzed using proc glimmix in SAS 9.3 (SAS Institute, 2003) for both years. Residuals homogeneity and normality were assessed and accounted for when needed using variance-grouping strategies. Treatment and year were considered as fixed effects, and block and its interactions were considered as random effects. When ANOVA showed a significant interaction between treatment and year, years were analyzed separately. When an effect was declared significant, means separation was conducted using Fisher's LSD at $\alpha=0.05$.

The soil $\text{NO}_3^- \text{-N}$ concentration was analyzed using proc glimmix in SAS 9.3 (SAS Institute, 2003). Each year was analyzed separately. Furthermore, within each year, preplant sampling time was analyzed alone, in-season sampling times were analyzed together, and postharvest was analyzed alone. Within the in-season sampling times, banded and BC treatments were analyzed together for 2013 growing season and separately for 2014 growing season, due to the change in BC sampling scheme in 2014. Residuals homogeneity and normality were assessed and accounted for when needed using log transformation and/or variance grouping strategies. For 2013 data, sampling time, treatment and location were considered fixed effects, and block and its interactions were considered as random effects. For 2014, sampling time, treatment and location for banded treatments, and sampling time and treatment for BC treatments were considered fixed effects, whereas block and its interactions were considered as random effects. No effort was made to model depth effects in preplant and

in-season sampling times in both years. Postharvest sampling time was analyzed separately for each year, where treatment and depth were considered fixed effects, and block and its interactions were considered random effects.

When ANOVA showed a significant interaction between sampling time (when appropriate), treatment and location (when appropriate), one factor was analyzed on the levels of the other factors. When no interaction was significant and a main effect was declared significant, main effects differences were evaluated. Means separation was conducted using Fisher's LSD at $\alpha=0.05$.

Results

Environmental Factors

Monthly accumulated rainfall in both years ranged from 17 to 224 mm. Total precipitation during the growing season (1 April through 31 October) totaled 550 and 589 mm in 2013 and 2014, respectively, lower than the 727 mm 30-year average (Table 2.2). Precipitation monthly pattern varied among years. In 2013, July and August were the driest months, and in 2014 July was the driest month overall. On the other hand, the wettest month recorded was June of 2014, totaling 224 mm, which was 136 mm more than the same month in 2013. Mean soil volumetric moisture varied from 2 to 49%, and it peaked following precipitation events (Fig. 2.5).

Soil temperature at gas sampling ranged from 9 to 28 °C in both years (Fig. 2.6), averaging 21.2 and 22.5 °C in 2013 and 2014, respectively. There were no differences in soil temperature among treatments. Air temperatures at gas sampling ranged from 8 to 35 °C in both

years (Fig. 2.6), averaging 26.6 and 26.9 °C in 2013 and 2014, respectively. Air temperature was higher than soil temperature at almost all sampling events.

Daily N₂O emissions

Daily N₂O emissions in 2013 varied in time and space (Fig. 2.7). Before fertilizer application, emissions were low even after precipitation events. However, after fertilizer was applied, N₂O emissions peaked following rainfall events, and then declined. The highest emission occurred under BC-Urea (113 g N₂O-N ha⁻¹ d⁻¹, DOY 211), whereas the control treatment always had the lowest fluxes. The main period of emissions lasted 48 days (from DOY 136 to 184) after fertilizer application, except for one late flux (DOY 211), which was the highest emission event for SSB-UAN and BC-Urea. Thereafter, fluxes remained at background levels even after precipitation events. The EEFs were efficient in reducing N₂O daily fluxes compared to their conventional counterparts. This effect was more evident and consistent with NI than with CU. On the major emission spikes, SSB-UAN+I emitted from 38 (DOY 152) to 79% (DOY 211) less N₂O than SSB-UAN, averaging 62% reduction across the main six emission events. For BC-CU, the reduction in emissions compared to BC-Urea was evident on the first three major spikes, when the use of CU promoted N₂O emission reductions from 45 (DOY 161) to 63% (DOY 140) compared to urea. However, emissions from BC-CU were 40% higher (DOY 175) and similar (DOY 179 and 211) compared to those of BC-Urea at later periods of the growing season.

Daily N₂O emissions in 2014 varied in time and space (Fig. 2.8). Before fertilizer application, emissions were low even after precipitation events. However, after the fertilizer was applied, N₂O emissions peaked following rainfall events, and then declined. Fluxes were of

higher magnitude in 2014 compared to 2013 for all N treatments. The highest emission occurred under SB-UAN ($270 \text{ g N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$, DOY 145), whereas the control treatment always had the lowest fluxes. The main period of emissions lasted 33 days (from DOY 137 to 170) after fertilizer application, except for two late fluxes (DOY 223 and 245), where BC-CU and SSB-UAN had higher emissions compared to other treatments. Thereafter, fluxes remained at background levels even after precipitation events. The EEFs efficiency in reducing daily N_2O emissions compared to their conventional counterparts followed the same pattern as 2013, but at a higher magnitude. On the major spikes, SSB-UAN+I emitted from 37 (DOY 145) to 84% (DOY 245) less N_2O than SSB-UAN, averaging 67% reduction across the main six emission events. On the other hand, BC-CU was only efficient in reducing N_2O emissions compared to BC-Urea on the first two main emission spikes, when CU emitted 55 (DOY 145) and 22% (DOY 154) less N_2O than urea. Thereafter, BC-CU emitted 3-fold (DOY 223) and 11-fold (DOY 245) more N_2O than BC-Urea.

Cumulative N_2O emissions

The effects of treatment, year and treatment \times year were significant. In 2013, all N treatments emitted significantly more N_2O than the control, except BC-UAN (Table 2.3, Fig. 2.9). Emissions were significantly higher under SSB-UAN ($2.4 \text{ kg N}_2\text{O-N ha}^{-1}$). Emissions were statistically the same between BC-CU and BC-Urea, whereas SSB-UAN+I emitted statistically less than SSB-UAN. Among the N treatments, BC-UAN emitted the least ($0.6 \text{ kg N}_2\text{O-N ha}^{-1}$).

In 2014, all N treatments emitted significantly more than the control, except for SSB-UAN+I (Table 2.3, Fig. 2.10). All N treatments emitted statistically the same (ranging from BC-CU= 3.51 to SSB-UAN= $2.44 \text{ kg N}_2\text{O-N ha}^{-1}$), except for SSB-UAN+I ($1.03 \text{ kg N}_2\text{O-N ha}^{-1}$).

Control emitted significantly lower than all other treatments (0.3 kg N₂O-N ha⁻¹). Overall, emissions in 2014 were higher than in 2013. The treatments that behaved differently from one year to the other were BC-Urea (1.63 to 3.37), BC-CU (1.35 to 3.51) and BC-UAN (0.6 to 2.68 kg N₂O-N ha⁻¹ in 2013 and 2014, respectively).

Fertilizer-Induced Emission Factor

The effect of treatment and year were significant, and their interaction was not significant. Averaged across both years, only SSB-UAN+I had a significantly lower FIEF (0.4%), while all other treatments did not differ statistically (Table 2.4). Averaged across treatments, 2013 FIEF (0.68%) was significantly lower than that of 2014 (1.38%).

Soil Nitrate

2013

In 2013, all treatments were sampled in a 2D fashion. Thus, both band and BC treatments were analyzed together. Within each sampling time, depths were analyzed individually.

The effects of treatment, location, sampling time, sampling time × treatment and location × treatment were significant for soil NO₃⁻ at the 0 to 5 cm depth. Since there were significant 2-way interactions, means are presented accordingly (Table 2.5 and 2.6).

At the 0-5 cm depth, on 2 June BC-CU, BC-UAN and SB-UAN had the highest values (Table 2.5), whereas control had the lowest. Interestingly the CU had NO₃⁻ concentration of 50 µg g⁻¹. On 21 June, BC-Urea, BC-UAN, SB-UAN and SSB-UAN had the highest values,

whereas control had the lowest. When comparing both sampling dates, BC-Urea, SSB-UAN and SSB-UAN+I had significantly higher values on 21 June compared to 2 June.

At the 0-5 cm depth, in location 0 SSB-UAN and SSB-UAN+I had the highest NO_3^- concentration, with control having the lowest (Table 2.6). In location 10, SB-UAN, BC-UAN and BC-CU had the highest levels, and control the lowest. In location 20, all BC treatments and SB-UAN were the highest, whereas the SSB treatments and control were the lowest. In location 30, all BC treatments were the highest, and all banded treatments and control were the lowest. When comparing a treatment across locations, all the banded treatments and control had one location that was higher than the others, whereas the BC treatments had all locations similar with no gradient. This indicates the placement of the band.

The effect of treatment, location, sampling time, sampling time \times treatment, location \times treatment and sampling time \times location were significant for soil NO_3^- at the 5 to 10 cm depth. Since there were significant 2-way interactions, means are presented accordingly (Table 2.7, 2.8 and 2.9).

At the 5-10 cm depth, on 2 June BC-UAN had the highest NO_3^- concentration, and control had the lowest (Table 2.7). On 21 June, SSB-UAN, BC-Urea, SB-UAN and BC-UAN had the highest values, and control had the lowest. BC-CU and BC-Urea were not statistically different, which was also observed between SSB-UAN+I and SSB-UAN (Table 2.7). However, on 21 June, NO_3^- levels for both BC-CU and SSB-UAN-I were statistically lower than their conventional counterparts. When comparing a treatment across sampling times, BC-CU, BC-UAN and control were statistically lower in 21 June compared to 2 June.

At the 5-10 cm depth, in location 0 SSB-UAN and SSB-UAN+I had the highest NO_3^- concentration, and control had the lowest (Table 2.8). The effect of location followed the same

pattern as that of 0-5 cm depth, with banded treatments presenting a gradient and BC treatments presenting a uniform concentration across all locations (Table 2.8). In location 10, BC-UAN, SSB-UAN, BC-Urea and SSB-UAN+I had the highest values, and control had the lowest. In location 20, BC-UAN, BC-Urea and SB-UAN had the highest values, and SSB-UAN+I and control had the lowest. In location 30, BC-CU, BC-UAN and BC-Urea had the highest, and control, SSB-UAN and SSB-UAN+I had the lowest. When comparing a treatment across locations, control and the banded treatments had one location with higher concentrations than the others, whereas the BC treatments had similar concentrations in all locations.

At the 5-10 cm depth, on 2 June, location 0 had the highest NO_3^- concentration, and all other locations were significantly lower (Table 2.9). On 21 June, location 0 had the highest concentration, and locations 20 and 30 had the lowest. This is probably due to plant uptake happening more at locations 20 and 30, the ones closer to the corn row. When comparing a location across sampling times, locations 20 and 30 were statistically lower on 21 June compared to 2 June.

The effect of treatment, location, sampling time \times location, location \times treatment, and sampling time \times location \times treatment were significant for soil NO_3^- at the 10 to 15 cm depth. Since there was a significant 3-way interaction, means are presented accordingly (Table 2.10).

At the 10-15 cm depth, on 2 June, at location 0, SSB-UAN+I had a significantly higher NO_3^- concentration than other treatments, and control and BC-Urea had the lowest concentration (Table 2.10). At the 10-15 cm depth, on both sampling times, BC-CU was always statistically equal to BC-Urea at every location (Table 2.10). However, SSB-UAN+I had significantly higher NO_3^- concentration on 2 June at location 0 when compared to SSB-UAN. At location 10, control was significantly lower than BC-UAN and SB-UAN. At location 20, SSB-UAN and

SSB-UAN+I were significantly lower than BC-UAN. At location 30, BC-UAN had a higher concentration than control, SB-UAN, SSB-UAN and SSB-UAN+I. When comparing a treatment across locations, on 2 June BC-UAN, SB-UAN, SSB-UAN and SSB-UAN+I had one location significantly higher than the others.

At the 10-15 cm depth, on 21 June, at location 0, SSB-UAN and SSB-UAN+I had significantly higher NO_3^- concentration, and control had the lowest (Table 2.10). At location 10, only BC-CU was significantly lower among N treatments, and control was the lowest. At location 20, BC-UAN, BC-Urea and SB-UAN had the highest concentrations, and BC-CU, control and SSB-UAN+I had the lowest. At location 30, BC-CU, BC-UAN, BC-Urea and SB-UAN had the highest concentrations, and control, SSB-UAN and SSB-UAN+I the lowest. When comparing a treatment across locations, on 21 June, BC-Urea was the only treatment that did not have a gradient, and the SSB treatments were the ones with the most evident gradient.

On 2 June, it was possible to observe the formation of a gradient not only under the banded treatments, but also under BC-UAN. Furthermore, although not significant, other BC treatments also presented a numerical gradient. However, the gradient between banded and BC at this depth was inversely related, with banded treatments presenting a higher NO_3^- concentration at location 0 whereas BC treatments presented a higher NO_3^- concentration at location 30. This is supported by plant uptake and fertilizer diffusion toward the depleted zone, nearby the root system. On 21 June, however, location 30 under BC treatments was the most depleted. At this stage (DOY 172), corn plants were expected to be taking up N at a fast rate, possibly causing the lower NO_3^- concentration values.

The effects of treatment and depth were significant for soil residual NO_3^- after corn harvest (Table 2.11). Averaged over depths, BC-CU had 3.9 kg N ha^{-1} left in the soil profile

with only 2.1 kg N ha⁻¹ in the 0N treatment (Table 2.11). Most of the residual N occurred in the 0 to 15 cm depth. The 45 to 60 and 60 to 90 cm layers had < 1 kg N ha⁻¹ suggesting very little leaching of N to these depths.

The cumulative residual soil profile NO₃⁻ after harvest was not impacted by treatment (p=0.6) (Table A.5. on Appendix). Nonetheless, BC-CU was the treatment with the highest numerical soil cumulative NO₃⁻ (19.4 kg ha⁻¹), whereas control had the least amount (10.3 kg N ha⁻¹).

2014

In 2014, band and BC treatments sampling schemes were readjusted. Band treatments were sampled on a 2D fashion, whereas BC treatments were sampled at random, with no regard to horizontal gradient. For that reason, band and BC treatments were split in different data sets and analyzed separately. Moreover, within each sampling time, depths were analyzed individually. Sampling times occurred on 21 June (DOY 172) and 8 August (DOY 221). BC-UAN was included in both datasets (band and BC).

There were no significant effects for 7 May at any depth for both band and BC treatments for soil NO₃⁻ concentration. The mean value (averaged over all factors) was 5 µg NO₃⁻-N g⁻¹ soil.

Band Treatments

All three depths had similar results, only changing in magnitude, with higher NO₃⁻ concentrations at 0-5 cm and decreasing levels as depth increases.

For 21 June and 8 August sampling times on band treatments, at the 0-5 cm depth, treatment, location, sampling time and sampling time \times location effects were significant. Since there was a significant 2-way interaction, means are presented accordingly (Table 2.12).

At the 0-5 cm depth on band treatments, on 21 June and 8 August locations 0 and 10 had a statistically higher NO_3^- concentration than locations 20 and 30 (Table 2.12). When comparing a location across different sampling times, location 0 had a statistically lower NO_3^- concentration on 8 August than on 21 June. For the treatment main effect, BC-UAN had statistically lower values compared to SSB-UAN and SSB-UAN+I. Depending of sampling time, different NO_3^- movement patterns can be observed. As NO_3^- gets taken up by the crops, NO_3^- concentration at different locations are impacted by the uptake rate at locations nearby the root system and the rate that NO_3^- diffuse from other locations toward the now-depleted location 0. BC-UAN had lower NO_3^- concentration compared to SSB-UAN and SSB-UAN+I, but it was not statistically different than SB-UAN. This could also be an effect of the rainfall. Even BC-UAN and SB-UAN being applied differently, the higher precipitation levels may have further incorporated BC-UAN and also caused a higher diffusion of the SB-UAN into the soil, making these two treatments to behave similarly.

For 21 June and 8 August sampling times on band treatments, at the 5-10 cm depth, treatment, location, sampling time and sampling time \times location effects were significant. Since there was a significant 2-way interaction, means are presented accordingly (Table 2.13).

At the 5-10 cm depth for band treatments, on 21 June, location 0 and 10 had the highest NO_3^- concentration, and location 0 had the lowest (Table 2.13). On 8 August, locations 0 and 10 had the highest, and 20 and 30 had the lowest concentrations. When comparing a location across different sampling times, location 0 and 10 were statistically lower on 8 August when

compared to 21 June. For the treatment main effect, BC-UAN was statistically lower than SSB treatments.

For 21 June and 8 August sampling times on band treatments, at the 10-15 cm depth, treatment, location, sampling time and sampling time \times location effects were significant. Since there was a significant 2-way interaction, means are presented accordingly (Table 2.14).

At the 10-15 cm depth for band treatments, on 21 June, location 0 and 10 had the highest NO_3^- concentration, and location 30 had the lowest (Table 2.14). On 8 August, 0 and 10 had the highest, and 30 had the lowest concentrations. When comparing a location across different sampling times, all locations were statistically lower on 8 August when compared to 21 June. For the treatment main effect, BC-UAN was statistically lower than SSB treatments.

On the previous year, more NO_3^- was observed at all the layers. The lower magnitude found in 2014 could be due to the more intensive precipitation pattern earlier in the season and also the sampling timing. In 2014, no difference in soil NO_3^- concentration was observed between SSB-UAN and SSB-UAN+I, at any given depth. Although, it is possible that the NI effect in decreasing NO_3^- occurred earlier in the growing season, when soil samples were not taken.

Broadcast Treatments

For 21 June and 8 August sampling times on broadcast treatments, at the 0-5 cm depth, there was no significant effect on soil NO_3^- concentration. The mean value (averaged over all factors) was $12 \mu\text{g NO}_3^- \text{-N g}^{-1}$ soil. This could be driven by the wetter spring, causing surface-applied fertilizer to be incorporated into the soil and moved transported deeper in the soil profile by water infiltration.

For 21 June and 8 August sampling times on broadcast treatments, at the 5-10 cm depth, only the treatment effect was significant (Table 2.15). At the 5-10 cm depth on broadcast treatments, BC-UAN and control had statistically lower NO_3^- concentration than BC-CU (Table 2.15).

For 21 June and 8 August sampling times on broadcast treatments, at the 10-15 cm depth, sampling time and treatment effects were significant (Table 2.16). At the 10-15 cm depth on broadcast treatments, only control had statistically lower NO_3^- concentration compared to other treatments. Sampling date 21 June was statistically higher than 8 August (Table 2.16). Although statistical differences were seen, the numerical difference was of small magnitude, ranging from 9 to 1 $\mu\text{g NO}_3^- \text{-N g}^{-1}$ soil over all BC treatments and both sampling times. As mentioned previously, this could be a result of higher rainfall events right after fertilizer application, which may have incorporated the fertilizer at a faster rate and made it available for plant uptake.

In 2014, no difference in soil NO_3^- concentration was observed between BC-Urea and BC-CU, at any given depth. Although, it is possible that the coating effect in decreasing NO_3^- occurred earlier in the growing season, when samples were not taken. Further, greater soil NO_3^- may have occurred later in the growing season under BC-CU than BC-Urea, driven by the rainfall events following the dry period, when N_2O emissions from BC-CU were higher.

Discussion

Daily N_2O emissions

Daily N_2O followed a common pattern of emissions. Before fertilizer application, low levels of NO_3^- in the soil (Table 2.1) were the driver for low, background emissions, even after

rainfall events. After fertilizer was applied, the emissions spiked following precipitation events. That was due to the fact that inorganic N concentration in the soil was high, whereas plant demand was not able to fully utilize soil NO_3^- . Therefore, N surplus coupled to increased soil moisture were the drivers for N_2O emission spikes. SSB-UAN+I had consistently low daily N_2O emissions, with the highest recorded daily emission being $24 \text{ g N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ (DOY 140), following the same pattern as the control, which had a highest recorded daily emission being $14 \text{ g N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ (DOY 211) (Fig. 2.7). In contrast, SSB-UAN was consistently among the highest daily emissions, with a highest recorded daily emission being $105 \text{ g N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ (DOY 211), about 4x higher than that of SSB-UAN+I.

Generally, emissions last 30-45 days after fertilizer application and then return to background levels thereafter. In 2013, the main emission period lasted about 48 days (Fig. 2.7). There was one emission spike out of this range, which occurred on DOY 211, 75 days after fertilizer application. That was driven by a precipitation event on DOY 210 of 13 mm. Although a small precipitation event, the rain was able to reach the soil surface and increase soil volumetric moisture to 41% (Fig. 2.5), triggering N_2O emissions. The previous rain event greater than 10 mm happened on DOY 178 (28 mm), 32 days earlier (Fig. 2.5). The month-long drought during a high-demand period caused soil volumetric moisture to be very low (4%, Fig. 2.5) 6 days prior to the 12-mm rain. We hypothesize that the dry period in 2013 decreased plant uptake, and the aerobic condition was conducive for NO_3^- build up, although this was not measured at the time. With increased soil NO_3^- , a change from 4 to 41% in soil volumetric moisture caused the most significant emission event of the growing season among all N treatments, of $113 \text{ g N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ under BC-Urea. Thereafter, daily fluxes remained at background levels, even after a 70-mm rainfall event on DOY 258 (Fig. 2.7).

In 2014, the main emission period was shorter than in 2013, lasting 33 days (Fig. 2.8). Despite the narrower window, 2014 emission occurred at a higher magnitude than in 2013, which can be visualized at the slope of increase on cumulative emissions between 2013 and 2014 (Fig. 2.7 and 2.8). BC-Urea was consistently among the highest emitting N treatments, whereas SSB-UAN+I and control were consistently among the least emitting treatments (Fig. 2.8). The highest recorded daily emission event happened under SB-UAN on DOY 145 ($270 \text{ g N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$). Two emission events were observed outside the main emission period, on DOY 223 and 245, 86 and 108 days after fertilizer application, respectively. The flux on DOY 223 was driven by a 23-mm rainfall event on DOY 222 (Fig. 2.5). On DOY 220, soil volumetric moisture was at 12% and increased to 36% after precipitation, on DOY 223 (Fig. 2.5). The previous rainfall greater than 10 mm occurred on DOY 166, a 57-day dry period. On DOY 220 (8 August), soil NO_3^- concentration was low for all treatments for all depths (Tables 2.12 through 2.16), ranging from 3 to $11 \mu\text{g NO}_3^- \text{-N g}^{-1}$ soil. From DOY 223 to 245, there were two rainfall events greater than 10 mm, on DOY 238 (12 mm) and DOY 243 (34 mm) (Fig. 2.5). No gas samples were taken right after DOY 238, although it is possible that a flux had happened. On DOY 245, N_2O emissions peaked mostly in SSB-UAN and BC-CU (20 and $56 \text{ g N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$, respectively). Soil NO_3^- concentrations at 0-5 cm depth at DOY 220 (8 August) were low for both treatments (11 and $12 \mu\text{g NO}_3^- \text{-N g}^{-1}$ soil, respectively, Table 2.12). However, it is possible that, for SSB-UAN, NO_3^- from lower layers was contributing to the N_2O peak, and in the case of BC-CU, N could have been released from the coating, which was not accounted for in the previous soil NO_3^- test. Many authors have observed N_2O emissions from CU to happen at a later stage of the growing season, when conventional sources would be at background emission levels (Halvorson et al., 2011; Sistani et al., 2011; Venterea et al., 2011; Drury et al.,

2012; Halvorson and Del Grosso, 2012; Fernández et al., 2014; Parkin and Hatfield, 2014). In those studies, CU delayed NO_3^- formation compared to urea, and the late release of NO_3^- from the coating induced by rainfall events was responsible for N_2O fluxes later in the growing season. In 2013, BC-CU had significantly lower NO_3^- levels compared to BC-Urea on 21 June at the 0-5 cm depth (Table 2.5) and 5-10 cm depth (Table 2.6). Further, in 2013, averaged over depths, BC-CU had significantly higher soil residual NO_3^- levels than urea (Table 2.11) after corn harvest. Dell et al. (2014), in a laboratory incubation experiment at 30% soil volumetric water, showed that CU delayed NO_3^- formation in soil compared to urea up to 9 days after fertilizer application. Thereafter, CU increased soil NO_3^- to same levels as urea at 21 days, and surpassed urea levels at 28 days. However, this type and magnitude of response can be different on field situations where soil water and temperature conditions are highly variable.

The magnitude of fluxes in different studies varies depending on many factors. For example, Dell et al. (2014), observed maximum daily emissions of about $40 \text{ g N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ under urea in one year, and about $250 \text{ g N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ under CU in the next year. The reason for the erratic pattern across both years was given by differences in rainfall timing and intensity. Similarly, Burzaco et al. (2013) found maximum daily emissions of 78 (SSB-UAN) and 41 (SSB-UAN+I) $\text{g N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ in one year, but much higher values ($230 \text{ g N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ under SSB-UAN and $200 \text{ g N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ under SSB-UAN+I) in the following year. The variation in magnitude was also affected by rainfall pattern.

Cumulative N_2O emissions

In 2013, SSB-UAN lost the most N_2O ($2.42 \text{ kg N}_2\text{O-N ha}^{-1}$) among all treatments (Table 2.3). Other studies have shown increased emissions from SSB than SB or BC (Drury et al.,

2006; Engel et al., 2010; Halvorson et al., 2011; Halvorson and Del Grosso, 2012), whereas others observed the opposite effect (Venterea et al., 2010). Engel et al. (2010) found that the band placement of urea-based fertilizer increased soil pH, favoring the accumulation of NH_4^+ , which caused NO_2^- levels to peak, promoting higher N_2O losses. In our case, we hypothesize that the slit opened during the SSB application promoted greater water channeling and infiltration in the band, thus increased soil moisture levels coupled with concentrated inorganic N led to enhanced N_2O losses. The use of NI significantly reduced N_2O losses, with SSB-UAN+I emitting $0.93 \text{ kg N}_2\text{O-N ha}^{-1}$, a reduction of 62% compared to SSB-UAN. Similarly, Burzaco et al. (2013) also observed a 24% reduction in N_2O emissions when UAN was applied with NI compared to UAN alone. This could be due to decreased NO_3^- levels in soil when NI is applied with the fertilizer. However, this trend was only observed on DOY 172 (21 June) at 5-10 cm depth in 2013 (Table 2.7), when soil NO_3^- levels were statistically lower under SSB-UAN+I than in SSB-UAN. BC-Urea ($1.63 \text{ kg N}_2\text{O-N ha}^{-1}$) and BC-CU ($1.35 \text{ kg N}_2\text{O-N ha}^{-1}$) were not significantly different, indicating that controlled-released fertilizer was not effective in reducing N_2O compared to its conventional counterpart. Many studies reported similar results in corn (Venterea et al., 2011; Nash et al., 2012; Dell et al., 2014) and wheat (Burton et al., 2008). This effect has been attributed to either abnormally dry conditions where denitrification is limited and N source becomes a secondary factor or when the delayed release of CU N increases N_2O emissions later in the season compared to urea (Dell et al., 2014). SB-UAN emitted 31% less than SSB-UAN. Drury et al. (2006) observed a similar result where shallow band (2-cm depth) UAN emitted 26% less than deep band (10-cm depth) UAN. SSB-UAN+I and BC-UAN were the only treatments that emitted significantly less than others, being BC-UAN not different from control. Although not measured, we hypothesized that BC-UAN low

emissions were possibly due to ammonia volatilization and/or N immobilization. This result can be corroborated by the lowest NFRE in 2013 being observed under BC-UAN (Chapter 3, Table 3.5).

In 2014, all treatments emitted more N₂O than during the previous year, with the BC treatments emitting significantly more compared to 2013 (Table 2.3). This was due to increased precipitation amounts received in 2014, especially earlier in the season, when N₂O emissions are more likely to happen. For example, the month of June received 224 and 88 mm in 2014 and 2013, respectively (Table 2.2). Furthermore, all N treatments emitted statistically the same, except for SSB-UAN+I (1.03 kg N₂O-N ha⁻¹), which was not different from the control (0.3 kg N₂O-N ha⁻¹) (Table 2.3). With a wetter spring, treatments that were not main emitters in 2013 had significantly increased emissions in 2014. It was the case for the BC treatments BC-Urea, BC-CU and BC-UAN, which emitted 52%, 62% and 78% more in 2014 compared to 2013, respectively. Higher precipitation amounts likely promoted more fertilizer incorporation in the soil by water infiltration and promoted continued elevated soil volumetric water content early in 2014, leading to increased losses. Although not significant due to increased variability, SSB-UAN+I emitted 58% less than SSB-UAN, indicating its potential in reducing N₂O losses under the different precipitation scenarios observed in 2013 and 2014. However, in 2014 no soil NO₃⁻ differences were observed between SSB-UAN and SSB-UAN+I at any depth or sampling time. It is possible that differences were observed earlier in the season, when soil NO₃⁻ data was not sampled. Burzaco et al. (2013), on an experiment where SSB-UAN and SSB-UAN+I were applied to corn, observed that soil NO₃⁻ concentration was the main driver for N₂O emissions in one year, but soil water content was the main driver on another year. Ciarlo et al. (2007) showed that increasing water-filled pore space from 40 to 120% significantly increased the amount of N

lost as N_2 compared to N_2O . Although not measured in the present study, N_2 losses could have been significantly higher in 2014, when flooded areas were observed after intense rainfall events in the spring, which did not happen in 2013.

Fertilizer-Induced Emission Factor

The values of FIEF ranged from 1.31% (BC-Urea) to 0.4% (SSB-UAN+I) (Table 2.4). The default FIEF value from agricultural soils used by IPCC is 1%, but it has a wide confidence interval (from 0.3 to 3%), which comprises the values observed in this study. In 2013, FIEF was lower than in 2014 due to the higher intensity of rainfall earlier in the 2014 season, which maintained soil volumetric moisture at levels between 28% and 38% during the 32 days following fertilizer application (Fig. 2.5). Only SSB-UAN+I was effective in reducing FIEF (0.4%) among all N treatments. BC-CU was not effective in reducing FIEF when compared to BC-Urea. Similar results were observed in other studies. Venterea et al. (2011) found no difference in FIEF between urea (0.26%) and PCU (0.31%) in a no-till corn field. Furthermore, Burton et al. (2008) observed no difference between urea (0.02%) and SU (0.1%). The lack of differences among conventional and EEFs in reducing FIEF has been attributed to higher emissions from EEF later in the season, especially under rainfed systems. Nonetheless, many studies reported PCU and/or SU as efficient alternatives to urea in reducing FIEF (Halvorson et al., 2010a, 2011; Halvorson and Del Grosso, 2012, 2013; Fernández et al., 2014). Halvorson and Del Grosso (2012) found FIEF values of in the order urea (0.69%) > UAN (0.38%) > CU (0.26%). Fernández et al. (2014) found FIEF values of 6.59% under urea and 4.2% under CU in one out of three years. The high values were observed under a year of frequent and intense precipitation events, whereas under dryer years, no difference was observed. In studies where N

sources such as urea and UAN were applied, both in conventional and EEF forms, urea alone had the highest FIEF values (Halvorson et al., 2011; Halvorson and Del Grosso, 2012, 2013). Although different UAN placements (BC, SB and SSB) had similar FIEF in the present study, Halvorson and Del Grosso (2013) observed consistent increases in FIEF when urea, UAN and PCU were SB (0.35%) rather than BC (0.22%) in both strip-till and no-till corn fields. Nelson et al. (2008) stated that EEFs would have the most beneficial impact when applied to either heavy soils where denitrification is enhanced by waterlogging or light soils where NO_3^- leaching is a major pathway of N loss. Our site does not fit in either scenarios, and thus EEF effects on FIEF were modest (when using NI) to none (when using coated-urea) compared to conventional fertilizers.

Soil Nitrate

2013

At the 0-5 cm depth, averaged over location, on 2 June BC and SB treatments had higher NO_3^- concentration than SSB treatments, which was expected since SSB application occurred at 10-cm depth (Table 2.5). SSB-UAN+I was not efficient in reducing NO_3^- levels compared to SSB-UAN at both sampling times, whereas BC-CU had lower NO_3^- levels than BC-Urea on 21 June only. Studies evaluating NO_3^- concentration as a result of N source application have shown contradictory results. For example, Venterea et al. (2011) and Nash et al. (2012) observed lower NO_3^- levels under BC-Urea than under BC-CU for most of their sampling dates. On the other hand, Halvorson et al. (2011) and Halvorson and Del Grosso (2012) observed BC-CU to be efficient in reducing NO_3^- concentration in soil compared to urea. Nonetheless, Halvorson and Del Grosso (2013) and Maharjan et al. (2014) observed no difference between the two sources

when evaluating NO_3^- in soil. Dell et al. (2014), under a controlled incubation study, showed that CU delayed NO_3^- accumulation compared to urea during the first 21 days after application, but it had a higher NO_3^- release later, which was able to reach and even surpass those levels observed under urea by the end of the study. In accordance, Parkin and Hatfield (2014) observed in a field study that during 37 days after fertilizer application, NO_3^- concentration in soil was lower under CU than urea, and 47 days after fertilizer application there was no difference among treatments. The effect of location was evident and followed the expected pattern (Table 2.6). Band treatments had a decreasing gradient from the band toward the plant rows, whereas BC treatments had a more even horizontal distribution of fertilizer. Furthermore, on location 0, banded treatments had a significantly higher NO_3^- concentration when compared to BC treatments, but significantly lower on locations 20 and 30 (Table 2.6).

At the 5-10 cm depth, averaged over treatments, the location effect was significantly different across sampling times (Table 2.9). On 2 June, only location 0 was higher than the others, whereas on 21 June locations 20 and 30 were statistically lower. This is probably due to plant uptake happening more at locations 20 and 30, the ones closer to the corn row.

At the 10-15 cm depth, on both sampling times, BC-CU was always statistically equal to BC-Urea at every location (Table 2.10). However, SSB-UAN+I had significantly higher NO_3^- concentration on 2 June at location 0 when compared to SSB-UAN. Although surprising, other authors have observed similar results, where the EEF surpasses the conventional counterpart (Venterea et al., 2011; Nash et al., 2012). On 2 June, it was possible to observe the formation of a gradient not only under the banded treatments, but also under BC-UAN. Furthermore, although not significant, other BC treatments also presented a numerical gradient. However, the gradient between banded and BC at this depth was inversely related, with banded treatments

presenting a higher NO_3^- concentration at location 0 whereas BC treatments presented a higher NO_3^- concentration at location 30. This is supported by plant uptake and fertilizer diffusion toward the depleted zone, nearby the root system. On 21 June, however, location 30 under BC treatments was the most depleted. At this stage (DOY 172), corn plants were expected to be taking up N at a fast rate, possibly causing the lower NO_3^- concentration values.

At the end of the season, soil residual NO_3^- was affected by treatment and depth (Table 2.11). BC-CU had the highest amounts of NO_3^- averaged over all depths. Although statistically significant, the magnitude between BC-CU and control (the lowest NO_3^- amount) was only 1.8 kg NO_3^- -N ha⁻¹. This is an indication of delayed N release from CU, in which case plant uptake was not able to utilize. Similar results were found by Halvorson and Del Grosso (2012) in one out of two years at 0-15 and 0-30 cm depth, where CU had higher NO_3^- levels after corn harvest compared to UAN, CU and SU. However, others have found no difference among urea, CU and SU after harvest (Halvorson and Del Grosso, 2013). In the same study, all N sources were applied either BC or banded, and placement also did not impact residual NO_3^- in soil. At depth, NO_3^- amounts were highest on the top layer, and significantly lower at the bottom layers. This may be an indication of the low potential for NO_3^- leaching of this location, previously observed by Harris (1993).

The results for cumulative residual soil profile NO_3^- show a trend for BC-CU to have higher NO_3^- amounts than other treatments (Table A.5. on Appendix). The use of CU provides a controlled release of N from the coating, which supposedly better match plant uptake. However, if N from the coating is released at a moment when plant demand is not able to fully utilize it, higher residual NO_3^- amounts will be left in the soil. However, it does not mean that the N is lost or unavailable, since it could still be utilized by the subsequent crop.

2014

In 2014, less statistical differences were observed possibly due to the higher rainfall amounts received following fertilizer application. For example, the month of June in 2014 had 120 mm more rain compared to the same month in 2013.

Band Treatments

All three depths had similar results, only changing in magnitude, with higher NO_3^- concentrations at 0-5 cm and decreasing levels as depth increases. Depending of sampling time, different NO_3^- movement patterns can be observed. As NO_3^- gets taken up by the crops, NO_3^- concentration at different locations are impacted by the uptake rate at locations nearby the root system and the rate that NO_3^- diffuse from other locations toward the now-depleted location 0.

Lower NO_3^- concentration were observed in BC-UAN compared to SSB-UAN and SSB-UAN+I, but it was not statistically different than SB-UAN. This could also be an effect of the rainfall. Even BC-UAN and SB-UAN being applied differently, the higher precipitation levels may have further incorporated BC-UAN and also caused a higher diffusion of the SB-UAN into the soil, making these two treatments to behave similarly. At depths 5-10 and 10-15 cm, similar trends were observed (Tables 2.13 and 2.14), only that NO_3^- levels were of a smaller magnitude. On the previous year, more NO_3^- was observed at the all layers. The lower magnitude found in 2014 could be due to the more intensive precipitation pattern earlier in the season and also the sampling timing.

Broadcast Treatments

At the 0-5 cm depth, there was no treatment or sampling time effect. This could be driven by the wetter spring, causing surface-applied fertilizer to be incorporated into the soil

and moved transported deeper in the soil profile by water infiltration. Averaged over sampling time, at the 5-10 cm depth BC-CU was significantly higher than BC-UAN and control (Table 2.15). At the 10-15 cm depth, only control was significantly lower, and 21 June was higher than 8 August (Table 2.16). Although statistical differences were seen, the numerical difference was of small magnitude, ranging from 9 to 1 $\mu\text{g NO}_3^- \text{-N g}^{-1}$ soil over all BC treatments and both sampling times. As mentioned previously, this could be a result of higher rainfall events right after fertilizer application, which may have incorporated the fertilizer at a faster rate and made it available for plant uptake.

Conclusions

Nitrogen fertilizer source and placement impacts N_2O losses from no-till continuous corn in Northeast Kansas. However, this effect is variable and weather dependent, especially due to rainfall frequency and intensity right after fertilizer application.

Subsurface band applied fertilizer promoted higher N_2O losses compared to surface band and broadcast when rainfall timing and intensity better followed crop water demand. However, no placement impact was observed on a year when rainfall was abundant right after fertilizer application.

The use of NI with fertilizer consistently decreased N_2O losses compared to fertilizer alone. Nevertheless, coated urea was not efficient in mitigating N_2O emissions when compared to conventional urea. Further, the addition of NI to subsurface-banded UAN was the only strategy that efficiently reduced FIEF. The addition of NI to UAN proved to be an efficient strategy in reducing overall N_2O losses in rainfed no-till corn systems in Northeast Kansas.

Further research should focus on N source, including EEFs, and placement under different soil and climate scenarios. EEFs have the potential to mitigate N₂O losses compared to conventional fertilizers, but the response is dependent on water availability. Water will dictate the incorporation of BC treatments, the release rate of N from CU, the plant uptake sink strength and, consequently, the potential for N₂O losses from the system.

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Figure 2.1. Treatment application for a) SSB-UAN and SSB-UAN+I, b) SB-UAN, c) BC-UAN and d) BC-Urea and BC-CU.



Figure 2.2. Chamber top a) in front view showing sampling port and thermometer, b) on a side view showing vent outlet, c) on an inside view showing vent tube, manifold and tubing branching to each quarter of the chamber, and d) a close up at the manifold.



Figure 2.3. 2D soil sampling scheme. a) Locations 0, 10, 20 and 30 from right to left. b) Soil core partitioned in 0-5, 5-10 and 10-15 cm depths.

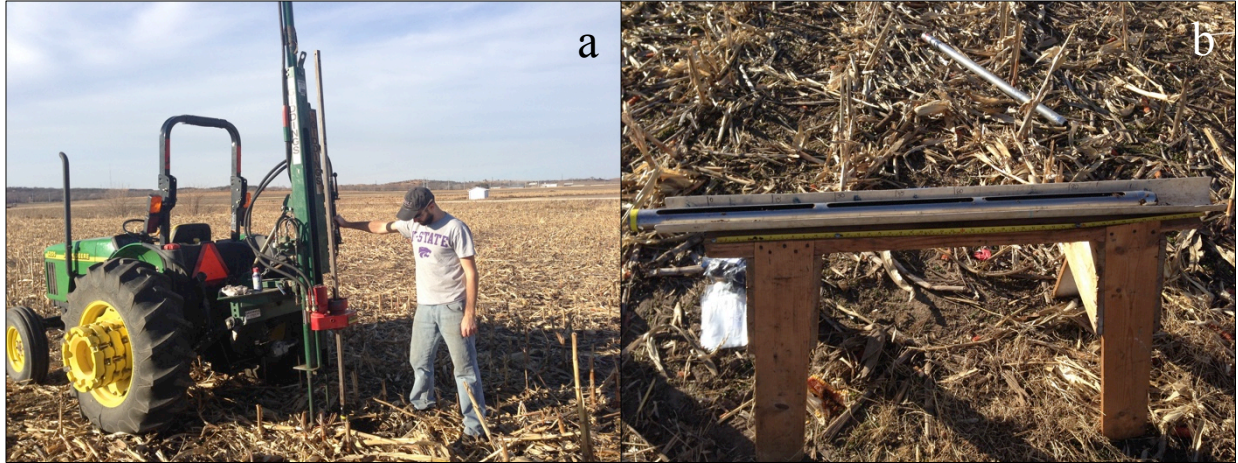


Figure 2.4. Soil sampling after corn harvest for soil residual NO_3^- . a) Sample acquisition. b) Sample depth cutting board.

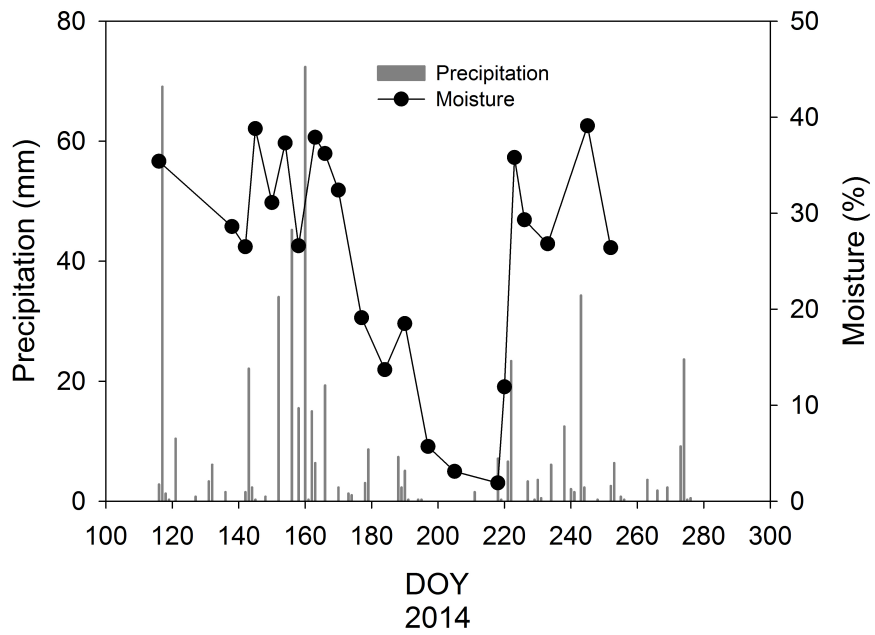
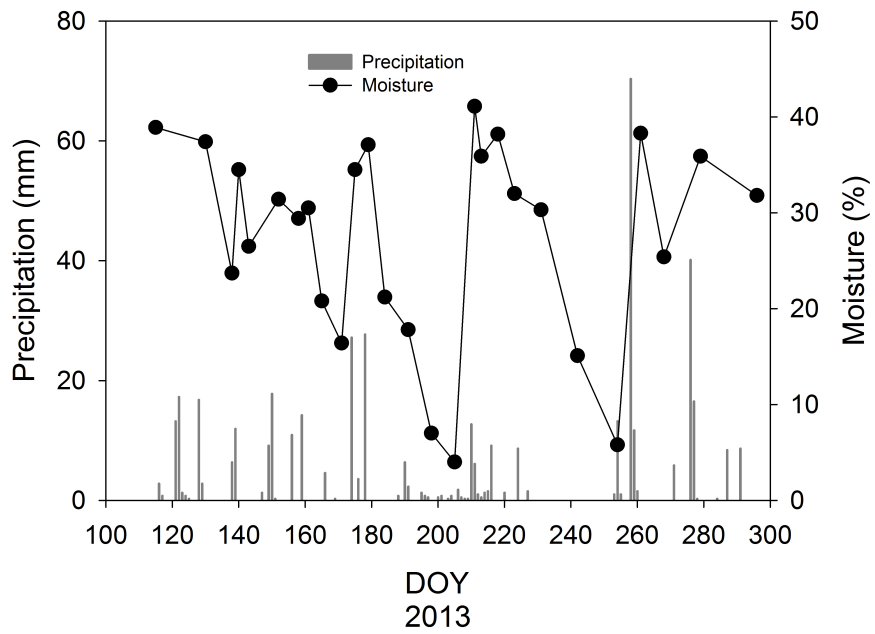


Figure 2.5. Precipitation (mm) and soil volumetric moisture (%) at gas sampling during 2013 and 2014. DOY = day of year.

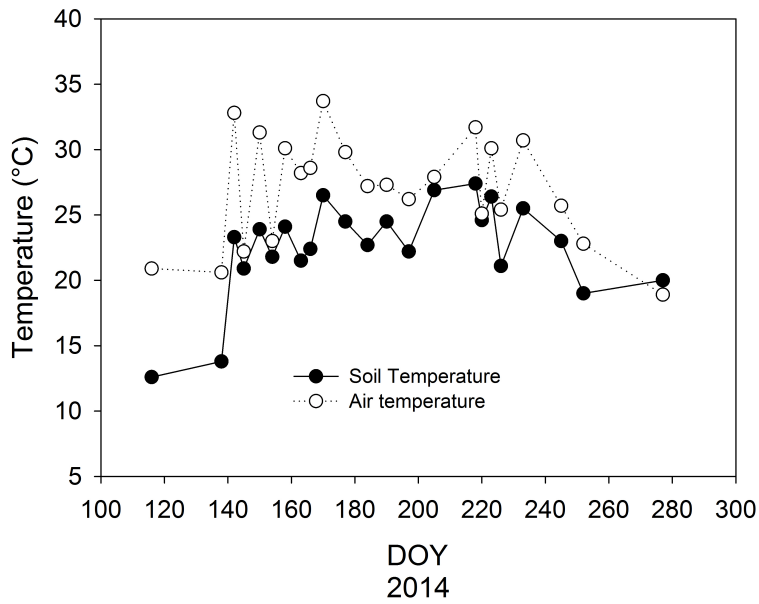
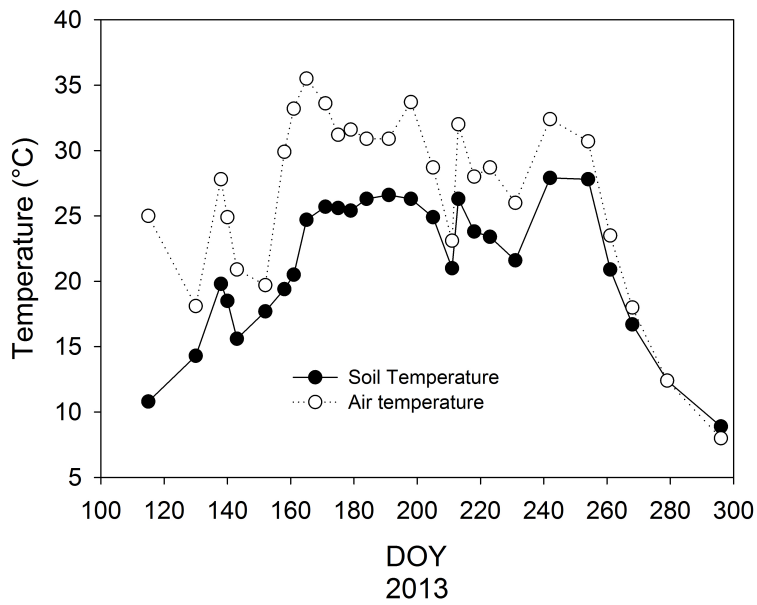


Figure 2.6. Soil (open circle) and air (closed circle) temperature at gas sampling during 2013 and 2014. DOY = day of year.

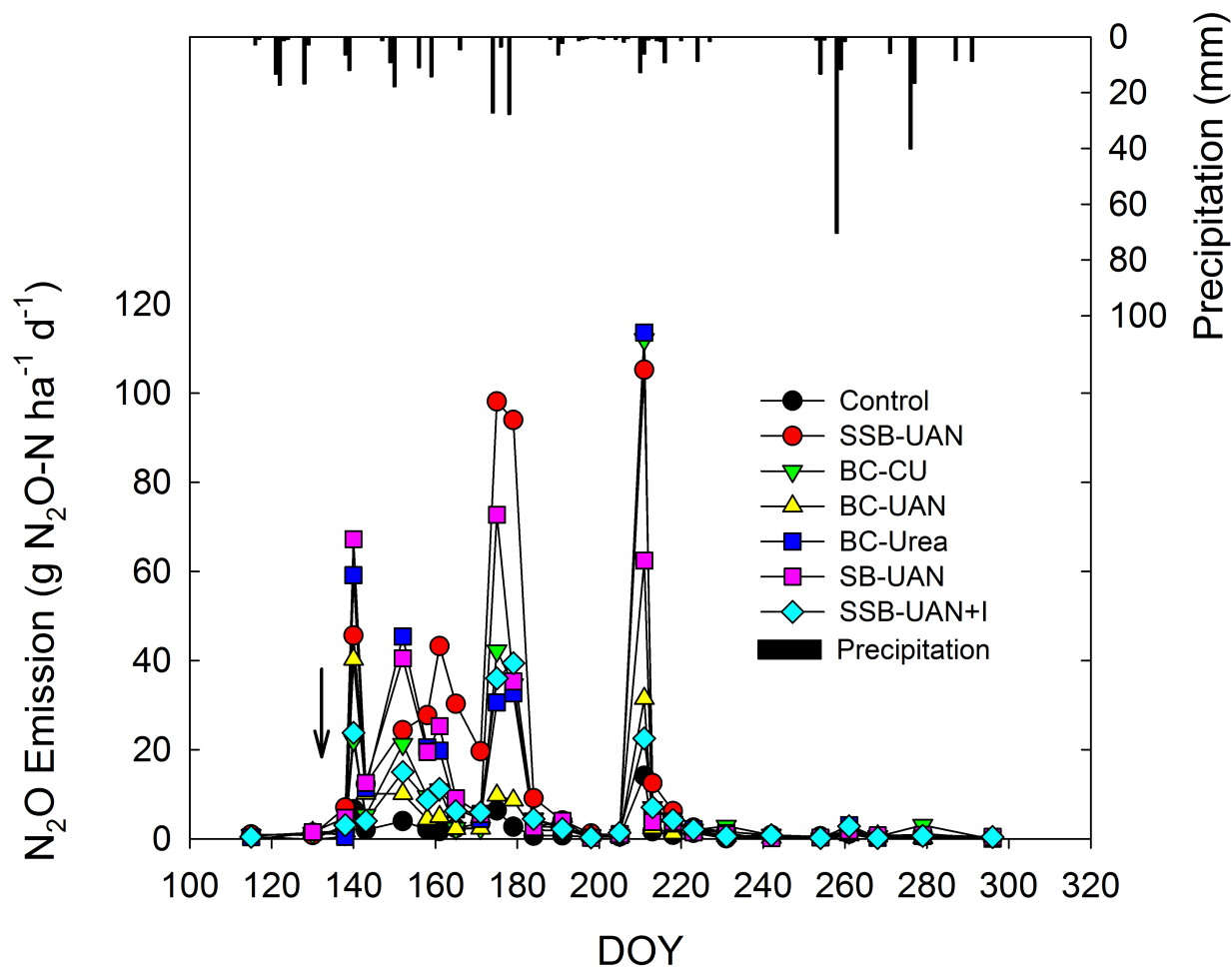


Figure 2.7. Daily mean N_2O emissions during 2013 under different treatments: control (no N), subsurface band UAN (SSB-UAN), broadcast coated urea (BC-CU), broadcast UAN (BC-UAN), broadcast urea (BC-Urea), surface band UAN (SB-UAN), and subsurface band UAN with NI (SSB-UAN+I). Arrow represents time of fertilizer application. Bars on top represent precipitation. DOY = day of year.

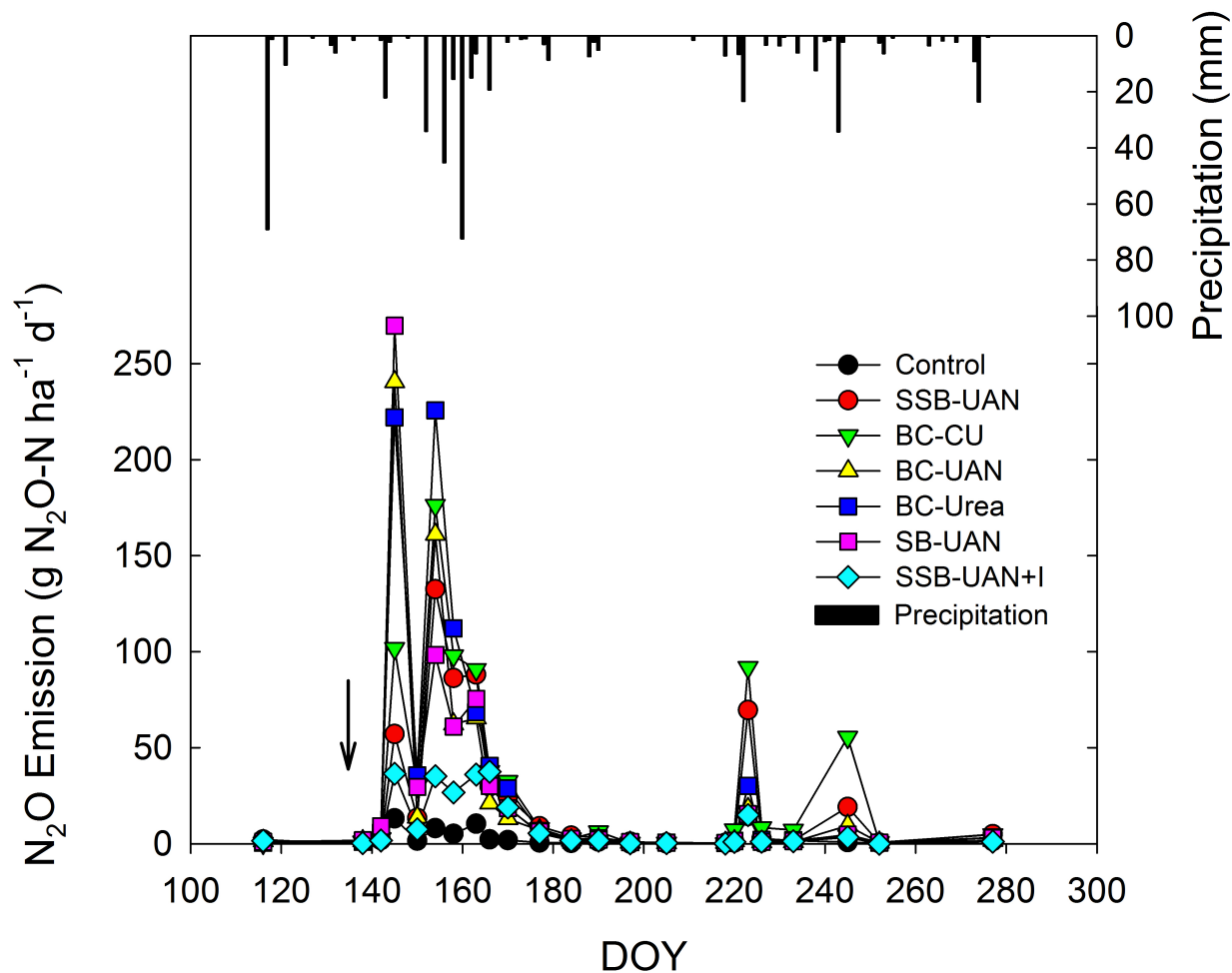


Figure 2.8. Daily mean N_2O emissions during 2014 under different treatments: control (no N), subsurface band UAN (SSB-UAN), broadcast coated urea (BC-CU), broadcast UAN (BC-UAN), broadcast urea (BC-Urea), surface band UAN (SB-UAN), and subsurface band UAN with NI (SSB-UAN+I). Arrow represents time of fertilizer application. Bars on top represent precipitation. DOY = day of year.

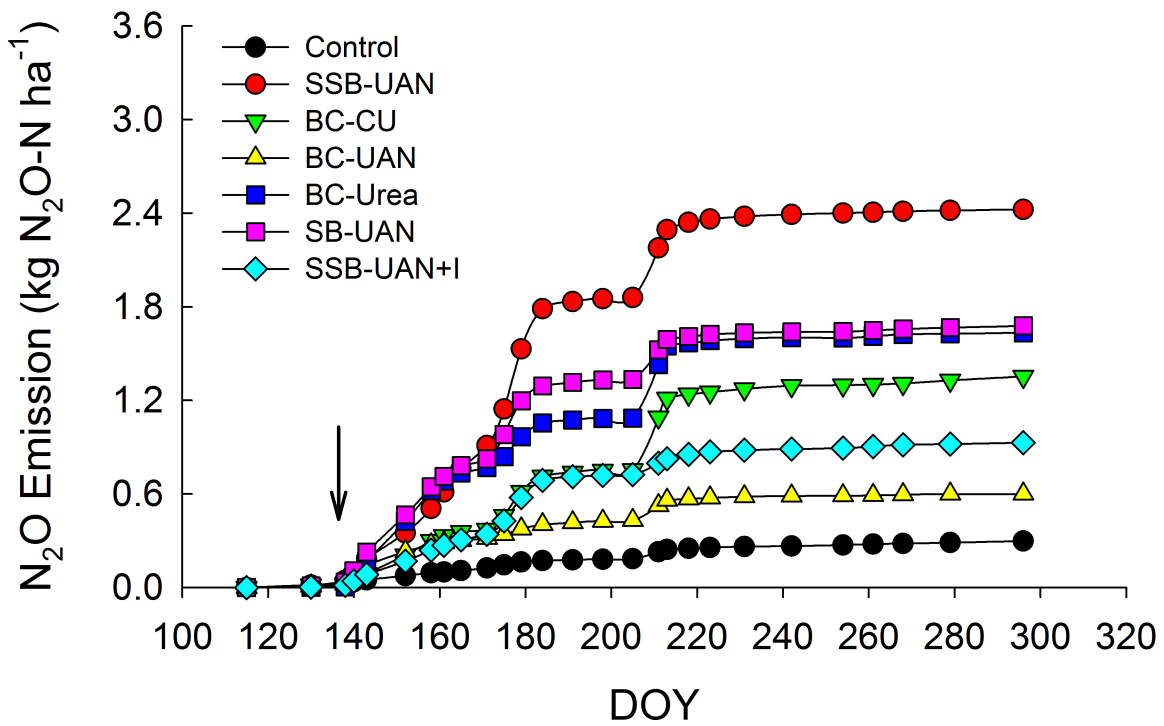


Figure 2.9. Mean cumulative N₂O emissions during 2013 under different treatments: control (no N), subsurface band UAN (SSB-UAN), broadcast coated urea (BC-CU), broadcast UAN (BC-UAN), broadcast urea (BC-Urea), surface band UAN (SB-UAN), and subsurface band UAN with NI (SSB-UAN+I). Arrow represents time of fertilizer application. DOY = day of year.

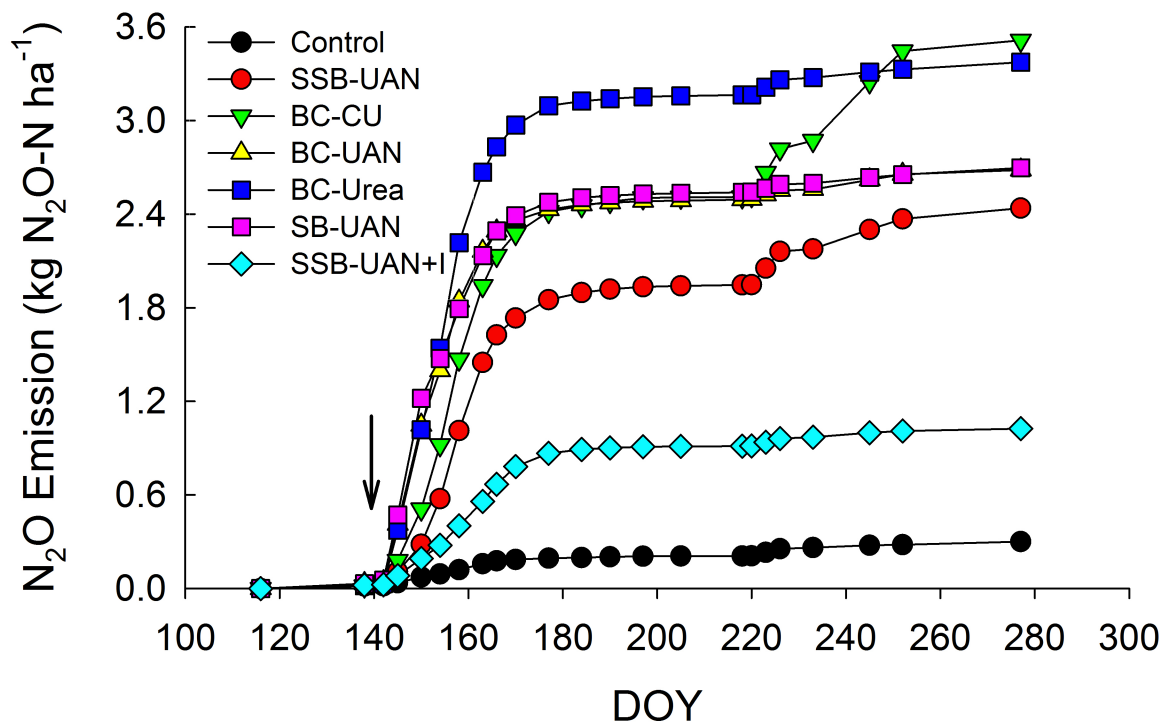


Figure 2.10. Mean cumulative N₂O emissions during 2014 under different treatments: control (no N), subsurface band UAN (SSB-UAN), broadcast coated urea (BC-CU), broadcast UAN (BC-UAN), broadcast urea (BC-Urea), surface band UAN (SB-UAN), and subsurface band UAN with NI (SSB-UAN+I). Arrow represents time of fertilizer application. DOY = day of year.

Table 2.1. Selected soil properties before experiment initiation in 2013.

| Depth | pH | SOC | SON | M3-P | M3-K | NO ₃ ⁻ -N | Sand | Silt | Clay |
|----------|-----|--------------------|-------|-------------------------|------|---------------------------------|------|------|------|
| | | g kg ⁻¹ | | μg g ⁻¹ soil | | | % | | |
| 0 to 5 | 7.4 | 0.166 | 0.016 | 44 | 465 | 0.3 | | | |
| 5 to 10 | 7.0 | 0.124 | 0.013 | 11 | 325 | 0.2 | | | |
| 10 to 20 | 6.9 | 0.109 | 0.011 | 11 | 235 | 0.1 | | | |
| 20 to 30 | 6.8 | 0.117 | 0.011 | 13 | 198 | 0.1 | | | |
| 0 to 20 | | | | | | | 20 | 58 | 22 |

SOC = soil organic carbon, SON = soil organic nitrogen.

§ M3-P = Mehlich-3 phosphorus. M3-K = Mehlich-3 potassium.

Table 2.2. Precipitation (mm) during 2013 and 2014 growing seasons and 30-year average for Manhattan, KS.

| Year | Precipitation | | | | | | | Total |
|------------|---------------|-----|------|------|------|-------|------|-------|
| | April | May | June | July | Aug. | Sept. | Oct. | |
| | mm | | | | | | | |
| 2013 | 88 | 99 | 88 | 37 | 24 | 105 | 110 | 550 |
| 2014 | 105 | 49 | 224 | 17 | 101 | 29 | 63 | 589 |
| 30-yr avg. | 81 | 129 | 145 | 112 | 105 | 87 | 68 | 727 |

Table 2.3. Cumulative N₂O emission during 2013 and 2014 under different treatments: subsurface band UAN (SSB-UAN), surface band UAN (SB-UAN), broadcast urea (BC-Urea), broadcast coated urea (BC-CU), subsurface band UAN with NI (SSB-UAN+I), broadcast UAN (BC-UAN), and control (no N) (significant treatment × year interaction).

| Treatment | Year | |
|-----------|--|---------------|
| | 2013 | 2014 |
| | ———— kg N ₂ O-N ha ⁻¹ ———— | |
| SSB-UAN | 2.4 (0.7) aA§ | 2.4 (0.5) abA |
| SB-UAN | 1.7(0.5) bA | 2.7 (0.5) aA |
| BC-Urea | 1.6 (0.9) bA | 3.4 (0.7) aB |
| BC-CU | 1.4 (0.7) bcA | 3.5 (0.7) aB |
| SSB-UAN+I | 0.9 (0.2) cdA | 1.0 (0.2) bcA |
| BC-UAN | 0.6 (0.4) deA | 2.7 (0.6) aB |
| Control | 0.3 (0.03) eA | 0.3 (0.05) cA |

§ Mean with standard error in parenthesis. Means in a column followed by the same lowercase letter and means in a row followed by the same uppercase letter are not significantly different at $\alpha=0.05$.

Table 2.4. Fertilizer-induced emission factor (FIEF) means for treatment and year main effects. Treatments are broadcast urea (BC-Urea), subsurface band UAN (SSB-UAN), broadcast coated urea (BC-CU), surface band UAN (SB-UAN), broadcast UAN (BC-UAN), and subsurface band UAN with NI (SSB-UAN+I) (no significant treatment × year interaction).

| Source | FIEF (%) |
|-----------|--------------|
| Treatment | |
| BC-Urea | 1.3 (0.3) a§ |
| SSB-UAN | 1.3 (0.2) a |
| BC-CU | 1.3 (0.3) a |
| SB-UAN | 1.1 (0.2) a |
| BC-UAN | 0.8 (0.3) ab |
| SSB-UAN+I | 0.4 (0.1) b |
| Year | |
| 2013 | 0.7 (0.1) a |
| 2014 | 1.4 (0.2) b |

§ Mean with standard error in parenthesis. Means in a column followed by the same lowercase letter are not significantly different at $\alpha=0.05$.

Table 2.5. Soil NO₃⁻ concentration in the 0-5 cm depth in 2013 2 June and 21 June sampling times (significant time × treatment interaction).

| Treatment | Sampling time | |
|-----------|---|---------|
| | 2 June | 21 June |
| | — μg NO ₃ ⁻ -N g ⁻¹ soil — | |
| BC-CU | 50 aA§ | 39 bcA |
| BC-UAN | 43 abA | 54 abcA |
| BC-Urea | 28 bcdA | 73 aB |
| Control | 10 eA | 8 dA |
| SB-UAN | 36 abcA | 58 abA |
| SSB-UAN | 22 cdA | 47 abcB |
| SSB-UAN+I | 19 dA | 33 cB |

§ Means in a column followed by the same lowercase letter and means in a row followed by the same uppercase letter are not significantly different at $\alpha=0.05$.

Table 2.6. Soil NO₃⁻ concentration in the 0-5 cm depth in 2013 2 June and 21 June sampling times (significant location × treatment interaction).

| Treatment | Location (cm) | | | |
|-----------|---|---------|--------|--------|
| | 0 | 10 | 20 | 30 |
| | ————— μg NO ₃ ⁻ -N g ⁻¹ soil ————— | | | |
| BC-CU | 60 bA§ | 53 abcA | 32 aA | 37 abA |
| BC-UAN | 56 bA | 57 abA | 43 aA | 38 abA |
| BC-Urea | 43 bA | 44 bcA | 45 aA | 49 aA |
| Control | 22 cA | 7 dB | 8 bB | 5 dB |
| SB-UAN | 46 bB | 101 aA | 40 aB | 23 bB |
| SSB-UAN | 236 aA | 40 bcB | 11 bC | 11 cC |
| SSB-UAN+I | 179 aA | 25 cB | 12 bBC | 8 cdC |

§ Means in a column followed by the same lowercase letter and means in a row followed by the same uppercase letter are not significantly different at $\alpha=0.05$.

Table 2.7. Soil NO₃⁻ concentration in the 5-10 cm depth in 2013 2 June and 21 June sampling times (significant sampling time × treatment interaction).

| Treatment | Sampling time | |
|-----------|---|---------|
| | 2 June | 21 June |
| | —— μg NO ₃ ⁻ -N g ⁻¹ soil —— | |
| BC-CU | 15 bA§ | 6 cB |
| BC-UAN | 31 aA | 12 abB |
| BC-Urea | 15 bA | 15 abA |
| Control | 7 cA | 2 dB |
| SB-UAN | 18 bA | 14 abA |
| SSB-UAN | 14 bA | 16 aA |
| SSB-UAN+I | 13 bA | 11 bA |

§ Means in a column followed by the same lowercase letter and means in a row followed by the same uppercase letter are not significantly different at $\alpha=0.05$.

Table 2.8. Soil NO₃⁻ concentration in the 5-10 cm depth in 2013 2 June and 21 June sampling times (significant location × treatment interaction).

| Treatment | Location (cm) | | | |
|-----------|---|--------|---------|--------|
| | 0 | 10 | 20 | 30 |
| | ————— μg NO ₃ ⁻ -N g ⁻¹ soil ————— | | | |
| BC-CU | 12 bA§ | 9 bA | 7 bcA | 10 abA |
| BC-UAN | 20 bA | 18 abA | 23 aA | 18 aA |
| BC-Urea | 14 bA | 14 abA | 12 abA | 21 aA |
| Control | 6 cA | 4 cAB | 3 dB | 4 cAB |
| SB-UAN | 20 bA | 32 aA | 13 abAB | 7 bB |
| SSB-UAN | 124 aA | 17 abB | 7 cC | 4 cD |
| SSB-UAN+I | 114 aA | 12 bB | 4 cdC | 3 cC |

§ Means in a column followed by the same lowercase letter and means in a row followed by the same uppercase letter are not significantly different at $\alpha=0.05$.

Table 2.9. Soil NO₃⁻ concentration in the 5-10 cm depth in 2013 2 June and 21 June sampling times (significant sampling time × location interaction).

| Location (cm) | Sampling time | |
|---------------|---|---------|
| | 2 June | 21 June |
| | μg NO ₃ ⁻ -N g ⁻¹ soil | |
| 0 | 26 aA§ | 23 aA |
| 10 | 15 bA | 11 bA |
| 20 | 11 bA | 6 cB |
| 30 | 12 bA | 5 cB |

§ Means in a column followed by the same lowercase letter and means in a row followed by the same uppercase letter are not significantly different at $\alpha=0.05$.

Table 2.10. Soil NO₃⁻ concentration in the 10-15 cm depth in 2013 2 June and 21 June sampling times (significant sampling time × location × treatment interaction).

| Treatment | 2 June | | | | 21 June | | | |
|-----------|---|--------|-------|--------|---|--------|---------|-------|
| | Location (cm) | | | | Location (cm) | | | |
| | 0 | 10 | 20 | 30 | 0 | 10 | 20 | 30 |
| | ————— μg NO ₃ ⁻ -N g ⁻¹ soil ————— | | | | ————— μg NO ₃ ⁻ -N g ⁻¹ soil ————— | | | |
| BC-CU | 9 cdA§ | 8 abA | 9 abA | 11 abA | 8 bA | 5 bA | 3 bcB | 9 aA |
| BC-UAN | 12 cB | 16 aAB | 13 aB | 28 aA | 15 bA | 15 aA | 13 aA | 5 abB |
| BC-Urea | 7 cdA | 7 abA | 6 abA | 10 abA | 8 bA | 11 abA | 7 abA | 7 abA |
| Control | 5 dA | 5 bA | 5 abA | 5 bA | 3 cA | 2 cAB | 1 cB | 1 cB |
| SB-UAN | 9 cdB | 17 aA | 7 abB | 6 bB | 13 bA | 13 aAB | 12.0 aA | 6 abB |
| SSB-UAN | 26 bA | 8 abB | 5 bB | 5 bB | 70 aA | 23 aB | 4 bC | 2 bcD |
| SSB-UAN+I | 72 aA | 7 abB | 4 bB | 4 bB | 60 aA | 14 aB | 2 cC | 1 cC |

§ Means in a column followed by the same lowercase letter within a given sampling time and means in a row followed by the same uppercase letter within a given sampling time are not significantly different at $\alpha=0.05$.

Table 2.11. Soil residual NO₃⁻ amounts after corn harvest in 2013 (no significant treatment × depth interaction).

| Source | Residual NO ₃ ⁻ |
|-----------|---|
| Treatment | kg NO ₃ ⁻ -N ha ⁻¹ |
| BC-CU | 3.9 (0.7) a§ |
| BC-UAN | 3.0 (0.7) b |
| SSB-UAN | 2.8 (0.7) bc |
| BC-Urea | 2.7 (0.7) bcd |
| SSB-UAN+I | 2.3 (0.6) bcd |
| SB-UAN | 2.2 (0.6) cd |
| Control | 2.1 (0.5) d |
| Depth | |
| 0 to 15 | 7.2 (0.3) a |
| 15 to 30 | 4.1 (0.3) b |
| 30 to 45 | 1.0 (0.2) c |
| 45 to 60 | 0.6 (0.1) d |
| 60 to 90 | 0.6 (0.0) d |

§ Mean with standard error in parenthesis. Means in a column followed by the same lowercase letter are not significantly different at $\alpha=0.05$.

Table 2.12. Soil NO₃⁻ concentration in the 0-5 cm depth in 2014 21 June and 8 August sampling times for band treatments (significant sampling time × location).

| Location (cm) | Sampling time | | Treatment | μg NO ₃ ⁻ -N g ⁻¹ soil |
|---------------|---|----------|-----------|---|
| | 21 June | 8 August | | |
| | μg NO ₃ ⁻ -N g ⁻¹ soil | | BC-UAN | 5 b§ |
| | | | SB-UAN | 7 ab |
| 0 | 39 aA§ | 11 aB | SSB-UAN | 11 a |
| 10 | 20 aA | 10 aA | SSB-UAN+I | 8 a |
| 20 | 5 bA | 4 bA | | |
| 30 | 2 cA | 3 bA | | |

§ Means in a column followed by the same lowercase letter and means in a row followed by the same uppercase letter are not significantly different at $\alpha=0.05$.

Table 2.13. Soil NO₃⁻ concentration in the 5-10 cm depth in 2014 21 June and 8 August sampling times for band treatments (significant sampling time × location).

| Location (cm) | Sampling time | | Treatment | μg NO ₃ ⁻ -N g ⁻¹ soil |
|---------------|---|----------|-----------|---|
| | 21 June | 8 August | | |
| | μg NO ₃ ⁻ -N g ⁻¹ soil | | BC-UAN | 2.0 b§ |
| | | | SB-UAN | 3.0 ab |
| 0 | 19 aA§ | 4.0 aB | SSB-UAN | 4.0 a |
| 10 | 10 aA | 4.0 aB | SSB-UAN+I | 3.0 a |
| 20 | 2.0 bA | 1.0 bA | | |
| 30 | 1.0 cA | 1.0 bA | | |

§ Means in a column followed by the same lowercase letter and means in a row followed by the same uppercase letter are not significantly different at $\alpha=0.05$.

Table 2.14. Soil NO₃⁻ concentration in the 10-15 cm depth in 2014 21 June and 8 August sampling times for band treatments (significant sampling time × location).

| Location (cm) | Sampling time | | Treatment | μg NO ₃ ⁻ -N g ⁻¹ soil |
|---------------|---------------|----------|-----------|---|
| | 21 June | 8 August | | |
| | | | BC-UAN | 1.0 b§ |
| | | | SB-UAN | 1.0 ab |
| 0 | 14 a§ | 1.0 a | SSB-UAN | 2.0 a |
| 10 | 9.0 a | 1.0 ab | SSB-UAN+I | 2.0 a |
| 20 | 3.0 b | 0 bc | | |
| 30 | 1.0 c | 0 c | | |

§ Means in a column followed by the same lowercase letter and means in a row followed by the same uppercase letter are not significantly different at $\alpha=0.05$.

Table 2.15. Soil NO₃⁻ concentration in the 5-10 cm depth in 2014 21 June and 8 August sampling times for broadcast treatments.

| Treatment | µg NO ₃ ⁻ -N g ⁻¹ soil |
|-----------|---|
| BC-CU | 9.0 a§ |
| BC-UAN | 3.0 b |
| BC-Urea | 5.0 ab |
| Control | 2.0 b |

§ Means in a column followed by the same lowercase letter are not significantly different at $\alpha=0.05$.

Table 2.16. Soil NO₃⁻ concentration in the 10-15 cm depth in 2014 21 June and 8 August sampling times for broadcast treatments.

| Source | µg NO ₃ ⁻ -N g ⁻¹ soil |
|---------------|---|
| Treatment | |
| BC-CU | 3.0 a§ |
| BC-UAN | 2.0 a |
| BC-Urea | 3.0 a |
| Control | 1.0 b |
| Sampling time | |
| 21 June | 3.0 a |
| 8 August | 1.0 b |

§ Means in a column followed by the same lowercase letter are not significantly different at $\alpha=0.05$.

Chapter 3 - N Fertilizer Source and Placement Impacts Grain Yield and N Use Efficiency in No-till Corn

Abstract

Nitrogen (N) is one of the most demanded nutrients by plants, and also one of the most limiting for crop growth and development. In the U.S., corn fields received 5 million tons of N fertilizer in the 2010 growing season, representing 44% of all N fertilizer used in the country. Nitrogen fertilizer source and placement choices are important tools when preparing an N fertilization plan as they impact both final grain yields, N loss potential and NUE. The objectives of this study were to evaluate how different N fertilizer source and placement combinations affect corn grain yield, yield-scaled N₂O emission (YSNE) and N fertilizer recovery efficiency (NFRE) in rainfed no-till continuous corn. The experiment was conducted at the Agronomy North Farm located at Kansas State University, Manhattan, KS. The soil was a moderately well-drained Kennebec silt loam. The treatments were broadcast urea (BC-Urea), broadcast urea ammonium nitrate (UAN) (BC-UAN), broadcast coated urea (BC-CU), surface-band UAN (SB-UAN), subsurface-band UAN (SSB-UAN), subsurface-band UAN + nitrification inhibitor (SSB-UAN+I) and a 0 N control. Treatments were arranged on a randomized complete block design with four replicates. In 2013, banded treatments had significantly higher grain yields (from 9.1 to 10.5 Mg ha⁻¹), whereas in 2014 fewer differences among N treatments were observed, ranging from 7.2 to 8.6 Mg ha⁻¹. Banded treatments had significantly lower grain yields in 2014 compared to 2013. Only BC-UAN and SSB-UAN+I had significantly lower YSNE, and 2013 had lower YSNE than 2014. In 2013, SSB-UAN had the greatest NFRE, whereas BC treatments had the lowest. In 2014, N treatments did not differ in

NFRE. SSB-UAN and SSB-UAN+I had significantly lower NFRE values in 2014 compared to 2013. Fertilizer source and placement have the potential to promote high yields and NFRE in corn, however, the response is dependent on rainfall pattern after fertilizer application.

Introduction

Nitrogen (N) fertilizer is one of the most limiting nutrients in crop production. It has been estimated that about 50% of the yields obtained in the past decades were in response to N fertilization (Cardwell, 1982). Fertilizer N is key to corn production in the U.S., where the crop received about 44% of all N applied nationally in 2010 (Economic Research Service, 2013). Different N fertilizer management options are suitable to specific soil, climate and crop scenarios. For example, banding N fertilizer in a high-residue no-till cropping system is more efficient from a crop yield perspective than broadcasting. Furthermore, using anhydrous ammonia (AA) or urea in a light-textured soil will decrease NO_3^- leaching potential when compared to NO_3^- -based fertilizers, which will impact crop yields and input use efficiencies. Moreover, many enhanced-efficiency fertilizers (EEFs) have become available for farmers in the past decade with the purpose of better matching fertilizer release pattern with plant demand. With that, crops may utilize the fertilizer more efficiently while the potential for N losses decrease. However, results in the literature are mixed in regard to EEF efficacy in promoting better yields and decreasing losses. Thus, there is a need for research to answer questions such as what EEF is more suitable for a location, when and how is the product applied, is there an economic return for the investment?

Nitrogen source and placement impacts on yield are variable in the literature. For example, Fernández et al. (2014) observed higher yields under polymer-coated urea (PCU)

compared to urea in two out of three growing seasons. Venterea et al. (2011) found PCU and urea to yield the same, but more than SU. Several authors did not observe grain yield increments from PCU and SU (Halvorson et al., 2010a; b; Sistani et al., 2011; Halvorson and Del Grosso, 2013; Dell et al., 2014) compared to urea. Additionally, a study comparing only PCU and urea also did not observe yield improvements (Drury et al., 2012). In contrast, Halvorson et al. (2011) and Halvorson and Del Grosso (2012) observed lower grain yields under urea+DCD+NBPT (SU) and PCU when compared to urea. On experiments evaluating urea-ammonium nitrate (UAN), no grain yield differences were observed when adding nitrification inhibitor (NI)+NBPT (Halvorson et al., 2010a; b; Sistani et al., 2011; Dell et al., 2014) and NI alone (Burzaco et al., 2013). Conversely, UAN resulted in higher grain yield than UAN with NI+NBPT in Colorado (Halvorson et al., 2011; Halvorson and Del Grosso, 2012).

Few studies have evaluated the impact of different N fertilizer placement on corn grain yields and N₂O losses where no confounding factor was present (e.g. N source, tillage system). Halvorson and Del Grosso (2012) observed no grain yield differences between BC and SB applications of urea, PCU and SU in corn. Similarly, Halvorson and Del Grosso (2013) found no difference between BC and SSB PCU. Mengel et al. (1982) found higher grain yields with UAN applied as SSB than BC in three site-years, but no difference was observed on 4 site-years in an Indiana corn crop. In agreement, Stecker et al. (1993) observed UAN to promote higher corn grain yields under SSB than SB and BC in 3 site-years, subsurface-band (SSB) to yield the same as broadcast (BC) but higher than surface-band (SB) in 1 site-year and no difference between the three placement options on the remaining 4 site-years.

Nitrogen fertilizer application has been well documented to increase N₂O emissions from soils. When striving for a sustainable cropping system, yields and environmental impacts

should be taken into account, in order to select the system that produces the most output at the least environmental cost. Yield-scaled N₂O emissions (YSNE) fits well in this role, since it is calculated as the cumulative N₂O losses divided by grain yield for a given system. Reported YSNE values from corn have ranged from 15 (Halvorson et al., 2011) to 1730 (Fernández et al., 2014) g of N₂O-N per Mg of grain. The benefits of EEF application compared to their conventional counterparts become more evident when looking at YSNE. Fernández et al. (2014) observed lower YSNE from PCU than urea in 1 out of 3 years in corn. Halvorson and Del Grosso (2013) and Venterea et al. (2011) found lower YSNE from SU compared to urea. Furthermore, Halvorson et al. (2011) and Halvorson and Del Grosso (2012) observed no difference between SU and PCU, but both were lower than urea. Halvorson et al. (2010a) found YSNE values in the order SU < PCU=urea under corn in Colorado. Accordingly, Maharjan et al. (2014) observed lower YSNE under SU than PCU. Sistani et al. (2011) found urea and SU to have the lowest YSNE, followed by PCU. In contrast, Drury et al. (2012) and Nash et al. (2012) did not observe differences between PCU and urea. For UAN, even more consistent results have been observed. Halvorson et al. (2011) found YSNE values for UAN with DCD+NBPT to not differ from UAN with Nfusion, but both were lower than UAN alone. In accordance, Halvorson et al. (2010a) and Halvorson and Del Grosso (2012) observed UAN + DCD+NBPT to have lower YSNE when compared to UAN. Furthermore, Burzaco et al. (2013) found UAN+NI to have lower YSNE than UAN. YSNE can be used to select management practices, including N fertilizer source and placement choice, to promote an efficient and sustainable cropping system.

The use of different N sources, especially EEFs, has been of research interest when striving for improved N use efficiency (NUE) and grain yields. For example, Halvorson and Bartolo (2014) observed 19% higher NUE when PCU was applied, compared to SU and urea in

continuous corn production. Furthermore, Burzaco et al. (2014) found increased NUE from UAN+NI compared to UAN alone, which was contrasting with the results from their meta-analysis showing no NUE difference from UAN with and without NI.

Variable responses regarding N source and placement can be found in the literature. In the case of EEFs, the variability in corn grain yield response has been attributed to different rainfall timing, amount and frequency, application method and soil properties (Nelson et al., 2008). EEFs have the potential to decrease losses as N₂O emissions, NH₃ volatilization and NO₃⁻ leaching. However, more studies are needed in order to better understand when and where these fertilizers would perform the best (Motavalli et al., 2008) and promote higher yields to cover the increased cost of these technologies.

The objectives of this study were to evaluate how different N fertilizer source and placement combinations affect corn grain yield, yield-scaled N₂O emission and N fertilizer recovery efficiency in rainfed no-till continuous corn. The hypothesis of this study were that i) CU would promote higher yield and NFRE and lower YSNE than urea, ii) UAN with NI would promote higher yield and NFRE and lower YSNE than UAN alone, iii) subsurface band would promote higher yield and NFRE and lower YSNE than surface band, and iv) surface band would promote higher yield and NFRE and lower YSNE than broadcast.

Materials and Methods

Site Description and Experimental Design

The site was located at the Kansas State University Agronomy North Farm, Manhattan, KS (39°11'30"N, 96°35'30"W). The soil was well-drained Kennebec silt loam (fine-silty, mixed, superactive, mesic Cumulic Hapludolls). Selected soil characteristics can be found in

Table 3.1. The region has a 30-year average temperature of 12.9 °C and precipitation of 833 mm yr⁻¹.

The experiment was conducted during the course of two growing seasons (2013 and 2014). Plots were the same for both years. Previously to the experiment initiation, the area had been planted to rainfed no-till continuous corn since 2010. Corn was planted on 16 May 2013 (DOY 136) and 15 May 2014 (DOY 136) at 76-cm rows. The average final population was 70,500 and 75,100 plants ha⁻¹ in 2013 and 2014, respectively. Plots were 7.6 m x 6 m, comprising 8 corn rows. Blocks were separated by 3-m alleys. Plots received 2-3 herbicide applications per growing season, and were hand weeded when necessary, to maintain plots weed free during the length of the experiment. The experimental design was a randomized complete-block, with four replicates.

N Fertilizer Source and Placement

Treatments consisted of specific combinations between N source and placement: broadcast urea (BC-Urea), broadcast urea-ammonium nitrate (UAN) (BC-UAN), broadcast coated urea (BC-CU), surface-band UAN (SB-UAN), subsurface-band UAN (SSB-UAN), subsurface-band UAN + NI (SSB-UAN+I) and a 0 N control. The coated urea used was ESN, and the NI used was Instinct. BC-Urea and BC-CU were applied by hand, whereas BC-UAN and SB-UAN were applied with a boom attach to a tractor. SSB-UAN and SSB-UAN+I were applied with a coulter attached to a tractor, to a depth of about 10 cm and 38 cm away from the row. SB-UAN boom nozzle spacing was 51 cm. SSB coulter spacing was 76 cm. Nitrogen fertilizer was applied at a rate of 168 kg N ha⁻¹, which was considered standard recommendation for the region, at DOY 136 and 137 in 2013 and 2014, respectively.

Soil Inorganic N Sampling and Analysis

Soil samples for NO_3^- -N determination in 2013 and 2014 were taken in the spring before corn planting, two times during the growing season, and after corn harvest for NO_3^- -N residual assessment. The preplant and in-season soil samples were taken with 2-cm diameter soil tubes, and post-harvest samples were taken with 4-cm diameter soil tubes.

In 2013, preplant sampling time occurred on 7 April (DOY 97), in-season sampling times occurred on 2 June (DOY 153) and 21 June (DOY 172), and postharvest sampling time occurred on 3 December (DOY 337). Before experiment initiation, sampling time 7 April was performed by taking 10 soil cores from each block, split in the depths 0-5, 5-10 and 10-15 cm, and pooled in a composite sample, as so each block would have 3 composite samples, one for each depth. Samples were taken on a 2-dimensional (2D) fashion (Fig. 2.3), with depth as the vertical vector (0-5, 5-10 and 10-15 cm segments) and location as the horizontal vector (0, 10, 20 and 30 cm). Samples were taken in this manner due to the presence of banded treatments, thus the horizontal variability was of interest. Location 0 was placed on top of the band for the banded treatments, and in the middle position between two corn rows for the BC treatments. One horizontal transect was taken per plot, where each location yielded one soil core that was further split in the three depths already mentioned. Thus, each plot would have a total of 16 samples (3 depths x 4 locations). On sampling time 3 December, samples were taken using a tractor and a Giddings deep soil sampler apparatus (Model GSRTS, Giddings Machine Co., Windsor, Colorado) (Fig. 2.4). Samples were taken to 90 cm depth, in the increments 0-15, 15-30, 30-45, 45-60 and 60-90 cm. Each plot was sampled three times for NO_3^- -N determination

and one time for bulk density determination. Each core x depth sample was bagged individually, for a total of 20 samples per plot.

In 2014, preplant sampling time occurred on 7 May (DOY 127), in-season sampling times occurred on 21 June (DOY 172) and 8 August (DOY 220), and postharvest sampling time occurred on 19 November (DOY 323). Sampling time 7 May was performed before corn planting and fertilizer application with banded treatments being sampled using the same 2D fashion as in-season sampling times of the previous year. However, in 2014 the banded treatments had a total of 3 transects sampled and pooled by depth x location (in 2013, only one transect was taken per plot). Furthermore, BC treatments did not have the location factor. Instead, 10 random sample cores were taken, split in the 0-5, 5-10 and 10-15 cm depth and pooled by depth. Sampling times 21 June and 8 August followed this same scheme (banded treatments sampled on 2D fashion, BC treatments sampled randomly with no location factor). Sampling time 19 November was only analyzed after the completion of this report, thus data concerning this event will not be shown here.

For both years and all sampling times, samples were brought to the lab and stored properly. If analysis could be performed within a week, samples were left in a cooler (4 °C). Otherwise, samples were stored in a freezer (-20 °C) until analysis. Sample inorganic N extraction was performed by weighing moist soil and adding 1 M KCl (1:4 ratio) to an erlernmeyer flask and shaking for 1h. After decanting, supernatant was poured on Whatman no. 42 paper filter and the collected portion was analyzed for NO_3^- -N using a continuous flow analyzer colorimetric analyzer (Lachat Instruments). Soil moisture was determined by weighing 10 g soil and drying at 105 °C until constant weight was obtained. Soil NO_3^- -N concentration

($\mu\text{g NO}_3^- \text{-N g}^{-1}$ soil) was calculated using the extract $\text{NO}_3^- \text{-N}$ concentration, soil moisture, KCl volume and moist soil mass used for extraction.

Corn Stover and Grain Biomass and N Uptake

Corn total biomass was determined by sampling plant stover and grain yield. Plant stover was determined by sampling 10 consecutive plants from a row adjacent to the harvested row. Samples were taken in the first week of September, when corn kernels were at $\frac{3}{4}$ milk line stage. Plants were cut at the soil level. Corn ears were discarded, and husks were left on the plant. All 10 plants were shredded in a chopper and a homogenous subsample was taken for moisture determination and further analysis. Corn grain yield was determined by hand-harvesting 4.6 m^2 (two rows, 3.05 m length) at physiological maturity. At this time, plant population was estimated by counting the number of plants from the harvested area. Ears were shelled and cobs were discarded.

Plant stover and corn grain samples were oven dried at $60 \text{ }^\circ\text{C}$ until constant weight was achieved, and results are expressed on an oven-dried basis for both variables. After drying, samples were ground in a Wiley mill and then in a ball mill until sample became a fine powder. Samples were weighed and analyzed for total N by dried combustion using a Thermo-Finnigan EA Flash 1112. Plant stover biomass was calculated using the average plant population, and grain yield biomass was calculated based on the harvested area.

Cumulative area-based N_2O flux ($\text{g N}_2\text{O-N ha}^{-1}$) was calculated using trapezoidal integration of flux and time. Yield-scaled N_2O emission ($\text{g N}_2\text{O-N Mg grain}^{-1}$) was calculated by dividing the treatment cumulative N_2O emission ($\text{g N}_2\text{O-N ha}^{-1}$) by its correspondent grain yield (Mg ha^{-1}).

NUE can be calculated and interpreted in different ways. In this study, NUE was assessed as N fertilizer recovery efficiency (NFRE). NFRE was calculated by subtracting total N uptake (stover and grain) (kg N ha^{-1}) of control plot from that of each N treatment, dividing it by the applied N rate (168 kg N ha^{-1}) and multiplying by 100.

N Balance

The total N uptake (stover and grain, kg N ha^{-1}) from the 0N control plot was used as an estimator of apparent N mineralization (ANM). For the N treatments, accounted N (A_N) was calculated by adding their respective values of cumulative N_2O losses ($\text{kg N}_2\text{O-N ha}^{-1}$), total plant N uptake (stover and grain, kg N ha^{-1}) and cumulative soil profile residual NO_3^- -N (kg N ha^{-1}). System plant available N (SPAN) was calculated as the summation of N fertilizer rate (168 kg N ha^{-1}) and ANM. Nitrogen balance (kg N ha^{-1}) was calculated as the difference between SPAN and A_N .

Data Analysis and Statistics

Grain yield, YSNE, NFRE, corn stover biomass, corn stover N uptake and corn grain N uptake and response variables were analyzed using proc glimmix in SAS 9.3 (SAS Institute, 2003) for both years, and N balance was analyzed for 2013 only. Residuals homogeneity and normality were assessed and accounted for when needed using variance-grouping strategies or log transformation. Treatment and year were considered as fixed effects, and block and its interactions were considered as random effects. When ANOVA showed a significant interaction between treatment and year, years were analyzed separately. When an effect was declared significant, means separation was conducted using Fisher's LSD at $\alpha=0.05$.

Results

Grain Yield

Treatment, year and treatment \times year interaction effects were significant for grain yield. Grain yield varied among treatments in a given year, and also from year to year for some of the treatments (Table 3.2). In 2013, SSB-UAN, SB-UAN and SSB-UAN+I were the highest yielding treatments (10.5, 9.8 and 9.1 Mg ha⁻¹, respectively), whereas control was the least yielding one (3.8 Mg ha⁻¹). In 2014, all N treatments yielded statistically the same (ranging from 7.2 to 8.6 Mg ha⁻¹), except for SSB-UAN+I (7.2 Mg ha⁻¹), which yield was significantly lower than BC-Urea (8.6 Mg ha⁻¹). When comparing a treatment across both years, SSB-UAN, SSB-UAN+I and SB-UAN yielded significantly less in 2014 compared to 2013 (30%, 21% and 19% less, respectively).

Treatment and year effects were significant for corn stover biomass (Table 3.3). The N treatments were all similar, varying from 10.6 (SB-UAN) to 10.1 (SSB-UAN+I) Mg of stover biomass ha⁻¹. Only the control was significantly lower (8.3 Mg ha⁻¹). Averaged over treatments, 2013 was significantly higher (11.2 Mg ha⁻¹) than 2014 (8.9 Mg ha⁻¹). The main difference among years was the rainfall pattern. In 2014, higher precipitation amounts were received in early spring, but a severe 57-day drought occurred between DOY 166 through 223 causing soil volumetric moisture to reach values as low as 1.9%.

Treatment was the only significant effect on corn stover N uptake (Table 3.4). SSB-UAN and SSB-UAN+I had the highest values (86 and 80 kg N ha⁻¹, respectively), and all other N treatments were not significantly different from one another. The lowest stover N uptake was observed under control (42 kg N ha⁻¹).

Treatment and treatment \times year effects were significant for corn grain N uptake (Table 3.5). In 2013, SSB-UAN had the highest values (150 kg N ha⁻¹), and control had the least (42 kg N ha⁻¹), and it followed a very similar pattern to grain yield treatment ranking (Table 3.2). Among N treatments, the BC treatments had the lowest corn grain N uptake, varying from 100 (BC-CU) to 82 (BC-UAN) kg N ha⁻¹. In 2014, there was no significant difference among N treatments, varying from 124 (BC-Urea) to 106 (SSB-UAN+I) kg N ha⁻¹. Nonetheless, control had the lowest value (53 kg N ha⁻¹). When comparing a treatment across years, BC-Urea and BC-UAN had higher corn grain N uptake in 2014 compared to 2013, whereas SSB-UAN had lower corn grain N uptake in 2014 compared to 2013.

Cumulative N₂O emissions

The effect of treatment, year and treatment \times year were significant. In 2013, all N treatments emitted significantly more N₂O than the control, except BC-UAN (Table 2.3, Fig. 2.9). Emissions were significantly higher under SSB-UAN (2.4 kg N₂O-N ha⁻¹). Emissions were similar between BC-CU and BC-Urea, whereas SSB-UAN+I emitted significantly less than SSB-UAN. Among the N treatments, BC-UAN emitted the least (0.6 kg N₂O-N ha⁻¹). In both years the unfertilized soil emitted 0.3 kg N₂O-N ha⁻¹.

In 2014, all N treatments emitted significantly more than the control, except for SSB-UAN+I (Table 2.3, Fig. 2.10). All N treatments emitted similarly (ranging from BC-CU=3.51 to SSB-UAN=2.44 kg N₂O-N ha⁻¹), except for SSB-UAN+I (1.03 kg N₂O-N ha⁻¹). Control emitted significantly lower than all other treatments (0.3 kg N₂O-N ha⁻¹). Overall, emissions in 2014 were higher than in 2013. The treatments that behaved differently from one year to the other

were BC-Urea (1.63 to 3.37), BC-CU (1.35 to 3.51) and BC-UAN (0.6 to 2.68 kg N₂O-N ha⁻¹ in 2013 and 2014, respectively).

Yield-Scaled N₂O emissions

The effects of treatment and year were significant for YSNE (Table 3.7). BC-Urea, BC-CU, SSB-UAN and SB-UAN had the highest YSNE values, ranging from 250 to 331 g N₂O-N Mg grain⁻¹. BC-UAN (149 g N₂O-N Mg grain⁻¹) and SSB-UAN+I (125 g N₂O-N Mg grain⁻¹) were the only N treatments that had significantly lower YSNE values, whereas the control had the lowest YSNE overall (38 g N₂O-N Mg grain⁻¹). YSNE should be interpreted in the context of both cumulative N₂O losses and grain yield for a given treatment, in order for one to fully assess the meaning of this parameter to sustainability of cropping systems. For BC-UAN, relative constant yields across both years (7.4 and 7.7 Mg ha⁻¹ in 2013 and 2014, respectively), coupled with significantly lower emissions in 2013 (0.6 kg N₂O-N ha⁻¹) and higher but on-average emissions in 2014 (2.68 kg N₂O-N ha⁻¹), were the causes for low YSNE. SSB-UAN+I had high yield in 2013 and on-average yield in 2014, whereas its emissions were consistently among the lowest, regardless of year, causing it to have a low YSNE value. On the other hand, BC-Urea, BC-CU, SSB-UAN and SB-UAN were the treatments with the highest YSNE. BC-Urea and BC-CU had high YSNE due to the fact that they yielded similarly across different years (Table 3.2), but had significantly higher cumulative N₂O loss in 2014 compared to 2013 (Table 3.6). YSNE values were equally high for SSB-UAN and SB-UAN, but those were caused by a different pattern. That was due to the fact that SSB-UAN and SB-UAN grain yields were statistically lower in 2014 compared to 2013 (Table 3.2), whereas their cumulative N₂O emission were consistent from year to year (Table 3.6), thus causing YSNE to increase.

Therefore, for the BC treatments, high YSNE values were observed due to differences in emissions in different years, whereas for the banded treatments the resulting high YSNE was given due to differences observed in grain yield in different years. The year of 2014 had significant higher YSNE (238 g N₂O-N Mg grain⁻¹) than 2013 (130 g N₂O-N Mg grain⁻¹) (Table 3.7). This was driven by both the banded treatments yielding less and BC treatments emitting more in 2014 compared to 2013, which was a result of rainfall pattern differences between both years, with 2014 being wetter in early season and drier during pollination compared to 2013.

N Fertilizer Recovery Efficiency

Treatment, year and treatment × year effects were significant for NFRE (Table 3.8). In 2013, the highest NFRE was observed under SSB-UAN (99%), whereas the lowest was observed under BC-UAN (36%). In 2014, there was no statistical difference in NFRE among N treatments, with values ranging from 53% (BC-Urea) to 45% (BC-UAN). Across both years, SSB-UAN and SSB-UAN+I were the treatments that had a NFRE value statistically lower in 2013 compared to 2014. The other treatments were not statistically different across both years.

N Balance

The ANM was estimated at 82 kg N ha⁻¹. This was the capacity of this soil to provide N from organic N mineralization during 2013 growing season, giving a SPAN value of 250 kg N ha⁻¹. The N balance values were the lowest under SSB-UAN (-15 kg N ha⁻¹), whereas BC-UAN had the highest (90 kg N ha⁻¹) (Table 3.9). Overall, banding fertilizer had a lower N balance than broadcasting. It means that, accounting for both N mineralized during the growing season

and N fertilizer inputs, N under banded treatments was conserved to a greater extent and better explained by plant N uptake, N₂O losses and soil residual NO₃⁻ than under broadcast treatments.

Discussion

Grain Yield

In 2013, the UAN banded treatments had the highest yields (Table 3.2). The positive effect of fertilizer banding on corn grain yields have been previously observed. Mengel et al. (1982) found higher yields when UAN was SSB compared to BC in 3 out of 7 site-years under no-till corn in Indiana. When pooling all 7 site-years together, Mengel et al. (1982) observed corn grain yields of 8.5, 7.4 and 7.7 Mg grain ha⁻¹ under SSB-UAN, BC-UAN and BC-Urea, respectively. The author suggested that SSB advantage over BC was due to decreased NH₃ volatilization and N immobilization, which are commonly observed when fertilizers are surface applied to no-till systems. In 2013, BC treatments had significantly lower NFRE compared to the SSB treatment (Table 3.8), suggesting increased volatilization and immobilization under the BC treatments. SSB-UAN+I (9.1 Mg ha⁻¹) yielded the same as its conventional counterpart SSB-UAN (10.5 Mg ha⁻¹). The same happened under BC-CU (8.2 Mg ha⁻¹) and BC-Urea (8 Mg ha⁻¹), with no yield advantage observed with the EEF option. Similar findings were observed by Dell et al. (2014), who suggested that the lack of significant differences was due to abnormally low rainfall during key crop stages. In 2014, fewer differences were observed among N treatments (Table 3.2), ranging from 8.6 (BC-Urea) to 7.2 (SSB-UAN+I) Mg ha⁻¹. Although 2014 received more precipitation amounts during the growing season when compared to 2013 (589 and 550 mm in 2014 and 2013, respectively), the rainfall timing played a role. In 2014, from DOY 166 to 223 there were no rainfall events greater than 10 mm. During this 57-day

period soil volumetric water decreased to about 2%. Since the corn crop was at pollination during this dry period, grain yields were reduced compared to 2013, when rainfall frequency was better synchronized with important crop growth stages. Nonetheless, the variable impact of fertilizer source in yield is commonly observed in the literature (Halvorson et al., 2010a, 2011; Sistani et al., 2011, 2014; Venterea et al., 2011; Drury et al., 2012; Halvorson and Del Grosso, 2012, 2013; Burzaco et al., 2013; Dell et al., 2014; Fernández et al., 2014; Halvorson and Bartolo, 2014; Maharjan et al., 2014). Normally, EEFs are more effective in reducing N losses than in promoting yield improvements, and it is generally assumed that this type of fertilizer do not cause crop yield loss (Hatfield and Parkin, 2014). Across both years, the surface-applied treatments had lower yields in 2014 compared to 2013 (Table 3.2), with reductions of 30%, 21% and 19% under SSB-UAN, SSB-UAN+I and SB-UAN in 2014 compared to 2013. This decrease in yield under banded treatments in a wetter year could be the result of higher amounts of fertilizer undergoing complete denitrification and being lost as N₂ when fertilizer was concentrated in the soil. Furthermore, enhanced NO₃⁻ leaching may have been promoted, where fertilizer is placed away from the rooting zone and becomes physically unavailable for plant uptake. These hypotheses are corroborated by the observed NFRE values (Table 3.8), which were significantly lower under SSB treatments in 2014 compared to 2013.

Corn stover biomass was similar across all N treatments (ranging from 10.6 to 10.1 Mg ha⁻¹) (Table 3.3), and only control was significantly lower (8.3 Mg ha⁻¹). Furthermore, 2013 had higher stover biomass (11.2 Mg ha⁻¹) than 2014 (8.9 Mg ha⁻¹). The main difference among years was the rainfall pattern. In 2014, higher precipitation amounts were received in early spring, but a severe 57-day period with limited rainfall occurred between DOY 166 through 223. The limited soil water caused stover biomass to decrease as water became limiting. Similar patterns

were observed by Halvorson et al. (2011), when no differences in corn stover biomass was observed, in any given year, under urea, CU, SU and UAN, with values ranging from 8.8 to 9.4 Mg ha⁻¹ in an irrigated strip-till cropping system in Colorado. Halvorson and Del Grosso (2012) observed the same pattern in one year, but in the other, PCU had significantly lower corn stover biomass (7.23 Mg ha⁻¹) than urea (8.62 Mg ha⁻¹).

Corn stover N uptake was highest under SSB-UAN (86 kg N ha⁻¹) and SSB-UAN+I (80 kg N ha⁻¹), and lowest for the control (42 kg N ha⁻¹) (Table 3.4). Halvorson and Del Grosso (2012) found urea (57 kg N ha⁻¹), SU (55 kg N ha⁻¹) and UAN (52 kg N ha⁻¹) to have similar values, and CU to be the lowest among N treatments (44 kg N ha⁻¹) in an irrigated corn system. Halvorson et al. (2011) also observed no differences in two years among urea, CU, SU and UAN, ranging from 50 to 63 kg N ha⁻¹. Halvorson and Del Grosso (2013) found no corn stover N uptake differences across no-till and strip-till corn systems in Colorado when urea (50 kg N ha⁻¹), CU (46 kg N ha⁻¹) and SU (48 kg N ha⁻¹) were applied, either BC (47.6 kg N ha⁻¹) or SB (48.9 kg N ha⁻¹). It is possible that stover N uptake was similar across different years, even under different precipitation regimes, due to translocation of N from stover to grain. This is explained by the significant differences observed on corn grain N uptake (Table 3.5).

In 2013, corn grain N uptake was highest under SSB-UAN (150 kg N ha⁻¹), and lowest under control (42 kg N ha⁻¹) (Table 3.5), and it followed a very similar pattern to grain yield treatment ranking (Table 3.2). In 2014, corn grain N uptake was similar across all N treatments (ranging from 124 to 106 kg N ha⁻¹), and control had the lowest value (53 kg N ha⁻¹). Halvorson and Del Grosso (2012) observed similar trends but at higher magnitudes (possibly due to the higher N rate applied than in our study) where urea, CU, SU and UAN corn grain N uptake were not significantly different, varying from 143 to 152 kg N ha⁻¹ over two years. Similarly,

Halvorson et al. (2011) observed no difference in corn grain N uptake in two growing seasons from urea, CU, SU and UAN, with values ranging from 139 to 157 kg N ha⁻¹. Venterea et al. (2011) did not find corn grain N uptake differences among urea, CU and SU, with values of ranging from 110 to 166 kg N ha⁻¹ for all treatments. Furthermore, Halvorson and Del Grosso (2013) did not observe corn grain N uptake differences among urea (137 kg N ha⁻¹), CU (136 kg N ha⁻¹) and SU (144 kg N ha⁻¹), either SB (137 kg N ha⁻¹) or BC (141 kg N ha⁻¹). While SSB-UAN corn grain N significantly decreased in 2014 compared to 2013 (150 vs. 108 kg N ha⁻¹), BC-Urea (94 x 124 kg N ha⁻¹, respectively) and BC-UAN (82 vs. 107 kg N ha⁻¹, respectively) corn grain N significantly increased in 2014 compared to 2013. SSB-UAN grain N uptake decreased in 2014 possibly due to the stress caused by the extended drought, which limited N diffusion from band toward the row. BC-Urea and BC-UAN grain N uptake increased in 2014 probably due to the more thorough incorporation of fertilizer by the rain movement into the soil early in the season, placing the fertilizer in closer contact to the roots.

Yield-Scaled N₂O Emissions

Previous research support our observation that PCU had the same YSNE as urea (Halvorson et al., 2010a; Drury et al., 2012; Nash et al., 2012). Halvorson et al. (2010a) found YSNE values for PCU and urea to not differ in one out two years, where PCU had a YSNE of 49.8 g N₂O-N Mg grain⁻¹ compared to 60.6 g N₂O-N Mg grain⁻¹ of urea. This was observed when either no grain yield difference is found between both sources and/or when PCU gives rise to higher emissions, especially toward the end of the growing season, compared to urea. Others have observed PCU to give lower YSNE than urea (Halvorson et al., 2011; Halvorson and Del Grosso, 2012; Fernández et al., 2014). Fernández et al. (2014) observed lower YSNE

for PCU (930 g N₂O-N Mg grain⁻¹) compared to urea (1560 g N₂O-N Mg grain⁻¹) in one out of three years, when rainfall amounts were exceedingly higher than normal. This response is found when lower cumulative N₂O emissions resulted from PCU due to better synchrony between N supply and plant demand, and/or increased grain yield under PCU. In this study, SSB-UAN (283 g N₂O-N Mg grain⁻¹) had higher YSNE compared to SSB-UAN+I (125 g N₂O-N Mg grain⁻¹), and this difference is attributed to lower cumulative emissions in different rainfall scenarios with the use of NI. This result is in agreement with Burzaco et al. (2013), who also found SSB-UAN (263 g N₂O-N Mg grain⁻¹) to have higher YSNE than SSB-UAN+I (203 g N₂O-N Mg grain⁻¹), where NI also decreased cumulative N₂O emissions compared to UAN alone.

N Fertilizer Recovery Efficiency

In 2013, SSB-UAN (99%) had the highest NFRE among all N treatments (Table 3.8). The NFRE magnitude of this treatment is exceedingly high and it may be possible that a source of error have influenced the result. Although the implement was calibrated prior to the treatment application, it is possible that a higher rate was applied, resulting in the abnormally high NFRE. Burzaco et al. (2014) observed NFRE under SSB-UAN+I about 10% higher than SSB-UAN when NI was used in their field study, but no difference in their meta-analysis (48% and 45% under UAN+I and UAN alone, respectively). The lowest NFRE was observed under BC-UAN (36%), along with one of the lowest N treatment grain yields and cumulative N₂O emissions (Tables 3.2 and 3.6). These results indicate other mechanisms competing with both plant uptake and N₂O losses, such as N immobilization by corn stover and/or NH₃ volatilization, commonly associated with BC-UAN applied to high-residue systems (Mengel et al., 1982). BC-Urea (50%) and BC-CU (48%) had similar NFRE values, whereas SSB-UAN+I (73%) had lower

values compared to SSB-UAN (99%). It is expected that EEFs such as NI and CU to better synchronize N supply to plant demand, thus increasing NFRE. From soil NO_3^- data, NI only decreased soil NO_3^- concentration compared to UAN alone only in one event (21 June, 5-10 cm depth, Table 2.7 on Chapter 2). BC-CU was able to delay NO_3^- formation more consistently compared to urea on 21 June at the depths 0-5 (Table 2.5 on Chapter 2) and 5-10 cm (Table 2.7 on Chapter 2). Similar findings were observed by Halvorson and Del Grosso (2013), when urea, PCU and SU, either broadcast or surface-banded, had similar total biomass N uptake values in one year of no-till continuous corn in Colorado. However, Venterea et al. (2011) observed PCU (about 40%) to have lower values than urea (about 50%) in one out of three years in a corn crop in Minnesota. They stated that controlled-release N fertilizers performance on NFRE is dependent on rainfall pattern, since the release of N from the fertilizer granule depends on water availability. In the present study, the lack of statistical differences among urea and CU could be due to asynchrony of N release from coating and plant demand (2013 growing season) or due to excessive rainfall in a short period of time stimulating high rates of N release from the EEF (2014 growing season). Dell et al. (2014), in a laboratory incubation experiment at 30% soil volumetric water, showed that CU delayed NO_3^- formation in soil compared to urea up to 9 days after fertilizer application. Thereafter, CU increased soil NO_3^- to same levels as urea at 21 days, and surpassed urea levels at 28 days. However, this type of response can be different on field situations where soil water and temperature conditions are highly variable. Halvorson and Bartolo (2014) observed higher NFRE under PCU (52%) than urea (42%), where the EEF seemed to have improved N synchrony with the plant demand in a furrow-irrigated continuous corn system at medium to medium-high N rates.

In 2014, there were no treatment effects on NFRE (Table 3.8). Since 2014 was a wetter year, less variability in soil NO_3^- was observed due to higher fertilizer incorporation through water moving into the soil. The more even conditions for fertilizer incorporation across different treatments caused NFRE to behave similarly across N treatments, ranging from 45% to 53%. When comparing a treatment across years, SSB-UAN and SSB-UAN+I had significantly lower NFRE in 2014 compared to 2013 (SSB-UAN: 99% vs 51% in 2013 and 2014. SSB-UAN+I: 73% vs 50% in 2013 and 2014). Since 2014 had more rainfall earlier in the season and flooded soil was observed right after intense precipitation events, increased NO_3^- leaching and complete denitrification could have played a role in increased N_2 losses from banded treatments. Ciarlo et al. (2007) showed that increasing water-filled pore space from 40 to 120% significantly increased the amount of N lost as N_2 compared to N_2O . In their experiment, right after incubation initiation, the WFPS values of 100 (saturation) and 120% (waterlogging) promoted N_2 emissions of about 110 and 235 $\text{g N}_2\text{-N kg}^{-1} \text{ soil h}^{-1}$, respectively, whereas N_2O emissions from the same treatments were around 14 $\text{g N}_2\text{O-N kg}^{-1} \text{ soil h}^{-1}$. This shows evidence that N_2 losses can be eight- to 16-fold greater than N_2O losses under saturated and waterlogged conditions, which were observed in the early 2014 growing season. This fact can help explain why SSB treatments had significantly lower NFRE values in 2014, as NO_3^- and continued saturation/waterlogging conditions were present in the band, promoting N_2 losses greater than those as N_2O . Furthermore, in 2014 there was a 57-day period of moisture stress that coincided with corn pollination. Decreased soil volumetric water coupled to SSB-applied fertilizer limited plant N uptake during a high-demanding stage. Sistani et al. (2014) observed lowest N uptake levels in a year when a drought period happened in June and July under SU, CU, urea and

ammonium nitrate, but UAN (ranging from 170 to 190 kg N ha⁻¹) and UAN+DCD+NBPT (ranging from 160 to 200 kg N ha⁻¹) had similar N uptakes regardless of rainfall pattern.

N Balance

The N balance in 2013 was greater for banded treatments compared to broadcast treatments (Table 3.9). SSB-UAN had a negative N balance value, which might be recurrent from erroneous N rate being applied to this treatment, as discussed previously on NFRE. Overall, banded treatments had less unaccounted N after deducting plant N uptake, N₂O losses and soil residual NO₃⁻ than under broadcast treatments. This could be the result of one or more unaccounted fates such as N immobilization in corn residue, NH₃ volatilization, NO₃⁻ leaching beyond 90 cm depth and N₂ losses. In the case of broadcast treatments, enhanced N immobilization and possibly NH₃ volatilization were the main drivers for the unaccounted N. We hypothesize that BC-Urea main loss mechanism was volatilization. Keller and Mengel (1986) observed that urea and UAN broadcast on no-till corn on a sandy loam soil lost as much as 30 and 9% of applied fertilizer as NH₃⁻ volatilization, with most of it being lost within 50 h after fertilizer application. However, those losses were of a lower magnitude under a silt loam soil, where broadcast urea and UAN lost about 11 and 5% of applied fertilizer as NH₃⁻ volatilization. In our study, after fertilizer application, there were two small rainfall events (6 and 12 mm) within 2 and 3 days, leaving a window of about 48 h during which the untreated urea was prone to NH₃ volatilization loss. Nonetheless, the use of CU did not provide any additional improvement on greater N synchrony over untreated urea. This result has been observed on the literature, most commonly under rainfed systems, where rainfall pattern is variable and erratic. In the case of BC-UAN, we hypothesize that N immobilization by the corn

residue was the major reason for the higher unaccounted N balance. Accordingly, Rice and Smith (1984) observed values ranging from 13 to 24% of broadcast applied $(\text{NH}_4)_2\text{SO}_4$ to become immobilized under no-till corn 35 d after application. This results are supported by the NFRE values observed in 2013, which followed the same treatment ranking as N balance, with the SSB UAN treatments having the highest and BC treatments having the lowest NFRE values.

Conclusions

Corn grain yields were higher when UAN was banded in 2013, when rainfall pattern conditions were more conducive to crop performance. However, N source and placement had little impact on yields under a drought stress situation at corn pollination in 2014. The use of EFF did not improve yields compared to their conventional form. Yield-scaled N_2O emissions were lowest when UAN was either BC or SSB with a NI. The use of NI with UAN promoted consistently lower N_2O losses and competitive grain yields. The use of CU was no efficient in reducing YSNE compared to urea. N fertilizer recovery efficiency was improved under banded UAN in 2013, a year with better precipitation distribution. However, NFRE was not impacted by N source or placement in 2014, when rainfall was abundant in early spring but limiting at pollination. Based on our results, recommendations of EFF use are limited due to lack of improved performance on grain yields in comparison to the conventional sources. Further research is needed under different soils, management practices and climate, especially in regard to precipitation volume and frequency, in order to broaden our understanding of EFF impact on yield.

N source and placement management have the potential to promote higher yields and improved NFRE, but the magnitude of the response is dependent on rainfall pattern in no-till continuous corn.

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Table 3.1. Selected soil properties before experiment initiation in 2013.

| Depth | pH | SOC | SON | M3-P | M3-K | NO ₃ ⁻ -N | Sand | Silt | Clay |
|----------|-----|------------------------|-------|-----------------------------|------|---------------------------------|-------|------|------|
| | | — g kg ⁻¹ — | | — μg g ⁻¹ soil — | | | — % — | | |
| 0 to 5 | 7.4 | 0.166 | 0.016 | 44 | 465 | 0.3 | | | |
| 5 to 10 | 7.0 | 0.124 | 0.013 | 11 | 325 | 0.2 | | | |
| 10 to 20 | 6.9 | 0.109 | 0.011 | 11 | 235 | 0.1 | | | |
| 20 to 30 | 6.8 | 0.117 | 0.011 | 13 | 198 | 0.1 | | | |
| 0 to 20 | | | | | | | 20 | 58 | 22 |

SOC = soil organic carbon, SON = soil organic nitrogen.

§ M3-P = Mehlich-3 phosphorus. M3-K = Mehlich-3 potassium.

Table 3.2. Grain yield in 2013 and 2014 growing seasons (significant treatment × year interaction).

| Treatment | Year | |
|-----------|---------------------------------|---------------|
| | 2013 | 2014 |
| | ————— Mg ha ⁻¹ ————— | |
| SSB-UAN | 10.5 (0.2) aA§ | 7.4 (0.2) abB |
| SB-UAN | 9.8 (0.2) aA | 7.9 (0.5) abB |
| SSB-UAN+I | 9.1 (0.3) abA | 7.2 (0.7) bB |
| BC-CU | 8.2 (0.6) bcA | 7.9 (0.6) abA |
| BC-Urea | 8.0 (0.5) bcA | 8.6 (0.7) aA |
| BC-UAN | 7.4 (0.3) cA | 7.7 (0.5) abA |
| Control | 3.8 (0.6) dA | 4.4 (0.3) cA |

§ Mean with standard error in parenthesis. Means in a column followed by the same lowercase letter and means in a row followed by the same uppercase letter are not significantly different at $\alpha=0.05$.

Table 3.3. Corn stover biomass for different treatments and years (no treatment × year significant interaction).

| Source | Stover biomass |
|-----------|-------------------------|
| Treatment | — Mg ha ⁻¹ — |
| SB-UAN | 10.6 (0.8) a§ |
| SSB-UAN | 10.5 (0.8) a |
| BC-UAN | 10.4 (0.6) a |
| BC-Urea | 10.2 (0.7) a |
| BC-CU | 10.1 (0.3) a |
| SSB-UAN+I | 10.1 (0.6) a |
| Control | 8.3 (0.5) b |
| Year | |
| 2013 | 11.2 (0.3) a |
| 2014 | 8.9 (0.2) b |

§ Mean with standard error in parenthesis. Means in a column followed by the same lowercase letter are not significantly different at $\alpha=0.05$.

Table 3.4. Corn stover N uptake for different treatments (no significant treatment × year interaction).

| Treatment | Stover N |
|-----------|-----------------------|
| | kg N ha ⁻¹ |
| SSB-UAN | 86 (7) a§ |
| SSB-UAN+I | 80 (7) a |
| BC-CU | 66 (4) b |
| SB-UAN | 66 (4) b |
| BC-Urea | 66 (5) b |
| BC-UAN | 61 (3) b |
| Control | 42 (2) c |

§ Mean with standard error in parenthesis. Means in a column followed by the same lowercase letter are not significantly different at $\alpha=0.05$.

Table 3.5. Corn grain N uptake for different treatments in 2013 and 2014 (significant treatment × year interaction).

| Treatment | 2013 | 2014 |
|-----------|-----------------------|-------------|
| | kg N ha ⁻¹ | |
| SSB-UAN | 150 (5) aA§ | 108 (7) aB |
| SB-UAN | 126 (4) bA | 109 (12) aA |
| SSB-UAN+I | 120 (7) bcA | 106 (7) aA |
| BC-CU | 100 (10) cdA | 112 (8) aA |
| BC-Urea | 94 (7) dA | 124 (14) aB |
| BC-UAN | 82 (5) dA | 107 (3) aB |
| Control | 42 (7) eA | 53 (5) bA |

§ Mean with standard error in parenthesis. Means in a column followed by the same lowercase letter and means in a row followed by the same uppercase letter are not significantly different at $\alpha=0.05$.

Table 3.6. Cumulative N₂O emission during 2013 and 2014 under different treatments: subsurface band UAN (SSB-UAN), surface band UAN (SB-UAN), broadcast urea (BC-Urea), broadcast coated urea (BC-CU), subsurface band UAN with NI (SSB-UAN+I), broadcast UAN (BC-UAN), and control (no N) (significant treatment × year interaction).

| Treatment | Year | |
|-----------|--|----------------|
| | 2013 | 2014 |
| | ———— kg N ₂ O-N ha ⁻¹ ———— | |
| SSB-UAN | 2.42 (0.7) aA§ | 2.44 (0.5) abA |
| SB-UAN | 1.68 (0.5) bA | 2.70 (0.5) aA |
| BC-Urea | 1.63 (0.9) bA | 3.37 (0.7) aB |
| BC-CU | 1.35 (0.7) bcA | 3.51 (0.7) aB |
| SSB-UAN+I | 0.93 (0.2) cdA | 1.03 (0.2) bcA |
| BC-UAN | 0.60 (0.4) deA | 2.68 (0.6) aB |
| Control | 0.30 (0.03) eA | 0.30 (0.05) cA |

§ Mean with standard error in parenthesis. Means in a column followed by the same lowercase letter and means in a row followed by the same uppercase letter are not significantly different at $\alpha=0.05$.

Table 3.7. Yield-scaled N₂O emissions in 2013 and 2014 (no significant treatment × year interaction).

| Source | YSNE |
|-----------|---|
| | g N ₂ O-N Mg grain ⁻¹ |
| Treatment | |
| BC-Urea | 331 (110) a§ |
| BC-CU | 313 (101) a |
| SSB-UAN | 283 (41) a |
| SB-UAN | 250 (48) ab |
| BC-UAN | 149 (57) bc |
| SSB-UAN+I | 125 (24) c |
| Control | 38 (9) d |
| Year | |
| 2013 | 130 (26) a |
| 2014 | 238 (48) b |

§ Mean with standard error in parenthesis. Means in a column followed by the same lowercase letter within a given source are not significantly different at $\alpha=0.05$.

Table 3.8. N fertilizer recovery efficiency in 2013 and 2014 (significant treatment × year interaction).

| Treatment | Year | |
|-----------|---------------|-------------|
| | 2013 | 2014 |
| | % | |
| SSB-UAN | 99 (6.1) aA§ | 51 (8.7) aB |
| SSB-UAN+I | 73 (13.7) bA | 50 (1.2) aB |
| SB-UAN | 60 (13.3) bcA | 48 (6.8) aA |
| BC-Urea | 50 (6.4) cdA | 53 (7.4) aA |
| BC-CU | 48 (3.7) cdA | 51 (7.1) aA |
| BC-UAN | 36 (7.3) dA | 45 (6.2) aA |

§ Mean with standard error in parenthesis. Means in a column followed by the same lowercase letter and means in a row followed by the same uppercase letter are not significantly different at $\alpha=0.05$.

Table 3.9. N balance under different N treatments in 2013.

| Treatment | N balance (kg N ha ⁻¹) |
|-----------|---------------------------------------|
| SSB-UAN | -15 (8) a§ |
| SSB-UAN+I | 33 (22) b |
| SB-UAN | 37 (12) bc |
| BC-CU | 70 (8) bc |
| BC-Urea | 72 (10) c |
| BC-UAN | 90 (16) d |

§ Mean with standard error in parenthesis. Means in a column followed by the same lowercase letter are not significantly different at $\alpha=0.05$.

Chapter 4 - Summary

Nitrogen (N) is one of the most required nutrients by plants, and also one of the most limiting for crop growth and development in both natural and managed systems. However, agricultural lands receiving N inputs are considered the primary source of N₂O, a potent greenhouse gas. If well planned and managed, N fertilization can promote high yields in corn, and at the same time, reduce the potential for N losses from the soil system.

N fertilizer management has shown variable effects on both N₂O losses and corn grain yield. This study assessed the impact of N source and placement on N₂O emissions, fertilizer-induced emission factor (FIEF), corn grain yield, yield-scaled N₂O emissions (YSNE) and N fertilizer recovery efficiency (NFRE).

The placement of urea-ammonium nitrate (UAN) in a subsurface band promoted the highest N₂O losses in 2013, a year where rainfall pattern was more evenly distributed throughout the growing season. The use of a nitrification inhibitor (NI) with UAN subsurface applied reduced N₂O losses by 62% compared to UAN alone in 2013. Broadcasting fertilizer in 2013 had low N₂O losses, but this increased for the BC treatments in 2014, when high amounts of rainfall happened early in the spring, right after fertilizer application. Subsurface-applying UAN with NI was the only strategy that reduced FIEF compared to other N source and placement combinations. NI was efficient in reducing N₂O losses both in 2013 and 2014, where different rainfall patterns were observed.

Grain yields were maximized with band-applied UAN, either on surface or subsurface, in 2013. The more evenly distributed rainfall pattern provided enough water and N movement from the band toward the plant roots. In 2014, there was no evidence that N placement or source impacted grain yields, when rainfall was abundant right after N application, incorporating

broadcasted treatments and decreasing the physical difference of placement. However, in 2014 a 57-day period of moisture stress was observed along with high temperatures, which comprised the corn pollination stage, causing grain yields to be lower than in 2013 for the banded treatments due to lower N diffusion from the band out.

The lowest YSNE occurred only when UAN was broadcasted or subsurface-band applied with NI. In the case of broadcasting UAN, the result was given by reduced emissions in 2013. However, due to decreased grain yield and N uptake, it is possible that the UAN applied on top of corn residue suffered N immobilization and/or ammonia volatilization, mechanisms that competed with both N₂O and plant uptake. In the case of subsurface-banded UAN with NI, the low YSNE was due to the consistent decreased N₂O losses provided by the NI, while yields responded positively to well-distributed rainfall events and negatively to extended drought conditions.

For NFRE banded UAN treatments were higher in 2013, which was promoted by the precipitation events being more adequately distributed. In 2014, all N source and placement combinations had similar NFRE, caused by the intense rainfall in early season stimulating N incorporation in the soil to the point where all treatments responded equally. Following the same pattern as for grain yield, NFRE values decreased in the wet-spring year under subsurface band UAN treatments. This effect was also driven by rainfall, when limited water availability decreased the N diffusion from the band, impacting N uptake by the roots.

The option of banding UAN without any additive promoted higher N₂O losses on a year when precipitation was well distributed, but also enhanced grain yield and NFRE. On the other hand, under the same precipitation conditions, broadcasting N fertilizer promoted lower N₂O losses, grain yield and NFRE, but those were all improved in a wet year. Therefore, the

subsurface band placement would be the best option under a normal year, whereas broadcasting fertilizer would be the best option under a wetter year. Further, the use of NI with subsurface band UAN turns this the most sustainable option, since the NI decreased N_2O losses compared to UAN alone in both years at the same time that the subsurface band placement promoted higher yields and NFRE in one year, and on-average results in the other.

In no-till systems, broadcasting fertilizer on top of residue should be avoided due to increased potential for NH_3 volatilization and N immobilization, processes that deviate N from plant uptake. In this case, subsurface banding fertilizer would avoid this problem, promoting higher N uptake and yield potential if water does not become limiting. However, SSB placement may significantly increase other losses, such as denitrification (N_2O and N_2). Nonetheless, the use of NI with banded fertilizer has shown potential in mitigating N_2O losses. Therefore, according to our results, subsurface banding UAN with NI would be the best management practice to promote yields and NFRE and to reduce N_2O losses and FIEF.

Further research should evaluate N source and placement combinations under different environments in order to better understand how they impact crop performance and the negative environmental aspects of N fertilization. It is important to test those treatments under different precipitation scenarios and look for trends that indicate the best N management option at the local level.

Appendix A - Tables with Interactions and Main Effects

Table A.1. Fertilizer-induced emission factor (FIEF) means for treatment and year main effects. Treatments are broadcast urea (BC-Urea), subsurface band UAN (SSB-UAN), broadcast coated urea (BC-CU), surface band UAN (SB-UAN), broadcast UAN (BC-UAN), and subsurface band UAN with NI (SSB-UAN+I) (no significant treatment × year interaction).

| Treatment | Year | | Mean |
|-----------|---------------|--------------|---------------|
| | 2013 | 2014 | |
| | ————— % ————— | | |
| SSB-UAN | 1.27 (0.15)§ | 1.27 (0.43) | 1.27 (0.2) a |
| SB-UAN | 0.82 (0.12) | 1.43 (0.29) | 1.12 (0.2) a |
| BC-Urea | 0.80 (0.15) | 1.83 (0.53) | 1.31 (0.3) a |
| BC-CU | 0.63 (0.15) | 1.92 (0.38) | 1.27 (0.3) a |
| SSB-UAN+I | 0.38 (0.10) | 0.43 (0.14) | 0.40 (0.1) b |
| BC-UAN | 0.18 (0.03) | 1.42 (0.21) | 0.80 (0.3) ab |
| Mean | 0.68 (0.1) a | 1.38 (0.2) b | |

§ Mean with standard error in parenthesis. Means followed by the same lowercase letter are not significantly different at $\alpha=0.05$.

Table A.2. Soil NO₃⁻ concentration in the 0-5 cm depth in 2013 2 June and 21 June sampling times.

| Treatment | 2 June | | | | | 21 June | | | | |
|-----------|---|-----|----|----|--------|---|----|----|----|--------|
| | Location (cm) | | | | Mean | Location (cm) | | | | Mean |
| | 0 | 10 | 20 | 30 | | 0 | 10 | 20 | 30 | |
| | ————— μg NO ₃ ⁻ -N g ⁻¹ soil ————— | | | | | ————— μg NO ₃ ⁻ -N g ⁻¹ soil ————— | | | | |
| BC-CU | 60§ | 46 | 47 | 47 | 50 a | 60 | 62 | 21 | 29 | 39 bc |
| BC-UAN | 57 | 50 | 30 | 39 | 43 ab | 55 | 65 | 62 | 38 | 54 abc |
| BC-Urea | 24 | 27 | 32 | 30 | 28 bcd | 77 | 71 | 65 | 78 | 73 a |
| Control | 19 | 8 | 9 | 6 | 10 e | 25 | 7 | 6 | 4 | 8 d |
| SB-UAN | 30 | 132 | 26 | 17 | 36 abc | 71 | 78 | 61 | 33 | 58 ab |
| SSB-UAN | 153 | 24 | 8 | 9 | 22 cd | 364 | 66 | 16 | 13 | 47 abc |
| SSB-UAN+I | 169 | 16 | 8 | 7 | 19 d | 190 | 40 | 18 | 9 | 33 c |
| Mean | 53 | 30 | 18 | 17 | | 85 | 46 | 26 | 20 | |

§ Means followed by the same lowercase letter are not significantly different at $\alpha=0.05$.

Table A.3. Soil NO₃⁻ concentration in the 0-5 cm depth in 2013 2 June and 21 June sampling times.

| Treatment | 2 June | | | | | 21 June | | | | |
|-----------|---|------|------|------|------|---|------|-----|-----|-------|
| | Location (cm) | | | | Mean | Location (cm) | | | | Mean |
| | 0 | 10 | 20 | 30 | | 0 | 10 | 20 | 30 | |
| | μg NO ₃ ⁻ -N g ⁻¹ soil | | | | | μg NO ₃ ⁻ -N g ⁻¹ soil | | | | |
| BC-CU | 16§ | 12 | 15 | 17 | 15 b | 9 | 7 | 4 | 5 | 6 c |
| BC-UAN | 25 | 24 | 32 | 48 | 31 a | 16 | 13 | 17 | 6 | 12 ab |
| BC-Urea | 11 | 14 | 13 | 24 | 15 b | 17 | 15 | 11 | 18 | 15 ab |
| Control | 7 | 7 | 7 | 9 | 7 c | 5 | 2 | 2 | 2 | 2 d |
| SB-UAN | 20 | 53 | 10 | 9 | 18 b | 19 | 19 | 18 | 5 | 14 ab |
| SSB-UAN | 103 | 10 | 9 | 4 | 14 b | 148 | 31 | 5 | 3 | 16 a |
| SSB-UAN+I | 118 | 11 | 6 | 4 | 13 b | 111 | 14 | 4 | 3 | 11 b |
| Mean | 26 a | 15 b | 11 b | 12 b | | 23 a | 11 b | 6 c | 5 c | |

§ Means followed by the same lowercase letter are not significantly different at $\alpha=0.05$.

Table A.4. Soil residual NO₃⁻ amounts after corn harvest in 2013 (no significant treatment × depth interaction).

| Treatment | Depth (cm) | | | | | Mean |
|-----------|-----------------------|-------------|-----------|-------------|-------------|---------------|
| | 0 to 15 | 15 to 30 | 30 to 45 | 45 to 60 | 60 to 90 | |
| | kg N ha ⁻¹ | | | | | |
| BC-CU | 8.7 (0.4)§ | 6.1 (0.9) | 2.4 (0.6) | 1.4 (0.5) | 0.8 (0.0) | 3.9 (0.7) a |
| BC-UAN | 7.8 (0.7) | 4.1 (1.0) | 1.4 (0.8) | 0.8 (0.5) | 0.7 (0.2) | 3.0 (0.7) b |
| BC-Urea | 7.5 (1.0) | 4.0 (1.1) | 0.8 (0.2) | 0.4 (0.1) | 0.6 (0.1) | 2.7 (0.7) bcd |
| Control | 5.9 (0.6) | 3.0 (0.5) | 0.6 (0.2) | 0.3 (0.2) | 0.5 (0.1) | 2.1 (0.5) d |
| SB-UAN | 6.8 (0.9) | 3.2 (0.6) | 0.4 (0.2) | 0.2 (0.1) | 0.4 (0.0) | 2.2 (0.6) cd |
| SSB-UAN | 7.5 (1.0) | 4.4 (1.0) | 1.0 (0.2) | 0.5 (0.1) | 0.6 (0.1) | 2.8 (0.7) bc |
| SSB-UAN+I | 6.4 (0.9) | 3.6 (0.4) | 0.8 (0.1) | 0.3 (0.1) | 0.5 (0.1) | 2.3 (0.6) cd |
| Mean | 7.2 (0.3) a | 4.1 (0.3) b | 1 (0.2) c | 0.6 (0.1) d | 0.6 (0.0) d | |

§ Mean with standard error in parenthesis. Means followed by the same lowercase letter are not significantly different at $\alpha=0.05$.

Table A.5. Cumulative soil profile NO₃⁻ after corn harvest in 2013.

| Treatment | kg N in profile ha ⁻¹ |
|-----------|----------------------------------|
| BC-CU§ | 19.4 (2) |
| BC-UAN | 14.8 (3) |
| SSB-UAN | 13.9 (2) |
| BC-Urea | 13.4 (2) |
| SSB-UAN+I | 11.6 (1) |
| SB-UAN | 11.0 (2) |
| Control | 10.3 (1) |

§ Mean with standard error in parenthesis. Means followed by the same lowercase letter are not significantly different at $\alpha=0.05$.

Table A.6. Soil NO₃⁻ concentration in the 0-5 cm depth in 2014 21 June and 8 August sampling times for band treatments.

| Treatment | 21 June | | | | | 8 August | | | | |
|-----------|---|------|-----|-----|------|---|--------|-----|-----|------|
| | Location (cm) | | | | | Location (cm) | | | | |
| | 0 | 10 | 20 | 30 | Mean | 0 | 10 | 20 | 30 | Mean |
| | ————— μg NO ₃ ⁻ -N g ⁻¹ soil ————— | | | | | ————— μg NO ₃ ⁻ -N g ⁻¹ soil ————— | | | | |
| BC-UAN | 13§ | 14 | 5 | 1 | 6 | 4 | 9 | 4 | 3 | 4 |
| SB-UAN | 38 | 14 | 4 | 2 | 8 | 16 | 8 | 5 | 2 | 6 |
| SSB-UAN | 76 | 32 | 11 | 3 | 17 | 20 | 9 | 4 | 3 | 7 |
| SSB-UAN+I | 61 | 25 | 3 | 2 | 10 | 10 | 17 | 4 | 4 | 7 |
| Mean | 39 a | 20 a | 5 b | 2 c | | 11.0 a | 10.0 a | 4 b | 3 b | |

§ Means followed by the same lowercase letter are not significantly different at $\alpha=0.05$.

Table A.7. Soil NO₃⁻ concentration in the 5-10 cm depth in 2014 21 June and 8 August sampling times for band treatments.

| Treatment | 21 June | | | | | 8 August | | | | |
|-----------|---|------|-----|-----|------|---|-----|-----|-----|------|
| | Location (cm) | | | | | Location (cm) | | | | |
| | 0 | 10 | 20 | 30 | Mean | 0 | 10 | 20 | 30 | Mean |
| | ————— μg NO ₃ ⁻ -N g ⁻¹ soil ————— | | | | | ————— μg NO ₃ ⁻ -N g ⁻¹ soil ————— | | | | |
| BC-UAN | 8§ | 8 | 3 | 1 | 3 | 2 | 1 | 1 | 1 | 1 |
| SB-UAN | 12 | 5 | 3 | 1 | 3 | 8 | 5 | 2 | 1 | 3 |
| SSB-UAN | 45 | 23 | 3 | 1 | 7 | 4 | 4 | 1 | 1 | 2 |
| SSB-UAN+I | 29 | 10 | 2 | 1 | 4 | 4 | 7 | 2 | 1 | 3 |
| Mean | 19 a | 10 a | 2 b | 1 c | | 4 a | 4 a | 1 b | 1 b | |

§ Means followed by the same lowercase letter are not significantly different at $\alpha=0.05$.

Table A.8. Soil NO₃⁻ concentration in the 10-15 cm depth in 2014 21 June and 8 August sampling times for band treatments.

| Treatment | 21 June | | | | | 8 August | | | | |
|-----------|---|-----|-----|-----|------|---|------|------|-----|------|
| | Location (cm) | | | | Mean | Location (cm) | | | | Mean |
| | 0 | 10 | 20 | 30 | | 0 | 10 | 20 | 30 | |
| | ————— μg NO ₃ ⁻ -N g ⁻¹ soil ————— | | | | | ————— μg NO ₃ ⁻ -N g ⁻¹ soil ————— | | | | |
| BC-UAN | 6§ | 7 | 3 | 1 | 3 | 1 | 0 | 0 | 0 | 0 |
| SB-UAN | 9 | 5 | 3 | 1 | 4 | 2 | 1 | 0 | 0 | 1 |
| SSB-UAN | 31 | 21 | 4 | 1 | 7 | 1 | 1 | 1 | 0 | 1 |
| SSB-UAN+I | 23 | 10 | 3 | 1 | 4 | 1 | 2 | 1 | 0 | 1 |
| Mean | 14 a | 9 a | 3 b | 1 c | | 1 a | 1 ab | 0 bc | 0 c | |

§ Means followed by the same lowercase letter are not significantly different at $\alpha=0.05$.

Table A.9. Soil NO₃⁻ concentration in the 0-5 cm depth in 2014 21 June and 8 August sampling times for broadcast treatments.

| Treatment | Sampling time | | Mean |
|-----------|---|----------|------|
| | 21 June | 8 August | |
| | —— μg NO ₃ ⁻ -N g ⁻¹ soil —— | | |
| BC-CU | 11§ | 15 | 13 |
| BC-UAN | 15 | 4 | 9 |
| BC-Urea | 14 | 9 | 12 |
| Control | 5 | 5 | 5 |
| Mean | 11 | 8 | |

§ Means followed by the same lowercase letter are not significantly different at $\alpha=0.05$.

Table A.10. Soil NO₃⁻ concentration in the 5-10 cm depth in 2014 21 June and 8 August sampling times for broadcast treatments.

| Treatment | Sampling time | | Mean |
|-----------|---|----------|------|
| | 21 June | 8 August | |
| | —— μg NO ₃ ⁻ -N g ⁻¹ soil —— | | |
| BC-CU | 4§ | 13 | 9 a |
| BC-UAN | 3 | 2 | 3 b |
| BC-Urea | 6 | 4 | 5 ab |
| Control | 2 | 2 | 2 b |
| Mean | 4 | 5 | |

§ Means followed by the same lowercase letter are not significantly different at $\alpha=0.05$.

Table A.11. Soil NO₃⁻ concentration in the 10-15 cm depth in 2014 21 June and 8 August sampling times for broadcast treatments.

| Treatment | Sampling time | | Mean |
|-----------|---|----------|------|
| | 21 June | 8 August | |
| | — μg NO ₃ ⁻ -N g ⁻¹ soil — | | |
| BC-CU | 3§ | 3 | 3 a |
| BC-UAN | 3 | 1 | 2 a |
| BC-Urea | 5 | 1 | 3 a |
| Control | 1 | 1 | 1 b |
| Mean | 3 a | 1 b | |

§ Means followed by the same lowercase letter are not significantly different at $\alpha=0.05$.

Table A.12. Yield-scaled N₂O emissions in 2013 and 2014 (no significant treatment × year interaction).

| Treatment | Year | | Mean |
|-----------|---|------------|-------------|
| | 2013 | 2014 | |
| | g N ₂ O-N Mg grain ⁻¹ | | |
| SSB-UAN | 282 (46)§ | 284 (75) | 283 (41) a |
| BC-Urea | 240 (119) | 457 (179) | 331 (110) a |
| SB-UAN | 193 (28) | 322 (78) | 250 (48) ab |
| BC-CU | 182 (72) | 537 (139) | 313 (101) a |
| SSB-UAN+I | 114 (16) | 137 (45) | 125 (24) c |
| BC-UAN | 67 (10) | 331 (52) | 149 (57) bc |
| Control | 34 (17) | 42 (9) | 38 (9) d |
| Mean | 130 (26) a | 238 (48) b | |

§ Mean with standard error in parenthesis. Means followed by the same lowercase letter are not significantly different at $\alpha=0.05$.

Table A.13. Corn stover biomass for different treatments and years (no treatment × year significant interaction).

| Treatment | Year | | Mean |
|-----------|---------------------|-------------|--------------|
| | 2013 | 2014 | |
| | Mg ha ⁻¹ | | |
| SB-UAN | 12.6 (0.1)§ | 8.7 (0.3) | 10.6 (0.8) a |
| SSB-UAN | 12.1 (0.9) | 8.8 (0.5) | 10.5 (0.8) a |
| BC-UAN | 11.6 (0.7) | 9.2 (0.5) | 10.4 (0.6) a |
| BC-Urea | 11.2 (1.2) | 9.2 (0.3) | 10.2 (0.7) a |
| SSB-UAN+I | 10.9 (1.1) | 9.3 (0.4) | 10.1 (0.6) a |
| BC-CU | 10.6 (0.5) | 9.6 (0.4) | 10.1 (0.3) a |
| Control | 9.3 (0.7) | 7.2 (0.4) | 8.3 (0.5) b |
| Mean | 11.2 (0.3) a | 8.9 (0.2) b | |

§ Mean with standard error in parenthesis. Means followed by the same lowercase letter are not significantly different at $\alpha=0.05$.

Table A.14. Corn stover N uptake for different treatments (no significant treatment × year interaction).

| Treatment | Year | | Mean |
|-----------|-----------------------|---------|----------|
| | 2013 | 2014 | |
| | kg N ha ⁻¹ | | |
| SSB-UAN | 98 (7)§ | 74 (8) | 86 (7) a |
| SSB-UAN+I | 85 (10) | 74 (10) | 80 (7) a |
| SB-UAN | 75 (2) | 57 (6) | 66 (4) b |
| BC-Urea | 69 (11) | 63 (3) | 66 (5) b |
| BC-UAN | 63 (5) | 60 (5) | 61 (3) b |
| BC-CU | 59 (3) | 73 (7) | 66 (4) b |
| Control | 40 (4) | 44 (3) | 42 (2) c |
| Mean | 70 (4) | 63 (3) | |

§ Mean with standard error in parenthesis. Means followed by the same lowercase letter are not significantly different at $\alpha=0.05$.