

MITIGATION OF NITRATE, NITROUS OXIDE, AND AMMONIA LOSS WITH
TIME AND SOURCE OF NITROGEN APPLICATION IN CORN

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Abstract

The large need of nitrogen (N) for crop production and the negative impacts of fertilizer on the environment result in a compelling need to identify new or advanced N management practices to reduce N losses while maintaining productivity and profitability. Nitrate (NO_3) leaching, nitrous oxide (N_2O) denitrification, and ammonia (NH_3) volatilization are the most common pathways of N loss when synthetic N fertilizer is applied in agricultural lands. The objectives of this 7-year study (2014-2020) were to evaluate the use of traditional management (urea applied at pre-plant) and advanced [enhanced efficiency fertilizers and split applications] N management practices on i) N losses (NO_3 , N_2O , and NH_3); ii) corn yield and profitability; and iii) cropping system N balance including plant N removal and soil N status. The field experiment was conducted at the University of Minnesota Southwest Research and Outreach Center, near Lamberton MN. Four treatments were applied and replicated four times in a randomized complete block design: a pre-plant application of 202 kg N ha⁻¹ of either urea (U) or polymer coated urea (PCU; ESN) (E) and 135 kg N ha⁻¹ as urea with urease inhibitor (Agrotain) sidedressed at development stage V4-6 with 67 kg N ha⁻¹ applied before planting as either urea (U/U+) or ESN (E/U+). Across the 7 years, the advanced management practice E/U+ increased corn grain yield (1 Mg ha⁻¹ or 10%) and total N uptake (TNU, plant + grain N; 18 kg N ha⁻¹) compared to the traditional management practice (U), while E and U/U+ had similar grain yields and TNU to the other treatments. Furthermore, while net economic returns (NER) were not statistically different between treatments, E/U+ generated numerically greater NER per hectare than U (\$63), E (\$52), and U/U+ (\$46). Nitrate-N leaching (measured from 2015 to 2020) was highly influenced by weather. Excess precipitation, especially after fertilizer application, increased NO_3 -N loads, which was lower for E compared to the other treatments; however, flow-weighted NO_3 -N concentration was not different between treatments, with only a trend for lower NO_3 -N concentrations for E. Nitrous oxide emissions (measured from 2018 to 2020) also increased with excess precipitation, especially after fertilizer application. Split application treatments and U did not reduce N_2O -N

loss, but in wet years N_2O -N loss was lower for E compared to the other treatments. This, however, was not observed in drier years or when precipitation was evenly distributed. Unlike NO_3 -N and N_2O -N losses, ammonia volatilization (measured from 2019 to 2020), decreased as the result of excess precipitation that helped incorporate the fertilizer deeper into the soil. Overall, NH_3 -N loss was lower for E compared to other treatments. Integration of all the variables measured into a N balance calculation showed to be a poor approach to estimate N efficiency or impact on environmental quality because plant N uptake overshadow treatment influence on N loss measurements. Our findings indicate that pre-plant ESN can be considered a strategy to reduce N losses while maintaining crop yield. While split treatments increased corn yield, they did not reduce N losses, which contrasts the common assumption held by many that split applications are better for the environment. Nonetheless, the traditional management practice of pre-plant urea was the least efficient, producing lower crop yields and increasing N losses compared to pre-plant ESN in wet years. This demonstrates that there are N management practices that can improve production and environmental protection and their merit should be explored and refined further.

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Chapter 1: Subsurface Nitrate Drainage, Corn Yield and Net Economic Return
Outcomes from Nitrogen Application Timing and Source

Overview

The use of advanced N management practices could minimize nitrate (NO₃-N) leaching from corn production (*Zea mays L.*) in poorly drained soils. Our objectives were to evaluate the effect of traditional (pre-plant application of urea) and advanced (enhanced efficiency fertilizers and split applications) nitrogen (N) management practices on i) NO₃-N loss in tile drainage water, ii) corn grain yield, iii) soil and plant nitrogen content and, iv) net economic return. Over 7 growing season (2014-2020), four treatments were applied to an experimental site near Lamberton, Minnesota: 202 kg N ha⁻¹ as urea before planting (U); 202 kg N ha⁻¹ as polymer coated urea (PCU; ESN) before planting (E); 67 kg N ha⁻¹ as either urea or ESN before planting and 135 kg N ha⁻¹ as urea with a urease inhibitor (Agrotain) at development stage V4-6 (U/U+) and (E/U+). Annual drainage ($R^2 = 0.85$) and NO₃-N load ($R^2 = 0.61$) increased exponentially with annual precipitation. Also, drainage was greatly influenced by precipitation distribution, as 49% of the total tile drainage occurred between April and June. Overall, annual flow-weighted NO₃-N concentration (AC) and before side-dress flow-weighted NO₃-N concentration (BSC) were not statistically different between treatments. The AC (4 to 14 mg L⁻¹) and BSC (1 to 23 mg L⁻¹) were at or above the maximum drinking water standard of 10 mg N L⁻¹ in 2016 and 2017. The E/U+ treatment significantly increased corn grain yield (1 Mg ha⁻¹ or 10%) and total N uptake (TNU, plant + grain N; 18 kg N ha⁻¹) compared to U, while E and U/U+ had similar grain yields and crop N uptake to the other treatments. Net economic return (NER) was not statistically different between treatments; however, E/U+ generated numerically greater NER per hectare than U (\$63), E (\$52), and U/U+ (\$46). Findings from this study indicate that, while using split application and ESN may result in greater corn yield, TNU and NER, these advanced N management practices are insufficient to substantially reduce NO₃-N leaching when N rates are near optimum for crop production.

Introduction

Nitrogen (N) fertilization is essential in intensive agriculture because this is the most limiting nutrient for crop production. Worldwide, agricultural N use has drastically increased in the last fifty years from 11.3 Tg N yr⁻¹ in 1961 to 107.6 Tg N yr⁻¹ in 2013 (Lu and Tian, 2017). The US ranks third with 11% of the global N consumption (Lu and Tian, 2017), of which the largest portion since 2000 is localized in the Midwest (Cao et al., 2018). This increase is also observable locally. For instance, in Minnesota, N fertilizer sales have increased by approximately 25% from 1989 to 2017 (MDA, 2017). This steep increase in agricultural N use has substantially contributed to food, feed, fuel, and fiber production for the growing world population. It is estimated that N fertilization is responsible for 41% of the corn production increase in the US (Stewart et al., 2005).

While helping increase corn productivity, N fertilization has also resulted in excess nitrate-N (NO₃-N) loading in the environment. Because NO₃-N is soluble in water, it moves readily with water and is susceptible to leaching losses from agricultural fields. Surplus NO₃-N in water can harm aquatic life, contaminate drinking water, and contribute to hypoxia, such as the dead zone in the Gulf of Mexico (EPA, 2020).

In addition to N fertilization, installation of subsurface tile drainage has exacerbated NO₃-N loss from agricultural fields (Dinnes et al., 2002; Schottler et al., 2014; Smith et al., 2018). Approximately 20 million ha (91% of total tile-drained area in the US) is in the Midwest, with the majority (84% of the total tile drained area in the US) concentrated in Iowa, Illinois, Minnesota, Indiana, Ohio and Michigan (NASS, 2019). Artificial drainage has been extensively used in the upper Midwest to help remove excess water from poorly drained soils and allow farmers to produce competitive yields. While N fertilizer and tile drainage are essential for profitable corn production, these factors have resulted in greater NO₃-N loss. It is imperative to find better ways to manage resources under tile-drained systems where N fertilization occurs. Drainage engineering or drastic changes in cropping systems, including the use of cover crops can help, but

they are often difficult to implement and are costly (Qi et al., 2011; Christianson et al., 2013; Xu et al., 2020). Advanced N management strategies to reduce N losses are generally much easier to implement and less expensive.

Timing of N fertilizer application may be an advanced strategy to reduce N losses. In Midwest corn production, most of the N is applied at or before planting, due to various reasons including logistical and economic advantages. However, because the amount of N required by corn plants during early developmental stages is low and excess precipitation normally occurs early in the growing season, applications of N before the crop is planted can result in considerable N loss. Conversely, applying N fertilizer later in the season, when corn N requirements are high, could reduce N loss and increase corn yields and N use efficiency (NUE). Some studies have shown reduced NO₃-N leaching (Bakhsh et al., 2002) and increase yield (Jaynes, 2015; Rutan and Steinke, 2018) with sidedress compared with pre-plant N application. However, other studies show no difference (Jaynes, 2013; Christianson and Harmel, 2015) except for sandy soils where a split application is advantageous (Mueller and Vyn, 2017; Clark et al., 2020). The lack of conclusive evidence, especially on NO₃-N leaching, highlights the need for additional research to determine the potential benefits of time of N application.

Nitrogen source could be another potential advanced strategy to reduce N losses. Specifically, controlled release N fertilizers such as polymer-coated urea (PCU) have shown to reduce N losses to the environment and increase N availability to crops. While a few studies have shown no benefits in increasing grain yield (Noellsch et al., 2009; Nash et al., 2015) or reducing NO₃-N leaching (Nash et al., 2014) with PCU, studies have shown the benefit of PCU in reducing NO₃-N leaching (Owens et al., 1999; Wilson et al., 2010) and increasing grain yield (Noellsch et al., 2009; Zhou et al., 2018; Larson et al., 2019). Despite the potential benefits of PCU, their higher cost compared with other common sources of N, makes PCU less common for extensive row-crop production (Zhou et al., 2018). However, studies have found that the increase in yield often makes PCU more profitability than conventional urea (Noellsch et al., 2009; Zhou et al.,

2018). Few studies that evaluated the effect of PCU in NO₃-N leaching losses were conducted in the Midwest in tile-drained fields. This type of study was mainly conducted in coarse-textured soils. More studies are needed across different soil textures to determine the effect of PCU in NO₃-N loss and yield responses.

The objectives of this study were to determine the effect of traditional (pre-plant application of urea) and advanced N management practices (ESN and split applications) in a poorly drained soil on i) NO₃-N loss in tile drainage water, ii) corn grain yield, iii) soil and plant nitrogen content and, iv) net economic return.

Materials and Methods

Site Description and Experimental Design

This field experiment was conducted between 2014 and 2020 on a tile drained site at the University of Minnesota Southwest Research and Outreach Center (SWROC) located near Lamberton, MN (44°14'11.0" N 95°18'41.7" W). The soils were classified as poorly drained Webster-Canisteo clay loams (fine-loamy, mixed, superactive, mesic Typic Endoaquolls and fine-loamy, mixed, superactive, calcareous, mesic Typic Endoaquolls, respectively). A continuous corn (*Zea mays L.*) cropping system was established in 2014 and was maintained for the duration of the study. Weather data were obtained from a weather station located near the study site (0.4 km distant). Monthly and annual mean air temperature and cumulative precipitation are presented for 2014 to 2020 along with the 30-year normal (1980-2009) (Tables 1.1 and 1.2, respectively).

The tile-drainage plots in this study were set up in 1994 and details are given in Zhao (1998). Succinctly, the site has sixteen individual subsurface tile-drainage 9.1 m by 18.2 m plots. Perforated tile lines with 0.1 m in diameter were buried 1 m deep and located 1.5 m away from the width edge of the plot. This arrangement simulated a tile drain spacing of 33 m. The perforated tile lines from each plot were connected to nonperforated PVC pipes that drained into monitoring wells located inside of culverts buried in the soil. To avoid possible lateral flow

between plots, the perimeter of each plot was isolated to a depth of 1.8 m by installing a 12 mil-thick plastic sheet.

Treatments and Agronomic Practices

Four N treatments were replicated four times in a randomized complete block design. The experimental treatments included a traditional N management practice and three advanced N management practices. The traditional N treatment consisted of 202 kg N ha⁻¹ as urea (46-0-0) applied before planting (U). The three advanced N treatments consisted of 202 kg N ha⁻¹ as the PCU ESN (44-0-0, Nutrien, Saskatoon, Canada) applied before planting (E); a split application of 135 kg N ha⁻¹ of urea treated with the urease inhibitor Agrotain (U+) (N-(n-butyl)-thiophosphoric triamide / Koch Fertilizer LLC, Wichita, KS) applied at development stage V4-6 where 67kg N ha⁻¹ was applied before planting either as urea (U/U+) or ESN (E/U+). All applications were broadcast applied and the N fertilizer applied immediately before planting (dates noted below) was incorporated 0.15 m using a field cultivator. The V4-6 side-dress application was done on 16 June 2014, 18 June 2015, 16 June 2016, 22 June 2017, 21 June 2018, 8 July 2019, and 15 June 2020. The 202 kg N ha⁻¹ fertilizer rate was chosen to represent farmers' typical N rate in the region of the study for a continuous corn rotation. The Maximum Return to N (MRTN) guideline from the University of Minnesota suggests 185 kg N ha⁻¹ with a range between 170 and 202 kg N ha⁻¹ (Kaiser et al., 2020).

Phosphorus and potassium amendments were applied when needed as triple-superphosphate (0-20-0; N-P-K) and potassium chloride (0-0-50; N-P-K) and other recommended agronomic practices for the region were used to optimize crop growth. Corn hybrid Dekalb DKC49-29-RIB was planted on 25 May 2014 and 9 May 2015, corn hybrid Pioneer P0157 AMX was planted on 16 May 2016 and 6 May 2017, corn hybrid DKC 39-27 RIB was planted on 31 May 2018, corn hybrid DKC 40-77 RIB was planted on 3 June 2019, and corn hybrid P0157 AMXT was planted on 11 May 2020. We used the best hybrids recommended for this area during

the study. Plant population target was 86,000 plants ha⁻¹ on 76-cm row spacing. Tillage was done in the fall with a chisel plow at a depth of 0.25 m.

Subsurface Drainage and Nitrate Concentration Measurements and Load Calculation

Water samples were not collected during the 2014 season because 2014 was an instrument setup and calibration year. Tipping buckets for each plot were installed in culverts used to measure the water flow drained from the tile lines from 2015 to 2017. Details of instrumentation setup are given in (Zhao et al., 2001). Each culvert housed two tipping buckets with a divider installed between them to prevent splash contamination. Tipping buckets were made from polyvinyl chloride (PVC) sheets with a capacity of approximately 410 mL. Composite flow proportionate water samples were obtained by taking 3mL of the water every other bucket tip through a tygon tube connected to an ISCO samplers.

In 2018 a new drainage water collection system was installed, similar to the one described by Lawlor et al. (2008). It consisted of a submersible pump (model 237, Liberty Pumps, Bergen, NY) for each plot that pumped drainage water through a PVC pipe fitted with a plated sprayer orifice nozzle and a 25 mm DLJ100C water meter (Daniel L Jerman Co., Inc., Hackensack, NJ) connected to a HOBO state data logger (Onset Computer Corporation) to record a timestamp for the flow. The back pressure created by the meter allowed collection of a flow-proportionate sample that was diverted through plastic tubing to a 3.8 L sampling bottle. The composite water samples were collected weekly or more frequently after rainfall by transferring a subsample to vials that were transported to the laboratory and frozen until analyzed for NO₃-N.

Water samples were analyzed for NO₃-N using the spectrophotometric determination method (Doane and Horwáth, 2003). When laboratory results values were below detection limit (0.05 mg L⁻¹), half the detection limit value was used (Yanai et al., 2018). Nitrate-N load (kg ha⁻¹) was calculated using the necessary unit conversions by multiplying the NO₃-N concentration (mg L⁻¹) by the drainage volume (L) measured between sampling days. Annual flow-weighted mean NO₃-N concentration was estimated by dividing annual NO₃-N load by annual flow. Before split

application flow-weighted mean $\text{NO}_3\text{-N}$ concentration was also calculated. Typically, measurements were not conducted during the end of December through most of March due to cold air temperatures (Table 1.1) and frozen soils that prevented water flow.

Drainage studies often have missing data due to equipment damage or failure and flooding events (Jaynes et al., 1999; Saadat et al., 2018). Here we describe missing data or unreliable data that was not included in the analysis. One of the plots consistently produced excessively low flow drainage that could not be corrected due to tile clogging. In 2016 three plots and 2019 two plots were not included in the analysis due to various electrical issues caused by rodent damage and pumps malfunctioning. In 2018, excessive rainfall in June and September produced more tile drainage than the actual precipitation due to flooding with water from adjacent fields. For those events, load was calculated only from reliable $\text{NO}_3\text{-N}$ data collected right before flooding or as soon as the collection system was restored and drainage was estimated from similar precipitation events without flooding during other years of the study, where the average percentage of precipitation lost as drainage per block was calculated for each plot in question.

Soil and Plant Measurements

Each year before planting and after grain harvest, two-core (40 mm diameter) soil samples were randomly collected within each plot from 0 to 30 cm, 30 to 60 cm, and 60 to 90 cm depth increments. After treatment application, a four core (19.1 mm diameter) composite soil sample was collected from each plot using a hand-held soil probe at development stages V4-6, V10-12 and, R1 from 0 to 30 and 30 to 60 cm depth increments. Soil samples were dried at 35°C to constant weight, ground and analyzed for ammonium ($\text{NH}_4^+\text{-N}$) (Bremner and Mulvaney, 1982) and $\text{NO}_3\text{-N}$ (Gelderman and Beegle, 2012) and total inorganic N (TIN) ($\text{NH}_4^+\text{-N}$ plus $\text{NO}_3\text{-N}$) was calculated.

Total dry biomass and N content was measured to calculate total N uptake from six aboveground whole plants collected at V6, V10, R1, and R6 development stages and from harvested grain. The R6 samples were partitioned into vegetative biomass and grain. Grain N

removal was calculated from the harvested grain. Plant and grain samples were dried at 60°C to constant weight, ground and analyzed for total N using the combustion method (Horneck & Miller, 1998). Grain harvest was generally done in October by combining the middle four crop-rows of each plot and grain yield was adjusted to 155 g kg⁻¹ moisture content.

Net Economic Return

The effect of N application timing and source on net economic return (NR) was evaluated using corn revenue and cost of fertilizer and application. Costs that did not differ by treatments (P and K fertilizer, seed, etc.) were not included in the NR calculation. Net economic return was calculated by subtracting fertilizer and application costs from corn revenue. Corn revenue was calculated by multiplying corn yield (Mg ha⁻¹) by corn price of US\$138 Mg⁻¹ (US\$3.5 bu⁻¹). The following prices were used for urea \$0.76 kg-N⁻¹ (\$ 0.34 lb-N⁻¹), ESN \$1.2 kg-N⁻¹ (\$ 0.54 lb-N⁻¹), and urea with Agrotain \$0.85 kg-N⁻¹ (\$ 0.39 lb-N⁻¹). The pre-plant application cost was \$11.1 ha⁻¹ and the split application cost was \$27.2 ha⁻¹. The values were based on local service supplier prices at the time the study was conducted.

Statistical Analysis

Analysis of variance was performed using R (R Core Team, 2020) linear mixed effects models and the restricted likelihood method with the lme4 package (Bates, et al., 2014). Treatment variables were analyzed as fixed effect and year and block as random effects. Although year was analyzed as a random effect to increase the inference space of the results from this study, these results are better understood in the context of yearly variability due to growing season conditions. For this reason, the yearly means are presented along with the mean separation analysis conducted across years. Assumptions of normality and homogeneity of variance (Levene's test) were assessed. Data were transformed when necessary to meet assumptions using the transformation suggested by the boxCox method with the car package (Fox, 2019). Back-transformed means are reported. Treatment differences were determined using Tukey's pairwise

comparisons with the emmeans package (Lenth, 2018). Statistical difference was declared when $P < 0.05$.

Results and Discussion

Weather and Subsurface Drainage

Annual mean monthly temperatures were within 2°C of the 30-year normal (Table 1.1).

Similarly, during the growing season (April to October) mean monthly temperatures were often within 2°C with and occasionally 3°C departure but never in consecutive months. The only exceptions were 2018 with 7°C below the normal in April and 2020 with 4°C below the normal in October, both followed by 3°C above the normal. Unlike the growing season, November through March had greater frequency of months with 3 to 8°C departures from the normal. Except for 2020, annual precipitation was greater than normal for all years (Table 1.2). Although there was more overall precipitation, across the 7 years, 84% (range 77 to 95%) or 708 mm of the total precipitation fell during the growing season (April-October), which is the same as the 30-yr normal of 83% (576 mm). On average, precipitation ranged from 40 to 45% greater than normal during the growing season in 2016, 2018, and 2019, from 6 to 27% greater than normal in 2014, 2015 and 2017, and 10% below normal in 2020.

Precipitation amounts greatly influence drainage (Table 1.2). Annual drainage had an exponential relationship to annual precipitation ($\text{Drainage} = 0.8516^{0.0041 * \text{precipitation}}$, $R^2 = 0.85$, data not shown). Across all years, the mean annual subsurface drainage volume was 25% of the total annual precipitation ranging from 11% in 2020 to 44% in 2019. This agrees with findings of Jaynes (2015) in central Iowa where subsurface drainage ranged from 5 to 30%. Positive deviations in precipitation from the normal resulted in greater drainage. Conversely, large negative deviations in precipitation from the normal resulted in little or no drainage. Precipitation timing and its distribution across the growing season also influenced drainage. A substantial portion (average of 49% across years) of the total tile drainage occurred between April and June, ranging from 36% in 2020 to 75% in 2015. Other studies conducted in the upper Midwest US

have reported even greater average tile drainage during these months. Randal et al. (2003) found an average of 62%, while Randall and Vetsch (2005) reported a total tile drainage of 71%. Moreover, in our study considerable drainage volumes (average of 20%) occurred in July during 4 of the 6 years (2016 and 2018 to 2020) when precipitation was 52 to 84 mm (157 to 191%) greater than normal.

Furthermore, evapotranspiration (ET) may have also influenced subsurface drainage. In 4 of the 6 years (2016 to 2019), on average 35% of the total drainage was observed during September and October, when precipitation was above normal, and ET is reduced as crops senesce. In 2020, warmer than normal air temperatures combined with greater than normal precipitation thawed the soil in March, before there were crops to use water, and resulted in substantial drainage relative to other years (Tables 1.1 and 1.2). This combined with the fact that precipitation in most months in 2020 were at or below the normal, resulted in 50% of the total annual drainage occurring in March. Consistent with previous studies (Mueller et al., 1997; Randall and Goss, 2008), most drainage occurred during relatively few events each year. Normally each year 3 to 6 rainy periods lasting anywhere from 1 to 13 days of intermittent rainfall each resulted in 70 to 95% of the total drainage.

A general trend for lower drainage for treatment E over the years resulted in lower drainage than U and U/U+ (Table 1.3). Nonetheless, we suspect drainage differences occurred by happenstance and not as a direct effect of the treatment. Only in 2019 drainage for E was substantially lower than the other treatments. Unfortunately, this can have a direct effect in treatment evaluation as $\text{NO}_3\text{-N}$ load is greatly influenced by drainage amounts (Randall and Goss, 2008). This problem has been observed previously and researchers often randomize treatments by drainage rather than by location within the field to circumvent this problem (Randall et al., 2003; Vetsch et al., 2019).

Nitrate-N Leaching Losses

Similar to annual drainage flow, annual NO₃-N load was influenced by precipitation amount. Nitrate-N load had an exponential relationship to precipitation ($\text{Load} = 0.3809^{0.0042 * \text{precipitation}}$, $R^2 = 0.61$, data not shown). Since both drainage and NO₃-N load show a similar positive relationship to precipitation, annual NO₃-N load had a linear response to annual drainage ($\text{Load} = 0.0664 * \text{drainage} + 2.1856$, $R^2 = 0.79$, data not shown). As with drainage, precipitation distribution and intensity influenced NO₃-N load. While the load amount was different between treatments, the pattern across the growing season was similar regardless of treatments, and the majority of NO₃-N load occurred in 3 to 5 distinct events each year (Appendix 2). For example, large increase in NO₃-N load happened when several small (<50mm) rain events occurred over a short period, including November 2015, March and May 2016, May 2017, July 2018, and April 2021. Substantial NO₃-N loads also occurred during large single rain events (>50mm) such as in June 2015, July and September 2016, October 2017, June and September 2018, July and September 2019, and June 2020. This illustrates the challenge it is to manage N since a few erratic rain events in the year produce the majority of NO₃-N loading.

In addition to precipitation amount and distribution, the time of precipitation in relation to fertilization events influenced NO₃-N load. While total precipitation amounts in 2015 and 2017 were similar to each other (779 vs 765 mm) and pre-plant fertilizer was applied under similar temperatures (Tables 1.1) in May, the wettest month of these years (Table 1.2), the NO₃-N loads in these two years were substantially different. In 2015 precipitation started 1 day after pre-plant fertilization and continued intermittently for 9 days in daily amounts of no more than 13 mm (Appendix 2), totaling 40% (55 mm) of the monthly precipitation (139 mm), and resulting in less than 10% (0.5 kg ha⁻¹) of the annual NO₃-N load. However, in 2017 precipitation started 9 days after pre-plant fertilizer and continued intermittently for 9 days in daily amounts that ranged from 3 to 40 mm (Appendix 2), totaling 73% (111 mm) of the monthly precipitation (152 mm), and resulting in 74% (17 kg ha⁻¹) of the total NO₃-N load. The difference in loading was likely because in 2015 the fertilizer had not had sufficient time to transform to NO₃-N before the wet

period, whereas in 2017 it did. The same is true for sidedress applications. Substantial precipitation occurred in several of the years (2015, 2016, 2018, and 2019) relatively soon after the sidedress application, which resulted in increased NO₃-N loads. This shows that split applications may not be as important to reducing NO₃-N load as it would be to avoid large amounts of precipitation soon after the application. Unfortunately, long-range forecasting for rain is difficult.

Overall annual NO₃-N load for E was lower than the other treatments (Table 1.4). This was especially true in wet years, such as 2019 where E had a 45% reduction in load relative to U, though this difference may be an artifact of less drainage for E than U. That said, in 2018, another wet year, U and E had virtually the same amount of drainage (Table 1.3), but E produced a 25% reduction in annual NO₃-N load compared to U. At the same time, the split application treatments that had substantially more drainage than U (and E), only increased NO₃-N loads by 2 kg ha⁻¹ compared to U. This indicates that E can be advantageous to reducing NO₃-N loads relative to U. This was also observed in most years and overall, across the years, but only as a trend, where NO₃-N load before side-dress application for E was lower than for U (Table 1.4). The lack of statistical difference between treatments on NO₃-N loads before side-dress application was also true across all four treatments even though N rates applied before planting were greater for U and E (202 kg ha⁻¹) than for U/U+ and E/U+ (67 kg ha⁻¹). The lack of difference may be due to organic matter (OM) mineralization. Other studies have suggested the potential contribution of OM mineralization on NO₃-N leaching losses (Addiscott, 1988; Cambardella et al., 1999; Randall and Goss, 2008). Further, under a similar location and soils to our study Gast et al. (1978) suggested that OM mineralization could explain higher soil NO₃-N accumulations for a treatment with 0 kg N ha⁻¹ compared to 20 kg N ha⁻¹.

As mentioned earlier, since NO₃-N loads are directly influenced by drainage amount, conducting analysis with flow-weighted NO₃-N concentration can be useful. The annual flow-weighted NO₃-N concentration (AC) ranged from 4 to 14 mg L⁻¹ and before side-dress flow-

weighted NO₃-N concentration (BSC) ranged from 1 to 23 mg L⁻¹ (Table 1.5). In 2016 and 2017 the AC and BSC were at or above the maximum drinking water standard of 10 mg L⁻¹ set by USEPA (USEPA, 2009). For these two years, annual mean NO₃-N concentrations from water samples averaged across treatments were also greater compared to the other years (Appendix 1). The fact that in those years BSC where only a portion of the total fertilizer was applied for the split application treatments was greater than AC is indicative of the fact that NO₃-N loss from mineralization and non-fertilizer sources early in the spring can be substantial. Further, the N rate used in this study was comparable to what farmers use in the region for continuous corn and is at the high end of the MRTN rate (Kaiser et al., 2020). This illustrates that it is possible to produce corn profitably while minimizing the environmental impact of N fertilizer when university guidelines developed through years of research are followed. Others have observed that reducing N rates below the MRTN often reduce grain yield with minimal improvements to nitrate loading (Randall and Sawyer, 2008; Struffert et al., 2016). At the same time, it is known that applying N above crop requirements does not increase yield, reduces profitability, and increases N loss to the environment (Randall and Sawyer, 2008; Greer and Pittelkow, 2018). For these reasons, efforts should be concentrated in helping farmers use research-based N rates developed by land-grant universities or similar counterparts and find ways to protect from leaching not only the N from fertilizer, but other sources naturally available in the soil that are also susceptible to loss.

There were no differences due to time or source of N applied for AC and BSC (Table 1.5). This illustrates that while best N management practices (also known as 4R's by the agriculture industry) such as the right source and time of application may be important, when N is applied at approximately the correct rate, additional "right" practices may not be additive and produce little or no additional improvement towards environmental protection. Others have come to similar conclusions. For example, Christianson and Harmel (2015) conducted a 40-year synthesis analysis and found no differences in N loading between N application timings. Our findings and those of others call into question the over emphasis currently placed on application

timing as a universal water quality improvement strategy. That said, while over generalization can be problematic, specific site and weather conditions are extremely important in evaluating the utility of best N management practices. Although we observed no differences in AC and BSC due to N source, others have observed that PCU can substantially reduce N loss in sites with contrastingly greater N loss potential relative to ours (Nelson et al., 2009; Wilson et al., 2010).

Corn Yield, Total Nitrogen Uptake, and Profitability

The advanced N management practice E/U+ significantly increased corn grain yield (1 Mg ha⁻¹ or 10%) and crop N uptake (18 kg N ha⁻¹) compared to the traditional N management practice (U), but E and U/U+ produced similar grain yield and crop N uptake to the other treatments (Table 1.6, Table 1.7). Furthermore, despite the few differences in corn yield between treatments in the current study, E showed a consistent trend for greater yields (0.7 Mg ha⁻¹) than U, which agrees with findings from Noellsh et al. (2009). Similarly, E/U+ had a consistent trend for greater yields (0.6 Mg ha⁻¹) than U/U+. Similar results were observed for crop N uptake (Table 1.7). These results demonstrate the potential benefits of using ESN to increase corn grain yields and N uptake or NUE. Corn grain yield typically follows a quadratic plus plateau response where yield near the MRTN is at the flattest portion of the response curve. For this reason, it is possible that the N rate used in this study lacked sensitivity and hinder our ability to detect treatment differences that might have been more obvious if we had used grain yield limiting N rates. We accepted this potential limitation in the experimental design because our emphasis was to evaluate treatments at a N rate representing current farmer practices.

Averaged across treatments, corn yield varied significantly between years, with greater yields in 2017 (12.6 Mg ha⁻¹) and 2020 (12.2 Mg ha⁻¹) compared to lower yields (9.8 to 10.7 Mg ha⁻¹) in the other years (Table 1.6). There was no relationship of grain yield with drainage, precipitation, or NO₃-N load (data not shown). This demonstrates that wetter years with greater potential for N losses do not necessarily reduce yields. It is possible that N loss in wet years may be compensated by N mineralization from organic matter.

While ESN and split N applications can lead to greater yield and N uptake, these practices are more expensive than the traditional pre-plant U application. Nonetheless, net economic return (NER) was not statistically different due to treatment (Table 1.8), and it ranged from \$1,053 to \$1,550 ha⁻¹. However, E/U+ showed a trend with the highest or second highest NER every year and U showed a trend with the lowest or second lowest NER in most years. Overall, compared with the other treatments, E/U+ generated numerically greater NER per hectare than U (\$63), E (\$52), and U/U+ (\$46). Our findings agree with Randall et al. (2003) who observed a trend for greater economic return with split applications compared to fall and spring N applications.

Plant and Soil Nitrogen

Averaged across years, plant N uptake differences were only observed at the development stage V4-6, which was due to the fact that U and E had more N available, but those differences disappeared later (Table 1.9). The fact that total N (table 1.7) at R6 was greatest for E/U+ and lowest for U indicate that applying a small amount of N (1/3) at pre-plant is sufficient to feed the crop until sidedress time in a cont. corn system. Averaged across years and treatments, plant N uptake increased with plant development from 8 kg N ha⁻¹ at V4-6 to 100 kg N ha⁻¹ at V10-12, and to 124 kg N ha⁻¹ at R1 (Table 1.9). Greater plant N uptake was observed in 2019 at V4-6 likely reflecting the latest planting for the study and latest sampling date for this development stage. Plant N uptake at V10-12 and R1 were generally greatest in 2017 and lowest in 2018 (Table 1.9). This follows what we observed with corn yield (Table 1.6), TNU (Table 1.7), and profitability (Table 1.8), even though 2017 had the greatest N loss (Table 1.5). As mentioned before, this likely reflects the capability of the soil to provide N through mineralization when considerable N losses are observed early in the season. Flooding events that lasted a few days before development stage V10 in 2018 likely diminished plant N uptake later in the season and reduced the yield potential as reflected in Table 1.6.

Soil samples were collected before planting (spring), throughout the growing season (V4-6, V10, and R1) and after harvest as another way to explain treatment differences in plant N uptake and N loss. Because N distribution in the soil profile was fairly consistent across years regardless of time of sampling or year and the fact that total N in the profile is the most important variable in relation to plant uptake and N loss, we only report mean $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ for the entire sampling depth (Table 1.10, 1.11). In general (averaged across years and treatments), soil $\text{NH}_4\text{-N}$ gradually increased from the spring sampling (34 kg N ha^{-1}) to the V10-12 sampling (42 kg N ha^{-1}), it decreased at R1 (31 kg N ha^{-1}) to levels similar to those observed in the spring sampling, and substantially increased by the post-harvest sampling (55 kg N ha^{-1}) (Table 1.10, Table 1.11). This pattern was consistent across years except for 2014 and 2017 where post-harvest levels remained low, similar to R1. In contrast, $\text{NO}_3\text{-N}$ increased substantially from 40 kg N ha^{-1} in the spring sampling to 81 kg N ha^{-1} at V4-6 due to fertilizer applications, progressively decreased during the growing season to 41 kg N ha^{-1} as corn uptake increased (Table 1.9), and slightly increased by post-harvest to 57 kg N ha^{-1} , likely as the result of nitrification of mineralized N after R6 when the crop no longer takes up N.

The relative distribution of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ in the soil profile during the spring sampling of the different years was approximately 50% of the total in the surface, 30% in the 30-60 cm, and 20% in the 60-90 cm depth (data not shown). Similar results were observed for $\text{NO}_3\text{-N}$ after harvest, but $\text{NH}_4\text{-N}$ distribution was approximately 65% in the surface, 20% in the 30-60 cm, and 15% in the 60-90 cm. Further, the relative distribution of $\text{NO}_3\text{-N}$ in the top 60 cm of the soil profile throughout the various sampling events in the growing season (V4-V6 to R1) remained constant. Approximately 56% of the $\text{NO}_3\text{-N}$ was in the top 30 cm and 44% in the 30-60 cm depth. Similar results were observed for $\text{NH}_4\text{-N}$ with the majority, approximately 70%, in the surface and 30% in the 30-60 cm depth.

While spring soil $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ were not influenced by treatment, post-harvest $\text{NO}_3\text{-N}$ was 51% greater for E/U+ compared to U (Table 1.10) despite the fact that E/U+ also had

greater N uptake by the crop (Table 1.7) and grain yield (Table 1.6) and similar $\text{NO}_3\text{-N}$ loss (Table 1.4 and Table 1.5) in comparison to U. The fact that by next spring residual soil N is similar across treatments, indicates that greater residual N in the fall does not contribute to the next crop and can potentially increase N loss to the environment. Greater soil N at post-harvest with split applications relative to the same application at pre-plant have been observed across the Midwest (Bandura et al., 2016). This may indicate that from an environmental protection standpoint, split applications may have limited utility.

Soil $\text{NO}_3\text{-N}$ at V4-6 for U/U+ and E/U+ was only around 40% of the levels measured for U and E (Table 1.9) and relate to the fact that at this point only 33% of the total N had been applied on the split application treatments. Compared to U, E had greater $\text{NH}_4\text{-N}$ at V4-6, and it was consistently observed in most years, reflecting the control release of N. Moreover, a consistent trend across most years for greater $\text{NO}_3\text{-N}$ may indicate less N loss with E relative to U early in the spring. Finally, the fact that across the years (2015-2020) and treatments there was 2.2 times more $\text{NO}_3\text{-N}$ than $\text{NH}_4\text{-N}$ at V4-6 compared to only 1.3 times at the spring sampling, shows that nitrification is occurring rapidly early in the spring under warm soil conditions. This, of course is a major challenge as nitrification increases the potential for N loss if weather conditions become excessively wet, something relatively common for this region.

As previously mentioned, as the growing season advanced, corn uptake increased (Table 1.9) and as a result, soil $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ decreased. While soil $\text{NH}_4\text{-N}$ was similar between treatments at V10-12, soil $\text{NO}_3\text{-N}$ concentrations for treatments U/U+ and E/U+ were, on average, 57% greater than U and 31% greater than E. Additionally, similar to the trend observed at V4-6, E had greater soil $\text{NO}_3\text{-N}$ at V10-12 compared to U, which demonstrates the controlled N release advantage of E compared to U to protect N from loss until the crop is ready to take it up. At tasseling (R1), soil $\text{NO}_3\text{-N}$ was, on average, 2.2 times greater for U/U+ and E/U+ in comparison to U and E, and soil $\text{NH}_4\text{-N}$ was greater for U/U+ compared to E. The addition of a split fertilization increased N availability in the soil, which in general improved corn grain yield

(Table 1.6), total N uptake (Table 1.7), and profitability (Table 1.8). However, NO₃-N loss (Table 1.5) was not reduced by the inclusion of a split application, which highlights the difficulty of improving environmental outcomes with additional best N management practices when the N fertilizer rate is near the optimum for crop production.

Conclusions

Tile drainage water and NO₃-N load are influenced by precipitation amount and distribution. When excess precipitation occurs, drainage and consequently NO₃-N load increase regardless of N best management practices targeting time and source of N. This is especially concerning as the frequency and intensity of erratic large rain events in the Midwest are predicted to increase and N management tools seem to be insufficient to successfully adapt to climate change. That said, advanced N management practices (split application and ESN) relative to conventional pre-plant practice (U) showed improvements in corn grain yield and N uptake. Our findings indicate that while using N best management practices is directionally correct, it is insufficient to substantially and consistently reduce NO₃-N leaching when N rates are near optimum for crop production. Using an N rate as suggested by university guidelines established through many years of research showed in general that flow-weighted NO₃-N concentrations in drainage water were below the USEPA drinking water standard (10 mg L⁻¹). Historically, University N guidelines have been primarily focused on agronomic outcomes. In the future, N rate studies should be designed to identify the optimum N rate for agronomic and environmental outcomes. Further, these studies should be holistic, focused in integrating other approaches (cropping systems and engineering solutions, to name a few) in conjunction with N best management practices that target various N loss mechanisms, not only NO₃-N leaching.

Table 1.1. Mean monthly and annual air temperature in °C for 2014 to 2020 and the 30-yr normal (1980-2009).

Month	2014	2015	2016	2017	2018	2019	2020	30-year Normal
	°C							
Jan	-13	-7	-9	-8	-10	-12	-9	-10
Feb	-13	-12	-4	-1	-12	-15	-8	-7
Mar	-4	1	4	0	-2	-4	1	-1
Apr	6	9	9	9	0	7	6	7
May	14	14	15	14	18	12	13	15
Jun	20	20	21	21	22	21	23	20
Jul	20	22	22	23	22	23	23	22
Aug	21	20	21	19	21	20	22	21
Sep	16	19	18	18	18	18	16	16
Oct	10	10	10	9	6	7	5	9
Nov	-4	4	6	0	-4	-2	3	0
Dec	-5	-3	-8	-7	-6	-6	-4	-8
Annual	6	8	9	8	6	6	8	7

Table 1.2. Monthly and annual cumulative precipitation (P) and subsurface drainage (D) in millimeters (mm) from 2014 to 2020 and 30-yr normal precipitation (1980-2009).

Month	2014		2015		2016		2017		2018		2019		2020		30-year Normal
	P	D [†]	P	D	P	D	P	D	P	D	P	D	P	D	P
	mm														
Jan	18	--	11	--	8	--	12	--	11	--	12	--	11	--	14
Feb	13	--	5	--	17	--	2	--	16	--	46	--	19	--	13
Mar	25	--	10	0	51	13	10	0	40	0	69	0	73	37	39
Apr	87	--	31	0	85	34	77	1	45	8	150	213	34	3	74
May	46	--	139	24	141	38	152	90	115	27	122	34	88	9	85
Jun	188	--	128	74	66	9	69	2	187	75	60	1	107	15	102
Jul	30	--	96	1	176	86	102	3	157	44	174	56	144	10	92
Aug	94	--	113	2	135	1	125	1	92	2	56	1	97	0	96
Sep	154	--	87	0	134	28	54	0	167	66	153	114	26	0	76
Oct	12	--	41	0	72	7	150	86	71	74	102	21	25	0	51
Nov	13	--	84	26	47	0	2	0	26	0	28	0	39	--	33
Dec	25	--	34	3	29	--	10	--	49	--	39	--	11	--	17
Annual	705	--	779	130	961	216	765	183	976	296	1011	440	674	74	692

[†] Drainage was not measured in 2014

Table 1.3. Mean cumulative subsurface tile drainage from 2015 to 2020 and 6-year mean as affected by N source [urea, ESN, and Urea with the urease inhibitor NBPT (Urea+)] and time of application [pre-plant at 202 kg N ha⁻¹ and split at 67/135 kg N ha⁻¹ (pre-plant at 202 kg N ha⁻¹ and split at 67/135 kg N ha⁻¹ (pre-plant/sidedress at V4 to V6 development stage)].

Treatment§	2015	2016	2017	2018	2019	2020	6-year mean
				mm			
Urea	142	276	173	224	515	68	216a†
ESN	90	145	147	225	330	46	156b
Urea/Urea+	157	226	177	269	458	47	207a
ESN/Urea+	90	176	179	280	434	71	199ab
Mean	114D‡	184C	173CD	273B	442A	62E	

† Means within a column with different lowercase letters are significantly different ($P < 0.05$)

‡ Means within a row with different uppercase letters are significantly different ($P < 0.05$)

§ Statistical analysis of subsurface tile drainage is based on transformed data suggested by boxCox, and back-transformed means are reported.

Table 1.4. Mean annual (A) and before side-dress application (BS) NO₃-N load leached for 2015 to 2020 and 6-year mean as affected by N source [urea, ESN, and Urea with the urease inhibitor NBPT (Urea+)] and time of application [pre-plant at 202 kg N ha⁻¹ and split at 67/135 kg N ha⁻¹ (pre-plant/sidedress at V4 to V6 development stage)].

Treatment	2015		2016		2017		2018		2019		2020		6-year mean	
	A	BS	A	BS	A	BS	A	BS	A	BS	A	BS	A	BS
	kg ha ⁻¹													
Urea	6	1	31	20	24	25	20	4	33	23	6	5	19a†	10
ESN	4	1	16	10	15	9	15	4	18	13	4	4	11b	7
Urea/Urea+	9	1	23	14	24	19	22	4	35	23	4	3	18a	9
ESN/Urea+	5	0.5	16	8	23	17	22	6	32	22	5	4	16a	8
Mean	6C‡	1D	19B	11B	22AB	19A	20B	4C	30A	20A	5C	4C		

† Means within a column with different lowercase letters are significantly different ($P < 0.05$)

‡ Means within a row with different uppercase letters are significantly different ($P < 0.05$)

§ Statistical analysis of NO₃-N load is based on transformed data suggested by boxCox, and back-transformed means are reported.

Table 1.5. Mean annual (A) and before side-dress application (BS) flow-weighted NO₃-N concentration for 2015 to 2020 and 6-year mean as affected by N source [urea, ESN, and Urea with the urease inhibitor NBPT (Urea+)] and time of application [pre-plant at 202 kg N ha⁻¹ and split at 67/135 kg N ha⁻¹ (pre-plant/sidedress at V4 to V6 development stage)].

Treatment	2015		2016		2017		2018		2019		2020		6-year mean	
	A	BS	A	BS	A	BS	A	BS	A	BS	A	BS	A	BS
	mg L ⁻¹													
Urea	5	3	10	13	13	20	9	7	6	7	8	8	8	9
ESN	4	3	11	14	11	13	7	8	6	6	9	9	7	9
Urea/Urea+	6	2	10	15	14	23	8	7	8	8	8	8	9	10
ESN/Urea+	8	1	10	13	14	22	8	8	7	7	7	7	8	8
Mean	6CD‡	2D	10AB	13B	13A	21A	8C	8C	7CD	7C	8BC	8C		

‡ Means within a row with different uppercase letter are significantly different ($P < 0.05$)

§ Statistical analysis of A and BS are based on transformed data suggested by boxCox, and back-transformed means are reported.

Table 1.6. Mean corn yield for different treatments from 2014 to 2020 and 7-year mean as affected by N source [urea, ESN, and Urea with the urease inhibitor NBPT (Urea+)] and time of application [pre-plant at 202 kg N ha⁻¹ and split at 67/135 kg N ha⁻¹ (pre-plant/sidedress at V4 to V6 development stage)].

Treatment	2014	2015	2016	2017	2018	2019	2020	7-year mean
	Mg ha ⁻¹							
Urea	9.3	10.3	9.9	12.2	9.2	10.2	11.0	10.3b†
ESN	10.3	9.9	10.7	13.1	10.8	10.5	12.0	11.0ab
Urea/Urea+	9.1	10.2	10.7	12.3	10.2	11.1	11.6	10.7ab
ESN/Urea+	10.4	10.8	11.1	12.8	10.5	11.2	12.2	11.3a
Mean	9.8C‡	10.3C	10.6BC	12.6A	10.2C	10.7BC	11.7AB	

† Means within a column with a different lowercase letter are significantly different ($P < 0.05$)

‡ Means within a row with different uppercase letter are significantly different ($P < 0.05$)

Table 1.7. Mean total N uptake (plant + grain) in corn for different treatments from 2014 to 2020 and 7-year mean as affected by N source [urea, ESN, and Urea with the urease inhibitor NBPT (Urea+)] and time of application [pre-plant at 202 kg N ha⁻¹ and split at 67/135 kg N ha⁻¹ (pre-plant/sidedress at V4 to V6 development stage)].

Treatment	2014	2015	2016	2017	2018	2019	2020	7-year mean
	kg ha ⁻¹							
Urea	139	151	119	180	144	120	137	142b†
ESN	146	138	130	198	157	145	160	154ab
Urea/Urea+	117	167	129	178	162	147	159	152ab
ESN/Urea+	138	168	137	193	167	151	162	160a
Mean	135CD‡	157B	129D	187A	158B	140BCD	154BC	

† Means within a column with a different lowercase letter are significantly different ($P < 0.05$)

‡ Means within a row with different uppercase letter are significantly different ($P < 0.05$)

Table 1.8. Mean net economic return from 2014 to 2020 and 7-year mean as affected by N source [urea, ESN, and Urea with the urease inhibitor NBPT (Urea+)] and time of application [pre-plant at 202 kg N ha⁻¹ and split at 67/135 kg N ha⁻¹ (pre-plant/sidedress at V4 to V6 development stage)].

Treatment	2014	2015	2016	2017	2018	2019	2020	7-year Mean
				\$ ha ⁻¹				
Urea	1116	1258	1201	1520	1106	1245	1347	1256
ESN	1170	1106	1217	1550	1235	1193	1397	1267
Urea/Urea+	1053	1202	1267	1480	1196	1316	1396	1273
ESN/Urea+	1198	1247	1293	1531	1216	1300	1447	1319
Mean	1134	1203	1245	1520	1188	1264	1397	

Table 1.9. Nitrogen plant uptake (kg N ha⁻¹) during different corn development stages (V4 to R1) for different years and across years as affected by N source [urea, ESN, and Urea with the urease inhibitor NBPT (Urea+)] and time of application [pre-plant at 202 kg N ha⁻¹ and split at 67/135 kg N ha⁻¹ (pre-plant/sidedress at V4 to V6 development stage)].

Sampling	Treatment	2014	2015	2016	2017	2018	2019	2020	Mean
		Kg ha ⁻¹							
V4-6	Urea	12	11	4	5	7	42	11	9a†
	ESN	13	11	4	6	8	36	10	10a
	Urea/Urea+	12	6	3	5	5	19	10	7b
	ESN/Urea+	14	8	4	5	5	21	8	7b
	Mean	13B‡	8CD	3F	5E	6DE	28A	9BC	
V10-12	Urea	120	98	111	107	58	103	75	96
	ESN	142	91	91	145	62	113	83	104
	Urea/Urea+	127	99	95	120	76	93	90	100
	ESN/Urea+	108	100	100	124	69	93	83	98
	Mean	124A	97B	102B	124A	66C	101B	83BC	
R1	Urea	131	117	113	156	87	102	150	122
	ESN	145	129	108	164	91	106	147	127
	Urea/Urea+	133	125	91	167	105	114	130	123
	ESN/Urea+	106	137	104	156	109	119	133	123
	Mean	129BC	127BC	104CD	161A	98D	110CD	140AB	

† Means within a column with a different lowercase letter are significantly different ($P < 0.05$)

‡ Means within a row with different uppercase letter are significantly different ($P < 0.05$)

Table 1.10. Soil nitrate-N, ammonium-N, and total inorganic N (nitrate-N plus ammonium-N) (TIN) content in kg N ha⁻¹ in the top 90 cm of the soil before planting (Spring) and post-grain harvest for different years and across years as affected by N source [urea, ESN, and Urea with the urease inhibitor NBPT (Urea+)] and time of application [pre-plant at 202 kg N ha⁻¹ and split at 67/135 kg N ha⁻¹ (pre-plant/sidedress at V4 to V6 development stage)].

Sampling	Treatment	2014	2015	2016	2017	2018	2019	2020	Mean
		NO ₃ -N							
Spring	Urea	48	88	16	31	18	20	39	30
	ESN	58	92	14	41	19	16	43	32
	Urea/Urea+	58	96	15	32	24	23	47	34
	ESN/Urea+	53	102	16	35	29	21	52	36
	Mean	53B‡	92A	15E	33C	21D	19DE	44B	
		NH ₄ -N							
	Urea	71	19	17	41	39	36	29	30
	ESN	70	22	18	46	42	26	28	30
	Urea/Urea+	83	23	21	43	42	30	25	31
	ESN/Urea+	62	19	21	44	38	26	23	29
	Mean	60A	20D	19D	43B	40B	28C	25C	
		TIN							
		116A	112A	34E	76B	62C	48D	70BC	
		NO ₃ -N							
Post-harvest	Urea	133	33	19	70	19	31	47	37b†
	ESN	158	28	36	78	24	35	78	46ab
	Urea/Urea+	187	23	24	28	29	62	101	45ab
	ESN/Urea+	160	48	31	59	26	42	139	56a
	Mean	157A	30CDE	24DE	47C	24E	39CD	79B	
		NH ₄ -N							
	Urea	27	50	56	18	58	110	84	53
	ESN	27	45	56	22	55	92	79	51
	Urea/Urea+	26	50	57	28	60	98	87	55
	ESN/Urea+	24	53	46	19	52	103	79	50
	Mean	26D	49C	53C	21D	56C	101A	82B	
		TIN							
		183A	81C	80C	63D	81C	142B	168AB	

† Means within a column with a different lowercase letter are significantly different ($P < 0.05$)

‡ Means within a row with different uppercase letter are significantly different ($P < 0.05$)

Table 1.11. Soil nitrate-N, ammonium-N, and total inorganic N (nitrate-N plus ammonium-N) (TIN) content in kg N ha⁻¹ in the top 60 cm of the soil during different corn development stages (V4 to R1) for different years and across years as affected by N source [urea, ESN, and Urea with the urease inhibitor NBPT (Urea+)] and time of application [pre-plant at 202 kg N ha⁻¹ and split at 67/135 kg N ha⁻¹ (pre-plant/sidedress at V4 to V6 development stage)].

Sampling	Treatment	2014	2015	2016	2017	2018	2019	2020	Mean
		NO ₃ -N							
V4-6	Urea	---	146	162	124	83	112	143	116a†
	ESN	---	184	153	149	112	164	121	136a
	Urea/Urea+	---	72	54	55	47	25	56	48b
	ESN/Urea+	---	73	51	60	57	37	56	53b
	Mean		106	84	84	68	62	82	
		NH ₄ -N							
V4-6	Urea	---	28	45	29	45	34	38	36b
	ESN	---	36	48	29	56	52	56	44a
	Urea/Urea+	---	24	38	25	47	30	40	32b
	ESN/Urea+	---	25	37	20	41	35	56	31b
	Mean		27BC‡	41A	25C	47A	36AB	45A	
		TIN							
		---	135	130	111	117	103	131	
		NO ₃ -N							
V10-12	Urea	36	26	28	74	32	36	81	38c
	ESN	102	62	34	118	41	42	121	61b
	Urea/Urea+	105	86	49	121	79	152	145	91a
	ESN/Urea+	130	61	43	88	77	136	172	86a
	Mean	76AB	52BC	34C	87AB	50BC	71AB	122A	
		NH ₄ -N							
V10-12	Urea	26	37	48	42	44	49	29	37
	ESN	32	49	45	47	44	56	45	43
	Urea/Urea+	26	38	38	103	47	62	30	42
	ESN/Urea+	33	35	33	99	41	57	32	40
	Mean	28E	39CD	40BCD	60A	43BC	53AB	32DE	
		TIN							
		108ABC	94BC	78C	156A	97BC	132AB	156A	
		NO ₃ -N							
R1	Urea	42	15	19	19	7	42	36	20b
	ESN	144	47	31	25	12	27	39	30b
	Urea/Urea+	103	48	33	110	39	79	53	53a
	ESN/Urea+	147	73	41	85	30	74	70	58a
	Mean	85A	34BC	27BC	42AB	16C	41AB	42AB	
		NH ₄ -N							
R1	Urea	27	26	33	30	42	22	33	31ab
	ESN	45	28	27	29	40	31	32	29b
	Urea/Urea+	35	27	34	48	47	32	30	33a
	ESN/Urea+	33	29	30	26	40	23	31	30ab
	Mean	30B	27B	30B	30B	42A	31B	30B	
		TIN							
		112A	62C	58C	74BC	60C	72BC	73BC	

† Means within a column with a different lowercase letter are significantly different ($P < 0.05$)

‡ Means within a row with different uppercase letter are significantly different ($P < 0.05$)

**Chapter 2: Nitrogen Application Timing and Source Affects Nitrate Leaching and
Nitrous Oxide and Ammonia Emissions in Continuous Corn**

Overview

Nitrate (NO_3) leaching, and nitrous oxide (N_2O) and ammonia (NH_3) emissions are the main pathways for nitrogen (N) loss in agriculture. A field experiment was conducted near Lamberton Minnesota during 2018 to 2020, in a poorly drained clay soil under continuous corn to evaluate the effects of traditional (pre-plant application of urea) and advanced N management practices (enhanced efficiency fertilizers and split applications) on i) N losses ($\text{NO}_3\text{-N}$ leaching, $\text{N}_2\text{O-N}$ denitrification, and $\text{NH}_3\text{-N}$ volatilization); ii) corn grain yield; iii) soil and plant N content and iv) crop-system N balance. Treatments were: 202 kg N ha^{-1} as urea applied before planting (U), 202 kg N ha^{-1} as polymer coated urea (PCU; ESN) applied before planting (E), 135 kg N ha^{-1} as urea with urease inhibitor (Agrotain) sidedressed at development stage V6 with 67 kg N ha^{-1} applied before planting as either urea (U/U+) or ESN (E/U+). Nitrogen losses were mostly influenced by weather. In general, when excess precipitation occurred, especially right after N fertilizer application, $\text{NO}_3\text{-N}$ and $\text{N}_2\text{O-N}$ losses increased. Conversely, excess precipitation after sidedress fertilizer application reduced $\text{NH}_3\text{-N}$ loss because precipitation incorporated the fertilizer into the soil. Timing of N application (pre-plan vs split) did not affect $\text{N}_2\text{O-N}$ loss, but E reduced losses in wet years. Similarly, across years, E reduced $\text{NH}_3\text{-N}$ losses by 90% compared to E/U+, 88% compared to U/U+, and 81% compared to U. Flow-weighted $\text{NO}_3\text{-N}$ concentrations were similar between treatments with a trend for smaller concentrations with E and were below the maximum drinking water standard of 10 mg L^{-1} . Corn grain yield and total nitrogen uptake (TNU) were lower for U (1 Mg ha^{-1} lower and 23 kg ha^{-1} lower) compared to the average of the other treatments. Nitrogen balance calculations varied considerably between treatments and years. This is a poor approach to calculating N efficiency or impact on environmental quality because the large TNU values overshadowed the contributions of the other parameters included in the nitrogen balance. Split applications of N can increase corn yield compared to pre-plant urea (U) but were not efficient in reducing N losses. The fact that E reduced N losses to the environment, especially in wet years, while outperforming U in corn grain yield and producing similar grain

yields to the split application treatments indicates that E may be a viable alternative to meet the need for improved agronomic production and mitigation of N loss to the environment.

Introduction

Nitrogen (N) is an important nutrient needed in great quantities to increase plant growth. Sources of N in agriculture include synthetic fertilizer, manure, biologically fixed N, plant residues, atmospheric deposition, and mineralized N. Unfortunately, N availability for crops is affected by many variables, making it necessary to find more efficient sources of N and ways to manage it. The most common source used in agriculture is synthetic fertilizer, supplying about 50 percent of all N required for global food production (Smil, 1999). Without N fertilizer, it would be impossible to produce high yields for many crops. Thus, synthetic N fertilizer has an important role in food production, especially as the world population is expected to rise to near 10 billion by 2050 (FAO, 2009).

One of the most widely used sources of synthetic fertilizer in the US is urea (USDA, 2019). When applied to the soil, urea converts quickly to ammonium and then to nitrate (NO_3). The NO_3 form is easily lost through leaching if precipitation exceeds the capacity of the soil to store water. Once NO_3 is leached, it can reach groundwater used for drinking or be discharged through tile drainage to water bodies. Nitrate in excess can accelerate algae blooms, leading to hypoxia zones and negatively impacting marine life. The largest hypoxia zone in the US occurs every summer in the Gulf of Mexico as nutrient loading, primarily from Midwest agriculture lands, occurs when excess precipitation induces NO_3 leaching, especially during the spring (EPA, 2008).

Nitrogen can also be lost to the atmosphere as nitrous oxide (N_2O) gas produced through denitrification when soils become saturated with water. Nitrous oxide is a greenhouse gas that has a 100-year average global warming potential, which is approximately 300 times more potent than carbon dioxide (Myhre and Shindell, 2013). The major sources of N_2O in agriculture are synthetic and organic fertilizers (EPA, 2019). In 2019, N_2O represented approximately 7% of all the US

greenhouse gas emissions, with agriculture being responsible for 75% of that amount (EPA, 2019).

Additionally, ammonia (NH_3) volatilization occurs when urea fertilizers are surface-applied and not sufficiently incorporated into the soil. Ammonia can also produce significant impacts to the environment, such as nutrient imbalances and eutrophication, and it can also cause human health concerns (NOAA, 2000; EPA, 2021). Agriculture activities are also the major source of NH_3 emissions in the US, accounting for approximately 60 to 85% of NH_3 emissions (USDA, 2014). A meta-analysis including 824 observations concluded that about 18% (ranging from 0.9 to 64%) of the applied synthetic fertilizer N was lost as NH_3 (Pan et al., 2016). Hence, it is imperative to improve N management practices and understand how N reacts in the landscape to enhance crop N use efficiency and minimize environmental degradation.

One of the most common management practices in the Midwest US is the application of urea only at or before planting. Nonetheless, a few advanced N management practices have been suggested due to their potential to synchronize N availability with N demand by the crop. Such practices could reduce the amount of N present early in the season when N uptake by crops is low and chances of losses are high due to typical wet conditions. Practices such as split application and enhanced-efficiency N fertilizers are among the practices that could achieve this synchronization. Split application consists of applying a portion of N fertilizer later in the season when crop N requirements are high. However, studies have shown inconsistent results. For instance, some studies showed that split applications reduced NO_3 (Bakhsh et al., 2002), N_2O (Drury et al., 2012; Fernández et al., 2016) and NH_3 loss (Ma et al., 2010), while others found no benefits of split applications on NO_3 (Christianson and Harmel, 2015), N_2O (Venterea and Coulter, 2015) and NH_3 loss (Pan et al., 2016).

Along with application time, enhanced-efficiency N fertilizers such as polymer coated urea (PCU) may help reduce environmental pollution from N. This type of fertilizer is designed to slowly release N over time. Studies have shown the potential benefits of PCU in reducing NO_3

(Wilson et al., 2010), N₂O (Hyatt et al., 2010; Fernández et al., 2015; Nash et al., 2015) and NH₃ loss (Nash et al., 2015; Liu et al., 2019). However, others have observed a lack of reduction in NO₃ (Nash et al., 2014), N₂O (Nash et al., 2012) and NH₃ (Zavaschi et al., 2014) loss with PCU. A potential reason why studies show seemingly contradictory results is that the various N loss pathways are interrelated. Conditions that increase one loss pathway may minimize another. Unfortunately, while there are studies investigating the effects of split application or PCU on a specific N loss pathways mechanism, studies simultaneously measuring NO₃, N₂O, and NH₃ losses are lacking.

The objectives of this study were to evaluate traditional (pre-plant application of urea) and advanced N management practices (ESN and split applications) in a poorly drained soil in a continuous corn cropping system on i) N losses (NO₃-N leaching, N₂O-N denitrification, and NH₃-N volatilization); ii) corn grain yield; iii) soil and plant N content and iv) N balance.

Material and Methods

Site Description and Experimental Design

The experiment was conducted from 2018 to 2020 at the University of Minnesota Southwest Research and Outreach Center (SWROC) near Lamberton, MN (44°14'11.0" N 95°18'41.7" W), on a poorly drained Webster-Canisteo clay loam soil (fine-loamy, mixed, superactive, mesic Typic Endoaquolls and fine-loamy, mixed, superactive, calcareous, mesic Typic Endoaquolls, respectively). Selected surface soil characteristics for the top 15 cm are presented in Table 2.1. The research was in a continuous corn cropping system established in 2014 and continued during the length of the study. Agronomic practices and corn hybrids used in the study are presented in chapter 1.

The study was set up in sixteen bottomless lysimeter plots (9.1 x 18.2 m, each with 12 0.76 m spacing corn rows) isolated from each other with a 12-mil plastic sheet to a depth of 1.8 m that was trenched around plot borders to prevent lateral water flow. A full description of these plots is given in Zhao et al., 1998. Concisely, subsurface tile lines were installed in 1994 in each

of the sixteen plots. The perforated plastic tile lines (0.1 m diameter) were installed 1 m deep and 1.5 m away from the plot width boundaries, simulating a tile line spacing of 33 m. Perforated tile lines were connected to nonperforated pipe that emptied drainage water into monitoring wells that housed equipment for two plots to measure water flow and obtain a flow-proportionate water sample for nitrate-N analysis.

The study was set up in a randomized complete block design with four treatments replicated four times. All treatments received each spring a total of 202 kg N ha⁻¹ but were divided in traditional and advanced N management practices. The traditional treatment was urea (46-0-0) (N-P-K) applied before planting (U). Three advanced treatments included the PCU fertilizer ESN (44-0-0, Nutrien, Saskatoon, SK Canada) applied before planting (E), and two split treatments that received two-thirds of the total N (135 kg ha⁻¹) at development stage V6 as urea treated with urease inhibitor Agrotain® (N-(n-butyl)-thiophosphoric triamide / Koch Fertilizer LLC, Wichita, KS) after receiving one-third (67 kg ha⁻¹) of the total N before planting as either urea (U/U+) or ESN (E/U+). All fertilizer was broadcast applied by hand and the N applied before planting was incorporated by a field cultivator at a depth of 0.15 m. The study was immediately planted after the fertilizer was tilled into the soil. Pre-plant applications were done on 31 May 2018, 3 June 2019, and 11 May 2020 and split applications were done on 21 June 2018, 8 July 2019, and 15 June 2020. The fertilizer rate was selected to mimic farmers' practice in the region. This rate was within the Maximum Return to N (MRTN) rate range (170 to 202 kg N ha⁻¹) suggested by the University of Minnesota guidelines (Kaiser et al., 2020).

Nitrate Leaching, Nitrous Oxide Denitrification, and Ammonia Volatilization

The monitoring wells were equipped with submersible pumps (model 237, Liberty Pumps, Bergen, NY). Flow drainage was recorded every 5 minutes by using Hobo® State dataloggers (Onset Computer Corporation) that were connected to 25 mm DLJ100C water flow meter (Daniel L Jerman Co., Inc., Hackensack, NJ). Composite water samples were collected weekly or more frequently dictated by precipitation patterns. Water samples were analyzed for NO₃-N using the

spectrophotometric determination method (Doane and Horwáth, 2003). When laboratory results values were below the detection limit (0.05 mg L^{-1}), half the detection limit value was used (Yanai et al., 2018). Nitrate-N load (kg ha^{-1}) was calculated by multiplying $\text{NO}_3\text{-N}$ concentration (mg L^{-1}) by drainage volume (mm) measured between sampling days. Annual flow-weighted $\text{NO}_3\text{-N}$ concentrations (mg L^{-1}) were estimated by dividing cumulative $\text{NO}_3\text{-N}$ load by annual flow. Water data from one of the plots was not used during the entire length of the study due to unreliable drainage caused by clogging of the tile line. In 2018, episodic excessive precipitation in June and September resulted in more tile drainage than precipitation as result of overland flow. For those events, estimations were used to calculate drainage flow as described in chapter 1. In 2019, water data from two plots were not used due to electrical issues with the sampling equipment.

Ammonia volatilization measurements were done in 2019 and 2020. The NH_3 volatilized was captured using a modified static ammonia sorber technique (Alexander et al., 2021). Two semi-open static collection chambers were installed in the middle of two rows after fertilization. The chamber consisted of a PVC cylinder (0.45 m in height and 0.2 m in diameter), which was pressed into the soil to a depth of 0.06 m and capped in a way that protected the inside from precipitation but allowing air movement. Polyurethane plastic foam sorbers were washed with 0.73 M phosphoric acid (H_3PO_4), rinsed two times with double deionized water, and soaked in a solution with ~35 ml of 0.73 M H_3PO_4 / 5% glycerol (v/v) solution. Two treated sorbers were installed in each chamber, 0 and 0.15 m away from the top of the chamber. The sorber on the bottom captured NH_3 from the soil and the top sorber captured ambient NH_3 . The bottom foam collection and replacement was target at 2, 4, 7, 14, 21, and 28 days after pre-plant and split fertilization. In 2019, the second set of measurements ended 30 days after the split application due to wet conditions that prevented field visits on the scheduled date. In 2019 sampling collection happened between June 6 and August 5, and in 2020 between May 12 and July 13. After collection, the sorbers were soaked overnight with 280 ml 2 M KCl solution and poured

into 30 ml vials that were stored at -20°C until analysis for ammonium (NH₄-N) concentrations. Cumulative NH₃-N (kg ha⁻¹) was calculated by adding emissions from planting to the time of the split N application and for 28 to 30 days after the split application.

Fluxes of N₂O from the soil were measured using non-steady-state stainless steel chambers (0.3 m wide by 0.5 m long) described by (Venterea et al., 2005). Flux sampling was conducted two to three times per week for at least 21 weeks (21 weeks in 2018, 23 weeks in 2019, and 23 weeks in 2020) after fertilizer application and less frequently thereafter, with a total of 27 (2018), 37 (2019) and 42 (2020) sampling dates during the growing seasons. One chamber anchor was inserted in each plot centered between two corn rows, with the short side parallel to the corn row. The anchors remained in the same place throughout the season. Sampling was generally done during the morning when the soil temperature in the upper 0.1 m was close to its daily mean value to minimize diurnal variability (De Klein & Harvey, 2012). At each sampling, chambers were secured onto anchors with binder clips, and gas samples were collected at 0, 0.5, 1, and 1.5 h after chamber deployment using a polypropylene syringe. The 12 mL-samples were immediately transferred to glass vials sealed with butyl rubber septa and analyzed within 2 weeks using a headspace autosampler (Teledyne Tekmar) connected to a 5890A gas chromatograph (Hewlett-Packard) equipped with an electron capture detector. Fluxes of N₂O gas were calculated from the rate of change in chamber N₂O concentration using the restricted quadratic regression procedure (Parkin et al., 2012) and the chamber bias correction method (Venterea, 2010). When quadratic regression was not met, linear regression was used instead. Cumulative growing season area scaled N₂O emissions (*a*N₂O) were calculated using daily N₂O fluxes (*d*N₂O) by trapezoidal integration (Parkin and Venterea, 2010). Indirect N₂O emissions were also estimated by multiplying cumulative NO₃⁻ leaching by 1.1% and by multiplying NH₃-N emissions by 1.0%, as suggested by Hergoualc'h et al. (2019). Total cumulative N₂O emissions (*t*N₂O) were the result of the sum of direct plus NO₃⁻-N and NH₃ indirect N₂O emissions. Cumulative yield scaled N₂O emissions (*y*N₂O) were also calculated by dividing *a*N₂O by grain yield.

Soil and Plant Measurements

Weather data was obtained from a weather station near the study site (0.4 km away). Soil volumetric water content (VWC) and temperature from 0 to 5, 5 to 10, 10 to 20, 20 to 30, and 30 to 60 cm depth increments were measured continuously during the growing season using TM-5 sensors and Em50 digital data loggers (Decagon Devices Inc).

Soil samples were collected at 0.15 m depth at each N₂O gas sampling day and oven-dried at 105 °C to determine moisture content. Soil cores were collected before planting and after harvest from 0-30, 30-60, and 60-90 cm depth increments using a hydraulic probe. Soil cores samples were also collected with a hand-held soil probe at development stage V6, V10, and R1 from 0-30 and 30-60 cm depth increments. Soil samples were oven dried at 35°C until constant weight, ground, and analyzed for ammonium (NH₄⁺-N) (Bremner and Mulvaney, 1982) and NO₃⁻-N (Gelderman and Beegle, 2012). Total inorganic nitrogen (TIN) was calculated by adding soil NH₄⁺-N and NO₃⁻-N concentrations.

Whole plants were collected at development stages V6, V10, R1, and R6. Twelve basal stalk samples, 20 cm each, were collected 15 cm above the soil surface at R6. The whole plants collected at R6 were partitioned into vegetative tissues and cobs and grain. Corn harvest was done in the four middle rows of the plots using a combine. Plant and grain samples were oven dried at 63°C until constant weight and weighed. Harvested grain and stover samples were further ground and analyzed for total N using the combustion method (Horneck & Miller, 1998). Basal stalks were analyzed for NO₃-N using the 2% Acetic Acid Extraction method (Gavlak et al., 2005). Total plant N uptake at different development stages was the product of dry biomass and N content. Total N uptake (TNU) was calculated as the sum of grain N removal and aboveground biomass at R6.

Nitrogen Balance

Nitrogen balance was calculated based on the procedure by Sainju (2017) as follows:

$$\text{Nitrogen balance} = N \text{ inputs} - N \text{ outputs} - \text{changes in soil total N}$$

where N inputs were N fertilization and atmospheric N deposition and N outputs were crop N removal (harvest grain N + R6 biomass N), and N losses ($\text{NO}_3\text{-N}$ from leaching, $\text{NH}_3\text{-N}$ from volatilization, direct + indirect $\text{N}_2\text{O-N}$ from denitrification) and changes in soil total N were the difference between soil total inorganic N at the end of each year (after harvest) by soil total inorganic N at the beginning of each year (before planting). Atmospheric N deposition estimates in the calculation were done from measurements conducted in 2019 and 2020 near the study site (Pagliari, personal communication). In this calculation N inputs from non-symbiotic N fixation and crop seed N, and N outputs from surface runoff and plant senescence were not included because they were likely relatively small (Sainju, 2017) and constant across treatments. A positive nitrogen balance indicates N is gained and a negative value indicates N is loss in the system.

Statistical Analysis

Data were analyzed using linear mixed-effects models and the restricted maximum likelihood method in the lme4 package (Bates, et al., 2014) using R (R Core Team, 2020) to test for differences between treatments. Treatment was considered a fixed effect and block a random effect. For the combined year analysis (3-year mean), when interaction between year and treatment was not significant, year was treated as a random effect, and separate analysis were done within each year using only treatment as a fixed factor. Assumptions of normality and homogeneity of variance (Levene's test) were assessed. When transformations were necessary to achieve normality, boxCox plot from the car package (Fox, 2019) was used to determine the appropriate transformation. Back transformed data is presented. Treatment differences were determined using Tukey's pairwise comparisons with the emmeans package (Lenth, 2018). Statistical difference was declared when $P < 0.05$.

Results and Discussion

Weather, Subsurface Drainage, and Soil Environment

The mean annual air temperature was 6°C in 2018, 6°C in 2019, and 8°C in 2020 and were within 2°C of the 30-year normal (Fig. 2.1a). The growing season mean air temperature was 15°C in all years of the study and were within 1°C of the 30-year growing season normal. Monthly air temperature differences bigger than 3°C from normal during the growing season were observed in April 2018 (7°C below normal) and October 2020 (4°C below normal). From June to September air temperatures were within 3°C of the normal in all years (Fig. 2.1a). Soil temperature was generally slightly lower than air temperature during the growing seasons (Fig. 2.1a).

Annual precipitation ranged from 676 mm in 2020 to 1010 mm in 2019, whereas the 30-year annual normal was 694 mm. The 2018 total growing season (April to October) precipitation was 45% greater than the 30-year normal of 576 mm, with the months of May to July, and September being excessively wetter than normal. April was drier than normal, and August was near normal. In 2019, total precipitation during the growing season was 42% greater than normal, with most monthly precipitation exceeding normal, but with June and August being drier than normal. The growing season precipitation in 2020 was 10% lower than normal, but as observed in the other years, July was wet (52 mm above the 92 mm normal). April, September, and October 2020 were dry, with approximately half the normal precipitation, while May, June and August had near normal precipitation.

Overall precipitation amounts and distribution were variable during the growing seasons and between years, which greatly influenced cumulative drainage water (Fig. 2.1b). On average, total annual drainage was 28% (11% in 2020 to 44% in 2019) of the total annual precipitation and 43% (36% in 2020 to 56% in 2019) of this drainage occurred between April and June. Overall, greater than normal precipitation resulted in greater drainage and lower than normal precipitation resulted in little or no drainage. Additionally, evapotranspiration seemed to influence subsurface drainage. In March 2020, when the crop was not planted yet, greater than normal precipitation (34 mm greater than normal) associated with greater than normal temperature (2°C above), resulted in 50% of the total annual drainage. Snow melt and precipitation in April 2019, when

evapotranspiration is low, resulted in 48% of the total annual drainage. In July, when crop evapotranspiration is high, greater than normal precipitation (52 mm in 2020 to 82 mm in 2019) resulted on average on 14% of the total drainage (13% in 2019 to 15% in 2018). Conversely, in September and October, when crop evapotranspiration is low, 47% (2018) and 31% (2019) of the total annual drainage occurred. On average, few precipitation events ranging from 2 to 11 days during each year were responsible for 88% of the total drainage. In 2018, 6 events lasting 4 to 11 days of intermittent precipitation with a total of 515 mm caused 93% of the total drainage. In 2019, 4 events lasting 2 to 8 days of intermittent precipitation totaling 441 mm resulted in 77% of the total drainage. In 2020, 4 events lasting 2 to 4 days totaling 213 mm of intermittent precipitation caused 95% of the total drainage.

Precipitation also largely influenced soil volumetric water content (VWC). The top layer (0-5 cm) was usually drier than the other layers during the entire season in all years (Fig 2.1c). Also, at the same depth, in 2018 and 2020, VWC was more variable and greatly influenced by precipitation. The mean annual VWC of the top layer was $0.26 \text{ m}^3 \text{ m}^{-3}$ in 2018, $0.27 \text{ m}^3 \text{ m}^{-3}$ in 2019, and $0.16 \text{ m}^3 \text{ m}^{-3}$ in 2020. Volumetric water content changes at the soil surface level can be especially important for gaseous N losses, where greater VWC can potentially means increased N emissions. Moreover, annual VWC means from the subsurface layers (5 to 60 cm) ranged from 0.31 to $0.32 \text{ m}^3 \text{ m}^{-3}$ in 2018, from 0.27 to $0.29 \text{ m}^3 \text{ m}^{-3}$ in 2019, and from 0.20 to $0.26 \text{ m}^3 \text{ m}^{-3}$ in 2020. The deeper layers (from 5 to 60) were usually wetter and followed similar patterns during the entire season, except for 2020, where the 5-10 cm depth was wetter compared to all other depths. However, compared to other years, at the same depth, VWC annual mean was lower in 2020 ($0.26 \text{ m}^3 \text{ m}^{-3}$) than in 2018 ($0.32 \text{ m}^3 \text{ m}^{-3}$) and 2019 ($0.28 \text{ m}^3 \text{ m}^{-3}$).

Corn Yield and Plant N Uptake

Progressive N accumulation across each of the growing seasons followed the typical pattern described by Abendroth et al. (2011) (Table 2.2). Plant N uptake differences between treatments were only observed at V6 in 2019 and for the 3-year mean (Table 2.2). The treatments receiving

all the N fertilizer before V6 (U and E) accumulated greater N amounts in the biomass than treatments that received a third of the total N fertilizer rate during this period (U/U+ and E/U+). Even though plant sampling and fertilizer application were targeted at V6, they were done near V7 in 2019, which may explain the higher N content in biomass in 2019 compared to 2018 and 2020. Regardless, plant N uptake at V10 and R1 were not different between treatments, indicating that a split application can be as effective as a pre-plant application to supply crop N needs. In other words, even though greater potential for immobilization of N in continuous corn often leads farmers to greater rates of N fertilization early in the season to avoid deficient supply (relative to corn after soybean, for example), these data indicate that a small amount of pre-plant N (67 kg N ha^{-1}) was sufficient until sidedress (Table 2.2). Ultimately, however, TNU was lower for U compared to the other treatments in 2019, 2020 and for the 3-year mean, and a similar trend was observed in 2018 (Table 2.2). Averaged across years, TNU was 13 to 16% lower for U compared to the other treatments. Our results showed a clear advantage with the advanced N management practices, especially ESN combined with a split application to supply N during the entire growing season.

Differences in basal stalk $\text{NO}_3\text{-N}$ were observed only in 2018 with greater concentrations for U/U+ in comparison to U and E (Table 2.2) and for the combined years where concentrations greater for U/U+ compared to all the other treatments (Table 2.2). Regardless, all values were considered marginal at best, signaling that N was deficient for the crop (Kaiser and Fernandez, 2020). While this study has only one N rate, other studies conducted in close proximity at the same time, which included five to seven N rates to determine the optimum yield and N rate, showed yield levels and optimum N rates that were comparable to this study (Fernandez, personal communication). This indicates that the basal stalk nitrate test by itself may have limited utility as an after the season evaluation tool. Others have observed similar limitations (Rubin et al, 2016).

Although treatment differences in grain yield occurred only in 2020, all years showed a similar trend that was reflected in the differences observed for the 3-yr mean where the traditional

treatment U produced lower yield (10.1 Mg ha^{-1}) than the three advanced management treatments (Table 2.2). As previously discussed in chapter 1, ESN fertilizer and split N applications are often considered to be costly and reduce profitability. However, these practices did not affect, and in fact slightly improved, profitability compared to U in our study (See chapter 1).

Nitrous Oxide

Daily mean N_2O flux ranged from <1 to $8177 \text{ ug N}_2\text{O-N m}_2 \text{ h}^{-1}$ in 2018, 0.31 to $2608 \text{ ug N}_2\text{O-N m}_2 \text{ h}^{-1}$ in 2019, and <1 to $1070 \text{ ug N}_2\text{O-N m}_2 \text{ h}^{-1}$ in 2020 (Fig 2.2). The annual daily N_2O flux mean for the combined years was greater for U ($49 \text{ ug N}_2\text{O-N m}_2 \text{ h}^{-1}$) compared to U/U+ ($29 \text{ ug N}_2\text{O-N m}_2 \text{ h}^{-1}$), E ($28 \text{ ug N}_2\text{O-N m}_2 \text{ h}^{-1}$), and E/U+ ($25 \text{ ug N}_2\text{O-N m}_2 \text{ h}^{-1}$). Similar range (12 to $31 \text{ ug N}_2\text{O-N m}_2 \text{ h}^{-1}$ or 0.20 to $0.74 \text{ mg N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$) of magnitudes of annual daily N_2O flux mean to the ones observed in this study were previously reported (Ussiri et al., 2009). The yearly fluxes averaged across treatments were greater in the wetter years, 2018 ($40 \text{ ug N}_2\text{O-N m}_2 \text{ h}^{-1}$) and 2019 ($35 \text{ ug N}_2\text{O-N m}_2 \text{ h}^{-1}$), than in the drier 2020 ($23 \text{ ug N}_2\text{O-N m}_2 \text{ h}^{-1}$).

A total of 1650 daily mean N_2O fluxes were measured from 2018 to 2020, and most of them (1641) ranged from 0 to $2000 \text{ ug N}_2\text{O-N m}^{-2} \text{ h}^{-1}$. Similar values were found by Fernández et al. (2016), who reported daily mean N_2O fluxes ranging from <1 to $1540 \text{ ug N}_2\text{O-N m}^{-2} \text{ h}^{-1}$. There were nine very high daily mean N_2O fluxes ranging from 2007 to $8177 \text{ ug N}_2\text{O-N m}^{-2} \text{ h}^{-1}$. Five of these values were observed eight days after split fertilizer application in 2018 (2121 to $8177 \text{ ug N}_2\text{O-N m}_2 \text{ h}^{-1}$) and one of the values thirty-five days after split fertilizer application in 2019 ($2007 \text{ ug N}_2\text{O-N m}_2 \text{ h}^{-1}$), all for treatments U/U+ and E/U+. The other three high fluxes were observed for treatment U thirteen days after fertilization in 2018 ($3874 \text{ ug N}_2\text{O-N m}_2 \text{ h}^{-1}$), twenty-one days after fertilization in 2019 ($2608 \text{ ug N}_2\text{O-N m}_2 \text{ h}^{-1}$) and sixteen days after split fertilization in 2019 ($2022 \text{ ug N}_2\text{O-N m}_2 \text{ h}^{-1}$). These high N_2O fluxes coincided with precipitation events ranging from 12 to 77 mm. Even though such high daily fluxes of N_2O are rarely observed, they are not without precedent (Venterea and Rolston, 2000). These high values were included in the analysis presented in this chapter, but a similar analysis without the high values is shown in Appendix 3.

Overall, temporal patterns of daily mean N₂O flux during the three growing seasons were similar, with most substantial (above baseline levels) emissions occurring within 5 to 6 weeks from fertilizer application during June and July. However, the emission amounts varied between years. Soil N₂O fluxes were low at the beginning of each season, right before and after planting, which happened in late May in 2018, early June in 2019 and early May in 2020. Substantial emissions occurred soon (within a few days) after application and continued for approximately 6 weeks. Fluxes normally returned to baseline levels and remained low from August to October. Daily N₂O flux measurements were not collected from 16 June to 24 June 2018 and 27 June to 7 July 2019 due to extreme precipitation (114 mm in 2018 and 101 mm in 2019) that resulted in flooding and restricted access to the field. Cumulative N₂O-N emissions from 2018 to 2020 is shown in Appendix 4. Because normally six to eight precipitation events induced most of the N₂O emissions during the study, and measurements were not collected during these critical periods in 2018 and 2019, it is likely that the total fluxes in the study are a conservative amount. This is, unfortunately, a limitation of soil N₂O flux measurement with static chambers.

The significant year by treatment interaction for *a*N₂O and *y*N₂O illustrates that N₂O emissions were substantially impacted by the amount and distribution of precipitation in relation to when fertilizer was applied and not as much by the timing of fertilizer application (pre-plant or split), but ESN can reduce emissions (Table 2.3 and Fig. 2.3). The year by treatment interaction for *a*N₂O and *y*N₂O was explained by ESN substantially reducing emissions relative to U in wet years (2018 and 2019) while no differences occurred in 2020 between these two treatments (or the other two split application treatments) because of less precipitation and better distribution. Within 30 days of the pre-plant fertilizer application there were 17 daily precipitation events totaling 187 mm in 2018 and 14 precipitation events totaling 119 mm in 2019, whereas only 9 precipitation events totaling 80 mm in 2020. Precipitation distribution is also important, within 60 days of pre-plant fertilization for 2018, 2019, and 2020, respectively there were 20, 21, and 13 days with consecutive precipitation events that lasted 2 to 7 days each, and for no precipitation

intervals the average number of days was 2.6, 2.3, and 3.2. It is clear that compared to U, E protected N from loss during the persistent wetter conditions in 2018 and 2019. Other studies have reported the potential benefits of ESN in wet years in the reduction of N₂O-N loss (Fernández et al., 2015). Further, the year by treatment interaction clearly showed that split applications may produce no benefit relative to U if substantial precipitation follows the sidedress application, as was the case in 2018 but not in 2019 and 2020. Within 20 days of the sidedress application there were 11 precipitation events totaling 149 mm in 2018, compared to only 9 events (85 mm) in 2019 and 7 events (60 mm) in 2020. Precipitation within 7 to 10 days after broadcast sidedress applications is important to move the fertilizer into the root-zone for crop uptake and to minimize the potential for ammonia volatilization losses, even when using a urease inhibitor. However, it was observed that within 7 days of sidedress, 5 days of precipitation totaling 70 mm in 2018 was sufficient to induce greater N₂O loss relative to 2019 (18 mm, 3 days of precipitation) and 2020 (20 mm, 1 day of precipitation). While logistically in commercial farming it is not always possible to sidedress at the best time, guiding the application based on a 5-to-7-day weather forecast can be beneficial.

Ammonia Volatilization

Ammonia emissions in 2019 followed a similar temporal pattern than 2020. However, losses were considerably smaller in magnitude in 2020 likely due to differences in weather conditions between the two years (Table 2.4, Fig. 2.4). Higher air temperature from day 1 to 5 (14°C greater) and from day 6 to 10 (7 °C greater) after pre-plant fertilization in 2019 compared to 2020 likely increased NH₃-N loss. Also, five days after split fertilization a 20 mm of precipitation in 2020 likely solubilized and moved the fertilizer into the soil, thus potentially decreasing NH₃ volatilization. Conversely, light precipitation (9 mm) three days after split fertilization in 2019 likely was sufficient to solubilize but not incorporate the fertilizer into the soil, thus increasing the potential for NH₃-N volatilization.

In 2019, for the first 28 days after fertilizer application $\text{NH}_3\text{-N}$ emissions for U increased continuously until it plateaus (Fig. 2.4). On the other hand, the full rate of ESN showed a small amount of NH_3 accumulation, similar to the split application treatments that had received only one-third of the fertilizer N. At the end of the 28-day period, the cumulative $\text{NH}_3\text{-N}$ volatilization mean for the advanced treatments E, U/U+, and E/U+ were approximately 80% lower than U (Table 2.4). After split N fertilizer application, NH_3 emissions continually increased during the entire sampling time for split treatments U/U+ and E/U+ (Fig. 2.4). The cumulative $\text{NH}_3\text{-N}$ volatilization at the end of the 30-day period after split fertilization was on average 98% greater for treatments U/U+ and E/U+ compared to U and E (Table 2.4). The total $\text{NH}_3\text{-N}$ loss during the 58 days of measurement were on average 77% greater for the split treatments (U/U+ and E/U+) compared to the single pre-plant applications (U and E) (Table 2.4).

Like 2019, for the first 28 days after fertilizer application NH_3 emissions for U increased continuously until it plateaus (Fig. 2.4). Cumulative $\text{NH}_3\text{-N}$ volatilization at the end of the 28-day period after pre-plant fertilizer were on average 90% lower for treatments E, U/U+ and E/U+ compared to U (Table 2.4). Unlike 2019, where substantial $\text{NH}_3\text{-N}$ emissions for treatments U/U+ and E/U+ started soon after fertilizer application and continued for the entire measurement period, in 2020, emissions increased during the 7-to-21-day period (Fig. 2.4). The cumulative $\text{NH}_3\text{-N}$ losses at the end of the 28-day period after split fertilization were on average 91% greater for treatments U/U+ and E/U+ compared to U and E (Table 2.4), which is similar to the results observed in 2019. Total cumulative $\text{NH}_3\text{-N}$ volatilization during the 56 days of measurement were on average 84% greater for treatments U, U/U+, and E/U+ compared to E (Table 2.4).

When averaged across two years, cumulative $\text{NH}_3\text{-N}$ volatilization at the end of the 28-day period after pre-plant fertilizer was on average 72% greater for treatment U compared to E. At the end of the second measurement period after split fertilization, $\text{NH}_3\text{-N}$ volatilization was on average 96% greater for the split treatments (U/U+ and E/U+) compared with the pre-plant treatments (U and E). Over the entire sampling period averaged across years, pre-plant ESN

reduced $\text{NH}_3\text{-N}$ losses by 90% compared to E/U+, 88% compared to U/U+, and 81% compared to U. The reduction in $\text{NH}_3\text{-N}$ volatilization observed with E compared to the traditional management practice (U) was similar to Nash et al. (2015) who reported a 73% reduction and Xu et al. (2013) who reported a 72% reduction. Lower volatilization losses of pre-plant ESN compared to U and the split application treatments indicate that E could be an important N source for production agriculture that meets both productivity and environmental protection goals.

Nitrate Leaching

Although drainage water, $\text{NO}_3\text{-N}$ load, and flow-weighted $\text{NO}_3\text{-N}$ concentrations were previously discussed in chapter 1 as part of a longer-term study, the 2018 to 2020 data are presented here to complete the discussion of N loss and N balance (Table 2.5). As previously described in chapter 1 and in this chapter, drainage amounts were greatly influenced by precipitation amounts and distribution. There were no differences in drainage between treatments during this three-year period, though the overall trend showed, as discussed in chapter 1, lower drainage for E than the other treatments (Table 2.5). Lower $\text{NO}_3\text{-N}$ load with E could be reflective of overall lower drainage, though despite similar drainage in 2018 $\text{NO}_3\text{-N}$ load for E was 15 kg ha^{-1} compared to 20 kg ha^{-1} for U, which may hint at a potential advantage of E over U. Because $\text{NO}_3\text{-N}$ load is greatly influenced by drainage amounts, flow-weighted $\text{NO}_3\text{-N}$ concentration, that account for differences in drainage flow, will be discussed in more detail. Flow-weighted $\text{NO}_3\text{-N}$ concentrations were not different between treatments, though there was a trend for lower flow-weighted $\text{NO}_3\text{-N}$ concentration for treatments with ESN. Furthermore, $\text{NO}_3\text{-N}$ concentrations were below the maximum drinking water standard of 10 mg L^{-1} set by USEPA (USEPA, 2009) in all three years of the study. Nonetheless, the study showed lack of benefits in using advanced N management practices (E, U/U+, and E/U+) over the traditional N practice (U). Cumulative $\text{NO}_3\text{-N}$ load from 2018 to 2020 is shown in Appendix 5. Other studies also observed no advantages when split application was used in comparison to single spring application (Jaynes, 2013; Christianson and Harmel, 2015). The lack of treatment difference in this study could be the result

of compounded variability as drainage and concentration measurements, each with their inherent variability, are combined in the calculation. This challenge has been observed by others (Randall and Vetsch, 2005). Moreover, in this study, N rate used was within the MRTN rate recommended by university guidelines (Kaiser et al., 2020), which demonstrates that when the right rate of N is applied, other N management practices, such as source or time of application, might provide limited additional benefit to reduce NO₃-N loss.

Soil N

Across years and treatments, soil NO₃-N increased substantially from 26 kg ha⁻¹ in the spring (pre-treatment) to 83 kg ha⁻¹ at V10 as a result of fertilizer applications (Table 2.6). As corn uptake increased throughout the growing season, soil NO₃-N considerably decreased to 33 kg ha⁻¹ at R1 (Table 2.2). Afterwards, soil NO₃-N slightly increased by post-harvest to 40 kg ha⁻¹, probably due to nitrification of mineralized N. Soil NH₄-N followed a similar pattern, but the magnitude of increase from spring to V10 was much smaller. Soil NH₄-N increased from 32 kg ha⁻¹ at spring (pre-treatment) to 43 kg ha⁻¹ at V10, slightly decreased to 35 kg ha⁻¹ at R1, and substantially increased again to 80 kg ha⁻¹ by post-harvest, likely as the result of organic matter mineralization after R6 when the crop no longer takes up N.

Soil NO₃-N at V6 was on average 2.6 times greater for U and E compared U/U+ and E/U+ due to the different amounts of fertilizer applied at pre-plant, total amount (202 kg ha⁻¹) for U and E and only one third (67 kg ha⁻¹) of the total N applied to the split treatments (Table 2.6). Soil NH₄-N at V6 was greater for E compared to the other treatments, even though the same amount of fertilizer was applied for U, which demonstrates the slow release of N present in ESN. Furthermore, a consistent trend across most years for greater NO₃-N may indicate less N loss with E relative to U in early spring (Table 2.6). For instance, excess precipitation after pre-plant fertilizer substantially induced NO₃-N leaching in 2018, but soil NO₃-N was numerically greater for E compared to U.

At V10, soil $\text{NO}_3\text{-N}$ was on average 2.3 times greater for U/U+ and E/U+ compared to U and E due to application of the remaining two thirds of the total fertilizer N done at V6 in the split treatments. At the same development stage, soil $\text{NH}_4\text{-N}$ was similar between treatments. However, like soil N amounts at V6, there was a trend across most years for greater soil $\text{NH}_4\text{-N}$ for treatment E compared to the other treatments, which demonstrates the controlled N release of ESN. At R1, on average, soil $\text{NO}_3\text{-N}$ was 2.4 times greater for U/U+ and E/U+ compared to U and E and soil $\text{NH}_4\text{-N}$ was similar between treatments. In general, the split application increased N availability in the soil, which improved corn grain yield and TNU (Table 2.2). However, N losses (Table 2.3 for $\text{N}_2\text{O-N}$; Table 2.4 for $\text{NH}_3\text{-N}$; and Table 2.5 for $\text{NO}_3\text{-N}$) were not reduced by the inclusion of a split application, especially in wet years, which demonstrates that split application might not be an efficient strategy to reduce N losses.

At post-harvest, soil $\text{NO}_3\text{-N}$ was 1.8 times greater for the split treatments (U/U+ and E/U+) compared to U, whereas E was similar to all other treatments, which was consistent across years (Table 2.6). Similar amounts of soil $\text{NO}_3\text{-N}$ at post-harvest were found by Spackman et al., (2019) and Clark et al., (2020). This pattern relates to the fact that treatment U produced lower crop yields and TNU than the other treatments (Table 2.2) due to lower soil N availability for plant uptake.

Nitrogen Balance

The N balance from 2018 to 2020 ranged from -93 to 29 kg ha^{-1} (Table 2.7). Positive N balance (N gain) was observed in 2018 for all treatments and negative N balances (N loss) were observed in most of the treatments in 2019 and 2020, except for U in 2020 (Table 2.7). Ideally, there should be no net gain or loss of N if this nutrient is recycled efficiently. However, this is rarely observed (Sainju, 2017).

Across years, N balance was lower for U compared to U/U+ and E/U+ (Table 2.7). However, this was mostly due to TNU, that accounted for 89% of the total N outputs (averaged across years and treatments) and was on average 14% lower for U compared to other treatments

(averaged across years). Furthermore, the sum of the N losses was greater for E/U+ compared to E and changes in soil N were similar between treatments. Nonetheless, since N balance was greatly influenced by TNU, inferences about how N losses and changes in soil N affected N balance are limited. Estimation of N balance has been suggested as a tool to help improve N use efficiency and reduce the potential for N losses (Pieri et al., 2011; Sainju, 2017). However, our findings demonstrate limitations of the N balance use, because TNU overshadowed differences from other parameters used in the calculation.

Despite the fact that N balance was not a good indicator of treatment performance and N impact on the environment, ultimately the study clearly showed that E overall reduced $\text{NO}_3\text{-N}$ leaching and $\text{NH}_3\text{-N}$ relative to U and split applications and E reduced $\text{N}_2\text{O-N}$ relative to U while split treatments produced intermediate results. This combined with N uptake and grain yield being better for E and the split treatments relative to U, demonstrates that there are better alternatives to U that need to be adopted more widely. Applying E is overall the best alternative because it produced as good of yield level as the split treatments and consistently reduced N losses, especially in wet years.

Conclusions

While N balance calculations provided little benefit as indicator of treatment performance and environmental quality, this study clearly showed that N loss of $\text{NO}_3\text{-N}$, $\text{N}_2\text{O-N}$, and $\text{NH}_3\text{-N}$ was mostly influenced by weather conditions, especially precipitation amount and distribution. When precipitation excess occurred, especially soon after fertilizer application, $\text{NO}_3\text{-N}$ and $\text{N}_2\text{O-N}$ loss increased. Conversely, excess precipitation reduced $\text{NH}_3\text{-N}$ after split application due to fertilizer incorporation by precipitation. Overall, advanced N management practices increased corn yield and TNU compared to the traditional management practice U. However, reduction in $\text{N}_2\text{O-N}$ and $\text{NO}_3\text{-N}$ loss was only observed in wet years when the advanced practice E was used compared to other treatments. Furthermore, E reduced $\text{NH}_3\text{-N}$ loss in all years. Our findings indicate that there

are better N management practices than the traditional U, such as E. Moreover, despite the generalized view by agronomists that split-N applications are superior to pre-plant applications to protect the environment, our findings demonstrate that while split fertilizer applications increased grain yield, they were not effective in reducing N losses to the environment relative to U. Despite the lower N losses and greater yield benefits associated with ESN, the higher cost of this source often deters farmers from using it more widely. Based on the results from this study, ESN use could have important benefits to reduce the impact of N fertilizers on the environment while maintaining high grain productivity. Additionally, future studies should be focused on evaluating the use of different rates of ESN and urea to determine what the ideal blend of these products should be to meet the goal of reducing N losses while maintaining or increasing grain yield and net economic return.

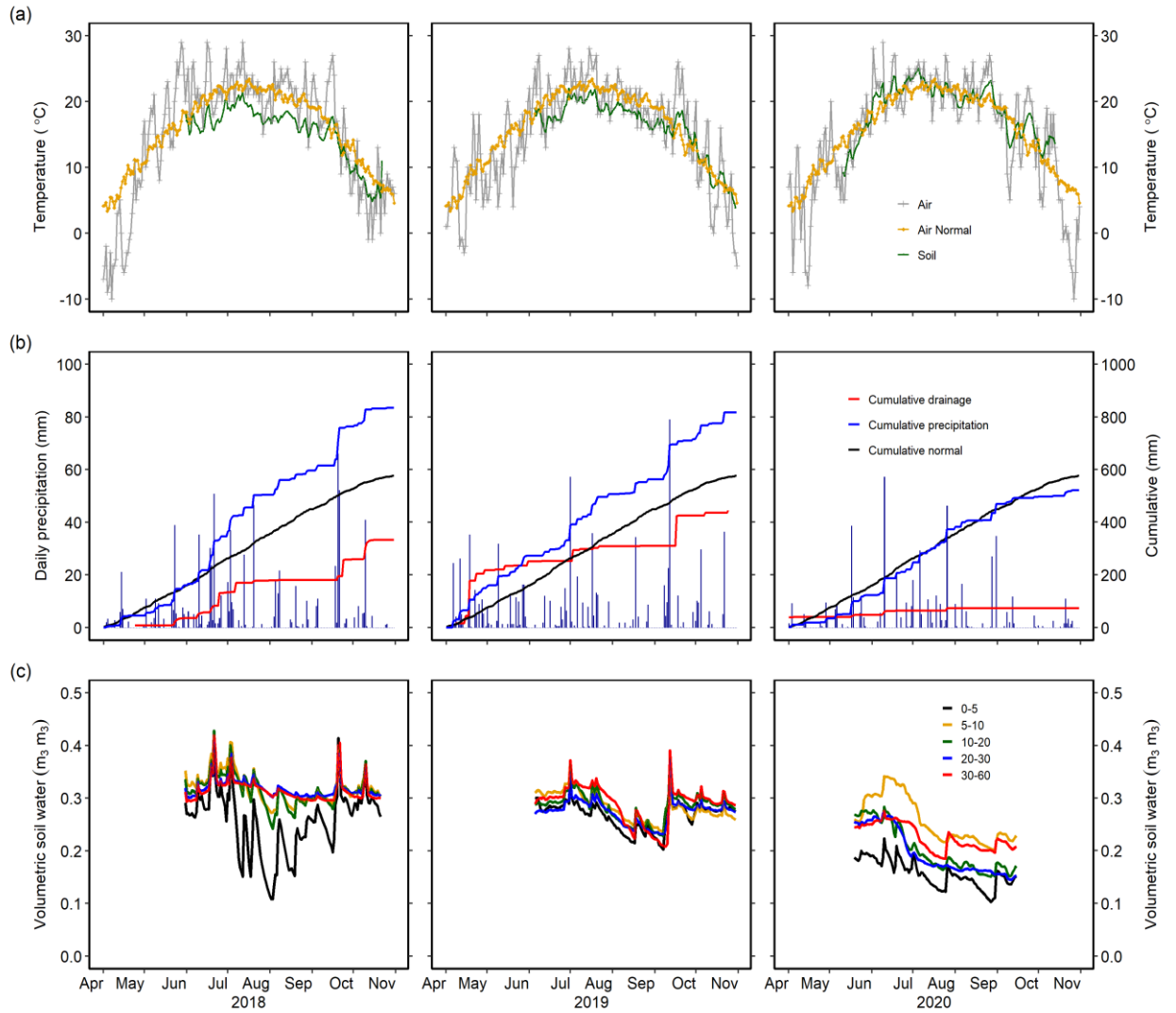


Figure 2.1. Mean daily soil, air, and 30-year normal air temperature (1980-2009) (a), cumulative drainage and precipitation and daily precipitation (b), volumetric soil water content from 0 to 60 cm (c) during 2018 to 2020.

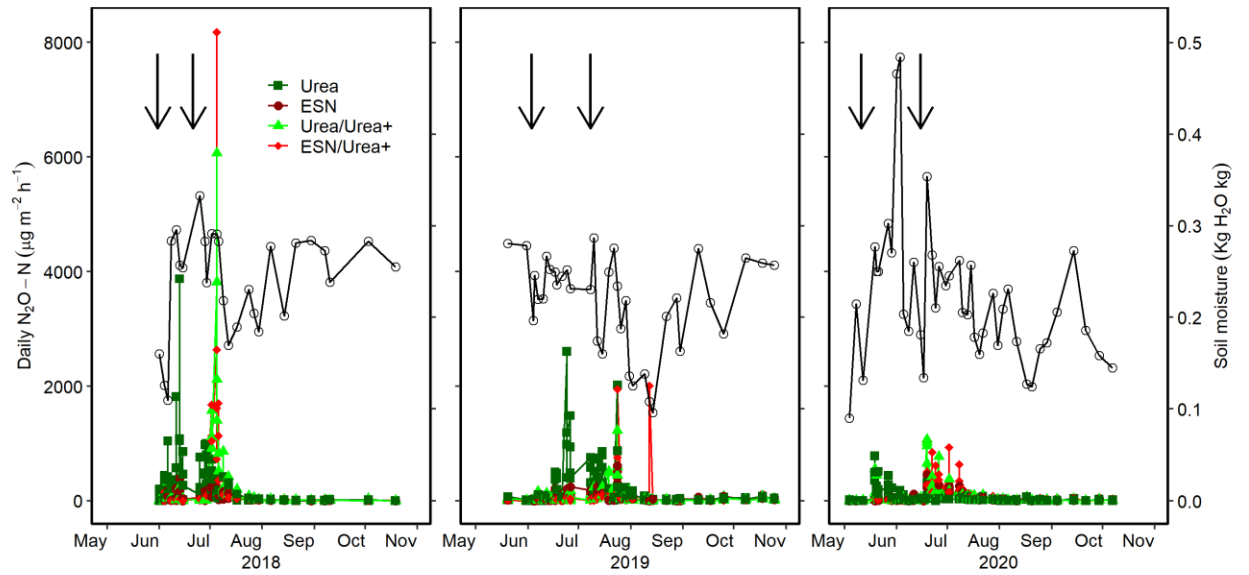


Figure 2.2. Daily N_2O-N emissions in response to treatment for 2018 to 2020 and soil moisture from the top layer (0-15 cm) for 2018 to 2020 (black line with black open circles). Downward pointing indicates the pre-plant and split fertilizer application dates.

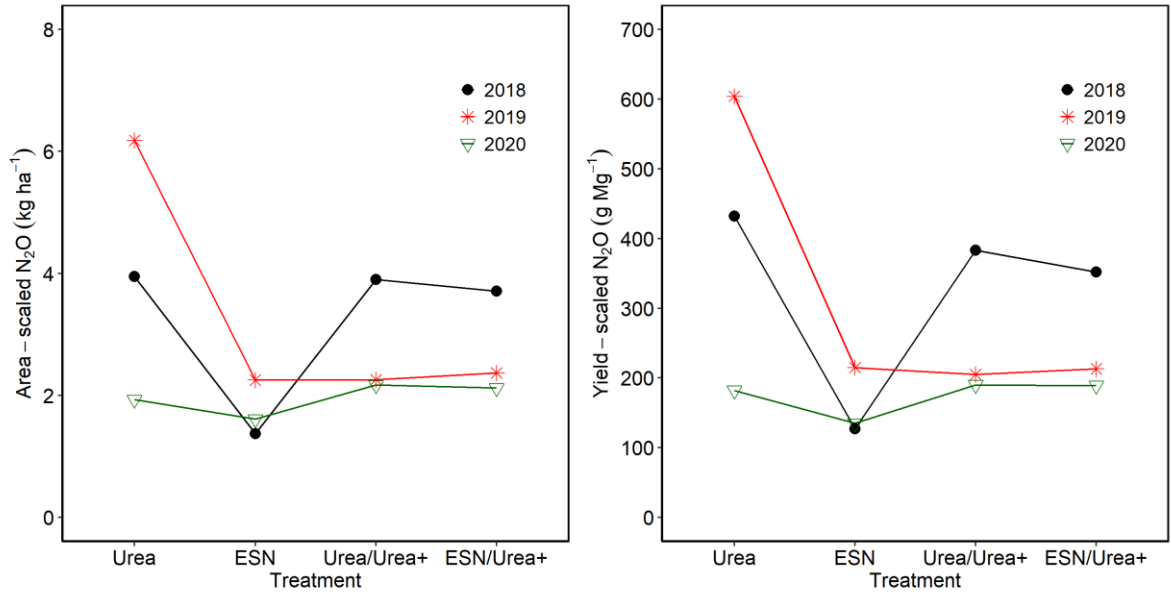


Figure 2.3. Year by treatment interaction for area-scaled N₂O-N and yield-scaled N₂O-N emissions.

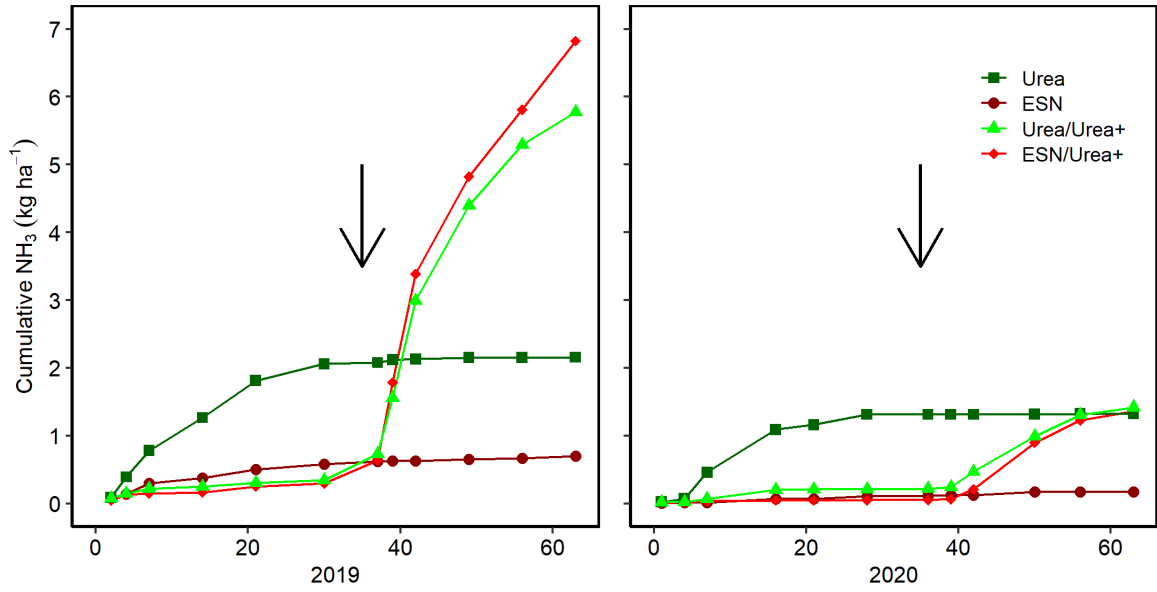


Figure 2.4. Cumulative NH₃-N volatilization loss as influenced by treatment over a 64-day period starting at pre-plant fertilizer application for 2019 and 2020. Downward pointing arrows indicate the split fertilizer application date.

Table 2.1. Phosphorus, potassium, organic matter and soil pH for top 15-cm depth for the 4-year mean (2017 to 2020).

Year	P [†]	K	OM	pH
	mg kg ⁻¹	mg kg ⁻¹	g kg ⁻¹	
Mean	18 (12)	196	46	8

[†] Bray P (Olsen P)

Table 2.2. Mean plant N uptake at V6, V10 and R1, total nitrogen uptake (TNU), basal stalk NO₃-N and grain yield from 2018 to 2020 and 3-year mean as affected by N source [urea, ESN, and Urea with the urease inhibitor NBPT (Urea+)] and time of application [pre-plant at 202 kg N ha⁻¹ and split at 67/135 kg N ha⁻¹ (pre-plant/sidedress at V4 to V6 development stage)].

Year	Treatment	Plant N uptake			TNU‡	Basal stalk nitrate	Grain Yield
		V6	V10	R1			
					kg N ha ⁻¹	mg N kg ⁻¹	Mg ha ⁻¹
2018	Urea	7	58	87	144	209b†	9.2
	ESN	8	62	91	157	85b	10.8
	Urea/Urea+	5	76	105	162	629a	10.2
	ESN/Urea+	5	69	109	167	342ab	10.5
2019	Urea	42a	103	102	120b	129	10.2
	ESN	36a	113	106	145a	245	10.5
	Urea/Urea+	19b	93	114	147a	613	11.1
	ESN/Urea+	21b	93	119	151a	241	11.2
2020	Urea	11	75	150	137b	161	11.0b
	ESN	10	83	147	160a	106	12.0a
	Urea/Urea+	10	90	130	159a	427	11.6ab
	ESN/Urea+	8	83	133	162a	201	12.2a
3-year Mean	Urea	14a	79	113	134b	126b	10.1b
	ESN	14a	86	115	154a	138b	11.1a
	Urea/Urea+	9b	87	116	156a	552a	11.0a
	ESN/Urea+	9b	82	120	160a	249b	11.3a

† Numbers within a column and year with different letters are significantly different ($P < 0.05$).

‡ Total nitrogen uptake (TNU) is the sum of plant N uptake at R6 and harvest grain N.

§ Statistical analysis presented are based on transformed data suggested by boxCox, and back-transformed means are reported.

Table 2.3. Least square means of selected N₂O-N response variables and significance of F values for fixed sources of variation and their interactions.

	Direct N ₂ O emissions		Direct + Indirect N ₂ O emissions
	Area-scaled N ₂ O Kg N ha ⁻¹	Yield-scaled N ₂ O g N Mg ⁻¹ grain ⁻¹	Area-scaled N ₂ O Kg N ha ⁻¹
Year (Y)			
2018	3.0	270	3.2
2019	2.9	240	3.3
2020	2.0	167	2.0
Treatment (T)			
Urea	3.8	386	4.0
ESN	1.6	148	1.8
Urea/Urea+	2.6	240	2.8
ESN/Urea+	2.5	226	2.8
Interaction			
Y*T	<0.05†	<0.05	<0.05

† Numbers within a column and variable with a different lowercase letter are significantly different.

§ Statistical analysis presented are based on transformed data suggested by boxCox, and back-transformed means are reported.

Table 2.4. Cumulative NH₃-N loss for two 28-day periods after pre-plant and sidedress fertilizer applications and as a total across measurement periods for 2019, 2020, and the 2-year mean as affected by N source [urea, ESN, and Urea with the urease inhibitor NBPT (Urea+)] and time of application [pre-plant at 202 kg N ha⁻¹ and split at 67/135 kg N ha⁻¹ (pre-plant/sidedress at V4 to V6 development stage)].

Treatment	28 days after pre-plant application			28 days after split application			Total NH ₃ †		
	2019	2020	2-year mean	2019	2020	2-year mean	2019	2020	2-year mean
	Kg ha ⁻¹								
Urea	1.8a‡	1.3a	1.6a	0.1b	0.1b	0.1b	2.2b	1.3a	1.6a
ESN	0.5b	0.1b	0.3b	0.1b	0.1b	0.1b	0.7b	0.2b	0.3b
Urea/Urea+	0.3b	0.2b	0.2b	5.3a	1.0a	2.3a	5.8a	1.2a	2.6a
ESN/Urea+	0.3b	0.1b	0.1b	6.5a	1.2a	2.8a	6.8a	1.2a	2.9a

† Total NH₃ is the sum of cumulative emissions collected during the two sampling periods. In 2019, the final sampling was 30 days after sidedress application.

‡ Numbers within a column with a different lowercase letter are significantly different ($P < 0.05$).

§ Statistical analysis presented are based on transformed data suggested by boxCox, and back-transformed means are reported.

Table 2.5. Mean annual tile water drainage, NO₃-N load leached, and flow-weighted NO₃-N concentration for 2018 to 2020 and 3-year mean as affected by N source [urea, ESN, and Urea with the urease inhibitor NBPT (Urea+)] and time of application [pre-plant at 202 k g N ha⁻¹ and split at 67/135 kg N ha⁻¹ (pre-plant/sidedress at V4 to V6 development stage)].

Treatment	Drainage				NO ₃ -N Load				Flow-weighted			
	2018	2019	2020	Avg	2018	2019	2020	Avg	2018	2019	2020	Avg
	mm				kg ha ⁻¹				mg L ⁻¹			
U	224	515	68	246	20	33a†	6	19a	8.8	6.3	8.0	7.8
E	225	330	46	188	15	18b	4	12b	6.9	5.9	8.6	7.2
U/U+	269	458	47	234	22	35a	4	18a	8.4	8.1	8.2	8.2
E/U+	280	434	71	256	22	32a	6	18a	8.1	7.4	6.6	7.4

† Numbers within a column with a different lowercase letter are significantly different ($P < 0.05$).

§ Statistical analysis of Drainage, NO₃-N load, and Flow-weighted are based on transformed data suggested by boxCox, and back-transformed means are reported.

Table 2.6. Soil nitrate-N and ammonium-N for pre-treatment (0-90 cm), in season (V6, V10, and R1; 0-60 cm) and post-harvest (0-90 cm) timings as affected by N source [urea, ESN, and Urea with the urease inhibitor NBPT (Urea+)] and time of application [pre-plant at 202 kg N ha⁻¹ and split at 67/135 kg N ha⁻¹ (pre-plant/sidedress at V4 to V6 development stage)].

Year	Treatment	Pre-treatment		V6		V10		R1		Post-harvest	
		NO ₃ ⁻	NH ₄	NO ₃ ⁻	NH ₄	NO ₃ ⁻	NH ₄	NO ₃ ⁻	NH ₄	NO ₃ ⁻	NH ₄
kg ha ⁻¹											
2018	Urea	18	39	83	45	32	44	7	42	19	58
	ESN	19	42	112	56	41	44	12	40	24	55
	Urea/Urea+	24	42	47	47	79	47	39	47	29	60
	ESN/Urea+	29	38	57	41	77	41	30	40	26	52
2019	Urea	20	36	112	34	36	49	42	22	31	110
	ESN	16	26	164	52	42	56	27	31	35	92
	Urea/Urea+	23	30	25	30	152	62	79	32	62	98
	ESN/Urea+	21	26	37	35	136	57	74	23	42	103
2020	Urea	39	29	143	38	81	29	36	33	47	84
	ESN	43	28	121	56	121	45	39	32	78	79
	Urea/Urea+	47	25	56	40	145	30	53	30	101	87
	ESN/Urea+	52	23	56	56	172	32	70	31	139	79
3-year mean	Urea	24	35	106a†	38b	42b	39	19b	36	27b	84
	ESN	23	32	120a	54a	58b	46	20b	33	36ab	76
	Urea/Urea+	27	32	40b	38b	116a	44	47a	37	49a	82
	ESN/Urea+	31	29	47b	38b	115a	41	47a	35	46a	78

† Means within a column with a different lowercase letter are significantly different ($P < 0.05$).

Table 2. 7. Total N inputs and outputs, change in soil N and N balance for 2018 to 2020 and 3-year mean as affected by N source [urea, ESN, and Urea with the urease inhibitor NBPT (Urea+)] and time of application [pre-plant at 202 kg N ha⁻¹ and split at 67/135 kg N ha⁻¹ (pre-plant/sidedress at V4 to V6 development stage)].

Year	Treatments	Total N inputs	Total N outputs	Change in soil	N balance
2018	Urea	221	171	21	29
	ESN	221	175	19	28
	Urea/Urea+	221	194	23	4
	ESN/Urea+	221	199	11	11
2019	Urea	221	155	85	-20
	ESN	221	161	85	-25
	Urea/Urea+	221	181	108	-68
	ESN/Urea+	221	192	98	-70
2020	Urea	221	145	63	13a†
	ESN	221	166	86	-31ab
	Urea/Urea+	221	167	116	-62ab
	ESN/Urea+	221	171	143	-93b
3-year mean	Urea	221	157	56	7a
	ESN	221	167	63	-10ab
	Urea/Urea+	221	180	82	-42bc
	ESN/Urea+	221	188	84	-51c

† Means within a column with a different lowercase letter are significantly different ($P < 0.05$)

Chapter 3: Conclusions

We found that N losses were mostly influenced by weather conditions, especially precipitation distribution and amount. When excess precipitation occurred, especially soon after fertilizer application, $\text{NO}_3\text{-N}$ and $\text{N}_2\text{O-N}$ losses increased. In contrast, under these same conditions, $\text{NH}_3\text{-N}$ loss decreased due to precipitation-induced fertilizer incorporation into the soil. Overall, while the advanced N management E/U+ increased grain yield by 10%, TNU by 18% and net economic return by 5% compared to U, the use of split application did not reduce N losses to the environment. Conversely, the advanced N management practice of pre-plant ESN reduced N losses in wet years relative to U and the split application treatments, produced comparable yields to the split application treatments and similar net economic return to the traditional management practice, despite the higher cost of ESN relative to urea. Furthermore, this study found that N balance was not a good indicator to assess environmental quality performance (N loss to the environment) of treatments, as total N uptake overshadowed differences from other parameters used in the calculation.

A few limitations with regards to sample collection and study design were identified and should be taken into consideration for future studies. One of the main issues was that some plots produced more drainage water than others. Ideally, study sites with the same problem should be randomized by drainage amount. We also experienced data loss due to power outages and rodent damage. Additionally, there were a few instances when nitrous oxide sampling was not possible due to extreme wetness of the field. The awareness of such issues is crucial for future researchers aiming to perform similar studies. Also, reliable automated sample and data collection systems should be considered to ensure consistency and avoid issues like the ones found herein.

Regardless of the challenges and complexities encountered, this study is well worth it, and we hope it serves to inspire other researchers to take a more integrative approach to measuring agronomic performance and losses to the environment in relation to weather conditions. The uniqueness of this study is the measurement of the most important N loss

pathways in agriculture, which allowed for a more comprehensive understanding of N loss. Because of it, we were able to identify that among the practices investigated, pre-plant ESN was the most efficient to reduce N losses to the environment, especially in wet years. This shows that ESN functions as it was designed to be a controlled-release N based on soil temperature and moisture. This demonstrates the importance of applying new technologies and continue to fine new and better ones to mitigate the negative impacts of N fertilizer to the environment. We encourage research institutions and companies to explore new technologies that take weather conditions into account as they develop new fertilizers. Further, an important consideration to improve adoption by end-users is to develop effective technologies that add minimally to the cost of the product.

Despite the lower N losses and greater yields associated with ESN, the higher cost of this fertilizer keeps farmers from using it more widely. Future studies should focus on evaluating the use of different blends of urea with ESN to find a balance between N loss reduction and optimal productivity and profitability. Furthermore, this study also found that $\text{NO}_3\text{-N}$ loss reduction was not observed when rates near optimum for crop production are used. These rates are based on University of Minnesota guidelines established through many years of research. In the future, N rate studies should be designed to identify the optimum N rate of different blends of urea and ESN (or other alternatives) not only for agronomic but also for environmental outcomes. Nonetheless, studies, including ours, have demonstrated that the use of 4 R's (right rate, right source, right time, and right place) practices alone are not enough to reduce N losses to the environment to pristine conditions as existed before commercial agriculture. Future studies should be holistic, focused on integrating N best management practices in conjunction with other practices such as, but not limited to, controlled drainage structures, recycling of drainage water which can allow the use of the saved water for irrigation, cover crops, crop rotation, and reduced tillage, which have shown not only benefits in the reduction of N losses to the environment, but

also improved soil health, decreased soil and nutrient losses by erosion and runoff, and increased productivity.

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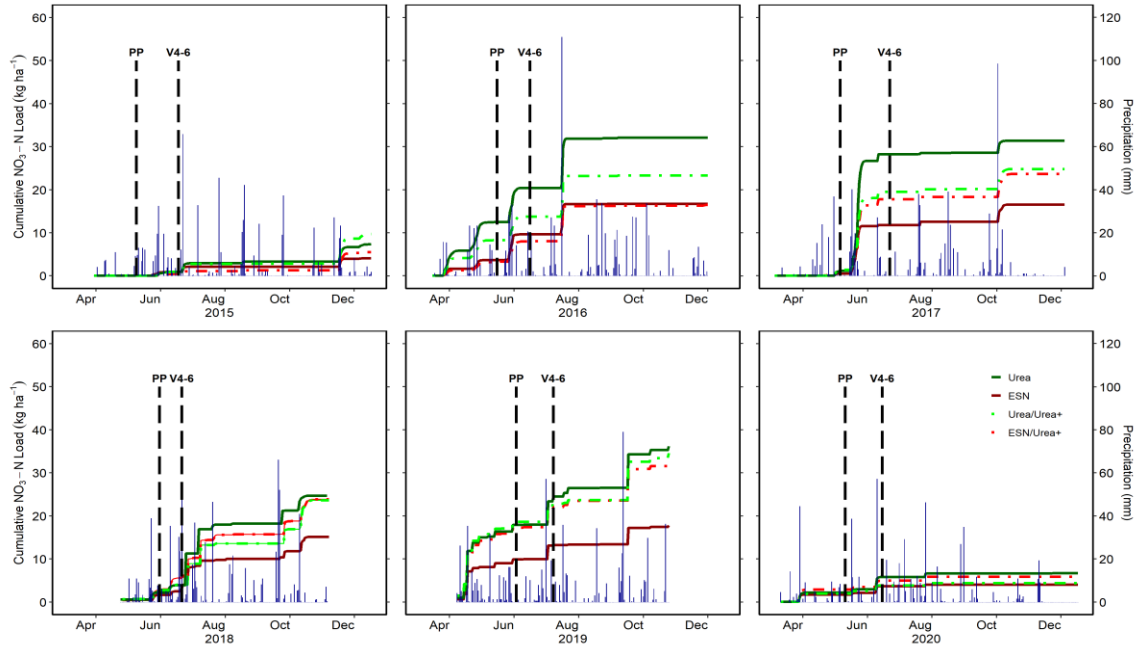
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Appendix

Appendix 1. Mean annual NO₃-N concentrations from water samples for 2015 to 2020 and 6-year mean as affected by N source [urea, ESN, and Urea with the urease inhibitor NBPT (Urea+)] and time of application [pre-plant at 202 kg N ha⁻¹ and split at 67/135 kg N ha⁻¹ (pre-plant/sidedress at V4 to V6 development stage)].

Treatment	2015	2016	2017	2018	2019	2020	6-year mean
	mg L ⁻¹						
Urea	9	13	20	8	8	9	10
ESN	9	14	12	7	7	6	8
Urea/Urea+	9	13	19	8	9	9	10
ESN/Urea+	8	12	19	7	8	6	9
Mean	8BC‡	12AB	17A	7C	8BC	7C	

‡ Means within a row with different uppercase letter are significantly different ($P < 0.05$)

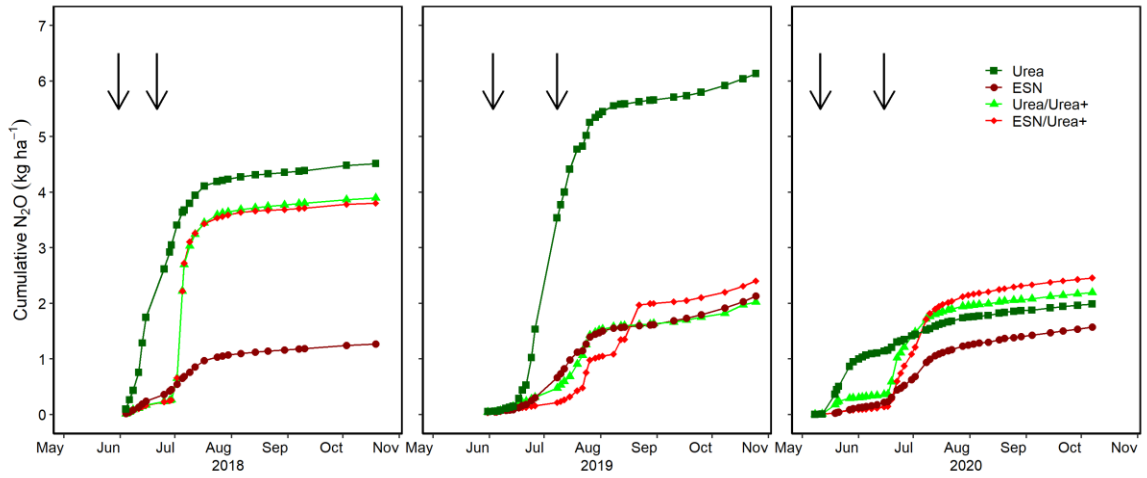


Appendix 2. Season-long cumulative NO₃-N load and daily precipitation (vertical bars) for 2015 to 2020. Pre-plant treatments Urea and ESN (solid lines) and split treatments Urea/Urea with the urease inhibitor NBPT (Urea+) and ESN/Urea+ (dashed lines). Vertical dashed lines represent pre-plant (PP) and split (V4-6) fertilizer applications.

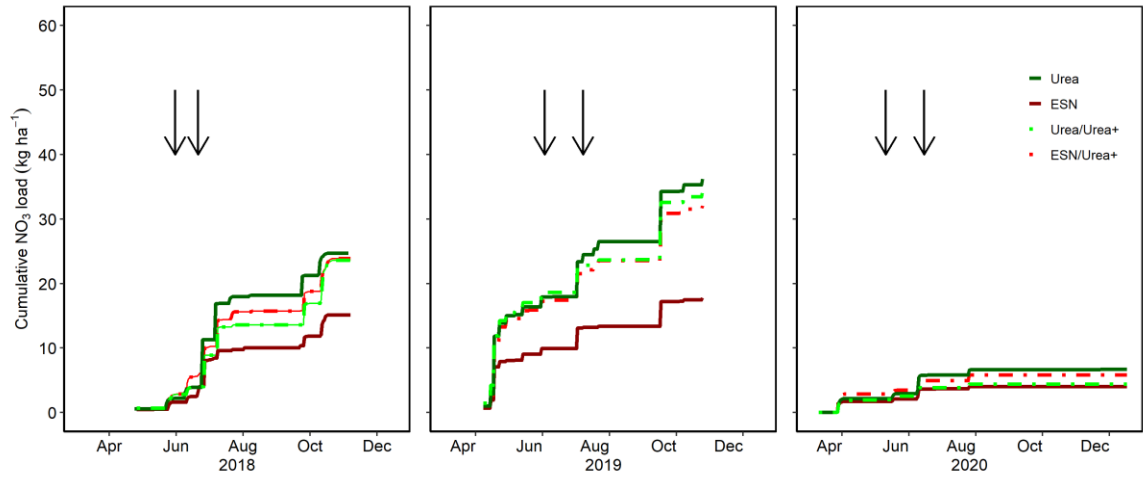
Appendix 3. Least square means of selected N₂O-N response variables without extreme values and significance of F values for fixed sources of variation and their interactions.

	Direct N ₂ O emissions		Direct + Indirect N ₂ O emissions
	Area-scaled N ₂ O Kg N ha ⁻¹	Yield-scaled N ₂ O g N Mg ⁻¹ grain ⁻¹	Area-scaled N ₂ O Kg N ha ⁻¹
Year (Y)			
2018	2.6	285	2.8
2019	2.9	309	3.3
2020	1.9	174	2.0
Treatment (T)			
Urea	3.8	400	4.0
ESN	1.6	159	1.8
Urea/Urea+	2.3	235	2.6
ESN/Urea+	2.3	229	2.6
Interaction			
Y*T	<0.05†	<0.05	<0.05

† Numbers within a column and variable with a different lowercase letter are significantly different.



Appendix 4. Cumulative N₂O-N emissions as influenced by treatment over the growing season from 2018 to 2020. Downward pointing arrows indicate the pre-plant and split fertilizer application dates.



Appendix 5. Cumulative NO₃-N load as influenced by treatment over the growing season from 2018 to 2020. Downward pointing arrows indicate the pre-plant and split fertilizer application dates.