# Advanced 4R Nitrogen Management Options for Corn in Sandy Soils of Manitoba, Canada

by

Kody F. L. Oleson

A Thesis

Submitted to the Faculty of Graduate Studies of

The University of Manitoba

in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Soil Science

University of Manitoba

Winnipeg, Manitoba

TABLE OF CONTENTS

# LIST OF ABBREVIATIONS

N – Nitrogen

NUE – Nitrogen use efficiency

EEF – Enhanced efficiency fertilizer

AE – Agronomic Efficiency

NRE – Apparent nitrogen recovery efficiency

EF – Emission Factor

EI – Emission Intensity

**ABSTRACT**

Pillars of 4R nutrient management - Right Source, Right Rate, Right Time, Right Place, have guided the development of best management practices in various soil-climatic conditions in recent decades. Nitrogen (N) management options that reduce environmental losses and/or improve N use efficiency must be investigated in various soil-climatic contexts to ensure food security and a more sustainable future. 4R research that investigates various measures of sustainability for multiple management practices remains in short supply. The objectives of this research were to compare growing season $N_2O$ emissions and N use efficiency measures between 1) at-planting sources of N (Urea, ESN/Urea, SuperU); 2) in-season sources of N (UAN, Agrotain, AgrotainPlus); 3) in-season placement depths of UAN (Surface dribble, Shallow, Deep) applied to corn in sandy soils of Manitoba, Canada. At three sites with similar soil and management characteristics, treatments were replicated four times in a randomized complete block design. Higher soil-moisture in spring of 2020 resulted in greater magnitudes of $N_2O$ emissions and a greater potential for N loss. Across three site-years, ESN/Urea had the lowest mean area-scaled emissions among at-planting sources, and agronomic benefits were apparent during the year with high soil-moisture at-planting. Among in-season sources of N, area-scaled emissions of AgrotainPlus were significantly lower than UAN Surface; UAN Deep consistently had the lowest area-scaled emissions among in-season placements. In summary, relatively dry conditions and timely rains after fertilization likely impeded the potential for enhanced efficiency fertilizers and placement depth to substantially reduce N losses and subsequently show agronomic benefit(s). However, enhanced efficiency fertilizers and shallow/deep placement tended to have greater residual N after corn harvest at each N rate compared to conventional urea and UAN. In dry conditions, reduced N losses may not translate

into yield or N uptake benefits, however, may give agronomic benefits during the following growing season(s).

# ACKNOWLEDGEMENTS

This research was conducted in southern Manitoba, on original lands of Anishinaabeg, Cree, Oji-Cree, Dakota, and Dene peoples, and on the homeland of the Métis Nation. I am extremely thankful for the farmers who dedicated part of their land and time to be involved in this research and make it all possible. This project would not have been possible without the help of many professors, technicians, farmers, and fellow students. Thank you all. I'd especially like to thank my supervisor Dr. Mario Tenuta for his guidance, knowledge, and support throughout this project. I greatly appreciate the opportunity to be involved in this research with such a great team: Brad Sparling, for managing gas and soil sampling operations as well as Emma Unruh for helping with gas sample analysis; Lanny Gardiner, for managing fertilization, seeding, site maintenance, and harvesting; all other students and technicians who helped collect and process samples in the field and lab; Dr. Paul Bullock and Dr. Martin Entz, for serving on my committee and giving excellent guidance throughout my degree; Dr. Francis Zvomuya, Dr. Brian Amiro, and Dr. Claudia Wagner-Riddle for giving me new-found perspectives on soils and the natural world; my fellow students, with whom I shared thoughts, ideas, and memories; and lastly, my family and friends for always being there for me. Thank you all for broadening my horizons during such a complicated time.

# LIST OF TABLES

Page

# LIST OF FIGURES

# 1. INTRODUCTION

## 1.1 Nitrogen in Agroecosystems

Nitrogen (N) is an essential element for plant growth, it is often the most limiting macronutrient in agroecosystems and greatly influences crop yield (Halvorson and Bartolo 2014). Over time, global food supplies have depended more and more on the additions of inorganic N (Smil 1997). Today's agricultural systems operate more frequently at large industrial scales, therefore high amounts of synthetic N fertilizer are applied to cereal crops such as corn (Galloway *et al.* 2017). As a result, the proportions of N recovered by crops have decreased at large spatial scales, resulting in greater amounts of N loss to the environment (Yan *et al.* 2014). On a global scale, some research argues that little progress has been made in the last several decades towards increasing the amount of N fertilizer that is recovered by crops (nitrogen use efficiency), while decreasing environmental losses caused by excessive application of N. However, the implementation of new technologies such as precision crop management and enhanced efficiency fertilizers (EEF's) have shown promise toward increasing nitrogen use efficiency in certain regions, such as the United States (Omara *et al.* 2019).

There are growing global concerns about greenhouse gas emissions from agricultural ecosystems, which account for roughly 9% of global emissions (Paul 2014). Emissions are projected to increase as the human population and the demand for food increases in the future; agriculture is currently the largest anthropogenic source of nitrous oxide ($N_2O$) which is produced through nitrification and denitrification processes in soils. Nitrous oxide is a potent greenhouse gas with an atmospheric lifetime of ~114 years, being an important influential factor for global climate change (Aneja *et al.* 2019). It is estimated that nitrous oxide accounts for approximately 6% of global radiative forcing (Myhre *et al*. 2013).

Farmers and industry suffer a loss in investment when N fertilizer is lost to the environment. Nitrogen fertilizer application rates largely dictate the magnitude of $N_2O$ fluxes from agricultural soils to the atmosphere; post-planting emissions ranged from 0–25kg $N_2O$-N $ha^{-1}$ during a long-term study conducted in Manitoba and Ontario, Canada (Tenuta *et al*. 2019). Additionally, gaseous losses of susceptible fertilizers through ammonia ($NH_3$) volatilization can account for 40–50% of N loss (Jones *et al*. 2007). Excessive N applications also pose a risk to groundwater resources through nitrate ($NO_3^-$) contamination, while various forms of N complement phosphorus loading in the eutrophication of surface water bodies, such as Lake Winnipeg (Lake Winnipeg Stewardship Board 2012, Singh *et al.* 2019). The various pathways for N loss pose a great risk to farmers and their communities from year to year. To improve socioeconomic benefit and mitigate environmental detriments of applied N fertilizer, it is necessary to investigate different management practices that increase the amount of N used by crops and/or decrease environmental losses.

## 1.2 Nitrogen Use Efficiency and the 4R's

Nitrogen use efficiency (NUE) is a complex term that evaluates the ability of crops to use N. There are many definitions of NUE encompassing various forms of N in soil, such as mineralization of organic matter, atmospheric deposition, and biological fixation. Nitrogen use efficiency values can be used as a tool to gauge the agronomic and environmental sustainability of various management practices (Omara *et al*. 2019). Agronomic efficiency (AE) and apparent N recovery efficiency (NRE) are measures that quantify the yield and N uptake benefits of fertilized crops relative to unfertilized crops, respectively. In addition to the quantification of various environmental loss pathways and environmental variables, AE and NRE aid in establishing the optimal management strategies needed to improve NUE and decrease $N_2O$ emissions.

In the past few decades, the 4R nutrient stewardship framework has guided best-management strategies to achieve socio-economic and/or environmental goals (Fixen 2020). The 4R framework optimizes N source, rate, timing, and placement of applied N fertilizer in various soil-climatic conditions. Due to the complexity and variability in soils, cropping systems, climate, management and many other factors, the 4R's must be investigated in different regions of the world to give agricultural communities different options to move further toward sustainability.

The primary goal of 4R nutrient management is to boost nutrient use efficiency, in other words, to maximize the amount of nutrient input used by crops and reduce environmental losses. The international fertilizer industry, farmers, stakeholders and researchers have demonstrated how enhanced efficiency fertilizers help to achieve this goal (Trenkel 2010). Examples of enhanced efficiency fertilizers include ESN, a polymer-coated urea, which is a controlled-release product; SuperU, urea containing urease and nitrification inhibitors; and UAN with AgrotainPlus, containing urease and nitrification inhibitors in solution (Halvorson *et al.* 2014). These products have been shown to reduce $NO_3^-$ leaching and gaseous emissions of $N_2O$ and $NH_3$ in many situations (Motavalli *et al.* 2008). Several studies have shown increased rates of ammonia volatilization when only nitrification inhibitors are used. Thus, dual inhibitors are recommended for urea-based fertilizers to reduce indirect $N_2O$ emissions, which occur when volatilized ammonia returns to the soil surface and undergoes nitrification or when leached $NO_3^-$

undergoes denitrification at a different location than where it originated (Zaman *et al.* 2009, Lam *et al.* 2017). Products that include urease and nitrification inhibitors together have been shown to decrease both emission pathways, while other combinations of placement and application timing can reduce gaseous emissions and boost yield (Randall *et al.* 2003, Gao *et al.* 2015, Drury *et al.* 2017). Nitrification inhibitors such as Dicyandiamide (DCD), nitrapyrin, and controlled-release fertilizers have also reduced nitrate leaching under various meteorological conditions and management strategies (Owens 1987, Shoji *et al.* 2001, Díez-López *et al.* 2008, Di and Cameron 2002).

### 1.3 Right Rate

Microbial communities vary greatly among and within agricultural soils while $N_2O$ can be produced via many different biogeochemical pathways. Additionally, crop growth, development and subsequent N uptake from year to year can be highly variable. In cold regions such as Manitoba, the largest $N_2O$ flux events are typically during spring-thaw and directly after spring fertilization, while crops such as corn require greater amounts of N later in the growing season (Tenuta *et al*. 2019). This leaves a gap for $N_2O$ production early in the growing season, particularly when all fertilizer N is applied at planting.

It is often difficult to gauge the optimal rate of N in rainfed systems. Greater N rates result in greater yield until the plateau of crop demand, while higher N rates have a greater risk for losses to the environment (Liu *et al.* 2013). Enhanced efficiency fertilizers (EEF’s) and split application of N are some examples of 4R strategies that are used to reduce N losses and effectively supply N to crops from year to year.

### 1.4 Right Source

Many studies have investigated the agronomic and environmental benefits of EEF's in the form of controlled-release, single inhibitor, and double inhibitor products in comparison to conventional urea or UAN (Eagle *et al*. 2017). For example, ESN is a slow-release (polymer-coated) urea; as urea is applied to soils, urease enzymes undergo urea hydrolysis to form $NH_4^+$, $CO_2$ and $H_2O$; this process consumes hydrogen ions and increases soil pH. Subsequently, $NH_3$ undergoes nitrification, which produces $N_2O$ as a by-product (details in Chapter 3). Controlled-release fertilizers such as ESN, delay the availability of N early in the growing season. For heavy clay soil in Manitoba, Asgedom *et al*. (2014) observed significantly lower cumulative $N_2O$ emissions using ESN compared to urea. Similarly, ESN and SuperU reduced cumulative $N_2O$ emissions by approximately 47% across four site-years and two different soil types for spring wheat in Manitoba (Gao *et al*. 2015). Both Asgedom *et al.* (2014) and Gao *et al*. (2015) found a significant correlation between soil-N concentrations (N intensity) and cumulative $N_2O$ emissions, implying the release of fertilizer N is a controlling factor for $N_2O$ emissions throughout each growing season. In a meta-analysis, Lam *et al*. (2017) found that nitrification inhibitors reduced direct $N_2O$ emissions by 0.2–4.5 kg $N_2O$-N $ha^{-1}$, however this effect may be negated by the subsequent indirect $N_2O$ emissions resulting from greater $NH_3$ volatilization and deposition. It is recommended that different measures be taken to decrease $NH_3$ volatilization and $N_2O$ emissions simultaneously to effectively reduce N losses and mitigate climate change. Many researchers have recommended the use of fertilizers that contain both urease and nitrification inhibitors (Lam *et al*. 2017; Woodley *et al.* 2020).

In addition to environmental benefits, EEF's have shown agronomic advantages in many situations. In fine-silty soils of Indiana, Burzaco *et al*. (2013) observed greater corn NUE and

NRE using UAN with nitrapyrin; however, their accompanied meta-analysis found inconsistencies in the observed agronomic effects of EEF's for spring-applied N. The effectiveness of EEF's at improving N uptake is highly dependent on environmental conditions from year to year. For example, Asgedom *et al*. (2014) observed the greatest yields with urea compared to ESN, SuperU, or manure applied to clay soils of Manitoba; Sahota (2020) notes how EEF's such as ESN can be detrimental to yield with slow N release in dry conditions, explaining why conventional fertilizers may have performed better than EEF's in this soil-climatic context. Manitoba has a semi-arid climate with a relatively high risk for corn-moisture stress compared to other regions of the world where enhanced efficiency fertilizers have shown agronomic benefit(s) (Nadler and Bullock 2011, Eagle *et al.* 2017). Most commonly, agronomic benefits have been observed using EEF's in wetter climates or in irrigated systems (Burzaco *et al*. 2013, Halvorson and Bartolo 2014). Agronomic benefits are most likely to be realized in Manitoba with environmental conditions that are favourable to substantial N losses through gaseous emission and/or leaching.

### 1.5 Right Time

With unpredictable environmental conditions throughout each growing season, fertilizer application timing, rate, and/or placement can interact with N source to affect yield, N uptake, and various N loss pathways differently in various soil-climatic contexts. Side-dress application of N is an effective way for farmers to improve NUE and decrease environmental losses from corn crops and enhanced efficiency fertilizers can also be applied during split-applications. In a meta-analysis of corn studies in the United States, Eagle *et al.* (2017) found that EEF's and side-dress of N each reduce $N_2O$ emissions by approximately 30%, noting how these management practices were more effective in warmer and wetter regions where corn productivity and N application rates are relatively high. Enhanced efficiency fertilizers such as Agrotain and AgrotainPlus further reduce N losses during in-season N applications.

Nitrous oxide emissions have an exponential relationship with N rate; EEF's and side-dress application can reduce $N_2O$ emissions by slowing the release of N and minimizing the amount of fertilizer N in the soil, respectively (Eagle *et al*. 2017). However, split application may result in greater cumulative $N_2O$ emissions when water-filled pore space and soil temperatures are high following mid-season application(s) (Burzaco *et al.* 2013); environmental conditions will influence the rate of $N_2O$ production and subsequent losses that result from various management decisions. The risk for corn moisture deficit is high in Manitoba, therefore farmers who apply N as side-dress may have a high risk for volatilization loss (Jones *et al*. 2007, Nadler and Bullock 2011). Application of liquid N fertilizers directly before precipitation events is recommended in order to incorporate N deeper in the soil and prevent volatilization loss. While volatilization losses are reduced and soil moisture is replenished by rain, risk is created for high $N_2O$ emission peaks directly after mid-season application of N. Nitrogen fertilizer products containing both urease and nitrification inhibitors have the potential to reduce $N_2O$ emissions of mid-season N applications by slowing the rates of urea hydrolysis and nitrification, respectively. For rainfed corn in Minnesota, EEF's significantly reduced $N_2O$ emissions for both single and split applications of urea (Venterea *et al.* 2016). However, Dell *et al.* (2014) and Sistani *et al*. (2011) did not observe significant differences between cumulative $N_2O$ emissions of EEF's applied mid-season; experiments with extended dry periods throughout the growing season(s) may result in low magnitudes of $N_2O$ flux, making it difficult to outline significant differences between N management practices. It is apparent that particular N management decisions are optimal for reducing gaseous N emissions depending on soil-climatic conditions from year to year, making it difficult to observe consistent results in rainfed systems.

Similarly, to $N_2O$ emissions - agronomic benefits with EEF's applied as split-application are variable and dependent on environmental conditions throughout each growing season. Venterea *et al.* (2016) observed similar yield, greater NRE, and lower $N_2O$ emissions using a 15% reduced rate of N applied as split application and/or applied with inhibitors compared to conventional fertilizer applied at planting. However, split applications alone did not reduce $N_2O$ emissions or improve yield/N uptake. This shows how source and timing can be combined to reduce environmental losses and give agronomic benefits.

Dell *et al.* (2014) and Beam (2012) observed no agronomic benefit using AgrotainPlus due to dry conditions; a meta-analysis by Li *et al.* (2018) suggests that yield and N uptake benefits by EEF's are rare in regions that receive less than 800mm of rainfall per year. In dry conditions where productivity is lower than expected, corn crops can rarely take advantage of improved N retention. Thus the use of EEF's may result in greater concentrations of residual soil-N compared to conventional fertilizers (Alonso-Ayuso *et al.* 2016). The culmination of 4R studies in various soil-climatic conditions shows great variability for split-applications to reduce environmental losses and provide economic benefits depending on soil-climatic conditions (Eagle *et al*. 2017).

### 1.6 Right Place

Alternatively, environmental losses resulting from side-dress applications of N can be mitigated by choosing the right placement method. Surface applications impose a high risk for volatilization losses unless timely rainfall incorporates N into deeper soil layers. For corn planted in Ontario, Woodley *et al.* (2020) found no significant difference in agronomic variables between broadcasted urea and injected UAN treatments due to low $NH_3$ losses. During their study, however, $NH_3$ volatilization and cumulative $N_2O$ emissions of injected treatments were significantly lower than broadcast and broadcast incorporated. The effect of N placement depth on $N_2O$ emissions depends on soil-climatic conditions and management (Kessel *et al*. 2013, Nash *et al*. 2012). Kessel *et al*. (2013) suggest nitrification and denitrification rates typically decrease at depth in no-till soils due to lower substrate supply and microbial activity than near the surface. Deep placement of inorganic N typically boosts $N_2O$ consumption, lowering net fluxes to the atmosphere (Chapuis-Lardy *et al*. 2007).

Deep placement of N has been shown to increase yield and NUE through more adequate placement for crop demand and greater adsorption of N to soil particles and organic matter (Steusloff *et al.* 2019). Deep and shallow banding are most likely to have a significant, positive effect on yield and NUE compared to surface dribble with conditions favourable for high volatilization losses (Halvorson and Del Grosso. 2013, Woodley *et al.* 2018). N placement may influence the distribution of soil N pools and subsequently influence the partitioning of energy and crop yield (Peng *et al.* 2012, Rochette *et al.* 2013). EEF's and deep/shallow banding may reduce environmental losses and thereby increase residual N (Pawlick *et al.* 2019, Woodley *et al*. 2020); Nitrogen fertilizer placement may influence residual N differently from year to year, depending on soil-climatic conditions that influence N release, N loss and crop N uptake (Halvorson and Grosso 2013).

For corn in semi-arid environments, other researchers have observed large variability between N rates, sources and experimental years due to meteorological variability. However, the treatments with the largest yields (SuperU at 150 lb N/ac and UAN side-dress with Agrotain at

50 and 100 lb N/ac) were consistent among growing seasons, showing greater leaf chlorophyll content and duration of green leaf area during grain-filling stage (Hatfield and Parkin 2011). This implies that specific treatments were ideal for particular soil-climatic situations, while other treatments inefficiently met crop N demand and/or showed greater environmental loss. However, although 4R strategies often show dualistic benefits, Asgedom *et al.* (2014) outlines the challenge of observing agronomic and environmental benefits simultaneously in some situations; in their study conducted in Manitoba, treatments with the greatest $N_2O$ emissions also had the greatest yield and N uptake. Crop N uptake and the pathways for N loss are controlled by complex abiotic and biotic factors that are highly variable in space and time (Waldo *et al.* 2019). Investigating multiple sets of management practices during the same site-years will give a better perspective on the optimal management practices to improve NUE and/or reduce environmental loss in various regions of the world. 4R management practices such as the use of enhanced efficiency fertilizers can interact with soil and meteorological conditions to influence nitrogen use efficiency and environmental losses from year to year.

## 1.7 Objectives

With such variability in environmental conditions, soils, and management it is necessary to investigate the viability of various 4R practices in Manitoba for the mitigation of $N_2O$ emissions and improvement of NUE. There is a limited body of research investigating multiple sets of management practices in the same site-year(s). With increasing knowledge of how 4R management combinations interact in various soil-climatic conditions, producers will be better equipped to achieve their socioeconomic and environmental goals in the future. At various N rates, the objectives of this study were to compare corn yield, AE, NRE, and residual soil N between 1) N sources applied at-planting (Urea (46-0-0), polymer coated urea (ESN (44-0-0))/Urea, nitrification and urease inhibited urea (SuperU (46-0-0)); 2) N sources surface-applied at the V4 stage (UAN Surface (28-0-0), Agrotain (urease inhibited UAN), AgrotainPlus (nitrification and urease inhibited UAN)); 3) Placements of UAN (28-0-0) applied at V4 (UAN Surface, UAN Shallow(1.5"), UAN Deep(3")). In 2019, the ESN treatment was changed to a mix of 70%ESN/30%Urea, therefore only 2019 and 2020 were included in statistical analyses. The ESN/Urea mixture will hereby be referred to as ESN for the remainder of this thesis; the UAN/Agrotain and UAN/AgrotainPlus treatments will hereby be referred to as Agrotain and AgrotainPlus, respectively.

## 1.8 Hypotheses (Chapter 2)

### 1.8.1 At-Planting Sources

Compared to urea, it was hypothesized that SuperU and ESN would significantly decrease cumulative $N_2O$ emissions by limiting microbial access to substrate and slowing the release of applied N, respectively (Alonso-Ayuso *et al*. 2016, Lam *et al.* 2017, Eagle *et al.* 2017, Sahota 2020). EEF efficacy in reducing emissions depends on environmental conditions, soil N pools, and the magnitude/frequency of $N_2O$ flux events throughout the growing season (Li *et al*. 2018, Woodley *et al*. 2020).

### 1.8.2 In-Season Sources

Relative to conventional UAN applied in-season, it was hypothesized AgrotainPlus would significantly reduce $N_2O$ emissions by urease and nitrification inhibition. Agrotain may increase emissions by retaining more ammoniacal N in soil solution as this product only contains a urease inhibitor and does not include a nitrification inhibitor (Lam *et al.* 2017, Woodley *et al.*

2020). EEF efficacies at reducing $N_2O$ emissions depend on soil-climatic conditions throughout the growing season (Li *et al.* 2018, Woodley *et al.* 2020).

### 1.8.3 In-Season Placements

The effect of N placement depth on $N_2O$ emissions depends on soil-climatic conditions and management (Kessel *et al.* 2013, Nash *et al.* 2012). Kessel *et al.* (2013) suggest nitrification and denitrification rates typically decrease at depth in no-till soils due to lower substrate supply and microbial activity than near the surface. Deep placement of inorganic N typically boosts $N_2O$ consumption, lowering net fluxes to the atmosphere (Chapuis-Lardy *et al*. 2007). It was hypothesized deep and shallow banded UAN would significantly reduce $N_2O$ emissions compared to surface dribble banded UAN.

**1.8.4 At-Planting Vs In-Season Conventional.** Yield and N uptake tend to be more variable for split-applications in rainfed systems, however they can be used to match crop N supply more adequately with N demand. Corn N demand is greater at later growth stages, therefor split applications can improve N uptake and yield in situations where there is a high risk for N loss at-planting and adequate moisture for the crop to realize benefits later in the growing season (Burzaco *et al.* 2013). Due to high risk of moisture deficit for corn grown in Manitoba (Nadler and Bullock 2011), it was hypothesized that urea applied at-planting would have significantly greater $N_2O$ emissions and yield compared to split application of UAN since both crops and microbes are likely to have greater access to N and soil moisture early in the growing season, particularly in sandy soils with low water-holding capacity.

## 1.9 Hypotheses (Chapter 3)

**1.9.1 At-Planting Sources.** It was hypothesized EEF's would not make a significant difference in yield, AE or NRE compared to conventional urea without warm, wet conditions that promote N losses and/or high corn productivity (Sistani *et al.* 2014). Although many studies have noted crop benefits with EEF's, few studies have shown notable increases in crop yield or NUE in dry conditions or sandy soils (Abalos *et al*. 2014, Gao *et al.* 2015). The risk of water deficit for corn is high in Manitoba and the risk of N leaching is low; corn crops are more likely to be water-limited than N limited with adequate fertilization from year–to–year (Paolo and Rinaldi 2008, Nadler and Bullock 2011). An appreciable amount of N loss is typically needed through gaseous emissions or leaching for EEF's to show a significant effect on yield, AE or NRE (Halvorson and Bartolo 2014). In dry climates, delayed N release by EEF's can decrease yield compared to conventional urea while the effects on crop N uptake tend to be more variable (Grant *et al.* 2012). EEF's are likely to increase residual soil N (Alonso-Ayuso *et al.* 2016).

**1.9.2 In-Season Sources.** Similarly, yield and NUE benefits for in-season applications have varied across studies, EEF's are more effective compared to UAN with warm, wet conditions that are conducive to N loss, either by gaseous emission or leaching (Akiyama *et al.* 2010, Gagnon *et al.* 2012, Watkins 2013, Woodley *et al.* 2018, Woodley et al. 2020). Timely precipitation patterns may influence treatment efficacy of reducing losses and giving crop benefits (Beam 2012, Hernández *et al.* 2015). Sistani *et al.* (2014) found no significant difference in grain yield between AgrotainPlus and UAN applied to corn in dry conditions. With a high moisture deficit risk for corn grown in Manitoba, it was hypothesized that EEF's would not show a significant effect on the above-mentioned parameters. Timely precipitation after in-season applications may negate the benefits that EEF's could have on yield and/or N uptake (Woodley *et al.* 2018, Woodley *et al.* 2020). Control release and inhibitor products will likely increase residual soil N (Alonso-Ayuso *et al.* 2016).

**1.9.3 In-Season Placements.** Deep banding has been shown to increase yield and NUE through more adequate placement for crop demand and greater adsorption of N to soil particles and organic matter (Steusloff *et al.* 2019). Deep and shallow banding are most likely to have a significant, positive effect on yield and NUE compared to surface dribble with dry, windy conditions that promote volatilization losses (Halvorson and Del Grosso. 2013, Woodley *et al.* 2018). N placement may influence the distribution of soil N pools and subsequently influence the partitioning of energy and crop yield (Peng *et al.* 2012, Rochette *et al.* 2013). It was hypothesized that EEF's (ESN, SuperU, Agrotain, AgrotainPlus) and deep/shallow banding would reduce environmental losses and thereby increase residual N (Pawlick *et al.* 2019). N placement may influence residual N differently from year to year, depending on soil-climatic conditions that influence N release, N loss and crop N uptake (Halvorson and Grosso 2013).

The effect of N placement depth on $N_2O$ emissions depends on soil-climatic conditions and management (Kessel *et al*. 2013, Nash *et al*. 2012). Kessel *et al*. (2013) suggest nitrification and denitrification rates typically decrease at depth in no-till soils due to lower substrate supply and microbial activity compared to near the surface. Deep placement of inorganic N gives more opportunity for $N_2O$ consumption, lowering net fluxes to the atmosphere (Chapuis-Lardy *et al*. 2007). It was hypothesized deep and shallow banded UAN would significantly reduce $N_2O$ emissions compared to surface dribble banded UAN.

**1.9.4 At-Planting Vs. In-Season Conventional.** Due to high risk of moisture deficit for corn grown in Manitoba (Nadler and Bullock 2007), it was hypothesized that urea would have significantly greater $N_2O$ emissions, EF, ad EI compared to split application of UAN since crops and microbes are likely to have greater access to N and soil moisture early in the growing season, particularly in sandy soils that have low water-holding capacity compared to heavy clay soils of the Red River Valley.

## 1.10 Structure of Thesis

This paper includes two research chapters. Chapter 2 investigates the effectiveness of various 4R management practices in reducing $N_2O$ emissions from corn crops in sandy soils. Comparisons of cumulative area-scaled emissions, emission factors, and yield-scaled emissions were made between treatments for each set of 4R practices. Chapter 3 focuses on the differences in yield, agronomic efficiency, agronomic recovery efficiency, and amount of residual soil inorganic nitrogen after harvest.

## 1.11 Contributions

I began working as a summer student in May of 2019 and participated in gas, soil, biomass sampling throughout the growing season. Due to the pandemic, I was unable to participate in field operations from May–September of 2020. Fertilizing and seeding was done by technicians and fellow students. With the help of many others, I was involved in corn harvesting for 2019, 2020 and 2021 (not included in this paper). I participated in biomass grinding, deep soil sample collection and organization, soil chopping, and soil N extractions. Data organization, calculations, visualization, and statistical analyses were conducted by myself with the help of Dr. Mario Tenuta and Dr. Francis Zvomuya. I have presented results from this research at MSSS, CSSS and Create Climate Smart Soils conferences.

### 1.12 References

Abalos, D., S. Jeffery, A. Sanz-Cobena, G. Guardia, and A. Vallejo. “Meta-Analysis of the Effect of Urease and Nitrification Inhibitors on Crop Productivity and Nitrogen Use Efficiency.” *Agriculture, Ecosystems & Environment* 189 (2014): 136–44. https://doi.org/10.1016/j.agee.2014.03.036.

Akiyama, Hiroko., X. Yan, and K. Yagi. “Evaluation of Effectiveness of Enhanced-Efficiency Fertilizers as Mitigation Options for $N_2O$ and NO Emissions from Agricultural Soils: Meta-Analysis.” *Global Change Biology* 16, no. 6 (2010): 1837–46. https://doi.org/10.1111/j.1365-2486.2009.02031.x.

Alonso-Ayuso, M., J. L. Gabriel, and M. Quemada. “Nitrogen Use Efficiency and Residual Effect of Fertilizers with Nitrification Inhibitors.” *European Journal of Agronomy 80,* (2016): 1–8.

Aneja, V. P., William H. Schlesinger, Qi Li, Alberth Nahas, and William H. Battye. “Characterization of Atmospheric Nitrous Oxide Emissions from Global Agricultural Soils.” *SN Applied Sciences* 1, no. 12 (2019): 1662.

Asgedom, H., M. Tenuta, D. N. Flaten, X. Gao, and E. Kebreab. “Nitrous Oxide Emissions from a Clay Soil Receiving Granular Urea Formulations and Dairy Manure.” *Agronomy Journal 106*, no. 2 (2014): 732–44. https://doi.org/10.2134/agronj2013.0096.

Beam, K. “ The effect of  Agrotain-Plus on strip-till corn with regards to N, P, K, Mg, Ca, S, Fe, Mn, B, Cu, Zn levels.” *Cantaurus,* no. 20 (2012); 5–9.

Burzaco, Juan P., D. R. Smith, and T. J. Vyn. "Nitrous Oxide Emissions in Midwest US Maize Production Vary Widely with Band-Injected N Fertilizer Rates, Timing and Nitrapyrin Presence." *Environmental Research Letters 8*, no. 3 (2013): 035031. https://doi.org/10.1088/1748-9326/8/3/035031.

Chapuis-Lardy, L., N. Wrage, A. Metay, J. Chotte, and M. Bernoux. "Soils, a Sink for $N_2O$? A Review." *Global Change Biology 13*, no. 1 (2007): 1–17. https://doi.org/10.1111/j.1365-2486.2006.01280.x.

Dell, C. J., K. Hun, R. B. Bryant, J. P. Schmidt. "Nitrous Oxide Emissions with Enhanced Efficiency Nitrogen Fertilizers in a Rainfed System" *Agronomy Journal 106,* no. 2 (2014): 723–31. https://acsess-onlinelibrary-wiley-com.uml.idm.oclc.org/doi/full/10.2134/agronj2013.0108.

Di, H. J., and K. C. Cameron. "The Use of a Nitrification Inhibitor, Dicyandiamide (DCD), to Decrease Nitrate Leaching and Nitrous Oxide Emissions in a Simulated Grazed and Irrigated Grassland." *Soil Use and Management 18*, no. 4 (2002): 395–403.

Díez-López, J. A., P. Hernaiz-Algarra, M. A. Sánchez, and I. C. Martín. "Effect of a nitrification inhibitor (DMPP) on nitrate leaching and maize yield during two growing seasons." *Spanish Journal of Agricultural Research 2,* (2008): 294-303.

Drury, C. F., X. Yang, W. D. Reynolds, W. Calder, T. O. Oloya, and A. L. Woodley. "Combining Urease and Nitrification Inhibitors with Incorporation Reduces Ammonia and Nitrous Oxide Emissions and Increases Corn Yields." *Journal of Environmental Quality 46,* no. 5 (2017): 939–49.

Eagle, A. J., L. P. Olander, K. L. Locklier, J. B Heffernan, and E. S. Bernhardt. "Fertilizer Management and Environmental Factors Drive $N_2O$ and $NO_3$ Losses in Corn: A Meta-Analysis" *Soil Science Society of America Journal 81*, no. 5 (2017): 1191–1202.

Fixen, Paul E. "A Brief Account of the Genesis of 4R Nutrient Stewardship." *Agronomy Journal 112*, no.5 (2020): 4511–4518. https://doi.org/10.1002/agj2.20315**.**

Gagnon, B., N. Ziadi, and C. Grant. "Urea Fertilizer Forms Affect Grain Corn Yield and Nitrogen Use Efficiency." *Canadian Journal of Soil Science 92*, no.2 (2012) https://doi.org/10.4141/cjss2011-074.

Galloway, J. N., A. M. Leach, J. W. Erisman, A. Bleeker, J. N. Galloway, A. M. Leach, J. W. Erisman, and A. Bleeker. "Nitrogen: The Historical Progression from Ignorance to Knowledge, with a View to Future Solutions." *Soil Research 55*, no. 6 (2017): 417–24.

Gao, X., H. Asgedom, M. Tenuta, and D. N. Flaten. "Enhanced Efficiency Urea Sources and Placement Effects on Nitrous Oxide Emissions." *Agronomy Journal 107*, no. 1 (2015): 265–77. https://doi.org/10.2134/agronj14.0213.

Grant, C. A., R. Wu, F. Selles, K. N. Harker, G. W. Clayton, S. Bittman, B. J. Zebarth, and N. Z. Lupwayi. "Crop Yield and Nitrogen Concentration with Controlled Release Urea and Split Applications of Nitrogen as Compared to Non-Coated Urea Applied at Seeding." *Field Crops Research 127* (2012): 170–80. https://doi.org/10.1016/j.fcr.2011.11.002.

Halvorson, A. D., and M. E. Bartolo "Nitrogen Source and Rate Effects on Irrigated Corn Yields and Nitrogen-Use Efficiency." *Agronomy Journal 106*, no. 2 (2014): 681–93.

Halvorson, A. D., and S. J. Del Grosso. "Nitrogen Placement and Source Effects on Nitrous Oxide Emissions and Yields of Irrigated Corn." *Journal of Environmental Quality 42*, no. 2 (2013): 312–22. https://doi.org/10.2134/jeq2012.0315.

Halvorson, A. D., Clifford S. Snyder, Alan D. Blaylock, and Stephen J. Del Grosso. "Enhanced-Efficiency Nitrogen Fertilizers: Potential Role in Nitrous Oxide Emission Mitigation." *Agronomy Journal 106*, no. 2 (2014): 715–22. https://doi.org/10.2134/agronj2013.0081.

Hatfield, J. L., and T. B. Parkin. "Nitrogen Management: Unraveling The Effects of Timing and Form." *North Central Extension-Industry Soil Fertility Conference 27*, (2011): 42–47.

Hernández, M., L. Echarte, A. Della Maggiora, M. Cambareri, P. Barbieri, and D. Cerrudo. "Maize Water Use Efficiency and Evapotranspiration Response to N Supply under Contrasting Soil Water Availability." *Field Crops Research 178* (2015): 8–15. https://doi.org/10.1016/j.fcr.2015.03.017.

Jones, C. A., R. T. Koenig, J. W. Ellsworth, B. D. Brown, and G. D. Jackson. "Management of Urea Fertilizer to Minimize Volatilization," *MSU Extension*, (2007): 1–12.

Kessel, C. V., R. Venterea, J. Six, M. A. Adviento-Borbe, B. Linquist, and K. J. V. Groenigen. "Climate, Duration, and N Placement Determine $N_2O$ Emissions in Reduced Tillage Systems: A Meta-Analysis." *Global Change Biology 19*, no. 1 (2013): 33–44.

Lake Winnipeg Stewardship Board. "Reducing nutrient loading to Lake Winnipeg and its watershed: Our collective responsibility and commitment to action." *Report to the Minister of Water Stewardship* (2012): 13–15.

Lam, S. K., H. Suter, A. R. Mosier, and D. Chen. "Using Nitrification Inhibitors to Mitigate Agricultural N2O Emission: A Double-Edged Sword?" *Global Change Biology 23*, no. 2 (2017): 485–89.

Li, T., W. Zhang, J. Yin, D. Chadwick, D. Norse, Y. Lu, X. Liu, X. Chen, F. Zhang, D. Powlson, Z. Dou. "Enhanced-Efficiency Fertilizers Are Not a Panacea for Resolving the Nitrogen Problem." *Global Change Biology 24*, no. 2 (2018): e511–521. https://doi.org/10.1111/gcb.13918.

Liu, J., L. Bu, L. Zhu, S. Luo, X. Chen, S. Li, R. L. Hill, and Y. Zhao. "Nitrogen Fertilization Effects on Nitrogen Balance and Use Efficiency for Film-Mulched Maize in a Semiarid Region."

*Acta Agriculturae Scandinavica, Section B — Soil & Plant Science 63*, no. 7 (2013): 612–22. https://doi.org/10.1080/09064710.2013.837192.

Motavalli, P. P., K. W. Goyne, and R. P. Udawatta. “Environmental Impacts of Enhanced-Efficiency Nitrogen Fertilizers.” *Crop Management 7*, no. 1 (2008): 1–15. https://doi.org/10.1094/CM-2008-0730-02-RV.

Myhre, G., Shindell, D., and Pongratz, J. “Anthropogenic and natural climate forcing.” *Climate Change* (2013).

Nadler, A. J., and P. R. Bullock. “Long-Term Changes in Heat and Moisture Related to Corn Production on the Canadian Prairies.” *Climatic Change 104*, no. 2 (2011): 339–52. https://doi.org/10.1007/s10584-010-9881-y.

Nash, P. R., P. P. Motavalli, and K. A. Nelson. “Nitrous Oxide Emissions from Claypan Soils Due to Nitrogen Fertilizer Source and Tillage/Fertilizer Placement Practices.” *Soil Science Society of America Journal 76*, no. 3 (2012): 983–93.

Omara, P., L. Aula, F. Oyebiyi, and W. R. Raun. “World Cereal Nitrogen Use Efficiency Trends: Review and Current Knowledge.” *Agrosystems, Geosciences & Environment 2*, no. 1 (2019): 1–8. https://doi.org/10.2134/age2018.10.0045.

Owens, L. B. “Nitrate Leaching Losses from Monolith Lysimeters as Influenced by Nitrapyrin.” *Journal of Environmental Quality 16*, no.1 (1987): 34–38.

Paolo, E. D.., and M. Rinaldi. “Yield Response of Corn to Irrigation and Nitrogen Fertilization in a Mediterranean Environment.” *Field Crops Research 105*, no. 3 (2008): 202–210. https://doi.org/10.1016/j.fcr.2007.10.004.

Paul, E. “Soil Microbiology, Ecology and Biochemistry”. *Academic Press*, (2014).

Pawlick, A. A., C. Wagner-Riddle, G. W. Parkin, and A. A. Berg. "Assessment of Nitrification and Urease Inhibitors on Nitrate Leaching in Corn (Zea Mays L.)." *Canadian Journal of Soil Science 99*, no. 1 (2019): 80–91.

Peng, Y., X. Li, and C. Li. "Temporal and Spatial Profiling of Root Growth Revealed Novel Response of Maize Roots under Various Nitrogen Supplies in the Field." *PLOS ONE 7*, no. 5 (2012): e37726. https://doi.org/10.1371/journal.pone.0037726.

Randall, G. W., J. A. Vetsch, J. R. Huffman "Corn Production on a Subsurface-Drained Mollisol as Affected by Time of Nitrogen Application and Nitrapyrin." *Agronomy Journal 95*, no. 5 (2003): 1213–1219.

Rochette, P.., D. A. Angers, M. H. Chantigny, M. Gasser, J. D. MacDonald, D. E. Pelster, and N. Bertrand. "Ammonia Volatilization and Nitrogen Retention: How Deep to Incorporate Urea?" *Journal of Environmental Quality 42*, no. 6 (2013): 1635–42. https://doi.org/10.2134/jeq2013.05.0192.

Sahota, T. S. "Environmentally Smart Nitrogen (ESN)—Potential for Improving Modern Crop Production and N-Use Efficiency." *Journal of Agricultural Science and Technology 10*, no. 6 (2020): 327–340.

Shoji, S., J. Delgado, A. Mosier, and Y. Miura. "Use Of Controlled Release Fertilizers And Nitrification Inhibitors To Increase Nitrogen Use Efficiency And Conserve Air And Water Quality," *Communications in Soil Science and Plant Analysis 32*, no. 7-8 (2001): 1051-1070.

Singh, S., L. Coppi, Z. Wang, M. Tenuta, and H. M. Holländer. "Regionalisation of Nitrate Leaching on Pasture Land in Southern Manitoba." *Agricultural Water Management 222* (2019): 286–300.

Sistani, K. R., M. Jn-Baptiste, N. Lovanh, and K. L. Cook. “Atmospheric Emissions of Nitrous Oxide, Methane, and Carbon Dioxide from Different Nitrogen Fertilizers.” *Journal of Environmental Quality 40*, no. 6 (2011): 1797–1805. https://doi.org/10.2134/jeq2011.0197.

Sistani, K. R., M. Jn-Baptiste, and J. R. Simmons. “Corn Response to Enhanced-Efficiency Nitrogen Fertilizers and Poultry Litter.” *Agronomy Journal 106*, no. 2 (2014): 761–70. https://doi.org/10.2134/agronj2013.0087.

Smil, V. “Global Population and the Nitrogen Cycle.” *Scientific American 277*, no. 1 (1997): 76–81.

Steusloff, T. W., K. A. Nelson, P. P. Motavalli, and G. Singh. “Fertilizer Placement Affects Corn and Nitrogen Use Efficiency in a Claypan Soil.” *Agronomy Journal 111*, no. 5 (2019): 2512–2522. https://doi.org/10.2134/agronj2019.02.0108.

Tenuta, M., B. D. Amiro, X. Gao, C. Wagner-Riddle, and M. Gervais. “Agricultural Management Practices and Environmental Drivers of Nitrous Oxide Emissions over a Decade for an Annual and an Annual-Perennial Crop Rotation.” *Agricultural and Forest Meteorology 276*, (2019): 107636.

Trenkel, M. E. “Slow-and controlled-release and stabilized fertilizers: An option for enhancing nutrient use efficiency in agriculture.” *International fertilizer industry association* (2010).

Venterea, R. T., J. A. Coulter, and M. S. Dolan. “Evaluation of Intensive ‘4R’ Strategies for Decreasing Nitrous Oxide Emissions and Nitrogen Surplus in Rainfed Corn.” *Journal of Environmental Quality 45*, no. 4 (2016): 1186–95. https://doi.org/10.2134/jeq2016.01.0024.

Watkins, P. H. “Nitrogen Management in Corn: Influences of Urea Ammonium Nitrate (UAN) Applications With and Without Nitrogen Stabilizer Products.” *University of Maryland, College Park* (2013). https://drum.lib.umd.edu/handle/1903/14181.

Woodley, A. L., C. F. Drury, X. M. Yang, W. D. Reynolds, W. Calder, and T. O. Oloya. "Streaming Urea Ammonium Nitrate with or without Enhanced Efficiency Products Impacted Corn Yields, Ammonia, and Nitrous Oxide Emissions." *Agronomy Journal 110*, no. 2 (2018): 444–54.

Woodley, Alex L., C. F. Drury, X. Y. Yang, L. A. Phillips, D. W. Reynolds, W. Calder, and T. Okello Oloya. "Ammonia Volatilization, Nitrous Oxide Emissions, and Corn Yields as Influenced by Nitrogen Placement and Enhanced Efficiency Fertilizers." *Soil Science Society of America Journal 84*, no. 4 (2020): 1327–41. https://doi.org/10.1002/saj2.20079.

Yan, X., C. Ti, P. Vitousek, D. Chen, A. Leip, Z. Cai, and Z. Zhu. "Fertilizer Nitrogen Recovery Efficiencies in Crop Production Systems of China with and without Consideration of the Residual Effect of Nitrogen," *Environmental Research Letters 9*, no. 9 (2014): 095002. https://iopscience.iop.org/article/10.1088/1748-9326/9/9/095002/meta.

Zaman, M., S. Saggar, J. D. Blennerhassett, and J. Singh. "Effect of Urease and Nitrification Inhibitors on N Transformation, Gaseous Emissions of Ammonia and Nitrous Oxide, Pasture Yield and N Uptake in Grazed Pasture System." *Soil Biology and Biochemistry 41*, no. 6 (2009): 1270–80.

# 2. INFLUENCE OF 4R NITROGEN MANAGEMENT FOR NITROGEN USE EFFICIENCY AND RESIDUAL SOIL NITROGEN OF CORN IN SANDY SOILS OF SOUTH-CENTRAL MANITOBA, CANADA.

## 2.1 Abstract

4R nutrient stewardship provides a framework to improve nutrient use efficiency and reduce environmental losses; evaluating the collective performance of multiple management practices within a soil-climatic condition. Corn crops in Canada typically require high nitrogen (N) addition rates to achieve high yield; more efficient use of N fertilizer provides socioeconomic benefit to farmers while reducing the environmental impact caused by $N_2O$ emissions and $NO_3^-$ leaching. Agronomic efficiency and apparent N recovery efficiency are indicators of yield and N uptake response to the nutrient addition, respectively. Three field trials were conducted on commercial farm fields in 2018, 2019 and 2020 in south-central Manitoba to compare corn grain yield, agronomic efficiency, apparent N recovery efficiency and residual soil inorganic N of 4R management treatments. The treatments were: 1) N sources applied at-planting (Urea (46-0-0), polymer-coated urea (ESN (44-0-0))/Urea, nitrification and urease inhibited urea (SuperU (46-0-0)); 2) N sources surface-applied at the V4 stage (UAN Surface (28-0-0), Agrotain (urease inhibited UAN), AgrotainPlus (nitrification and urease inhibited UAN)); and 3) Placements of UAN (28-0-0) applied at V4 stage (UAN Surface, UAN Shallow, UAN Deep). Treatment plots were replicated four times and arranged in a randomized complete block design with a split-plot treatment structure. Each growing season had lower amounts of precipitation than normal, however, rains occurred within days of in-season N applications and minimized N losses for these treatments. We found no consistent yield or N uptake differences among at-planting sources, however, ESN and SuperU tended to have greater amounts of after-

harvest inorganic soil N at each N rate and the ESN/Urea blend had greater yield and N uptake in 2020, the year with highest soil-moisture content at planting. For in-season treatments, UAN Surface had greater yield, N uptake, and after harvest inorganic soil N at N rates of 56 and 84 kg N $ha^{-1}$ rates among the other in-season sources and placements. In dry conditions, low yield potential combined with low risk for N losses likely decreased the potential of corn crops to realize major agronomic benefits from the 4R treatments examined here.

## 2.2 Introduction

### 2.2.1 Importance of Nitrogen in Cropping Systems

Adequate nitrogen (N) supply is essential for high productivity in cereal crops, such as corn; N fertilizer influences corn's photosynthetic capacity, yield, and grain quality (Muchow 1998). Factors including the expansion of cropland, better management, and increases in synthetic N fertilizer inputs enabled the doubling of global food production during the 20$^{th}$ century. Synthetic fertilizer inputs increased from approximately 11 to 94 Tg N $yr^{-1}$ from 1960 to 2010 (Zhang *et al.* 2021). Extensive N fertilizer application has resulted in low nitrogen use efficiency (NUE) and high proportions of applied N being lost to the environment on a global scale (Omara *et al.* 2019). Inefficient fertilizer usage also poses a great economic burden to farmers, with estimates of $680 million – $1 billion per year being lost in Canada alone (Biswas and Ma 2016). Corn production is of particular concern since it requires a relatively large amount of N to reach full growth potential and harbours a greater risk for N loss to the environment than other cereals (Olson *et al.* 1982).

Nitrogen losses from agricultural fields impact freshwater and marine ecosystems through eutrophication while contributing to atmospheric greenhouse gas accumulation, ozone depletion, and biodiversity loss (Tilman 1999, Zhang *et al.* 2021). With regard to N management, there have been great technological advancements to reduce environmental impacts during recent decades, such as through the development of enhanced efficiency fertilizers (EEF's) (Dimkpa *et al.* 2020). Despite these advancements, Omara *et al.* (2019) argue there is still much progress to be made in order to improve NUE at a global scale. Figure 1 and Figure 2 provide a visualization for the sources of $N_2O$ and other environmental loss pathways for N in agroecosystems.

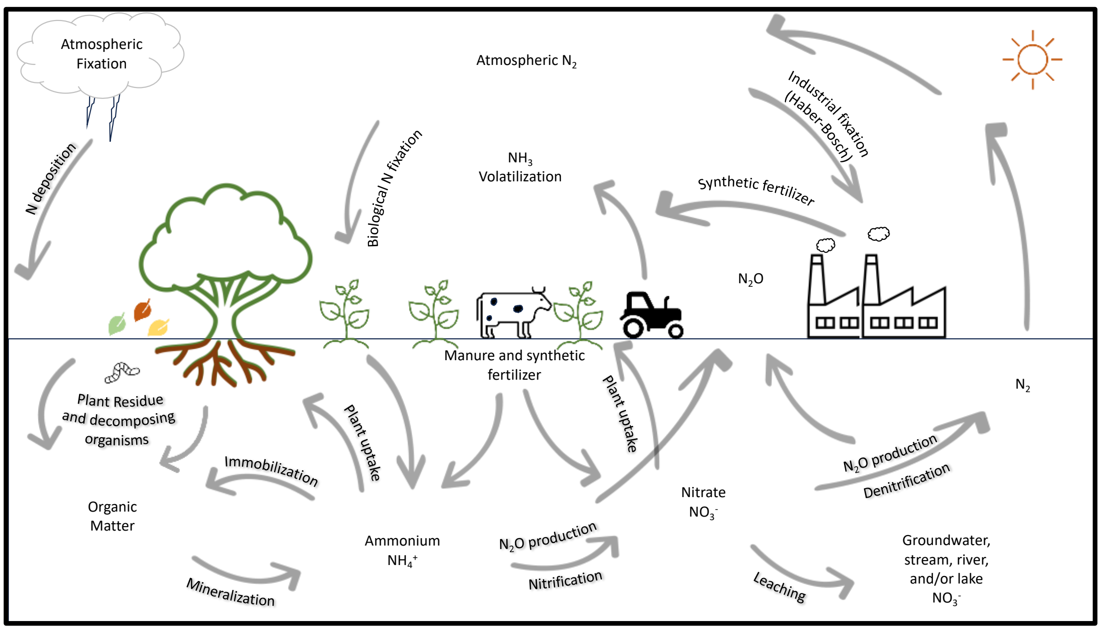



Figure 2.1: Visualization of the nitrogen cycle.

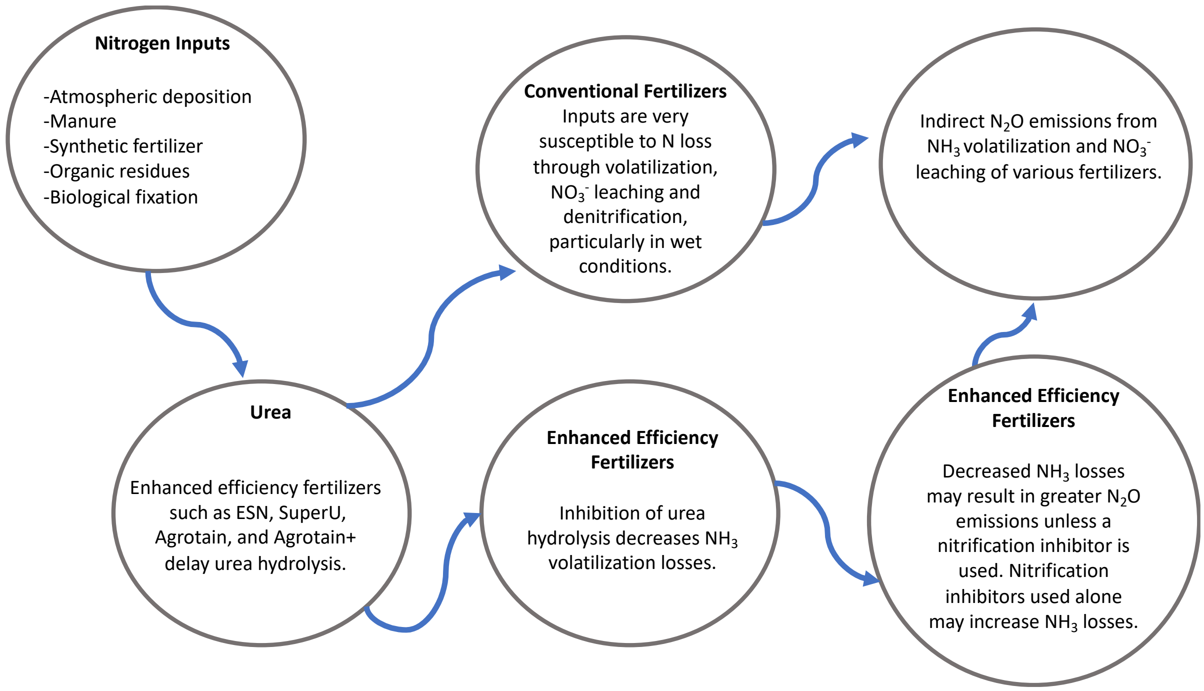



Figure 2.2: Gaseous nitrogen loss pathways for various conventional and enhanced efficiency fertilizers.

### 2.2.2 Measures of Nitrogen Use Efficiency

Nitrogen use efficiency (NUE) is a term used to measure how efficiently plants use and retain soil nitrogen. In agricultural contexts, NUE typically refers to the proportion of applied N that is taken up by crops in a growing season. Nitrogen use efficiency is high when a low proportion of applied N is lost and/or remains in the soil after harvest (Sharma and Bali 2017). Researchers and producers investigating the nutrient response of various crops can evaluate NUE using apparent nitrogen recovery efficiency (NRE), defined as the difference in N uptake of above-ground plant biomass between fertilized and unfertilized plants relative to the application rate. Agronomic efficiency (AE) is another term used to reflect the direct economic benefit of a given fertilizer treatment, calculated as the difference in yield between fertilized and unfertilized plants relative to difference in application rate (Omonode and Vyn 2019). Management practices that improve crop productivity, soil fertility and/or reduce environmental losses are most easily identified by evaluating a combination of NUE and environmental loss parameters over several site years. For example, particular N treatments may not significantly benefit crop productivity, however, may reduce environmental losses, boost residual soil N, and decrease N requirements for the following crop(s) (Dourado-Neto *et al.* 2010). For example, in tropical agroecosystems Dourado-Neto *et al.* (2010). For example, Alonso-Ayuso *et al.* (2016) conducted a three year-field study using the nitrification inhibitor DMPP (3,4-dimethylpyrazole phosphate) which allowed a 23% reduction of N fertilizer application during the second site-year by increasing residual soil N.

### 2.2.3 Environmental Influences on Nitrogen Use Efficiency

Field trials evaluating the efficiency of fertilizer N use have been conducted within a plethora of soil-climatic conditions (Eagle *et al.* 2017). However, many biological, chemical and physical factors interact in soils to influence crop responses to N management and create great variability between and within fields, particularly for coarse-textured soils and rainfed systems (Thapa *et al.* 2016). In a meta-analysis of rainfed corn across China, Gao *et al.* (2012) found that maximum yields were strongly correlated to the yield of unfertilized crops, suggesting that management and environmental conditions (e.g., soil type and rainfall) influenced the variability in average yields between regions. The authors discuss how soils with high organic matter content, for example, provide benefits toward water-holding capacity and nutrient availability while coupling N mineralization with plant uptake in the rhizosphere. These benefits reduce N requirements for maximum yield and the potential for N loss, shrinking the gap between average and maximum yield (Gao *et al.* 2012). This example shows how corn response to N varies greatly depending on environmental conditions and how management actions needed to reach full yield potential will spatiotemporally differ depending on soil-N and water interactions during crop development (Hernández *et al.* 2015). Corn NUE and yield highly depend on the integrated management of soil, crops, water, nutrients, and pests (Cassman *et al.* 2003). For the past few decades, NUE studies have revolved around one or more pillars of the 4R framework (Right Source, Right Rate, Right Time, Right Place) to shape best management practices in various soil-climatic conditions (Venterea *et al.* 2016, Fixen 2020, Woodley *et al.* 2020). This framework aims to benefit economically while reducing environmental losses from N fertilizer application.

### 2.2.4 Right Source

Concerning the Right Source of N, EEF's have shown great potential to increase NUE, yield, and decrease environmental loss through decreased leaching and gaseous emissions. However, research has shown mixed results due to the inherent variability in soil-climatic conditions from year to year (Li *et al.* 2018). 4R metadata has previously been used for identifying trends across space and time. However, these trends are not universal, considering the great variability in soil-climatic conditions (Thapa *et al.* 2016). For at-planting and mid-season applications of N, several studies have shown yield, NUE, and/or residual N benefits for corn in wet conditions by using EEF's such as ESN, SuperU, Agrotain, and AgrotainPlus (Halvorson and Bartolo 2014, Drury *et al.* 2017; Pawlick *et al.* 2019). These studies suggest that the efficacy for EEF's to improve yield and NUE is greatest under warm, wet conditions conducive to high N losses and corn productivity. Nitrogen use efficiency improvements using EEF products that contain nitrification or urease inhibitors may be less significant in clay soils due to interactions between inhibitors, organic particles and clay colloids (McGeough *et al.* 2016). Woodley *et al.* (2020) observed slight yield benefits when using EEF's in a clay loam soil while reducing ammonia volatilization and $N_2O$ emissions. Asgedom *et al.* (2014) observed similar $N_2O$ losses and higher yield/N uptake with Urea compared to ESN or SuperU in clay soils of Manitoba. Southern Manitoba has a semi-arid climate, and dry conditions after the application of granular fertilizers can prolong the release of N into soil, slow-release (polymer-coated) EEF's can be detrimental to yield and N uptake under these circumstances (Sahota 2020). Similarly, the efficacy of mid-season fertilizers such as Agrotain and AgrotainPlus to benefit corn production is highly dependent on soil N and water interactions throughout the growing season (Hernández *et al*. 2015). Due to a lack of precipitation, Beam (2012) found no yield or N uptake benefits with AgrotainPlus compared to conventional UAN. Since corn requires a high amount of water to reach full yield potential, it is rare to observe yield or N uptake benefits from improved soil N retention in dry conditions unless N losses from conventional fertilizers are substantial (Drury *et al.* 2017).

### 2.2.5 Right Rate

After choosing the right source of N for given soil climatic conditions, producers must determine the optimal rate of N to match nutrient supply with crop demand. The optimal source can vary depending on environmental conditions and will influence how fertilizer N becomes available to crops throughout the growing season, which then influences the optimal rate of N to apply. The recommended rate of N is dependent on soil-climatic conditions and producers must use soil-testing a apply fertilizers relative to the amounts of residual soil N and potentially mineralizable N across their fields. Corn typically shows a quadratic or linear-plateau yield response as the N rate increases, with higher NUE at lower rates of N. Excessive N applications can result in N toxicity and high N losses. Given the numerous biogeochemical pathways for N fertilizer, matching crop supply and demand is particularly challenging in rainfed systems. Sometimes, EEF's or side-dress applications can significantly reduce N loss and lower N rates while producing similar or improved yield and N uptake (Ma *et al.* 2010, Halvorson and Bartolo 2014, Venterea *et al.* 2016).

### 2.2.6 Right Time and Right Place

Producers often use split-application timings to match crop N supply and demand more efficiently, N applied as a split application rather than at-planting has been shown to benefit yield and/or N uptake while reducing environmental losses (Ma *et al*. 2010, Burzaco *et al.* 2013, Venterea *et al.* 2016). However, the optimal timing for N application depends on soil-climatic conditions (Spackman *et al.* 2019). For example, fertilizers may be more susceptible to N loss during certain application timings. In Manitoba, volatilization losses can account for a significant proportion of applied N and pose a great risk for producers; Lasisi *et al.* (2019) observed on average 3–28% mean volatilization losses from conventional urea applied in the spring across two growing seasons. The risk of moisture deficit for corn is high in Manitoba, which promotes hot, dry conditions and high volatilization losses from liquid fertilizers, such as UAN (Nadler and Bullock 2011, Ma *et al.* 2010). Timely precipitation following mid-season application promotes the movement of N to deep soil layers (Barker and Sawyer 2017). Injection of UAN rather than surface application is another option to increase soil contact with ammoniacal N to reduce volatilization losses and boost crop productivity; deep placement depth of N has also shown benefits toward yield and NUE by reducing losses and providing better supply of N to plant roots (Rochette *et al.* 2013; Steusloff *et al.* 2019). This situation gives promise toward timing and placement combinations in Manitoba.

### 2.2.7 Objectives

The accumulated body of research focusing on 4R management suggests that N source, rate, timing, and placement interact with management, soil properties, and climatic conditions to influence crop productivity and NUE (Rochette *et al.* 2013, Fixen 2020). With such inherent variability in field research, evidence-based 4R nutrient stewardship is still under development and there is a lack of studies that evaluate multiple sets of practices over multiple site-years. With increasing knowledge of how 4R management combinations interact in various soil-climatic conditions, producers will be better equipped in the future to achieve their socioeconomic and environmental goals. The objectives of this study were to compare corn yield, AE, NRE, and residual soil N between: 1) N sources applied at-planting (Urea (46-0-0), polymer-coated urea (ESN (44-0-0))/Urea, nitrification and urease inhibited urea (SuperU (46-0-0)); 2) N sources surface-applied at the V4 stage (UAN Surface (28-0-0), Agrotain (urease inhibited UAN), AgrotainPlus (nitrification and urease inhibited UAN); and 3) Placements of UAN (28-0-0) applied at V4 (UAN Surface, UAN Shallow (1.5”), UAN Deep (3”)). These comparisons were made between N treatments at various N rates (56, 84, 112, 164 kg ha$^{-1}$). Replicated field trials were conducted on commercial farm fields in 2018, 2019, 2020.

### 2.2.8 Hypotheses

**2.2.8.1 At-Planting Sources.** The risk of water deficit for corn is high in Manitoba and the risk of N leaching is low; corn crops are more likely to be water-limited than N-limited with adequate fertilization from year–to–year (Paolo and Rinaldi 2008, Nadler and Bullock 2011). It was hypothesized that EEF's would not give benefits toward yield, AE or NRE compared to conventional urea without warm, wet conditions that promote N losses and/or high corn productivity (Abalos *et al*. 2014, Sistani *et al.* 2014). It was hypothesized that EEF's would increase residual N due to reductions in environmental losses.

**2.2.8.2 In-Season Sources.** Similarly, yield and NUE benefits for in-season applications have varied across studies, EEF's are more effective compared to UAN with warm, wet conditions that are conducive to N loss, either by gaseous emission or leaching (Akiyama *et al.* 2010, Gagnon *et al.* 2012, Watkins 2013, Woodley *et al.* 2018, Woodley *et al*. 2020). Timely precipitation after in-season applications may negate EEF's benefits on yield and/or N uptake (Woodley *et al.* 2018, Woodley *et al*. 2020). With a high risk for moisture deficit risk for corn grown in Manitoba, it was hypothesized that EEF's would not give agronomic benefit but may increase residual N by reducing environmental losses.

**2.2.8.3 In-Season Placements.** Deep banding may increase yield and NUE through more adequate placement for crop demand and greater N adsorption to soil particles and organic matter (Steusloff *et al.* 2019). It was hypothesized that deep and shallow banding would have a significant, positive effect on yield and NUE compared to surface dribble banded UAN with conditions favourable for high volatilization losses (Halvorson and Del Grosso. 2013, Woodley *et al.* 2018). Deep and shallow banding may negatively affect crop productivity in wet conditions that promote $NO_3^-$ leaching (Rochette *et al*. 2013).

**2.2.8.4 At-Planting Vs. In-Season Conventional.** Yield and N uptake tend to be more variable for split-applications in rainfed systems, however they can be used to match crop N supply more adequately with N demand. Corn N demand is greater at later growth stages, therefor split applications can improve N uptake and yield in situations where there is a high risk for N loss at-planting and adequate moisture for the crop to realize benefits later in the growing season (Burzaco *et al.* 2013). Due to high risk of moisture deficit for corn grown in Manitoba (Nadler and Bullock 2011), it was hypothesized that urea applied at-planting would have significantly greater $N_2O$ emissions and yield compared to split application of UAN since both crops and microbes are likely to have greater access to N and soil moisture early in the growing season, particularly in sandy soils with low water-holding capacity.

## 2.3 Materials and Methods

### 2.3.1 Site Description

For three years (2018, 2019, 2020), field experiments were conducted on level to gently undulating sandy lacustrine soils of the Lower Assiniboine Delta situated in the rural municipalities of Dufferin and Grey, Manitoba. This is an area where fine-clay soils of the Red-River Valley transition to coarse-textured regosols that developed through cycles of interbedded sand and silt deposits throughout the existence of post-glacial Lake-Agassiz (Boyd 2007). Imperfectly drained sandy soils that are influenced by high water tables can facilitate high potential for leaching of N fertilizers with improper management (Agriculture and Agri-food Canada 1999. Boyd 2007). In 2018, a field experiment was conducted North of Carman, Manitoba (49°32’52”N, 98°00’48”W) in soils mapped as Almasippi very fine sand; the 2019 experiment was conducted in Haywood, Manitoba (49°40’54”N, 98°11’57”W) in soils mapped as Almasippi loamy fine sand; the 2020 field experiment was conducted North of Carman, Manitoba (49°32’52”N, 98°00’30”W) in soils mapped as Almasippi very fine sand (Agriculture and Agri-Food Canada 1999). These soils are characterized as level with minimal erosion, non-stony and non-saline; Table 2.1 shows soil characteristics for each site-year. Study sites were alternated each year and corn seed (Dekalkb DK 33-78RIB) with a relative maturity of 83 and 2450 CHU requirement was planted following soybeans in each year.

Table 2.1 Soil parameters observed at planting for each site-year, 2018–2020. Composite samples were sent to Farmers Edge for analysis, $NO_3^-$ and $SO_4^-$ were analyzed at 0–6" and 6–18" depths and summed together; other parameters were only tested from 0–6" depth.

| | Year | | |
|---|---|---|---|
| Soil Parameter | 2018 | 2019 | 2020 |
| pH | 7.6 | 8.5 | 8.2 |
| EC (mS/cm) | 0.23 | 0.15 | 0.28 |
| Organic matter (%) | 2.1 | 3.7 | 2.5 |
| $NO_3^-$ (mg/kg) | 5.5 | 6.4 | 3.0 |
| $PO_4$ -Olsen P (mg/kg) | 13 | 8.4 | 5.2 |
| K (mg/kg) | 140 | 54 | 150 |
| $SO_4^-$ (mg/kg) | 2.3 | 7.5 | 4 |
| Zn (mg/kg) | 0.99 | 0.55 | 0.7 |
| Cu (mg/kg) | 0.27 | 0.26 | 0.4 |

### 2.3.2 Experimental and Treatment Design

For each site-year, a split-plot layout with 34 treatments was replicated in a randomized complete block design with fertilizer source/placement as main plot and N rate as sub-plot (Figure 2.3). Each block included plots with one of two timings (at-planting and in-season), and 1 of 4 N rates (0.5, 0.75, 1.0, 1.5 times recommended) of various N sources and various placement depths. To compare at-planting N-sources; Urea, ESN70%:Urea30%, and SuperU were broadcast-incorporated in 2019 and 2020. In 2018, at -planting N sources were Urea, ESN, and SuperU. To compare mid-season N sources, mid-season treatments received 35 kg N $ha^{-1}$ of side-banded urea at planting, later receiving the remaining proportional rate (0.5, 0.75, 1.0, 1.5 of recommended) as UAN, UAN/Agrotain or UAN/AgrotainPlus by surface dribble-band application at the V4-V5 stage. To compare mid-season N placements, mid-season UAN treatments were applied as surface dribble (surface), shallow side-dress, or deep side-dress (Table 2.2). Shallow and deep band treatments were placed 5.08cm to the side of seed placement at 3.81cm and 7.62cm depth, respectively.

Table 2.2: Fertilizer treatments used for field experiments in each site-year, each including 4 randomized plots receiving N rates of 56, 84, 112, and 168 kg N $ha^{-1}$.

| Nitrogen Source | Time | Placement |
|---|---|---|
| Urea | At-planting | Broadcast incorporated |
| ESN/Urea | At-planting | Broadcast incorporated |
| SuperU | At-planting | Broadcast incorporated |
| Urea + UAN | V4–V5 stage | Shallow side dribble |
| Urea + UAN/Agrotain | V4–V5 stage | Shallow side dribble |
| Urea + UAN/AgrotainPlus | V4–V5 stage | Shallow side dribble |
| Urea + UAN | V4–V5 stage | Shallow band (3.81cm depth) |
| Urea + UAN | V4–V5 stage | Deep band (7.62cm depth) |
| None | None | None |
| Urea (35 kg $ha^{-1}$) | At-planting | Side band |

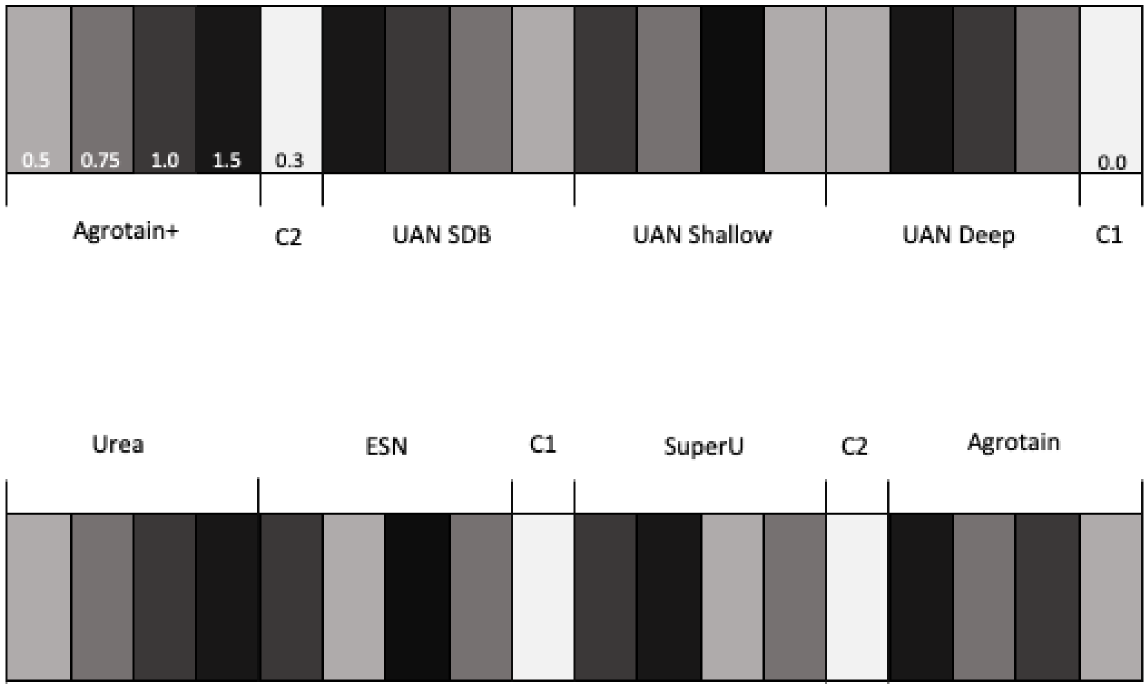



Figure 2.3 Visualization for four-row corn plots within one block of a randomized complete block design. C1 represents control plots receiving 0 kg N $ha^{-1}$ and C2 represents mid-season control plots receiving 35 kg N $ha^{-1}$. Black lines separate ‘main plots’ of N sources that contain ‘subplots’ which are given either 0.5, 0.75, 1.0, or 1.5 times the recommended N rate. Note: The spacing between ‘half blocks’ are not to scale.

### 2.3.3 Field Operations

On the day of planting (May 25$^{th}$) in 2018, the Urea, ESN, and SuperU treatments were broadcasted by hand and incorporated with a tandem disc. A phosphate (0-45-0) and potash (0-0-60) blend of (2:1) was applied at 115 kg $ha^{-1}$ (half of the target rate due to mechanical issues, there were no visual effects on the crop throughout the growing season). Roundup Weather Max 540 was applied on June 7$^{th}$ (0.25 L $ha^{-1}$) and June 20$^{th}$ (1.5L $ha^{-1}$). In-season N fertilizer was applied on June 26$^{th}$ (DOY 177) with a John Deere 1050 applicator while corn was at V4-V5 stage. Biomass sampling and combine harvesting took place on October 29$^{th}$ and 30$^{th}$. Post-harvest soil sampling was done immediately after corn harvesting.

In 2019, at-planting treatments were broadcasted and incorporated on May 6$^{th}$. Background fertilizer was a 16:8:1:1 blend of phosphate: potash: zinc: copper applied at 218 kg ha$^{-1}$ as corn was planted on May 9$^{th}$. Glyphosate was applied on June 11$^{th}$ and June 18$^{th}$ (1.5L ha$^{-1}$ with 270 L ha$^{-1}$ water); 2-4D amine 600 was also applied on June 18$^{th}$ to target volunteer soybeans (0.45 L ha$^{-1}$) and didn't affect the corn crop in the long term. Mid-season N application took place on June 28$^{th}$ (DOY 179) in the same fashion as 2018 and alleyways between blocks were mowed on July 11$^{th}$. Biomass sampling and combine harvesting took place on October 23$^{rd}$ and 24$^{th}$ and post-harvest soil samples were taken from October 30$^{th}$ – November 1$^{st}$.

In 2020, at-planting treatments were broadcasted and incorporated on May 6$^{th}$. Background fertilizer was a 26:20:2:1 blend of TSP: Potassium Sulfate: Copper: Zinc applied at 275 kg ha$^{-1}$ as corn was planted on May 11$^{th}$. Urea was side-banded to various depth and 2" to the side of the seed for mid-season treatments on May 11$^{th}$. Glyphosate was applied on June 19$^{th}$, mid-season N was applied on June 30$^{th}$ (DOY 182) and alleyways between blocks were mowed on July 9$^{th}$. Biomass sampling occurred from October 2$^{nd}$ - October 6$^{th}$ and combine harvest occurred October 6$^{th}$. Post-harvest soil samples were taken October 7$^{th}$, 8$^{th}$,9$^{th}$ and 13$^{th}$.

### 2.3.4 Meteorological Data Collection

In 2018 and 2019, Watchdog® weather-stations were positioned within the field at the Southwest edge of blocks to measure wind gust, direction, speed, air temperature, dew-point temperature, solar radiation, precipitation, and relative humidity at 1-hour intervals from the time of seeding (late May) to harvest (late October). Data from nearby weather stations were used for years 1 and 3 due to equipment complications and the global pandemic, respectively (Environment and Climate Change Canada 2020).

### 2.3.5 Yield, Agronomic Efficiency and Apparent Nitrogen Recovery Efficiency

Corn biomass and grain yield were determined by weighing eight whole plants from each plot's second and third (middle) corn-rows by hand (shears were used to cut each plant at the soil surface). Plants were weighed in the field, cobs were then picked by hand, weighed separately, and threshed using a plot combine in stationary mode. A 300–700g subsample of grain was transported back to the lab in a paper bag. In 2018 and 2020, three of the previously harvested plants and three of the threshed cobs were then mowed in the field, mixed thoroughly by hand and a 300–700g subsample of biomass was transported back to the lab in a paper bag (Mixture of mowed stalks, leaves, and threshed cobs). Biomass and grain subsamples were weighed before being placed in a drying room at approximately 45 ºC and being placed in a drying oven at 65-77 ºC for 24-72 hours. Samples were then re-weighed to quantify moisture loss and dry biomass/grain yield. These samples were also used as samples for biomass and grain N content analysis. Dried samples were stored in darkness at room temperature for 3–12 months and biomass samples were ground through a 1 mm screen on a Wiley Mill (Thomas Wiley Laboratory Mill Model 4). Grain samples were ground with handheld grinders, then analyzed dried and ground for N concentration using an Elementar Vario Macro C-N analyzer® (Halvorson *et al.* 2010). Biomass and grain samples from 2019 and 2020 were sent to be analyzed by Agvise Laboratories in the same fashion as the 2018 samples.

In 2019, field conditions were too wet for stationary threshing of grain and mowing of biomass in the field. Biomass and cobs were transported back to the lab in mesh bags and placed in a drying room at approximately 45 °C, samples were then re-weighed at 4% moisture content and grain was threshed at an indoor facility at the University of Manitoba. For each plot, a 300–700g subsample of grain was taken for N content analysis. Biomass and cob samples were then ground separately; subsamples were taken from ground material of 3 plants and 3 cobs, respectively. For this reason, cob N content was analyzed separately from biomass subsamples in 2019. Total N content of cobs and biomass were then added together for each plot for a measure of N in above-ground biomass. Apparent nitrogen recovery efficiency and agronomic efficiency values were then calculated for each fertilized treatment using the following equations;

(1) $$NRE\ (\%) = \frac{\text{TNF} - \text{TNC}}{\text{Change in N applied}}$$

(2) $$AE\ (kg/kg)\ = \frac{\text{GYF and GYC}}{\text{Change in N applied}}$$

Where NRE (%*)* is apparent nitrogen recovery efficiency, TNF and TNC represent total plant N uptake of fertilized and control treatments, respectively. If the control treatment is 0 kg N $ha^{-1}$, 'Change in N applied' would be the amount of N fertilizer applied.

Where AE is agronomic efficiency, GYF and GYC represent grain yield (15% moisture) of fertilized and control treatments, respectively (Omonode and Vyn 2019).

### 2.3.6 Soil Sampling, Storage and Analysis

Prior to each growing season, three subsamples of soil were taken at 0–6 and 6–24" depth to gauge residual soil N prior to each experiment. Each Soil sampling began following N application at seeding and subsequently every month of the growing season until directly after harvest when soil samples from 0–15.24cm, 15.24–60.96cm, and 60.96–121.92cm depths were taken using a tractor-mounted hydraulic probe. For in-season soil sampling, triplicate sub-samples were taken for each plot (two within rows and one between) at 0 – 15.24cm and 15.24 – 60.96cm depths. End-of-season, hydraulic core samples were taken in triplicate, throughout the 8 m length of each plot down the middle corn row. All soil samples were then transported on ice for 1–2 hours to the University of Manitoba and then stored at approximately 4ºC until organized (1–5 days) and transferred to -25ºC for longer-term storage. Samples were thawed, chopped by hand, and stored at -25ºC until $NH_4NO_3$ extraction and analysis for gravimetric moisture content.

Soil N extractions were done by mixing 5g soil with 25 mL of 2M KCL solution, shaking for 1 hour (150 epm), placing on a centrifuge for 3.5 minutes at 1350 x *g*, and stored frozen (Maynard *et al.* 1993) prior to analysis by colorimetry for $NH_4^+$ and $NO_3^-$ using a segmented flow analyzer (Technicon AAII). Samples were analyzed colorimetrically for $NH_4^+$ using the Berthelot reaction, $NO_2^-$ by azo dye formation from reaction with sulfanilamide and N-napthylethylene-diamine dihydochloride, and $NO_3^-$ by reduction using Cu-Cd to $NO_2^-$ before azo dye formation, as described by Gao *et al.* (2015). Bulk density of 1.15, 1.25, and 1.35 Mg $m^{-3}$ were assumed for 0 – 15.24cm, 15.24 – 60.96cm, and 60.96 – 121.92cm depths, respectively. Root-zone extractable inorganic N was calculated as the sum of extractable N from 0 – 15.24cm and 15.24 – 60.96cm depths for each plot while Total extractable inorganic N was calculated as the sum of extractable N from 0 – 15.24cm, 15.24 – 60.96cm, and 60.96 – 121.92cm depths.

### 2.3.7 Economically Optimal Nitrogen Rate Models

Using the relationship between grain yield and N rate, quadratic-plateau models were used to calculate the EONR by using the ratio of fertilizer and grain market prices (Hong *et al*. 2007). For this study, Manitoba's lowest available fertilizer prices for 2019 or 2020 were used. Corn grain price was 0.15991 CAD $kg^{-1}$ as of July 2020 (Manitoba Agriculture 2021). Bulk fertilizer prices used for this study are shown in Table 2.3. Quadratic models were fit using PROC NLIN in SAS. Models were fit for each N treatment across the applied rate, residual soil N before planting was included.

Table 2.3: Fertilizer prices from three retail sources in Manitoba used to calculate the EONR for each treatment. (Tenuta 2022, personal communication)

| | Fertilizer prices (CAD $ per kg of N or per kg of UAN used) | | | | | |
|---|---|---|---|---|---|---|
| Source | Urea/Tonne (46-0-0) | ESN/Tonne (44-0-0) | SuperU/Tonne (46-0-0) | UAN/Tonne (28-0-0) | Agrotain | Agrotain+ |
| Source 1 | 1.08 | 1.46 | 1.32 | | | |
| Source 2 | | | | 1.12 | | |
| Source 3 | | | | | 0.172 | 0.247 |

Note: Each kg of UAN mixed with Agrotain costs 1.292$.

### 2.3.8 Statistical Analyses

Separate analyses of variance were performed for at-planting N sources (Urea, ESN/Urea, SuperU), mid-season N sources (UAN Surface, UAN/Agrotain, UAN/AgrotainPlus), and mid-season N placements (UAN Surface, UAN Shallow, UAN Deep) using PROC GLIMMIX in SAS. Treatment means of grain yield, AE, NRE, and residual N were compared at each N rate using Fischer's protected LSD method for post-hoc comparisons ($P$=0.05). Block and site-year were treated as random variables. Block was also a random variable when analyzing data within a site-year. Data were checked for normality and homogeneity of variance using PROC UNIVARIATE in SAS and scatterplots of residual versus predicted values, respectively (Spackman *et al.* 2019). Non-normal distributions were log-transformed for statistical analysis; all figures and tables show non-transformed data. The control treatment was not included in statistical analyses for better comparisons between N treatments. Only two years of data (2019 and 2020) for the ESN/Urea treatment were used in the analyses; in 2018 this treatment was 100% ESN rather than a 70/30 split. There were no significant interactions between site-year and treatment for the parameters tested in this paper ($P < 0.05$).

## 2.4 Results

### 2.4.1 Soil-Climatic Conditions

In general, South-central Manitoba experienced hot and dry conditions compared to climate normal conditions. Table 2.4 shows most months for each growing season had greater mean temperature and lower amounts of precipitation than normal. In 2018, Carman, MB received approximately 2460 corn heat units and 273 mm of precipitation; in 2019, Haywood, MB received approximately 3130 corn heat units and 365.4 mm of precipitation, 193 mm of which precipitated in September and October. In 2020, Carman, MB received approximately 2725 corn heat units and 187 mm of precipitation from the time of planting to the end of harvest. However, October of 2019 had much more precipitation than normal which resulted in relatively high soil moisture in the spring of 2020.

Table 2.4: Mean monthly temperatures and precipitation throughout the 2018–2020 growing seasons for Carman, Manitoba. Climate normals were calculated using Environment and Climate Change Canada historical datasets for Carman MB 1991– 2020. Meteorological data from Carman, MB were used to represent climate normal values for each location included in this study (Carman, Haywood, Carman).

| | May | June | July | August | September | October |
|---|---|---|---|---|---|---|
| Mean temperature (°C) | | | | | | |
| 2018 | 14.7 | 19.0 | 19.9 | 19.0 | 10.5 | 2.8 |
| 2019 | 9.6 | 17.7 | 20.4 | 17.9 | 12.8 | 2.9 |
| 2020 | 10.7 | 18.2 | 20.2 | 18.7 | 12.3 | 2.2 |
| Climate Normal | 11.4 | 17.2 | 19.4 | 18.5 | 13.4 | 5.4 |
| Total Precipitation (mm) | | | | | | |
| 2018 | 47.9 | 98.3 | 42.9 | 31.0 | 43.2 | 21.8 |
| 2019 | 38.0 | 27.2 | 72.1 | 34.5 | 155.3 | 38.4 |
| 2020 | 27.5 | 70.7 | 54.0 | 24.3 | 10.8 | 16.1 |
| Climate Normal | 79.1 | 90.8 | 70.1 | 66.6 | 53.2 | 41.0 |

### 2.4.2 Yield

**2.4.2.1 At-Planting Sources.** Across site-years, each N source had greater mean yield than the control. Relative to other site-years, the control treatment had the greatest yield in 2019; this field had greater organic matter content than the commercial fields used in 2018 and 2020 (Table 2.1). In general, yields increased as N rate increased. Urea and ESN had significantly greater mean yield compared to SuperU at 112 kg ha$^{-1}$ (Table 2.5). Yield results were not consistent between treatments in 2018, however Urea had the greatest mean yield for 84, 112, and 168 kg ha$^{-1}$ in 2019. In 2020, wet soil conditions at the time of planting enabled a quicker release of N by EEF's compared to other years, which provided greater protection from N loss compared to urea and resulted in significantly greater yield and NRE at 84 kg ha$^{-1}$ (Table 2.A3 and 2.A9).

**2.4.2.2 In-Season Sources.** Across site-years, UAN Surface tended to have the greatest yield, AE and NRE at lower N rates (56 and 84 kg ha$^{-1}$) compared to UAN/Agrotain or UAN/AgrotainPlus (Tables 2.5 and 2.8), this trend was most pronounced in 2019 however, treatments did not have significant differences in yield in any individual site-year.

**2.4.2.3 In-Season Placements.** Mid-season placements followed similar trends to mid-season sources, with UAN Surface outperforming UAN Shallow and UAN Deep (Table 2.5); Although no significant differences were found across site-years, UAN Surface tended to have greater yield at lower N application rates of 56 and 84 kg ha$^{-1}$(Figure 2.4).

**2.4.2.4 At-planting Vs. In-season Conventional.** Urea had greater yields than UAN Surface at each N rate excluding 84 kg N ha$^{-1}$ (Table 2.6). Across site-years, there was no significant difference in yield between Urea applied at-planting and UAN applied as side-dress at the V4 stage of growth.

Table 2.5**:** Means and ±1 standard error for corn grain yield (15% moisture) across site-years, at each N rate for Urea, ESN blend, and SuperU (abc); UAN Surface, Agrotain, and AgrotainPlus (ABC); UAN Surface, UAN Shallow, and UAN Deep (xyz).
For each set of comparisons, different letters indicate significant differences using LSD means (*P* <0.05). 2018 ESN blend left out. Results for UAN Surface are given twice for comparison between in-season sources and in-season placements. Source effects were significant at *P* < 0.05 while < 0.1 indicates a trend.

| | | Yield (Mg ha$^{-1}$) | | | | |
|---|---|---|---|---|---|---|
| | N rate (kg ha$^{-1}$) | 0 | 56 | 84 | 112 | 168 |
| At-planting sources | Control | 4.39±0.4 | | | | |
| | Urea | | 7.23±0.7 | 7.32±0.6 | 8.18±0.7a | 8.91±0.5 |
| | ESN | | 6.52±0.7 | 7.39±0.5 | 7.58±0.5a | 9.59±0.7 |
| | SuperU | | 6.97±0.5 | 7.65±0.5 | 7.06±0.6b | 8.91±0.6 |
| In-season sources | UAN Surface | | 6.85±0.7 | 7.82±0.7 | 7.50±0.6 | 8.50±0.5 |
| | UAN/Agrotain | | 6.63±0.4 | 7.25±0.4 | 7.50±0.5 | 8.57±0.5 |
| | UAN/Agrotain+ | | 6.34±0.5 | 7.20±0.4 | 8.09±0.5 | 8.71±0.5 |
| In-season placements | UAN Surface | | 6.85±0.7 | 7.82±0.7x | 7.50±0.6 | 8.50±0.5 |
| | UAN Shallow | | 6.30±0.4 | 7.17±0.4xy | 7.70±0.4 | 8.63±0.3 |
| | UAN Deep | | 5.93±0.3 | 6.60±0.4y | 7.46±0.4 | 8.20±0.4 |
| | **Anova** | | | | | |
| | Planting sources | | 0.8358 | 0.5654 | 0.0227 | 0.3405 |
| | Season sources | | 0.4711 | 0.3575 | 0.3963 | 0.9101 |
| | Season placements | | 0.2343 | 0.0710 | 0.9128 | 0.6619 |

Table 2.6**:** Means and ±1 standard error for corn grain yield (15% moisture), agronomic efficiency (AE), and apparent nitrogen recovery efficiency (NRE) for Urea and UAN Surface across site-years. For each set of comparisons, different letters indicate significant differences using LSD means (*P* <0.05). 2018 ESN blend left out. Results for UAN Surface are given twice for comparison between in-season sources and in-season placements. Source effects were considered significant with *P* < 0.05 while < 0.1 indicates a trend.

| | N rate (kg N ha$^{-1}$) | 56 | 84 | 112 | 168 |
|---|---|---|---|---|---|
| | | | Yield (Mg ha$^{-1}$) | | |
| Urea | | 7.23±0.7 | 7.32±0.6 | 8.18±0.7 | 8.91±0.5 |
| UAN Surface | | 6.85±0.7 | 7.82±0.7 | 7.50±0.6 | 8.50±0.5 |
| Anova | | 0.3261 | 0.3284 | 0.2273 | 0.3827 |
| | | | AE (kg kg-N$^{-1}$) | | |
| Urea | | 49±8 | 34±3 | 32±4 | 25±2 |
| UAN Surface | | 42±8 | 40±6 | 26±5 | 23±4 |
| Anova | | 0.3677 | 0.2995 | 0.1833 | 0.4512 |
| | | | NRE (%) | | |
| Urea | | 78±13 | 52±4a | 61±7 | 44±3 |
| UAN Surface | | 80±12 | 70±9b | 54±6 | 49±4 |
| Anova | | 0.8808 | 0.0797 | 0.3331 | 0.2762 |

### 2.4.3 Agronomic Efficiency and Apparent Nitrogen Recovery Efficiency

**2.4.3.1 At-Planting Sources.** In general, AE and NRE decreased as N rate increased. Across site-years, SuperU had significantly lower AE at 112 kg ha$^{-1}$ compared to Urea and ESN while there were no significant differences for NRE (Table 2.7 and 2.8); however, ESN and SuperU had greater NRE at 168 kg N ha$^{-1}$ ($P$<0.1). In 2018 and 2019, there were no significant differences between treatment means of AE or NRE; in 2020, ESN and SuperU had significantly greater AE than Urea at the 84 kg ha$^{-1}$ rate. **(**Table 2.A4–6). Urea had significantly lower NRE than ESN and SuperU at 84 and 168 kg ha$^{-1}$, and ESN at 168 kg ha$^{-1}$. (Table 2.A7–9)

**2.4.3.2 In-Season Sources.** Apparent nitrogen recovery efficiency of UAN Surface was greatest for each site-year and rate (Table 2.A7–9). Across site-years, mean NRE of UAN Surface at 84 kg ha$^{-1}$ was significantly greater than Agrotain and AgrotainPlus with approximately a 20% increase in recovered N (Table 2.8). The same trend for NRE was observed at 56 kg N ha$^{-1}$ ($P$<0.01), and although not significant, greater N uptake was accompanied by greater average yield and AE at low N rates (Tables 2.5 and 2.7).

**2.4.3.3 Mid-season Placements.** Mid-season placements followed similar trends to mid-season sources. Although no significant differences were found across site-years, UAN Surface tended to have greater AE and NRE at lower N application rates of 56 and 84 kg ha$^{-1}$(Tables 2.7 and 2.8). Across site years, UAN surface showed a trend for greater NRE ($P$<0.1) and increased NRE by more than 40% compared to UAN deep at rates of 56 and 84 kg N ha$^{-1}$ in 2019.

**2.4.3.4 At-Planting Vs. In-Season Conventional.** Across site-years, there were no significant differences for AE or NRE between urea applied at planting and split application (Table 2.6). In 2018, Urea consistently had greater AE and NRE, however UAN Surface tended to outperform Urea in 2019 and 2020, particularly at low N rates of 56 and 84 kg N ha$^{-1}$.

Table 2.7**:** Means and ±1 standard error for corn agronomic efficiency (15% moisture) across site-years. At each rate, mean comparisons were made between Urea, ESN, and SuperU (abc); UAN Surface, Agrotain, and AgrotainPlus (ABC); UAN Surface, UAN Shallow, and UAN Deep (xyz) using LSD means. For each set of comparisons, different letters indicate significant differences using LSD means (*P* <0.05). 2018 ESN blend left out. Results for UAN Surface are given twice for comparison between in-season sources and in-season placements. Source effects were considered significant with *P* < 0.05 while *P* < 0.1 indicates a trend.

| | | Nitrogen Rate (kg ha$^{-1}$) | | | |
|---|---|---|---|---|---|
| | N Rate (kg ha$^{-1}$) | 56 | 84 | 112 | 168 |
| | | Corn agronomic efficiency (kg kg$^{-1}$) | | | |
| At-planting sources | Urea | 49±8 | 34±3 | 32±4a | 25±2 |
| | ESN | 46±7 | 38±6 | 29±4a | 28±4 |
| | SuperU | 46±6 | 37±5 | 23±4b | 26±4 |
| In-season sources | UAN Surface | 42±8 | 40±6 | 26±5 | 23±4 |
| | UAN/Agrotain | 39±5 | 33±3 | 27±3 | 23±3 |
| | UAN/Agrotain+ | 33±6 | 32±4 | 31±4 | 24±3 |
| In-season placements | UAN Surface | 42±8 | 40±6x | 26±5 | 23±4 |
| | UAN Shallow | 34±6 | 31±6xy | 27±4 | 23±3 |
| | UAN Deep | 26±7 | 25±4y | 26±3 | 22±3 |
| | Anova | | | | |
| | Planting sources | 0.8348 | 0.6989 | 0.0375 | 0.6332 |
| | Season sources | 0.4289 | 0.3071 | 0.5046 | 0.8936 |
| | Season placements | 0.2101 | 0.0634 | 0.9866 | 0.8309 |

Table 2.8**:** Means and ±1 standard error for above-ground corn apparent N recovery efficiency (0% moisture) across site-years. At each rate, mean comparisons were made between Urea, ESN, and SuperU (abc); UAN Surface, Agrotain, and AgrotainPlus (ABC); UAN Surface, UAN Shallow, and UAN Deep (xyz). For each set of comparisons, different letters indicate significant differences using LSD means (*P* <0.05). 2018 ESN blend left out. Results for UAN Surface are given twice for comparison between in-season sources and in-season placements. Source effects were considered significant with *P* < 0.05 while *P* < 0.1 indicates a trend.

| | N Rate (kg ha$^{-1}$) | | | | |
|---|---|---|---|---|---|
| | N Rate (kg ha$^{-1}$) | 56 | 84 | 112 | 168 |
| | | Apparent nitrogen recovery efficiency (% N applied) | | | |
| At-planting sources | Urea | 78±13 | 52±4 | 61±7 | 44±3b |
| | ESN | 65±10 | 64±8 | 53±8 | 58±8a |
| | SuperU | 79±6 | 68±6 | 52±5 | 56±5a |
| In-season sources | UAN Surface | 80±12A | 70±9A | 54±6 | 49±4 |
| | UAN/Agrotain | 52±8B | 50±3B | 46±6 | 46±5 |
| | UAN/Agrotain+ | 47±12B | 51±6B | 51±7 | 46±5 |
| In-season placements | UAN Surface | 80±12x | 70±9x | 54±6 | 49±4 |
| | UAN Shallow | 56±11xy | 57±9xy | 56±7 | 45±5 |
| | UAN Deep | 42±12y | 45±8y | 53±6 | 51±4 |
| | ANOVA | | | | |
| | Planting sources | 0.7518 | 0.1287 | 0.4855 | 0.0843 |
| | Season sources | 0.0578 | 0.0461 | 0.5218 | 0.8442 |
| | Season placements | 0.0632 | 0.0774 | 0.9366 | 0.5260 |

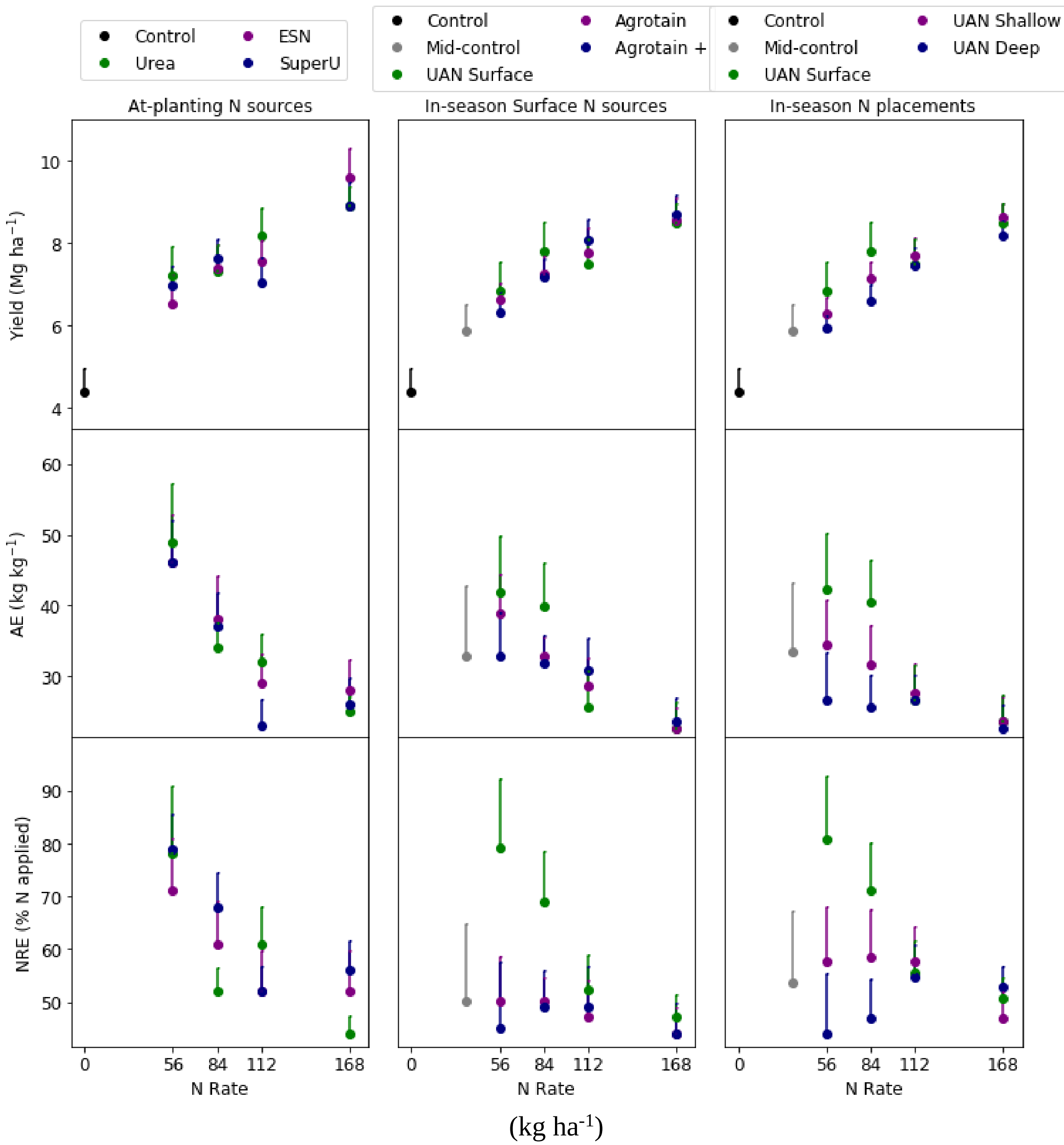



Figure 2.4: Mean Yield, agronomic efficiency, and apparent nitrogen recovery efficiency across three site-years. Error bars represent +1 standard error of the mean.

### 2.4.4 Residual Inorganic Nitrogen

**2.4.4.1 At-Planting Sources.** Across site-years, total inorganic extractable N to 121.92cm depth was greater for ESN and SuperU compared to Urea across N rates, with Urea having a significant difference from ESN at 168 kg $ha^{-1}$(Table 2.9). All treatments had significantly different residual N to 60.96cm depth at 168 kg $ha^{-1}$ and urea consistently had the lowest mean residual N at each N rate with trends of $P < 0.1$ (Table 2.10). Urea had the lowest residual N for most application rates in each site-year, with significant differences in certain situations (Tables A10–15).

**2.4.4.2 Mid-Season Sources.** Total (Table 2.9) and root-zone (Table 2.10) residual N followed a similar pattern to yield; UAN Surface had greater residual N at lower N rates of 56 and 84 kg N $ha^{-1}$. Conversely, Agrotain and/or AgrotainPlus consistently had greater residual N at higher N rates of 112 and 168 kg $ha^{-1}$ throughout site-years (Tables A10–12)

**2.4.4.3 Mid-season placements.** UAN Surface tended to have the greatest total residual N at lower N rates of 56 and 84 kg N $ha^{-1}$; at 84 kg N $ha^{-1}$ UAN Surface. In 2019 and across site-years, UAN Shallow had significantly greater residual inorganic N at 112 kg $ha^{-1}$ (Table 2.9 and Table 2.A11).

**2.4.4.4 At-Planting Vs. In-Season Conventional.** Across site-years, UAN had greater mean residual N from 0–4’ depth at each N rate (Table 2.9). This trend was most pronounced in 2020, when UAN had more than three times the residual N compared to urea at 168 kg $ha^{-1}$.

Table 2.9**:** Means and ±1 standard error for total residual N post-harvest (0–121.92cm depth) across site-years. At each rate, mean comparisons were made between Urea, ESN, and SuperU (abc); UAN Surface, Agrotain, and AgrotainPlus (ABC); UAN Surface, UAN Shallow, and UAN Deep (xyz). For each set of comparisons, different letters indicate significant differences using LSD means (*P* <0.05). 2018 ESN blend left out. Results for UAN Surface are given twice for comparison between in-season sources and in-season placements. Source effects were considered significant with *P* < 0.05 while *P* < 0.1 indicates a trend.

| | | Total extractable inorganic N (kg N ha$^{-1}$) | | | | |
|---|---|---|---|---|---|---|
| | N Rate (kg ha$^{-1}$) | 0 | 56 | 84 | 112 | 168 |
| At-planting sources | Control | 40±12 | | | | |
| | Urea | | 42±7 | 47±10 | 52±10 | 60±10b |
| | ESN/Urea | | 37±4 | 39±8 | 55±9 | 76±17a |
| | SuperU | | 47±8 | 52±8 | 66±12 | 82±15a |
| In-season sources | UAN Surface | | 53±11 | 59±10 | 56±7 | 82±11 |
| | UAN/Agrotain | | 38±8 | 49±7 | 62±11 | 85±11 |
| | UAN/Agrotain+ | | 41±5 | 55±7 | 61±7 | 103±17 |
| In-season placements | UAN Surface | | 53±11 | 59±10 | 56±7y | 82±11 |
| | UAN Shallow | | 51±6 | 55±8 | 84±17x | 92±15 |
| | UAN Deep | | 42±6 | 41±5 | 64±11xy | 89±16 |
| | Anova | | | | | |
| | Planting sources | | 0.2214 | 0.6490 | 0.1320 | 0.0368 |
| | Season sources | | 0.6166 | 0.4936 | 0.7295 | 0.4767 |
| | Season placements | | 0.4361 | 0.2012 | 0.0745 | 0.7467 |

Table 2.10**:** Means and ±1 standard errors for root-zone N post-harvest (0–60.96cm depth) across site-years. At each rate, mean comparisons were made between Urea, ESN, and SuperU (abc); UAN Surface, Agrotain, and AgrotainPlus (ABC); UAN Surface, UAN Shallow, and UAN Deep (xyz). For each set of comparisons, different letters indicate significant differences using LSD means (*P* <0.05). 2018 ESN blend left out.  Results for UAN Surface are given twice for comparison between in-season sources and in-season placements. Source effects were considered significant with *P* < 0.05 while *P* < 0.1 indicates a trend.

| | N Rate (kg  ha$^{-1}$) | 0 | 56 | 84 | 112 | 168 |
|---|---|---|---|---|---|---|
| | | | Root-zone extractable inorganic N (kg N ha$^{-1}$) | | | |
| | | 22±4 | | | | |
| At-planting sources | Urea | | 21±2b | 23±3 | 28±4b | 29±4b |
| | ESN | | 23±3ab | 23±4 | 29±3ab | 45±7a |
| | SuperU | | 25±3a | 24±3 | 35±5a | 43±9ab |
| In-season sources | UAN Surface | | 25±3 | 30±4 | 32±4 | 51±8 |
| | UAN/Agrotain | | 24±3 | 28±2 | 36±5 | 53±8 |
| | UAN/Agrotain+ | | 22±2 | 28±4 | 30±3 | 62±13 |
| In-season placements | UAN Surface | | 25±3 | 30±4x | 32±4 | 51±8 |
| | UAN Shallow | | 22±2 | 24±2y | 33±6 | 44±7 |
| | UAN Deep | | 20±2 | 23±3y | 30±4 | 44±7 |
| | Anova | | | | | |
| | Planting sources | | 0.0920 | 0.3981 | 0.0620 | 0.0008 |
| | Season sources | | 0.6689 | 0.7942 | 0.4772 | 0.7214 |
| | Season placements | | 0.1953 | 0.0922 | 0.7433 | 0.6827 |

### 2.4.5 Economically Optimal Nitrogen Rate Models

It was determined that calculations of EONR were inaccurate in such dry conditions where N losses were limited and the N rates included in this study were not high enough to reach the plateau of yield response to N fertilizer. Inherent variability between yield, blocks, site-years, grain and fertilizer pricing influence the EONR of various fertilizers differently. As shown in

Figure 2.5, the plateau of crop yield was predicted to be at unreasonably high N rates in most situations (See appendices Table 2.A19– 2.A21).

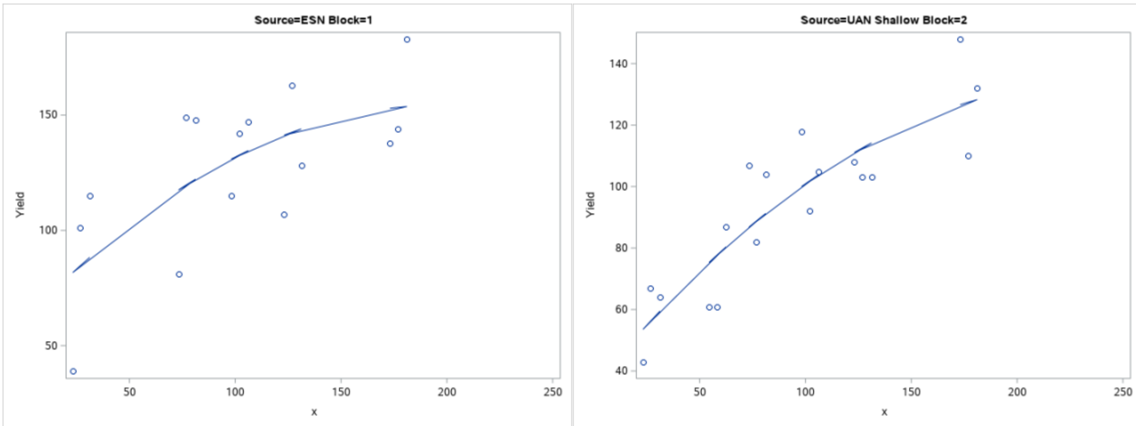



Figure 2.5: Quadratic models produced to estimate economically optimal nitrogen rates in SAS. X = applied fertilizer rate plus background soil inorganic nitrogen. X represents the N rate applied plus residual N at-planting.

## 2.5 Discussion

### 2.5.1 At-Planting Sources

The efficacy of various management practices at achieving specific goals, such as increasing yield, is highly dependent on soil-climatic conditions; Gao *et al*. (2012) discuss how factors such as organic matter content and precipitation patterns can influence maximum yields, noting how corn production of fertilized treatments are spatially dependent on site-specific factors and the productivity of unfertilized soils. Dry conditions were persistent with the exception of September and October of 2019; antecedent conditions led to wetter soil conditions during the spring of 2020 compared to other site-years. Dryer than normal conditions continued throughout the following growing season. This situation shows how contrasting soil moisture conditions affect N release and losses from broadcast incorporated, granular fertilizers applied at-planting; contrasting conditions give a better perspective of how EEF's can be used to give agronomic benefit in different situations. Table (3.2) shows soil moisture was at its peak in the spring of 2020 compared to other site-years, coinciding with the greatest daily fluxes of $N_2O$ from conventional urea throughout the study period. SuperU and ESN also had significantly greater yield, NUE, and NRE at 84 kg $ha^{-1}$ compared to urea in 2020. SuperU and ESN gave agronomic benefits at each N rate although not significant (Table 2.A3, 6, 9). High levels of soil moisture at the time of fertilizer application renders conventional urea vulnerable to volatilization, $N_2O$ emissions, leaching, run-off and denitrification losses, thus decreasing the amount of available N compared to control release and double inhibitor products such as ESN and SuperU, respectively.

Although many researchers have observed agronomic benefits using EEF's such as ESN and SuperU, controlled-release fertilizers can be detrimental to corn production in dry conditions due to the delayed release of N in soil (Sahota 2020). SuperU also delays urea hydrolysis and subsequent nitrification of ammonia, influencing the form of plant available N throughout the growing season. Particularly in dry conditions, urea undergoes hydrolysis more rapidly than EEF's and $NH_4^+$ is quickly converted to $NO_3^-$; Urea had greater $NO_3^-$ concentrations compared to SuperU and ESN on DOY 151 of 2018 in this study (Chapter 3).

Contrasting agronomic responses to different fertilizer sources in each site-year make it difficult to outline trends across only three site-years, however, these results give a better perspective of how EEF's applied at planting can either be beneficial or detrimental to crop productivity depending on environmental conditions. Wetter conditions promote N loss and allow crops to take advantage of greater N retention by EEF's throughout the growing season. Dry conditions restrict N loss and decrease the likelihood of realizing crop benefits from improved N retention.

Root-zone N was the lowest in 2020 due to wetter soil conditions promoting greater N losses, reflecting the agronomic benefit EEF's had on the crop, particularly ESN. EEF's are more likely to benefit yield and/or NUE in warm, wet conditions where N losses are more substantial (Sistani *et al.* 2014). Many studies have noted how EEF's promote soil N retention through decreased N losses; both controlled-release and inhibitor products slow the transformation of soil N through urea hydrolysis and nitrification; Halvorson and Bartolo (2014) observed yield benefits and greater soil retention using ESN compared to Urea. Pawlick *et al.* (2019) observed greater residual N by SuperU than Urea in rainfed corn. We did not measure leaching in this study and only measured volatilization losses qualitatively at the 112 kg N ha$^{-1}$ rate, however, our residual N results agree with findings from past studies to show that EEF's reduce N loss through various pathways and retain soil N for longer periods of time.

### 2.5.2 In-Season Sources

Similar to at-planting sources, it was challenging to outline consistent agronomic trends among mid-season sources of N. Results in the current study indicate that UAN/agrotain and UAN/AgrotainPlus did not significantly improve yield, NUE or NRE compared to conventional UAN; with the exception that conventional UAN had significantly greater NRE at 56 and 84 kg N ha$^{-1}$, in 2019. Beam (2012) found no significant difference in yield or N uptake between UAN and AgrotainPlus in dry conditions due to limited crop productivity and N losses. As reflected by the meteorological conditions observed in this study, the risk of moisture deficit is high for corn grown in Manitoba and precipitation is more likely to be a limiting factor for productivity rather than N, particularly at higher N rates (Nadler and Bullock 2011). However, despite dry conditions in each site-year, precipitation events of at least 5 mm occurred within a few days of mid-season N application, Woodley *et al*. (2018) emphasize how timely precipitation after in-season N application limits volatilization losses by incorporating N into deeper soil layers (Afshar *et al.* 2018, Woodley *et al.* 2018). In 2018, mid-season application occurred June 26$^{th}$ (DOY 177) before 29.7 mm precipitation on June 29$^{th}$ (DOY 180); in 2019, fertilizer was applied June 28$^{th}$ (DOY 179) before 5.2 mm precipitation on June 29$^{th}$ (DOY 180); in 2020, fertilizer was applied June 30$^{th}$ (DOY 182) prior to 24.2mm precipitation the same day. Timely precipitation events decrease volatilization losses and move N to deeper soil layers (Lasisi *et al.* 2019). UAN Surface likely had greater N uptake at low N rates due to more readily available forms of inorganic N during early vegetative growth stages, which are periods of high N demand for corn. We observed timely rainfall directly after in-season N application in each site-year. Barker and Sawyer (2017) found a lack of response to inhibitor products with timely rainfall after application, suggesting that N from conventional products was moved to deeper soil profiles where temperatures were lower and microbial transformation of N was slowed; this explains why we observed significantly greater NRE in 2019 using UAN Surface compared to AgrtoainPlus and Agrotain at 84 kg N ha$^{-1}$; total residual N was also greater at low N rates. Therefore, when timely rains occur directly after N application, results from this study suggest that surface placement of conventional UAN is an optimal management decision to reduce environmental loss, improve nitrogen use efficiency, and/or increase soil N retention; the 4R management decisions that achieve these goals most efficiently are spatially dependent on environmental conditions from year to year (Eagle *et al.* 2017).

More consistent trends would likely have been observed between treatments with the absence of timely rainfall and greater volatilization losses by UAN Surface compared to EEF's. However, we observed greater residual N for UAN Surface at lower N rates where the concentration of $NH_3$ at the soil surface is relatively low and the risk for volatilization loss is lower than at high N rates (Ma *et al.* 2010). AgrotainPlus had the greatest residual N at 168 kg $ha^{-1}$, and compared to low N rates, the difference in $NH_3$ concentration between the soil surface and the atmosphere is much greater. Urease and nitrification inhibitors have more potential to reduce volatilization loss and retain soil N at higher N rates and thus improve nitrogen use efficiency compared to conventional fertilizers applied at similar N rates (Ma *et al.* 2010). When timely precipitation is not received soon after N application, Agrotain and AgrotainPlus have more potential to reduce N losses, particularly through volatilization since they contain a urease inhibitor (Jones *et al.* 2007).

### 2.5.3 In-Season Placements

Similarly, significant differences in yield, AE, and/or NRE were difficult to outline with such timely rainfall after mid-season application; the main goal of shallow and deep placement in this context was to reduce volatilization losses, which were likely minimized in each site-year due to timely rainfall (Woodley *et al.* 2018). Timely precipitation events may have negated the potential agronomic benefits that shallow and deep placement would have had compared to conventional fertilizer, since volatilization losses were likely minimized. Alternatively, Deep placement depth may promote downward movement of N compared to surface applications, resulting in greater N losses by leaching (Rochette *et al.* 2013). Placement depth is a double-edged sword in this situation, and the agronomic results highly depend on soil-climatic conditions from year to year.

Soil-water interactions throughout the growing season influence N loss and soil N retention and subsequent nitrogen use efficiency. Decreased N losses may result in agronomic benefits, however this is more common in warm, wet conditions (Noellsch *et al.* 2009). Woodley *et al.* (2018) found injection of UAN reduced volatilization losses while boosting corn yield and NUE, compared to surface application. Drury *et al.* (2017) observed similar results; these studies were conducted in clay soils, at high N rates (130 kg $ha^{-1}$) where water-holding capacity is greater than in sandy soils and corn yield potential is greater than in dry conditions. The risk for volatilization increases with N rate, thus increasing the potential for EEF's, shallow, or deep placement to mitigate losses and provide agronomic benefit. Contrastingly in this study, the risk for volatilization loss was low with timely precipitation events occurring within five days of N application in each site-year. This explains why we observed greater yield and NUE for UAN Surface at low N rates of 56 and 84 kg N $ha^{-1}$. UAN Surface provided more readily available, diverse N pools during a growth stage with high crop N demand.

### 2.5.4 At-Planting Vs. In-Season Conventional Sources

Corn begins more rapid uptake of water and nutrients near the V6 stage of growth, therefor split-applications of N have great potential to reduce N losses and improve NUE (Abendroth *et al.* 2011). The decision to apply N at-planting or in-season is largely dependent on socioeconomic and environmental factors, however split application of N has increased yield and/or N uptake compared to at-planting in many situations (Clark 2020). For claypan soils in Kansas, Sweeney and Diaz (2021) observed up to 15% greater yield with split application compared to at-planting application of N; in a meta-analysis of nitrogen application timing for corn in the United states, Clark (2020) observed greater grain yield when split applications were used in coarse textured soil with high potential for N loss and regions that received consistent rainfall near the time of side-dress application; single applications at-planting produced greater yield in soil with high cation exchange capacity, silt content, or clay content to provide nutrient and water retention benefits. We observed contrasting agronomic benefits when comparing urea applied at-planting to a split application of urea and UAN.

Drought conditions prevailed for most of the study period, however, precipitation events occurred within days of in-season N application in each site-year, which minimized $NH_3$ volatilization losses (Woodley *et al.* 2018). In 2018, we qualitatively observed the greatest $NH_3$ volatilization losses from UAN Surface directly after in-season application (Figure 3.6); Urea likely outperformed UAN surface at most N rates due to greater N losses in this site-year using split-application. The urea treatment took advantage of early season soil-moisture and greater concentrations of soil N in this site-year.

In 2019, UAN outperformed Urea at low N rates (56 and 84 kg N $ha^{-1}$) while Urea outperformed UAN at high N rates (112 and 168 kg N $ha^{-1}$). At high N rates, there is a greater risk for volatilization loss when the amount of ammoniacal N is high in soil solution as compared to the atmosphere (Ma *et al.* 2010); surface placement of UAN is highly susceptible to volatilization loss with high soil temperatures in the middle of the growing season (Liu *et al.* 2020). Given the dry conditions throughout most of each growing season, urea granules were less susceptible to environmental loss and more adequately met crop N demand at high N rates. At low N rates, soil N pools were kept at relatively low levels throughout the growing season by using split applications, which minimized the potential for N loss and synchronized the timing of N application with N demand to improve NUE.

Yield and NUE measures that result from various at-planting and in-season applications methods are highly dependent on soil-climatic conditions from year to year. In 2020, high soil moisture conditions rendered at-planting N applications more susceptible to N loss and resulted in UAN outperforming urea; UAN had greater yield ($P < 0.1$ at 112 kg N $ha^{-1}$), AE, and NRE (*P*

< 0.05 at 168 kg N ha$^{-1}$) at each N rate excluding 56 kg N ha$^{-1}$ (Table 2.A18). These results agree with past studies suggesting that split-applications are most beneficial for grain yield and N uptake in wet conditions with high potential for N loss (Clark 2020); antecedent soil moisture conditions increased the potential for N losses from at-planting treatments early in the growing season. Simultaneously, precipitation events that occurred shortly after in-season application reduced the potential for environmental losses by in-season N application by incorporating N into deeper soil layers (Woodley *et al*. 2020). The environmental losses of N and the subsequent nitrogen use efficiency of N application timing is highly dependent on soil and meteorological conditions from year to year.

Across site-years, we did not observe a significant difference in grain yield or AE when comparing Urea to UAN Surface, however, NRE of UAN Surface was significantly greater than Urea at 84 kg N ha$^{-1}$. Results from this study show that side-dress application was not detrimental to corn productivity and can improve NUE in situations where N applied at planting is susceptible to loss, such as in 2020. Although split applications of N do not consistently provide agronomic benefits in rainfed corn crops of Manitoba, there is still great potential to reduce environmental losses through $NH_3$ volatilization, $N_2O$ emission, $NO_3^-$ leaching, and runoff (Clark 2020).

### 2.5.5 Economically Optimal Nitrogen Rate Models

In medium-textured soils, Tremblay *et al*. (2012) observed increases of yield response to applied N above 134 kg N ha$^{-1}$; there is inherent spatial and temporal variability in corn yield response to N and also great variability in estimation of the EONR. Very dry conditions from 2018–2020 may have limited N losses at higher N rates while underlying silt and clay layers enabled corn crops to take advantage of higher soil inorganic-N concentrations (Boyd 2007). Economically optimal nitrogen rate models would be improved with the addition of site-years with greater amounts of N losses and/or the addition of higher N application rates, which may reveal a more accurate prediction for the plateau of yield response to N rate.

## 2.6 Conclusion

It is unlikely for EEF's applied at-planting to give benefits toward yield, AE or NRE compared to conventional urea without warm, moist conditions that promote N losses and/or high corn productivity (Sistani *et al.* 2014). Although many studies have noted crop benefits with EEF's, few studies have shown notable increases in crop yield or NUE in dry conditions or sandy soils (Abalos *et al.* 2014, Gao *et al*. 2015). The risk of water deficit for corn is high in Manitoba and the risk of N leaching is low; corn crops are more likely to be water-limited than N limited with adequate fertilization from year–to–year (Paolo and Rinaldi 2008, Nadler and Bullock 2011). An appreciable amount of N loss is typically needed through gaseous emissions or leaching for EEF's to positively affect on yield, AE or NRE (Halvorson and Bartolo 2014). ESN had greater yield and N uptake than Urea at the majority of applied N rates in 2020 when soil-moisture conditions were relatively high at-planting; SuperU was less consistent. These results confirm that control release and double inhibitor products applied at-planting have potential to give agronomic benefits to corn crops in this context.

Across site-years, we did not observe a significant difference in grain yield or AE when comparing Urea to UAN Surface, however, NRE of UAN Surface was significantly greater than Urea at 84 kg N $ha^{-1}$. Results from this study show that side-dress application was not significantly detrimental to corn productivity and can improve NUE in situations where N applied at-planting is susceptible to loss. Split applications of N can be used to more adequately meet crop N demand when in-season applications are managed precisely and environmental losses are minimized. Aside from other in-season N sources and placements, UAN Surface also outperformed urea at low N rates of 56 and 84 kg N $ha^{-1}$ in 2019. Minimizing soil N pools throughout the growing season and applying in-season fertilizer at the optimal time before precipitation events resulted in the greatest yield, NUE, and NRE at low N rates.

Deep and shallow banding are most likely to have a significant, positive effect on yield and NUE compared to surface dribble with conditions favourable of high volatilization losses (Halvorson and Del Grosso 2013, Woodley *et al.* 2018). N placement may influence the distribution of soil N pools and subsequently influence the partitioning of energy and crop yield (Peng *et al*. 2012, Rochette *et al.* 2013). UAN Surface performed better than shallow and deep placement at low N rates, where the potential for volatilization loss is lower than at high N rates (Ma *et al.* 2010).

In conclusion, the results of this study were influenced by precipitation patterns and soil-moisture conditions that limited the ability for crops to realize agronomic benefits from various N treatments; additional site-years with greater amounts of precipitation will further improve our understanding of how different 4R N management decisions influence yield and N uptake of corn in sandy, no-till soils of Manitoba.

## 2.7 References

Abalos, D., S. Jeffery, A. Sanz-Cobena, G. Guardia, and A. Vallejo. “Meta-Analysis of the Effect of Urease and Nitrification Inhibitors on Crop Productivity and Nitrogen Use Efficiency.”

*Agriculture, Ecosystems & Environment 189* (2014): 136–44. https://doi.org/10.1016/j.agee.2014.03.036.

Abendroth, L. J., Elmore, R. W., Boyer, M. J., & Marlay, S. K. "Corn Growth and Development." (2011).

Agriculture and Agri-food Canada. "Soils and Terrain. An Introduction to the Land Resource.". Information Bulletin (1999).

Akiyama, H., X. Yan, and K. Yagi. "Evaluation of Effectiveness of Enhanced-Efficiency Fertilizers as Mitigation Options for $N_2O$ and NO Emissions from Agricultural Soils: Meta-Analysis." *Global Change Biology 16*, no. 6 (2010): 1837–46. https://doi.org/10.1111/j.1365-2486.2009.02031.x.

Alonso-Ayuso, M., J. L. Gabriel, and M. Quemada. "Nitrogen Use Efficiency and Residual Effect of Fertilizers with Nitrification Inhibitors." *European Journal of Agronomy 80* (2016): 1–8. https://doi.org/10.1016/j.eja.2016.06.008.

Asgedom, H., M. Tenuta, D. N. Flaten, X. Gao, and E. Kebreab. "Nitrous Oxide Emissions from a Clay Soil Receiving Granular Urea Formulations and Dairy Manure." *Agronomy Journal 106*, no. 2 (2014): 732–44. https://doi.org/10.2134/agronj2013.0096.

Barker, D., and J. Sawyer. "Evaluation of Nitrogen Fertilizer Additives for Enhanced Efficiency in Corn on Iowa Soils." *Crop, Forage & Turfgrass Management 3*, no. 1 (2017): 1–6. cftm2017.02.0010. https://doi.org/10.2134/cftm2017.02.0010.

Beam, K. " The effect of  Agrotain-Plus on strip-till corn with regards to N, P, K, Mg, Ca, S, Fe, Mn, B, Cu, Zn levels." *Cantaurus*, no. 20 (2012); 5–9.

Biswas, D. K., and B. Ma. “Effect of Nitrogen Rate and Fertilizer Nitrogen Source on Physiology, Yield, Grain Quality, and Nitrogen Use Efficiency in Corn.” *Canadian Journal of Plant Science 96*, no. 3 (2016): 392–403. https://doi.org/10.1139/cjps-2015-0186.

Boyd, M. “Early Postglacial History of the Southeastern Assiniboine Delta, Glacial Lake Agassiz Basin.” *Journal of Paleolimnology 37*, no. 3 (2007): 313–29. https://doi.org/10.1007/s10933-006-9044-3.

Burzaco, Juan P., D. R. Smith, and T. J. Vyn. “Nitrous Oxide Emissions in Midwest US Maize Production Vary Widely with Band-Injected N Fertilizer Rates, Timing and Nitrapyrin Presence.” *Environmental Research Letters 8*, no. 3 (2013): 035031. https://doi.org/10.1088/1748-9326/8/3/035031.

Cassman, K. G., Dobermann, A., Walters, D. T., & Yang, H. “Meeting cereal demand while protecting natural resources and improving environmental quality.” *Annual Review of Environment and Resources 28*, no. 3 (2003): 315-358.

Clark, J. “When to Use a Single or Split Application of Nitrogen Fertilizer in Corn.” *Crops & Soils 53*, no. 5 (2020): 20–24. https://doi.org/10.1002/crso.20070.

Dimkpa, C. O., J. Fugice, U. Singh, and T. D. Lewis. “Development of Fertilizers for Enhanced Nitrogen Use Efficiency – Trends and Perspectives.” *Science of The Total Environment 731* (2020): 139113. https://doi.org/10.1016/j.scitotenv.2020.139113.

Dourado-Neto, D., D. Powlson, R. Abu Bakar, O. O. S. Bacchi, M. V. Basanta, P. Cong, G. Keerthisinghe, M. Ismaili, S. M. Rahman, K. Reichardt, M. S. A Safwat, R. Sangakkara, L. C. Timm, J. Y. Wang, E. Zagal, C. V. Kessel. “Multiseason Recoveries of Organic and Inorganic Nitrogen-15 in Tropical Cropping Systems.” *Soil Science Society of America Journal 74*, no. 1 (2010): 139–52. https://doi.org/10.2136/sssaj2009.0192.

Drury, C. F., X. Yang, W. D. Reynolds, W. Calder, T. O. Oloya, and A. L. Woodley. "Combining Urease and Nitrification Inhibitors with Incorporation Reduces Ammonia and Nitrous Oxide Emissions and Increases Corn Yields." *Journal of Environmental Quality 46*, no. 5 (2017): 939–49. https://doi.org/10.2134/jeq2017.03.0106.

Eagle, A. J., L. E. Christianson, R. L. Cook, R. D. Harmel, F. E. Miguez, S. S Qian, D. A. R. Diaz. "Fertilizer Management and Environmental Factors Drive $N_2O$ and $NO_3^-$ Losses in Corn: A Meta-Analysis" *Agronomy Journal 109*, no.6 (2017): 2441–2449. https://acsess-onlinelibrary-wiley-com.uml.idm.oclc.org/doi/full/10.2136/sssaj2016.09.0281.

Fixen, P. E. "A Brief Account of the Genesis of 4R Nutrient Stewardship." *Agronomy Journal* 112, no.5 (2020): 4511–4518. **https://doi.org/10.1002/agj2.20315.**

Gagnon, B., N. Ziadi, and C. Grant. "Urea Fertilizer Forms Affect Grain Corn Yield and Nitrogen Use Efficiency." *Canadian Journal of Soil Science 92*, no.2 (2012) https://doi.org/10.4141/cjss2011-074.

Gao, Q., C. Li, G. Feng, J. Wang, Z. Cui, X. Chen, and F. Zhang. "Understanding Yield Response to Nitrogen to Achieve High Yield and High Nitrogen Use Efficiency in Rainfed Corn." *Agronomy Journal 104*, no. 1 (2012): 165–68. https://doi.org/10.2134/agronj2011.0215.

Gao, X., H. Asgedom, M. Tenuta, and D. N. Flaten. "Enhanced Efficiency Urea Sources and Placement Effects on Nitrous Oxide Emissions." *Agronomy Journal 107*, no. 1 (2015): 265–77. https://doi.org/10.2134/agronj14.0213.

Halvorson, A. D., S. J. Del Grosso, and F. Alluvione. "Nitrogen Source Effects on Nitrous Oxide Emissions from Irrigated No-Till Corn." *Journal of Environmental Quality 39*, no. 5 (2010): 1554–62. https://doi.org/10.2134/jeq2010.0041.

Halvorson, A. D., and S. J. Del Grosso. "Nitrogen Placement and Source Effects on Nitrous Oxide Emissions and Yields of Irrigated Corn." *Journal of Environmental Quality 42*, no. 2 (2013): 312–22. https://doi.org/10.2134/jeq2012.0315.

Halvorson, A. D., and M. E. Bartolo. "Nitrogen Source and Rate Effects on Irrigated Corn Yields and Nitrogen-Use Efficiency." *Agronomy Journal 106*, no. 2 (2014): 681–93. https://doi.org/10.2134/agronj2013.0001.

Hernández, M., L. Echarte, A. D. Maggiora, M. Cambareri, P. Barbieri, and D. Cerrudo. "Maize Water Use Efficiency and Evapotranspiration Response to N Supply under Contrasting Soil Water Availability." *Field Crops Research 178*, (2015): 8–15. https://doi.org/10.1016/j.fcr.2015.03.017.

Hong, N., P. C. Scharf, J. G. Davis, N. R. Kitchen, and K. A. Sudduth. "Economically Optimal Nitrogen Rate Reduces Soil Residual Nitrate." *Journal of Environmental Quality 36*, no. 2 (2007): 354–62. https://doi.org/10.2134/jeq2006.0173.

Jones, C. A., R. T. Koenig, J. W. Ellsworth, B. D. Brown, and G. D. Jackson. "Management of Urea Fertilizer to Minimize Volatilization," *MSU Extension*, (2007): 1–12.

Lasisi, A. A., Olalekan O. Akinremi, and Darshani Kumaragamage. "Efficacy of a New N-(n-Butyl) Thiophosphoric Triamide Formulation in Reducing Ammonia Volatilization from Urea-Based Fertilizers." *Canadian Journal of Soil Science 99*, no. 4 (2019): 395–405. https://doi.org/10.1139/cjss-2018-0072.

Li, T., W. Zhang, J. Yin, D. Chadwick, D. Norse, Y. Lu, X. Liu, X. Chen, F. Zhang, D. Powlson, Z. Dou. "Enhanced-Efficiency Fertilizers Are Not a Panacea for Resolving the Nitrogen Problem." *Global Change Biology 24*, no. 2 (2018): e511–521. https://doi.org/10.1111/gcb.13918.

Liu, L., X. Zhang, W. Xu, X. Liu, Y. Li, J. Wei, Z. Wang, and X. Lu. "Ammonia Volatilization as the Major Nitrogen Loss Pathway in Dryland Agro-Ecosystems." *Environmental Pollution 265* (2020): 114862. https://doi.org/10.1016/j.envpol.2020.114862.

Ma, B. L., T. Y. Wu, N. Tremblay, W. Deen, N. B. McLaughlin, M. J. Morrison, and G. Stewart. "On-Farm Assessment of the Amount and Timing of Nitrogen Fertilizer on Ammonia Volatilization." *Agronomy Journal 102*, no. 1 (2010): 134–44. https://doi.org/10.2134/agronj2009.0021.

Manitoba agriculture. " Manitoba Markets Historic Crop Prices Monthly, 1987–2022". (2022) online: https://www.manitoba.ca/agriculture/markets-and-statistics/crop-statistics/grains-oilseeds-market-prices-current-year.html.

Maynard, D. G., Y. P. Kalra., and J. A. Crumbaugh (1993). Nitrate and exchangeable ammonium nitrogen. *Soil sampling and methods of analysis*, *1*, 25-38.

McGeough, K. L., C. J. Watson, C. Müller, R. J. Laughlin, and D. R. Chadwick. "Evidence That the Efficacy of the Nitrification Inhibitor Dicyandiamide (DCD) Is Affected by Soil Properties in UK Soils." *Soil Biology and Biochemistry 94* (2016): 222–32. https://doi.org/10.1016/j.soilbio.2015.11.017.

Muchow, R. C. "Nitrogen Utilization Efficiency in Maize and Grain Sorghum." *Field Crops Research*, Nutrient Use Efficiency in Rice Cropping Systems *56*, no. 1 (1998): 209–16. https://doi.org/10.1016/S0378-4290(97)00132-9.

Nadler, A. J., and Paul R. Bullock. "Long-Term Changes in Heat and Moisture Related to Corn Production on the Canadian Prairies." *Climatic Change 104*, no. 2 (2011): 339–52. https://doi.org/10.1007/s10584-010-9881-y.

Noellsch, A. J., P. P. Motavalli, K. A. Nelson, and N. R. Kitchen. “Corn Response to Conventional and Slow-Release Nitrogen Fertilizers across a Claypan Landscape.” *Agronomy Journal 101*, no. 3 (2009): 607–14. https://doi.org/10.2134/agronj2008.0067x.

Olson, R. A., and L. T. Kurtz. “Crop Nitrogen Requirements, Utilization, and Fertilization.” *Nitrogen in Agricultural Soils 22*, (1982): 567–604. https://doi.org/10.2134/agronmonogr22.c15.

Omara, P., L. Aula, F. Oyebiyi, and W. R. Raun. “World Cereal Nitrogen Use Efficiency Trends: Review and Current Knowledge.” *Agrosystems, Geosciences & Environment 2*, no. 1 (2019): 1–8. https://doi.org/10.2134/age2018.10.0045.

Omonode, R. A., and T. J. Vyn. “Tillage and Nitrogen Source Impacts on Relationships between Nitrous Oxide Emission and Nitrogen Recovery Efficiency in Corn.” *Journal of Environmental Quality 48*, no. 2 (2019): 421–29. https://doi.org/10.2134/jeq2018.05.0188.

Paolo, E. D., and M. Rinaldi. “Yield Response of Corn to Irrigation and Nitrogen Fertilization in a Mediterranean Environment.” *Field Crops Research 105*, no. 3 (2008): 202–210. https://doi.org/10.1016/j.fcr.2007.10.004.

Pawlick, A. A., C. Wagner-Riddle, G. W. Parkin, and A. A. Berg. “Assessment of Nitrification and Urease Inhibitors on Nitrate Leaching in Corn (Zea Mays L.).” *Canadian Journal of Soil Science 99*, no. 1 (2019): 80–91. https://doi.org/10.1139/cjss-2018-0110.

Peng, Y., X. Li, and C. Li. “Temporal and Spatial Profiling of Root Growth Revealed Novel Response of Maize Roots under Various Nitrogen Supplies in the Field.” *PLOS ONE 7*, no. 5 (2012): e37726. https://doi.org/10.1371/journal.pone.0037726.

Rochette, P., D. A. Angers, M. H. Chantigny, M. Gasser, J. D. MacDonald, D. E. Pelster, and N. Bertrand. “Ammonia Volatilization and Nitrogen Retention: How Deep to Incorporate Urea?”

*Journal of Environmental Quality 42*, no. 6 (2013): 1635–42. https://doi.org/10.2134/jeq2013.05.0192.

Sahota, T., S. "Environmentally Smart Nitrogen (ESN)—Potential for Improving Modern Crop Production and N-Use Efficiency." *Journal of Agricultural Science and Technology B 10,* no. 6 (2020). https://doi.org/10.17265/2161-6264/2020.06.002.

Sharma, L., and S. Bali. "A Review of Methods to Improve Nitrogen Use Efficiency in Agriculture." *Sustainability 10,* no. 2 (2017): 51. https://doi.org/10.3390/su10010051.

Sistani, K. R., M. Jn-Baptiste, and J. R. Simmons. "Corn Response to Enhanced-Efficiency Nitrogen Fertilizers and Poultry Litter." *Agronomy Journal 106*, no. 2 (2014): 761–770. https://doi.org/10.2134/agronj2013.0087.

Spackman, J. A., F. G. Fernandez, J. A. Coulter, D. E. Kaiser, and G. Paiao. "Soil Texture and Precipitation Influence Optimal Time of Nitrogen Fertilization for Corn." *Agronomy Journal 111*, no. 4 (2019): 2018–30. https://doi.org/10.2134/agronj2018.09.0605.

Steusloff, T. W., K. A. Nelson, P. P. Motavalli, and G. Singh. "Fertilizer Placement Affects Corn and Nitrogen Use Efficiency in a Claypan Soil." *Agronomy Journal 111*, no. 5 (2019): 2512–2522. https://doi.org/10.2134/agronj2019.02.0108.

Sweeney, D. W., and D. A. R. Diaz. "Corn Response to Tillage and Side-Dress Nitrogen Management on Claypan Soil." *Agrosystems, Geosciences & Environment* 4, no. 3 (2021): e20206. https://doi.org/10.1002/agg2.20206.

Thapa, R., A. Chatterjee, R. Awale, D. A. McGranahan, and A. Daigh. "Effect of Enhanced Efficiency Fertilizers on Nitrous Oxide Emissions and Crop Yields: A Meta-analysis" *Soil Science Society of America Journal 80,* no.5 (2016): 1121–1134. **https://acsess.onlinelibrary.wiley.com/doi/abs/10.2136/sssaj2016.06.0179.**

Tilman, D. "Global Environmental Impacts of Agricultural Expansion: The Need for Sustainable and Efficient Practices." *Proceedings of the National Academy of Sciences 96*, no. 11 (1999): 5995–6000. https://doi.org/10.1073/pnas.96.11.5995.

Tremblay, N., Y. M. Bouroubi, C. Bélec, R. W. Mullen, N. R. Kitchen, W. E. Thomason, S. Ebelhar, D. B. Mengel, W. R. Raun, D. D. Francis, E. D. Vories, and I. Ortiz-Monasterio "Corn Response to Nitrogen Is Influenced by Soil Texture and Weather." *Agronomy Journal 104*, no. 6 (2012): 1658–71. https://doi.org/10.2134/agronj2012.0184.

Venterea, R. T., J. A. Coulter, and M. S. Dolan. "Evaluation of Intensive '4R' Strategies for Decreasing Nitrous Oxide Emissions and Nitrogen Surplus in Rainfed Corn." *Journal of Environmental Quality 45*, no. 4 (2016): 1186–95. https://doi.org/10.2134/jeq2016.01.0024.

Watkins, P. H. "Nitrogen Management in Corn: Influences of Urea Ammonium Nitrate (UAN) Applications With and Without Nitrogen Stabilizer Products." *University of Maryland, College Park* (2013). https://drum.lib.umd.edu/handle/1903/14181.

Woodley, A. L., C. F. Drury, X. M. Yang, W. D. Reynolds, W. Calder, and T. O. Oloya. "Streaming Urea Ammonium Nitrate with or without Enhanced Efficiency Products Impacted Corn Yields, Ammonia, and Nitrous Oxide Emissions." *Agronomy Journal 110*, no. 2 (2018): 444–54.

Woodley, A. L., C. F. Drury, X. Y. Yang, L. A. Phillips, D. W. Reynolds, W. Calder, and T. Okello Oloya. "Ammonia Volatilization, Nitrous Oxide Emissions, and Corn Yields as Influenced by Nitrogen Placement and Enhanced Efficiency Fertilizers." *Soil Science Society of America Journal 84*, no. 4 (2020): 1327–41. https://doi.org/10.1002/saj2.20079.

Zhang, X., T. Zou, L. Lassaletta, N. D. Mueller, F. N. Tubiello, M. D. Lisk, C. Lu, R. T. Conant, C. D. Dorich, J. Gerber, H. Tian, T. Bruulsema, T. M. Maaz, K. Nishina, B. L. Bodirsky, A.

Popp, L. Bouwman, A. Beusen, J. Chang, P. Havlik, D. Leclère, J. G. Canadell, R. B. Jackson, P. Heffer, N. Wanner, W. Zhang, E. A Davidson "Quantification of Global and National Nitrogen Budgets for Crop Production." *Nature Food 2*, no. 7 (2021): 529–40. https://doi.org/10.1038/s43016-021-00318-5

# 3. 4R Management Options to Reduce $N_2O$ Emissions from Corn in Sandy Soils of South-Central Manitoba, Canada.


### 3.1 Abstract

Nitrogen (N) management options that reduce environmental losses and improve N use efficiency must further be investigated to ensure food security and foster sustainability in the future. To achieve these goals, pillars of 4R nutrient stewardship - Right Source, Right Rate, Right Time, and Right Place have guided the development of best management practices in various soil-climatic conditions around the world. However, 4R research investigating multiple practices simultaneously remains in short supply. Experimental trials were conducted on commercial corn fields from 2018–2020 to 1) compare area-scaled $N_2O$ emissions, Emission factor (EF) and Yield intensity (EI) between at-planting sources of N (Urea, ESN/Urea, SuperU); in-season sources of N (UAN, Agrotain, AgrotainPlus); in-season placement depths of UAN (Surface dribble, Shallow, Deep); and timing of conventional fertilizer (Urea, UAN Surface) applied to grain corn; 2) Provide a qualitative assessment of ammonia volatilization for the same treatments. Treatments were replicated four times in a randomized complete block design and triplicate gas samples were collected from static-vented chambers at four twenty-minute time intervals (0, 20, 40, 60min) from plots given the recommended rate of N (112 kg N $ha^{-1}$) throughout each growing season. Particularly during years with relatively high soil-moisture conditions, urea had the greatest mean area-scaled emissions, EF, and EI among at-planting sources, however treatments did not have significant differences across three site-years; area-scaled emissions of AgrotainPlus were significantly lower than UAN Surface across site-years ($p<0.1$); UAN Deep consistently had the lowest area-scaled emissions, EF, and EI among in-season placements; Split-application of UAN consistently reduced area-scaled $N_2O$ emissions

compared to urea applied at planting. With the exception of high soil moisture conditions in the fall of 2019 and spring of 2020; relatively dry conditions throughout each growing season combined with timely precipitation after fertilization lowered the potential for gaseous N loss throughout the growing seasons of 2018–2020.

## 3.2 Introduction

### 3.2.1 Nitrogen in Agroecosystems

Nitrogen is often a limiting nutrient to achieve high yield in field crops such as grain corn. During the early 20th century, the Haber-Bosch synthesis of ammonia enabled more widespread use of nitrogen (N) fertilizer, an important factor that allowed for increased food production around the world (Smil 1997). Since then, steady-state conditions of the global N cycle have further been disrupted as synthetic fertilizers and manures have been applied at larger industrial scales around the world. Over time, greater N application rates have promoted greater rates of nitrification and denitrification, increasing the risk for N losses to the environment. Tian *et al.* (2020) indicate that human-induced $N_2O$ emissions increased by 30% in the past 40 years and are expected to increase further as agroecosystems around the world seek to increase yield potential. At present, agriculture accounts for approximately 10% of Canada's total greenhouse gas emissions in $CO_2$ eq per year (Rodríguez 2019). The atmospheric concentration of $N_2O$ has risen at a rate of ~0.25% per year during the 21st century and $N_2O$ is a greenhouse gas that accounts for approximately 6% of global radiative forcing (Myhre *et al.* 2013). Nitrous oxide has an atmospheric residence time over 100 years and increased $N_2O$ emissions pose great risks in the context of climate change (Eagle *et al.* 2017, Prather *et al.* 2015). Globally, there is still much progress to be made in order to boost nitrogen use efficiency (NUE) and decrease environmental losses of N fertilizers from agricultural soils (Omara *et al*. 2019).

### 3.2.2 Environmental Influences On Gaseous Emissions From Agroecosystems

Even with optimal management, there is still risk for N loss through various pathways. Ammonia volatilization is of particular concern for agricultural communities since urea-based fertilizers are the most prominently used N source worldwide for corn and other crops due to low cost and widespread availability (Pawlick *et al.* 2019). As urea is applied to soil, it quickly undergoes hydrolysis by urease enzymes to form $NH_4^+$, $CO_2$ and $H_2O$; this process consumes hydrogen ions and increases soil pH. In turn, higher pH decreases the $NH_4^+/NH_3$ ratio in the soil and promotes $NH_3$ volatilization (Cantarella *et al.* 2018). When urea-based fertilizers are broadcast incorporated or placed close to the surface, volatilization can account for major losses (~50%) from soil-cropping systems; the risk of high volatilization loss is greatest in soils with low buffering capacity, cation exchange capacity and/or high pH (Ferguson *et al.* 1984, Fillery *et al.* 1984, Schepers and Raun 2008). Ammonia volatilization is influenced by the amount of total ammoniacal N in soil solution in tandem with the soil resistance to volatilization. Total ammoniacal N throughout the growing season is affected by the rate of fertilization, soil temperature, soil-water content, pH, urease activity, clay and organic matter content; soil resistance to volatilization is influenced by rainfall, soil compaction, soil disturbance, texture, and fertilizer placement depth, among other factors (Ma *et al*. 2010, Awale and Chatterjee 2017).

Ammonia volatilization losses are also dependent on N fertilizer source. For example, the volatilization losses resulting from application of granular, broadcasted-incorporated urea are greatest with high temperature, rapid air exchange, and high soil-water content at the time of fertilization, unless sufficient precipitation/irrigation moves N to deeper soil layers. Ammonia volatilization losses typically decrease as the magnitude of rain events that occur after N application increases (Ernst and Massey 1960, Fillery *et al.* 1984, Bouwmeester *et al.* 1985). For liquid fertilizers such as UAN, dry and windy conditions promote volatilization loss and timely precipitation events after fertilization reduce $NH_3$ losses (Woodley *et al.* 2018). EEF's containing urease inhibitors slow the accumulation of ammoniacal N in soil solution and may reduce volatilization losses (Schepers and Raun 2008, Upadhyay 2012, Qiao *et al.* 2015). In contrast, EEF's containing nitrification inhibitors alone can prolong the retention of $NH_4^+$ in soil and boost volatilization losses. Similarly, mitigating $NH_3$ volatilization may increase the magnitude of $N_2O$ emissions by conserving a greater amount of N in soil, or volatilized $NH_3$ can be deposited and nitrified elsewhere to produce $N_2O$ during nitrification and denitrification (Lam *et al.* 2017). Split-applications of N and placement below the surface have proven to reduce volatilization losses by reducing the amount of ammoniacal N in solution throughout the growing season and increasing soil contact with ammoniacal N, respectively.

### 3.2.3 Nitrous Oxide Production in Agroecosystems

Fertilizer N applied to soils can produce high fluxes of $N_2O$ as a by-product of nitrification and denitrification. Nitrification is a two-step process carried out by ammonia and nitrite oxidizing bacteria and archaea. Ammonia oxidizers convert $NH_3$ to hydroxylamine ($NH_2OH$) by the ammonia monooxygenase enzyme and $NH_2OH$ to nitrite ($NO_2^-$) by the hydroxylamine oxidoreductase enzyme; nitrite oxidizers convert $NO_2^-$ to nitrate ($NO_3^-$) by nitrite oxidoreductase. Nitrite can be reduced to $N_2O$ during this reaction in the absence of electrons for $NH_2OH$ oxidation (Ward 2008). Denitrification is the reduction of $NO_3^-$ to $N_2$, involving four steps that are catalyzed by various enzymes; denitrification requires anoxic conditions since the synthesis of denitrification enzymes is inhibited by dissolved oxygen (Di Capua *et al.* 2019). Nitrous oxide is produced as an intermediate when denitrifying organisms use $NO_3^-$ as an electron acceptor during complete denitrification; incomplete denitrification occurs when nitrous oxide reductase enzymes are inhibited under less anaerobic conditions, resulting in $N_2O$ flux to the atmosphere. The proportions of $N_2O$ produced by nitrification and denitrification change with water-filled pore space; denitrification may be limited in dry conditions, causing relatively low magnitudes of $N_2O$ flux in some studies (Davidson *et al.* 2000).

Recent research has revealed that ammonia oxidizing bacteria and archaea are accompanied by complete-oxidizing bacteria "Comammox" that are able to convert $NH_3^+$ to $NO_3^-$ themselves (Wang *et al.* 2017). Microbial communities differ greatly among soil ecosystems and $N_2O$ emissions change based on microbial responses to the environment and the availability of various N pools (Lehtovirta-Morley 2018). For example, $NH_3$ oxidizing bacteria are typically more resilient to very dry conditions and release more $N_2O$ compared to ammonia oxidizing archaea at similar abundancies (Placella and Firestone 2013, Hink 2017). Different management practices and environmental conditions strongly influence the soil environment, microbial communities, and the biogeochemical fate of fertilizer N applied to cropping systems. Different types of N fertilizer, application method, timing, and rate of N fertilizer will influence soil N pools and the potential for crop uptake and/or environmental loss by gaseous emission and/or leaching (Johnston and Bruulsema 2014, Liu *et al.* 2020).

### 3.2.4 Environmental Influences on Nitrous Oxide Emissions

There are several physical, chemical, and environmental factors that interact in soils to influence microbial communities and N cycling at an ecosystem scale. For example, soil moisture is critical for microbial function and crop health, acting as a resource, solvent and medium for transportation (Schimel 2018). This is an important factor to consider in a semi-arid climate, particularly for crops with high water demand, such as corn. Fluxes of $N_2O$ and NO to the atmosphere are controlled by factors that influence nitrification and denitrification rates in soil (Conrad *et al.* 1983, Khalil *et al.* 2004). Factors that influence nitrification rates include temperature, nitrifier abundance, soil moisture, pH, oxygen supply, substrate concentration and substrate availability (O'Sullivan *et al.* 2013). Denitrification rates increase as carbon content and volumetric soil moisture content increase, however, denitrification is still important in dry conditions. For example, temperature and moisture regimes vary throughout soil aggregates, leading to spatial differences in $O_2$ and substrate supply (Sahrawat 2008, Højberg *et al.* 1994). The optimal conditions for nitrification and denitrification differ throughout microbial communities and the soil matrix over time (Davidson *et al.* 2000, Sahrawat 2008).

### 3.2.5 4R Management Practices to Reduce Nitrous Oxide Emissions

Research efforts aiming to improve NUE and reduce N losses serve a mutual benefit for the biosphere and overall socioeconomic welfare. The 4R nutrient stewardship framework aims to address the challenges associated with fertilizer usage by guiding best management practices for various crops, soils, and climates (Johnston and Bruulsema 2014). The 4R framework aims to match the right source, timing, rate, and placement of fertilizer application in order to boost nutrient use efficiency and reduce environmental losses by $NH_3$ volatilization, $N_2O$ emission, $NO_3^-$ leaching, and denitrification. There is a vast amount of research focusing on the four pillars of the 4R framework in many different soil-cropping systems to investigate optimal management practices (Pan *et al.* 2016, Fixen 2020). For example, enhanced efficiency fertilizers (EEF's), including slow-release (polymer-coated) fertilizers such as Environmentally Smart Nitrogen (ESN), and products containing urease and/or nitrification inhibitors, such as SuperU and AgrotainPlus, have proven to reduce $N_2O$ emissions in various soil-climatic contexts (Akiyama *et al.* 2009, Eagle *et al.* 2017, Lam *et al.* 2017).

Several studies have outlined the potential benefits of the 4R framework in Manitoba. Among other factors, $N_2O$ emissions are highly dependent on N application rates (Tenuta *et al.* 2019). Enhanced efficiency fertilizers have great potential to reduce $N_2O$ emissions by delaying microbial access to applied N that is applied in the spring or at-planting (Akiyama *et al.* 2009, Lam *et al.* 2017). Tenuta *et al.* (2019) identified that approximately 50% of growing season $N_2O$ emissions in spring and following fertilizer application over a 10-year crop rotation in clay soils of Manitoba; this outlines the importance of adopting management practices to reduce early growing season $N_2O$ emissions, particularly enhanced efficiency fertilizers such as ESN and SuperU applied at-planting.

For five site-years of Canadian hard red spring wheat in Manitoba, Wood (2018) observed an average 40% reduction in $N_2O$ emissions by SuperU compared to fall and spring applied urea. ESN delayed $N_2O$ release in some cases and resulted in slightly greater emissions than products containing nitrification inhibitors. For wheat grown in sandy soil of Manitoba, Gao *et al.* (2015) observed a significant reduction of $N_2O$ emissions with double-mid-row banded ESN or SuperU compared to broadcast-incorporated urea; side-row and mid-row banded urea also reduced emissions compared to broadcast-incorporated urea.

Alternative to EEF's, which typically cost more than conventional fertilizers, split application of N can improve yield and/or reduce N losses. In a meta-analysis for corn crops in North America, Eagle *et al.* (2017) estimate that nitrification inhibitor products and side-dress application of N reduce $N_2O$ emissions by approximately 30%. Among other factors that influence $N_2O$ emissions, substrate availability and soil moisture are of utmost importance (O'Sullivan *et al.* 2013). Split applications of N fertilizer can reduce $N_2O$ emissions by reducing soil N concentrations throughout the growing season and more efficiently supplying the crop with N at later growth stages, when N demand is high. Soil moisture and precipitation patterns will also influence $N_2O$ fluxes as timely precipitation after in-season applications will incorporate N into the root-zone where it is less susceptible to gaseous losses. Contrastingly, a very dry growing season may limit N uptake of in-season applications and increase residual soil N; this may increase annual $N_2O$ emissions compared to at-planting applications (Clark 2020). A preliminary meta-analysis of 4R studies on corn, canola, and potato in Manitoba showed that split-applications of N reduced cumulative $N_2O$ emissions by approximately 50% compared to at-planting applications (Tenuta 2022, personal communication)

For in-season application of N, various placement methods can be used to increase NUE and reduce environmental losses. Compared to surface dribble banded UAN, deep placement of UAN has potential for reducing $N_2O$ emissions since deep placement of N promotes downward movement into the root-zone (Rochette *et al.* 2013). Kessel *et al.* (2013) suggest nitrification and denitrification rates typically decrease at depth in no-till soils due to lower substrate supply and microbial activity compared to near the surface. Deep placement of N can result in greater $NO_3^-$ leaching and as a result, less $N_2O$ production. Additionally, deep placement of inorganic N may boost $N_2O$ consumption by denitrification as gases must travel a further distance to reach the soil-atmosphere interface (Chapuis-Lardy *et al.* 2007). The above mentioned management practices are of interest to farmers in Manitoba in order to reduce environmental losses and potentially improve yield and N uptake.

The studies that have shown the potential to increase crop yield using EEF's, are those conducted under conditions of high N loss potential. Sahota (2020) suggest that polymer coated EEF's can actually be detrimental to crop yield in dry conditions where fertilizer granules remain intact for longer periods of time. Additionally, it is not guaranteed for EEF's to reduce $N_2O$

emissions. For example, An *et al.* (2020) found no significant yield benefit or $N_2O$ reduction by EEF's for winter wheat in Alberta. Similarly, Asgedom *et al.* (2014) highlight the challenge of meeting crop demand while reducing $N_2O$ emissions in certain situations; this Manitoba study showed that urea had the greatest $N_2O$ emissions but also the greatest yield. Yield, N uptake, and $N_2O$ emissions may respond to various management practices differently depending on soil-climatic conditions (Eagle *et al.* 2017).

Although many studies have evaluated the effectiveness of various 4R practices to provide agronomic benefit and/or reduce N losses, there is a lack of studies that focus on multiple sets of management practices within the same site-year(s). The quantification of fluxes that result from various management practices will add to the national greenhouse gas inventory and support more accurate predictions of $N_2O$ fluxes from Canadian agroecosystems. The objective of this study was to investigate the effectiveness of EEF's at reducing in-season $N_2O$ emissions for both at-planting and in-season application timings,. For in-season application, we also investigate the effectiveness of deep (7.62cm) and shallow (3.81cm) banded UAN at reducing $N_2O$ emissions compared to surface dribble banded UAN; urea at-planting and UAN surface applied in-season were also compared in this study. Field research investigating several management practices in the same site-year(s) is needed to advance the current knowledge of 4R nutrient stewardship within different soil-climatic contexts. The objectives of this study were to 1) compare cumulative $N_2O$ fluxes, emission factors, and emission intensities for at-planting N sources (Urea, ESN, and SuperU); in-season surface N sources (UAN Surface, Agrotain, AgrotainPlus); in-season UAN placement (UAN Surface, UAN Shallow, UAN Deep); timing of conventional fertilizer (Urea, UAN Surface). 2) Provide a qualitative assessment of $NH_3$ emissions between treatments.

### 3.2.6 Hypotheses

**3.2.6.1 At-Planting Sources.** Compared to urea, it was hypothesized that SuperU and ESN would significantly decrease cumulative $N_2O$ emissions by limiting microbial access to substrate and slowing the release of applied N into soil, respectively (Alonso-Ayuso and Quemada 2016, Lam *et al.* 2017, Eagle *et al.* 2017, Sahota 2020); EEF efficacy at reducing emissions depends on environmental conditions, soil N pools, and the magnitude/frequency of $N_2O$ flux events throughout the growing season (Li *et al.* 2018, Woodley *et al.* 2020).

**3.2.6.2 In-Season Sources.** Relative to conventional UAN applied in-season, it was hypothesized that UAN/AgrotainPlus would significantly reduce $N_2O$ emissions while UAN/Agrotain may increase emissions by retaining more ammoniacal N in soil solution (Lam *et al.* 2017, Woodley *et al*. 2020); EEF efficacies at reducing $N_2O$ emissions depend on soil-climatic conditions throughout the growing season (Li *et al.* 2018, Woodley *et al.* 2020).

**3.2.6.3 In-Season Placements.** The effect of N placement depth on $N_2O$ emissions depends on soil-climatic conditions and management (Kessel *et al*. 2013, Nash *et al.* 2012). Kessel *et al.* (2013) suggest nitrification and denitrification rates typically decrease at depth in no-till soils due to lower substrate supply and microbial activity compared to the surface. Additionally, deep placement of inorganic N may boost $N_2O$ consumption, lowering net fluxes to the atmosphere (Chapuis-Lardy *et al.* 2007). It was hypothesized deep and shallow banded UAN would significantly reduce $N_2O$ emissions compared to surface dribble banded UAN.

**3.2.6.4 At-Planting s. In-Season Conventional.** Due to high risk of moisture deficit for corn grown in Manitoba (Nadler and Bullock 2007), it was hypothesized that urea would have significantly greater $N_2O$ emissions, EF, ad EI compared to split application of UAN since crops and microbes are likely to have greater access to N and soil moisture early in the growing season, particularly in sandy soils that have low water-holding capacity compared to heavy clay soils of the Red River Valley.

## 3.2 Materials and Methods

### 3.3.1 Site Description, Experimental Design, and Field Operations

A detailed description of experimental site, design, field operations, and biomass sampling are given in Chapter 2 of this thesis.

### 3.3.2 Sampling Operations

Nitrous oxide gas sampling was done for each plot given the recommended rate of N (112 kg N $ha^{-1}$) and control treatments (0 and 35 kg N $ha^{-1}$). Gas sampling took place from May $28^{th}$– Oct $17^{th}$ (DOY 148–290) in 2018; from May $16^{th}$– Oct $16^{th}$ (DOY136–289) in 2019 and; from May $15^{th}$– Oct $1^{st}$ (DOY 136–275) in 2020. Gas sampling was done using rectangular, plastic (white), static-vented chambers and commenced each year after seeding/fertilization. Gas sampling took place 2–3 times per week until September when emissions were expected to decrease and sampling was done one-to-two times every two weeks. For 2018, 2019, and 2020, gas sampling was done for a total of 21, 21, and 30 days respectively. One chamber was placed on the corn-row while two chambers were placed between rows directly after planting and fertilization (Figure 3.A1). See Table 3.A1 for a detailed list of all treatments included in this study. Plant(s) grew inside the chambers until they could no longer be contained during gas sampling (4–6 weeks).

### 3.3.3 Area-Scaled Nitrous Oxide Emissions, Emission Factors, and Emission Intensities

Chamber lids were equipped with weather strips and placed onto pre-installed static-vented chambers (3–5 cm soil depth) to create a seal and enable gas accumulation. 20mL gas samples were collected at four time intervals (0, 20, 40 and 60 minutes) through a rubber septum by using a plastic syringe (Becton-Dickinson) equipped with a 23g needle (BD PrecisionGlide$^{TM}$); accumulated gases were mixed by three re-injections before collecting each gas sample. Due to a shortage of resources in 2020, five ambient air samples were taken during the first twenty-minute intervals to represent the initial gas concentrations for each chamber in each block; initial gas concentrations were taken from each chamber in 2018 and 2019. Gas samples were transferred to 12mL exetainers rinsed twice with helium (or hydrogen gas as substitute) and thrice evacuated (Westphal *et al.* 2018). A thin layer of silicon was placed on the vial lids to prevent gas leakage (Mastercraft, Canadian Tire Corp). Shaded soil temperature and volumetric moisture content measurements were taken for each plot and gas volumes were converted to standard atmospheric temperature using the average of four air temperature measurements, taken at the beginning of gas sampling for each block.

Gas samples were stored in darkness at room temperature until analyzed. A gas chromatograph calibrated with dilutions of pure $N_2O$ gas (Welders Supply, Winnipeg, MB) was used to determine $N_2O$ concentrations in collected gas samples. Implemented with the HMR package in R, as described by Asgedom *et al.* (2014), daily fluxes were calculated using the change in gas concentration through four 20-minute time intervals. The gas chambers used were fairly large (40 x 20 x 15cm) and rarely showed non-linear gas accumulation trends in one hour. For each plot and sampling day, average daily emissions were calculated; linear interpolation was then used to provide an estimate of $N_2O$ flux for each day of the growing season and cumulative emissions were given by summing them together. This gave four replicates of cumulative $N_2O$ flux for each treatment, per year.

Following Asgedom *et al.* (2014), yield scaled emissions (EI) were calculated as $\sum N_2O$/yield (g N $Mg^{-1}$). Emission Factors (EF), expressed as the percentage of total N applied that was emitted as $N_2O$, were calculated as

$$EF = \frac{\sum N_2O_{\mathrm{Fert}} - \sum N_2O_{\mathrm{Cont}}}{\sum N_2O_{\mathrm{Fert}}} \ X\ 100 \quad (1)$$

### 3.3.4 Ammonia Volatilization

For each plot given the 1x recommended rate (112 kg N $ha^{-1}$) and control treatment plots (0 and 35 kg N $ha^{-1}$), dosimeter tubes were installed near each plot's centre to qualitatively measure $NH_3$ volatilization, following methods described by Van Andel *et al*. (2017). We used 59 L recycling bins (Nova Products, Canadian Tire Corp) drilled with ten 0.9525cm holes dispersed throughout each side of the bin. Bins were placed tight to the soil surface to surround wooden stakes that positioned dosimeters 15–20cm above the soil surface using elastic bands. Dosimeters were qualitatively checked for ammonia absorption at the time of $N_2O$ gas sampling and were replaced accordingly. Dosimeter chambers were moved to a different area for each plot on sampling dates that followed rain events. These measurements were solely qualitative and were not intended for statistical analysis because we were unable to estimate a flux of $NH_3$ using the dosimeter tubes alone, however the dosimeter results can be used to assess the potential exchange of pollutants ($N_2O$, $NH_3$) for each treatment throughout each growing season.

### 3.3.5 Soil Sampling and Analyses

Pre-plant nutrient tests were taken in triplicate in each site year from 0–15.24cm and 15.24–60.96cm (Table A2). For in-season soil sampling, triplicate sub-samples were taken for each plot (two within rows and one between) at 0–15.24cm and 15.24–60.96cm depths using 15.24cm augers and 45.72cm tube-samplers, respectively; deep soil samples were taken from the same spot directly after 0–15.24cm depth samples were taken. All soil samples were then transported on ice and stored at ~4ºC until organized (0–5 days) and transferred to -25ºC for longer-term storage. Soil samples were thawed, disaggregated and homogenized fresh, by hand and stored again at -25ºC until $NH_4$/$NO_3$ extraction and analysis for gravimetric moisture content. Gravimetric moisture content was used to calculate the concentrations of ammonium and nitrate per kg of dry soil in each soil sample.

Soil N extractions were done by mixing 5g of fresh soil (thawed) with 25ml of 2 mol $L^{-1}$ KCL solution, shaking for one hour (150 epm), placing on a centrifuge for 3.5 minutes at 1350 x g, and then transferring 15mL of supernatant to sterile vials using a mechanic pipette (Maynard *et al*. 1993). Vials of extracted solution were stored at -25ºC prior to thawing and colorimetric analysis using a Technicon colorimetric analyzer. Colorimetric analysis was done using the Berthelot method described by Gao *et al.* (2015). Soil samples taken at 0–15.24cm depth were used to evaluate N concentrations throughout the growing season and calculate $NO_3^-$ exposure for each treatment, in a similar way to cumulative $N_2O$ emissions (Asgedom *et al*. 2014). The Applied Soil Ecology Lab has previously found strong positive relationships between cumulative $N_2O$ emissions and nitrate exposure for soils in Manitoba.

### 3.3.6 Statistical Analyses

Separate analyses of variance were used for each objective in this experiment to compare cumulative seasonal $N_2O$ emissions, EF and EI using PROC GLIMMIX in SAS. Fischers protected LSD method for post-hoc comparisons was used at a significance level of 0.05 ($P$<0.1

included in the appendices). Block was treated as a random variable and was nested within site-year to compare treatments across site-years. Normality was tested using PROC UNIVARIATE and residuals were transformed to fit a normal distribution using a log transformation if necessary. Homogeneity of variance was checked using scatterplots of the model residuals. This experiment was part of a larger split-plot design, however this analysis was treated as a complete randomized block design since $N_2O$ measurements were only taken for the 1x recommended rate (112 kg $ha^{-1}$).

## 3.4 Results

### 3.4.1 Soil-Climatic Conditions

In general, Southern Manitoba experienced warm, dry conditions throughout each growing season in this study; mean monthly air temperatures were higher than the climate normal values for Carman, MB from May–August, and lower in September and October. Precipitation was less than the climate normal average for each site-year (Table 3.1). Crops received adequate corn heat unit requirements, however the region experienced persistent dry conditions throughout site-years, particularly in May and August (Figure 3.1). A notable exception was September of 2019 with 155mm of precipitation, almost three times the climate normal for September. Figure 3.1 shows the differences in precipitation between each month of each year while Figure 3.2 shows how antecedent conditions of 2019 contributed to high volumetric moisture content values in May and June of 2020.

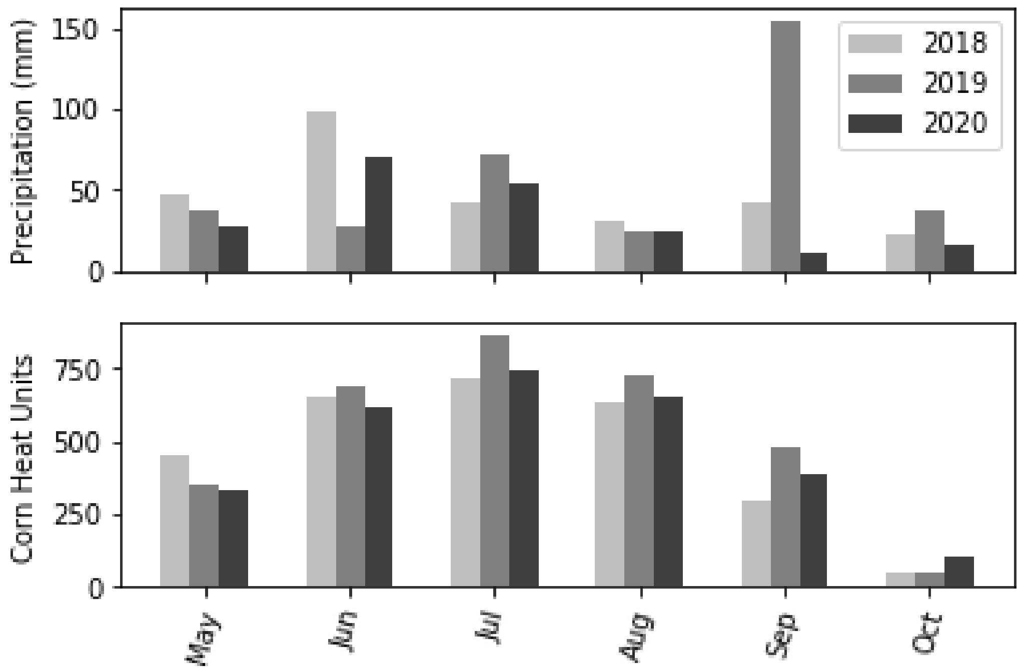


Figure 3.1: Total monthly precipitation and corn heat unit accumulation for the 2018, 2019, 2020 growing seasons. For calculation of CHU, minimum thresholds for maximum and minimum daily temperature were set to 10 and 4.4 °C, respectively.

Table 3.1: Mean monthly temperatures and precipitation throughout the 2018–2020 growing seasons for Carman MB. Climate normals were calculated using Environment and Climate Change Canada historical datasets for Carman, MB 1991– 2020.

| | May | June | July | August | September | October |
|---|---|---|---|---|---|---|
| Mean temperature (°C) | | | | | | |
| 2018 | 14.7 | 19.0 | 19.9 | 19.0 | 10.5 | 2.8 |
| 2019 | 9.6 | 17.7 | 20.4 | 17.9 | 12.8 | 2.9 |
| 2020 | 10.7 | 18.2 | 20.2 | 18.7 | 12.3 | 2.2 |
| Climate Normal | 11.4 | 17.2 | 19.4 | 18.5 | 13.4 | 5.4 |
| Total Precipitation (mm) | | | | | | |
| 2018 | 47.9 | 98.3 | 42.9 | 31.0 | 43.2 | 21.8 |
| 2019 | 38.0 | 27.2 | 72.1 | 34.5 | 155.3 | 38.4 |
| 2020 | 27.5 | 70.7 | 54.0 | 24.3 | 10.8 | 16.1 |
| Climate Normal | 79.1 | 90.8 | 70.1 | 66.6 | 53.2 | 41.0 |

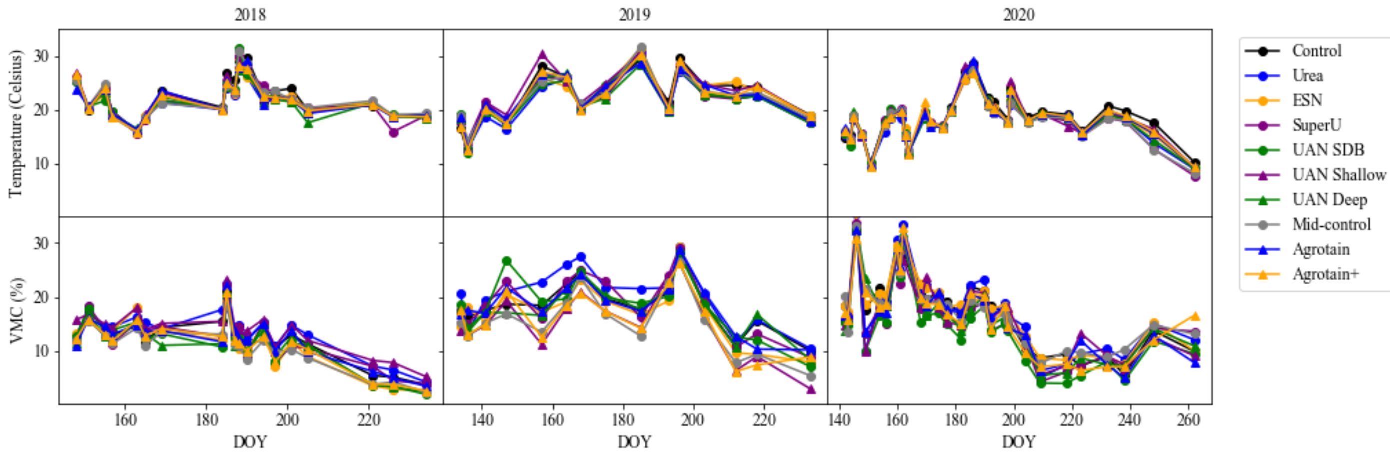



Figure 3.2: Mean soil temperature and VMC measurements taken 2–5 cm from the soil surface at the time of gas sampling for each treatment and site-year.

### 3.4.2 Daily $N_2O$ Emissions, Area-Scaled Emissions, Emission Factors, and Emission Intensity

**3.4.2.1 At-Planting Sources.** Daily $N_2O$ emissions were influenced by the timing of N application and precipitation patterns for each site-year included in this study (Figures 3.3–3.5). In 2018, ESN and AgrotainPlus delayed peak $N_2O$ emissions after application; whereas in 2019 and 2020, ESN and SuperU (deep, and shallow banding) reduced emission peaks that occurred following periods with heavy rainfall after fertilization. Soil moisture conditions also influenced the magnitude and variability of $N_2O$ fluxes from year-to year. Wetter soil conditions and greater $N_2O$ emission peaks in the spring of 2020, compared to other site-years (Figures 3.2 and 3.5). Mean soil temperature and soil moisture values were similar between treatments on each sampling date of each year.

Urea consistently had the greatest area scaled emissions, EF, and EI in each site-year and also had significantly greater area scaled $N_2O$ emissions across site-years ($P$<0.1). Area-scaled

$N_2O$ emissions of each at-planting treatment was significantly different from the control in 2020 and across site-years ($P<0.05$) (Table 3.2). Urea had the greatest EF and EI throughout site-years, however no significant differences were found between treatments. ESN tended to have greater EF, but lower EI in comparison to SuperU. EI of each fertilized treatment were significantly different from the control at a $P$ value of 0.1. (Table A3.4 and A3.5).

**3.4.2.2 In-Season Sources and Placements.** Similar to at-planting sources of N, area-scaled $N_2O$ emissions for in-season N sources were influenced by precipitation and soil moisture patterns throughout each growing season. The greatest peak emissions were observed in 2019 after in-season application; AgrotainPlus had much lower daily emissions on DOY 196 compared to UAN Surface and Agrotain (Figure 3.4). Across site-years, AgrotainPlus was the only treatment with area-scaled emissions that were not significantly different from the control ($P<0.05$) (Table 3.2). Agrotain had the lowest cumulative emissions in 2018 while AgrotainPlus had the lowest in 2019 and 2020. With the exception of 2019, UAN Surface had the greatest area-scaled emissions, resulting in greater mean $N_2O$ flux across site-years. AgrotainPlus had significantly lower area-scaled emissions compared to UAN Surface across site-years ($P<0.1$). There were no significant differences between in-season UAN placements, however deep placement had the lowest area-scaled emissions, EF, and EI in each site year (Table 3.2-4). Each placement depth had significantly greater $N_2O$ emission compared to the control in 2020 and across site-years ($P<0.05$).

**3.4.2.3 At-planting Vs. In-Season Conventional Sources.** Urea applied at-planting consistently had greater area-scaled $N_2O$ emissions and EF compared to UAN Surface; urea had significantly greater area-scaled emissions in 2018 ($P$<0.1), however there was no significant difference across site-years. Urea consistently had greater emissions peaks after fertilization in each site-year and UAN Surface only had comparable daily emissions in 2019 (Figure 3.3–5). Urea had the greatest EI in 2018 and 2020 and both fertilizer treatments were significantly greater than UAN across site-years; Urea also had significantly greater EF compared to UAN in 2018.

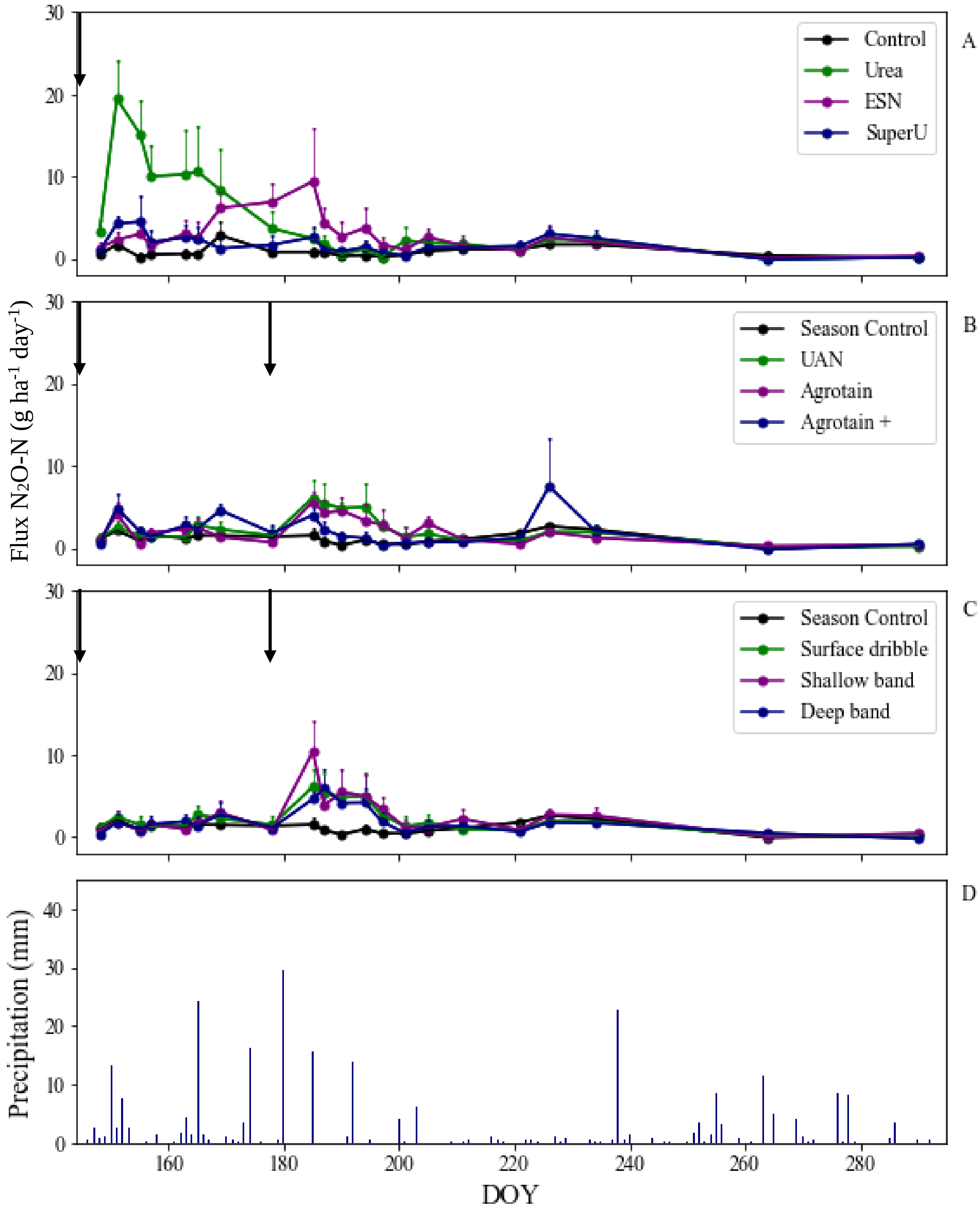



Figure 3.3**:** Daily $N_2O$ fluxes for at-planting N sources (a), in-season N sources (b), in-season N placements (c) and precipitation (d) for Carman, MB in 2018. Arrows represent the time of at-planting and in-season N applications.

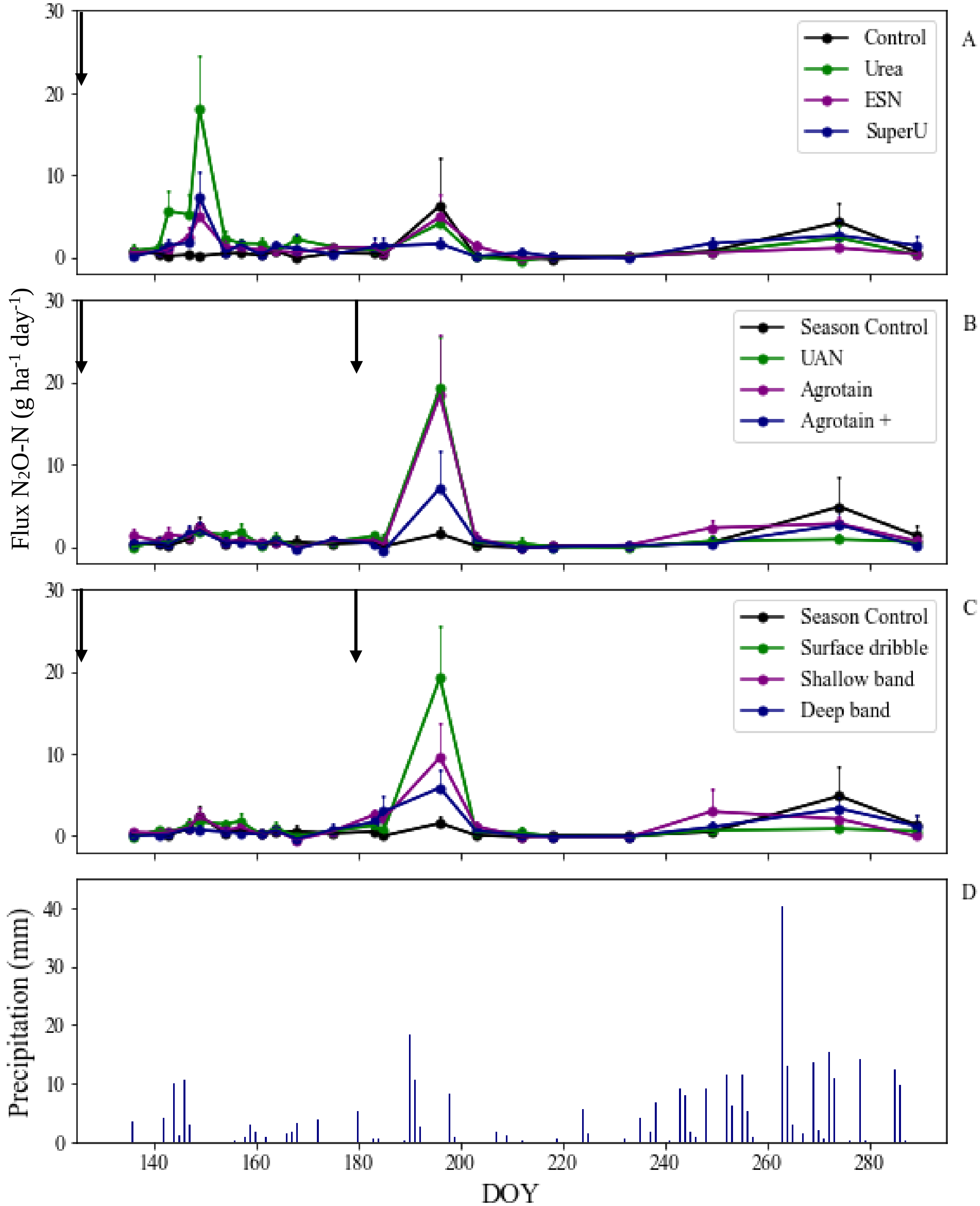
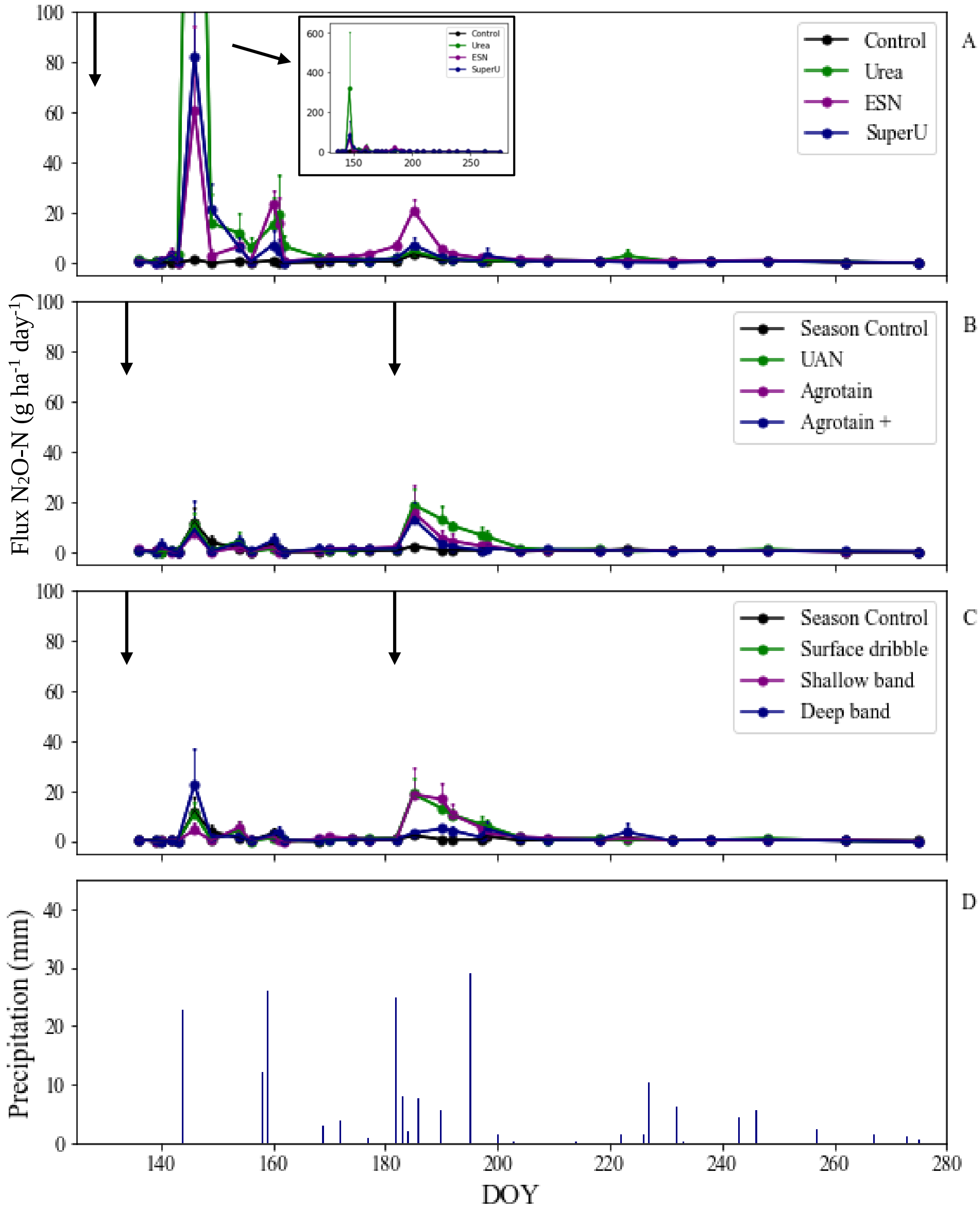



Figure 3.4: Daily $N_2O$ fluxes for at-planting N sources (a), in-season N sources (b), in-season N placements (c) and precipitation (d) for Haywood, MB in 2019. Arrows represent the time of at-planting and in-season N applications.




.

Figure 3.5: Daily $N_2O$ fluxes for at-planting N sources (a), in-season N sources (c), in-season N placements (d) and precipitation (e) for Carman, MB in 2020. Vertical arrows represent the time of at-planting and in-season N application.

Table 3.2: Area-scaled $N_2O$ emissions (g $N_2O$-N $ha^{-1}$) and standard errors for at-planting sources (abc), in-season sources (ABC) and in-season placements (xyz).

| Treatment | 2018 | 2019 | 2020 | All |
|---|---|---|---|---|
| Urea | 465±14 | 290±70 | 1300±855a | 685±295a |
| ESN | | 157±61 | 548±116a | 249±67a |
| SuperU | 230±50 | 189±41 | 494±223a | 304±81a |
| Control | 139±44 | 193±96 | 87±20b | 140±35b |
| | | | | |
| UAN Surface | 246±36 | 258±50 | 323±55A | 276±27A |
| Agrotain | 224±39 | 322±76 | 215±81AB | 254±39A |
| AgrotainPlus | 261±53 | 178±66 | 198±89BC | 212±39AB |
| Control | 139±44 | 193±96 | 87±20C | 140±35B |
| | | | | |
| UAN Surface | 246±36 | 258±50 | 323±55x | 276±27x |
| UAN Shallow | 297±43 | 240±45 | 307±88x | 282±34x |
| UAN Deep | 217±47 | 199±13 | 227±61x | 214±24x |
| Control | 139±44 | 193±96 | 87±20y | 140±35y |
| ANOVA | | | | |
| Planting Source | 0.0762 | 0.3196 | 0.0191 | 0.0006 |
| Season Source | 0.1586 | 0.2907 | 0.0109 | 0.0029 |
| Season Placement | 0.0630 | 0.4978 | 0.0049 | 0.0002 |

Different letters indicate significant differences between fertilized treatments LSD method for post-hoc comparisons. (*P* =0.05)

Table 3.3: Mean area-scaled emission factors (% N applied) and standard errors for at-planting sources (abc), in-season sources (ABC) and in-season placements (xyz). ESN 2018 not included.

| Treatment | 2018 | 2019 | 2020 | All |
|---|---|---|---|---|
| Urea | 0.29±0.11 | 0.09±0.09 | 1.08±0.75 | 0.49±0.26 |
| ESN | | -0.03±0.05 | 0.41±0.09 | 0.19±0.06 |
| SuperU | 0.08±0.07 | 0.00±0.06 | 0.36±0.21 | 0.15±0.08 |
| | | | | |
| UAN Surface | 0.09±0.01 | 0.06±0.1 | 0.21±0.05 | 0.12±0.04 |
| Agrotain | 0.07±0.03 | 0.12±0.06 | 0.11±0.06 | 0.10±0.03 |
| AgrotainPlus | 0.11±0.08 | -0.01±0.08 | 0.10±0.07 | 0.06±0.04 |
| | | | | |
| UAN Surface | 0.09±0.01 | 0.06±0.1 | 0.21±0.05 | 0.12±0.04 |
| UAN Shallow | 0.14±0.06 | 0.04±0.07 | 0.20±0.07 | 0.13±0.04 |
| UAN Deep | 0.07±0.01 | 0.01±0.08 | 0.13±0.06 | 0.07±0.04 |
| | | | | |
| ANOVA | | | | |
| Planting Source | 0.7850 | 0.2751 | 0.5542 | 0.5033 |
| Season Source | 0.5627 | 0.7119 | 0.2409 | 0.1820 |
| Season Placement | 0.7402 | 0.4298 | 0.1996 | 0.1651 |

Different letters indicate significant differences between fertilized treatments using protected LSD method for post-hoc comparisons. (*P* =0.05) Log-normal distribution was used.

Table 3.4: Mean yield-scaled $N_2O$ emissions (g $N_2O$-N $Mg^{-1}$) and standard errors for at-planting sources (abc), in-season sources (ABC) and in-season placements (xyz).

| Treatment | 2018 | 2019 | 2020 | All |
|---|---|---|---|---|
| Urea | 49±17 | 34±8 | 246±160 | 110±57 |
| ESN | | 18±6 | 84±19 | 48±10 |
| SuperU | 26±5 | 29±5 | 100±45 | 51±17 |
| Control | 27±13 | 34±17 | 36±18 | 32±9 |
| | | | | |
| UAN Surface | 33±9 | 36±4 | 48±10A | 39±5 |
| Agrotain | 32±5 | 36±7 | 30±9B | 33±4 |
| AgrotainPlus | 35±7 | 19±6 | 27±12B | 27±5 |
| Control | 27±13 | 34±17 | 36±18AB | 32±9 |
| | | | | |
| UAN Surface | 33±9 | 36±4 | 48±10 | 39±5 |
| UAN Shallow | 37±3 | 32±8 | 43±13 | 37±5 |
| UAN Deep | 26±5 | 25±2 | 42±14 | 31±5 |
| Control | 27±13 | 34±17 | 36±18 | 32±9 |
| | | | | |
| ANOVA | | | | |
| Planting Source | 0.3428 | 0.3708 | 0.3156 | 0.0866 |
| Season Source | 0.8649 | 0.3497 | 0.0278 | 0.1004 |
| Season Placement | 0.4858 | 0.8331 | 0.7341 | 0.4199 |

Different letters indicate significant differences between fertilized treatments using a protected LSD method for post-hoc comparisons. (*P* =0.05)

Table 3.5: Area-scaled $N_2O$ emissions (g $N_2O$-N $ha^{-1}$) and standard errors for at-planting sources (abc), in-season sources (ABC) and in-season placements (xyz).

| Treatment | 2018 | 2019 | 2020 | All |
|---|---|---|---|---|
| Urea | 465±14 | 290±70 | 1300±855 | 685±295 |
| UAN Surface | 246±36 | 258±50 | 323±55 | 276±27 |
| Control | 139±44 | 193±96 | 87±20 | 140±35 |
| | | | | |
| Anova | | | | |

Different letters indicate significant differences between fertilized treatments using a protected LSD method for post-hoc comparisons. (*P* =0.05).

### 3.4.3 Ammonia Volatilization

Ammonia volatilization losses from the control treatments were lower than fertilized treatments in each site-year. For at planting N sources, ESN had greater volatilization losses following the precipitation events that occurred from DOY 175–200 in 2018 and 2019, resulting in greater cumulative volatilization losses. In contrast, Urea and SuperU had greater emissions after planting in 2020 while ESN gradually released $NH_3$ throughout the growing season, resulting in lower cumulative fluxes of $NH_3$ (Figure 3.6–8). It is noted that these results are qualitative and may not be representative of actual $NH_3$ fluxes resulting from these N sources.

Regarding in-season N sources, Agrotain and AgrotainPlus reduced cumulative $NH_3$ volatilization compared to UAN Surface in 2018; volatilization losses were very similar in 2019 while UAN Surface was slightly higher in 2020. For in-season placements of UAN; deep and shallow banding greatly reduced cumulative volatilization loss in 2018 but had greater losses than UAN Surface in 2019. Compared to UAN Surface, shallow banding had the greatest volatilization losses while deep banding had the lowest in 2020 (Figures 3.6–8)

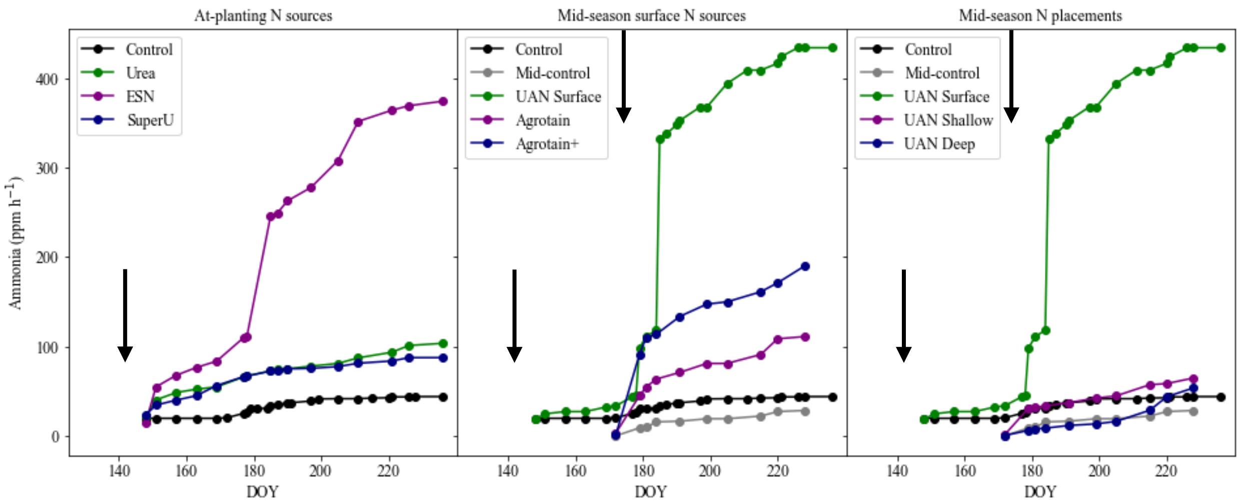



Figure 3.6: Cumulative $NH_3$ emissions of each treatment at Carman, MB in 2018. Due to limited equipment supplies, not all treatments had measurements before in-season application. Black arrows represent the time of N application.

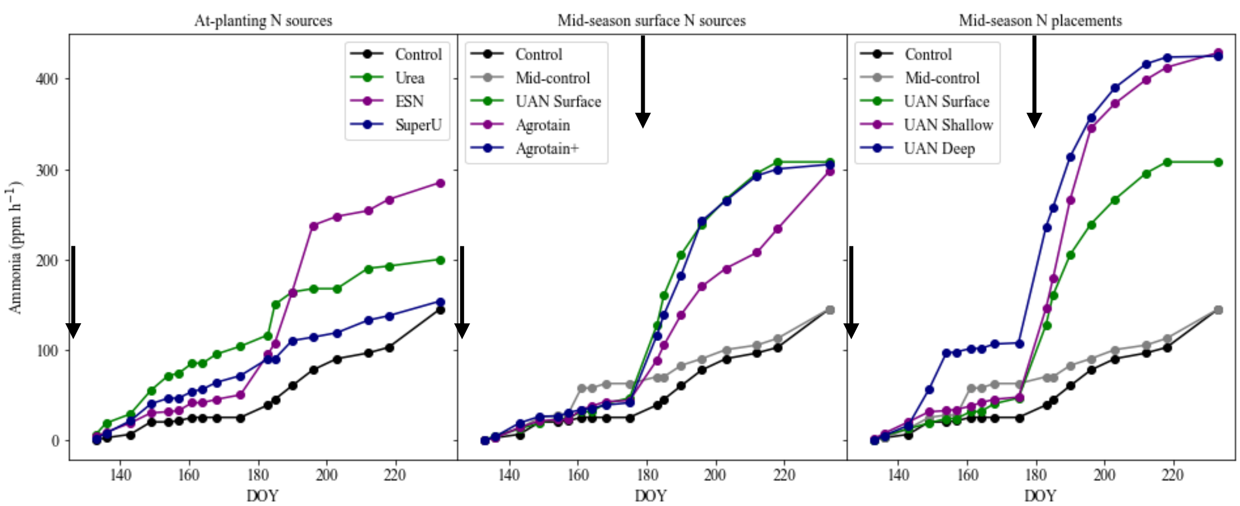



Figure 3.7: Cumulative $NH_3$ emissions of each treatment at Haywood, MB in 2019. Black lines represent the time of in-season N application. Black arrows represent the time of N application.

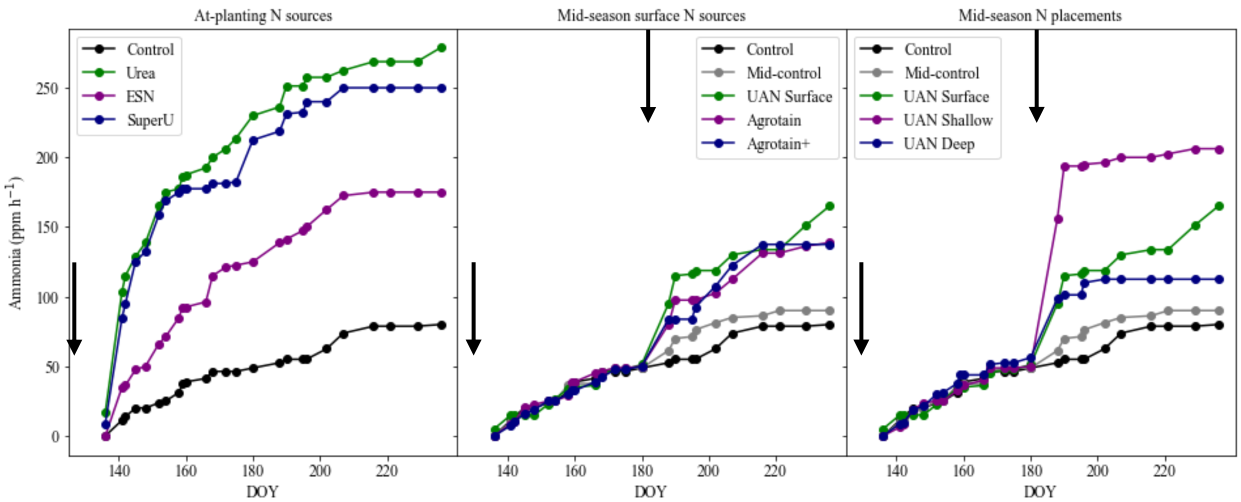



Figure 3.8: Cumulative $NH_3$ emissions of each treatment at Carman, MB in 2020. Black arrows represent the time of N application.

### 3.4.4 Soil Inorganic Nitrogen and Nitrate Intensity

For each treatment and site-year, soil $NH_4^+$ and $NO_3^-$ concentrations peaked following N fertilization, then decreased throughout the growing season (Figures 3.9–11). For the majority of each growing season, SuperU and ESN maintained higher soil $NH_4^+$ and $NO_3^-$ concentrations compared to urea at-planting, with the exception of June 6th 2018 (DOY 157), and July 2nd 2020 (DOY 183); urea also had greater $NO_3^-$ concentrations than ESN from the time of application to August 6th in 2019 (DOY 218). Soil N concentrations seemed to show a general trend for in-season N sources and placements; Agrotain and AgrotainPlus maintained higher levels of soil $NH_4^+$ while UAN Surface had greater $NO_3^-$ concentrations throughout each growing season; enhanced efficiency fertilizers delay the accumulation of $NO_3^-$ in most soils (Dell *et al.* 2014). However, on July 13th 2018 (DOY 194) each treatment reached peak concentrations with Agrotain having the highest $NO_3^-$ concentration. UAN shallow had the greatest peak N concentrations after fertilization in 2018 (DOY 194) while UAN Deep had the greatest peak concentrations in 2019 (DOY 196) and 2020 (DOY 201).

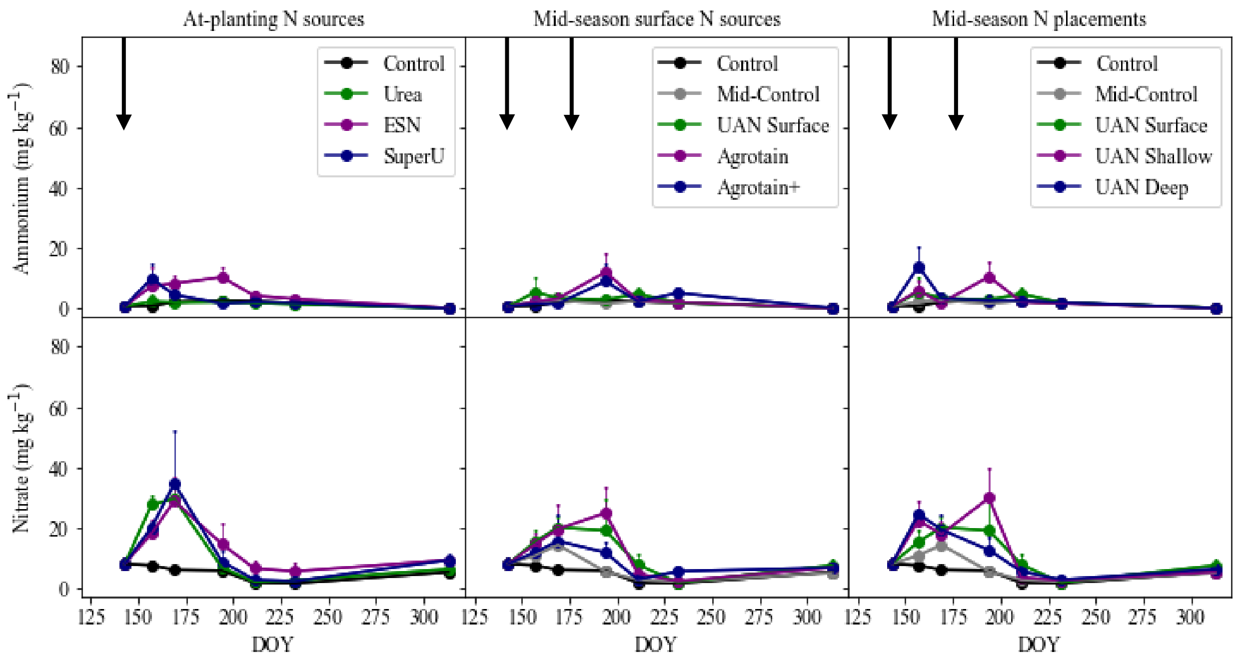



Figure 3.9**:** Daily soil ammonium and nitrate concentrations from 0–15.24cm depth at Carman, 2018. Legends represent treatments for top and bottom figures. Black arrows represent the time of N application.

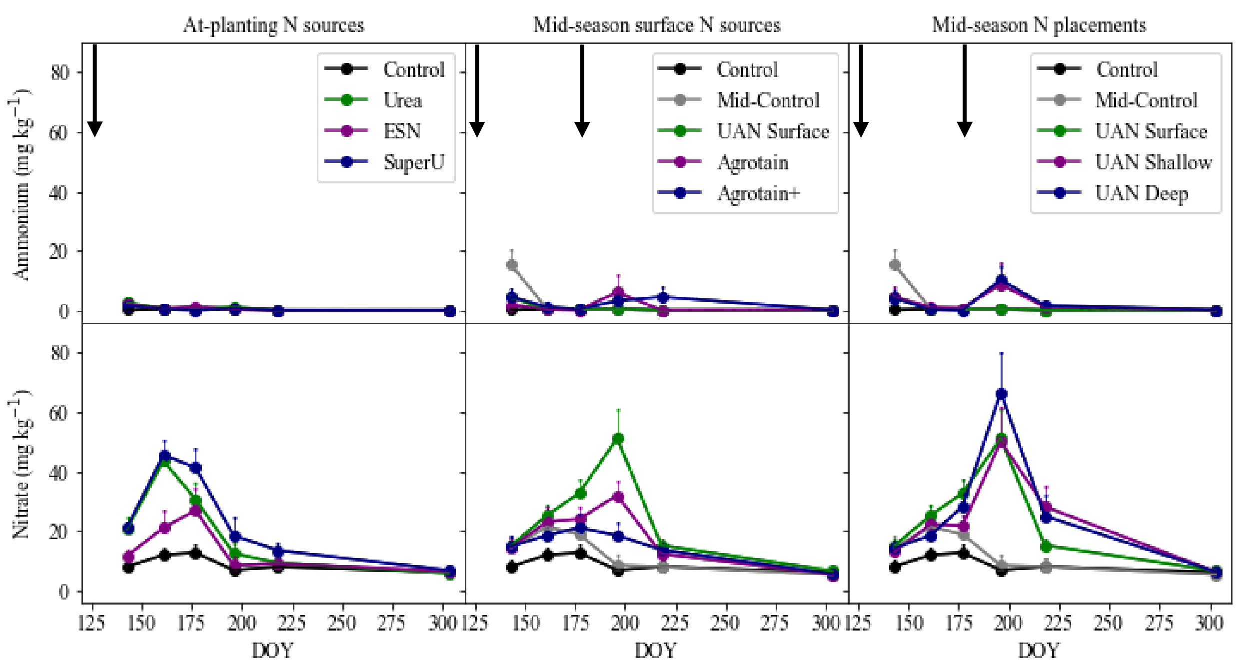



Figure 3.10: Daily soil ammonium and nitrate concentrations from 0–15.24cm depth at Haywood, 2019. Black arrows represent the time of N application.

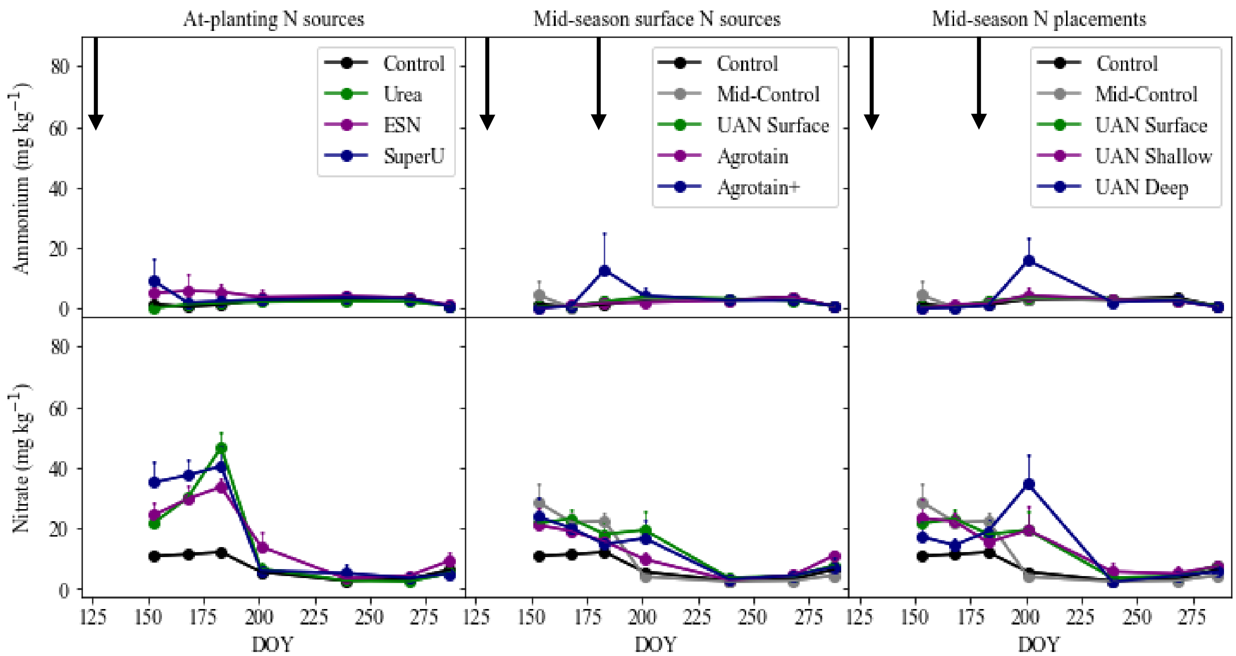


Figure 3.11: Daily soil ammonium and nitrate concentrations from 0–15.24cm depth at Carman, 2020. Black arrows represent the time of N application.

Control treatments had the lowest nitrate exposure in each site year.. Otherwise, there were no consistent trends for nitrate exposure throughout site-years (Figure 3.12). Compared to other studies, we did not observe strong relationships between nitrate exposure and cumulative $N_2O$ emissions (Asgedom *et al*. 2014). Figure 3.13 shows the strongest relationship observed was in 2020 ($r^2$ 0.57, P=0.08). Among all fertilized treatments, AgrotainPlus consistently had lower nitrate exposure values compared to other treatments and also had very low cumulative emissions of $N_2O$; in contrast, SuperU consistently had high nitrate exposure values compared to other treatments and also had low cumulative $N_2O$ emissions (Figure 3.12 and 3.13).

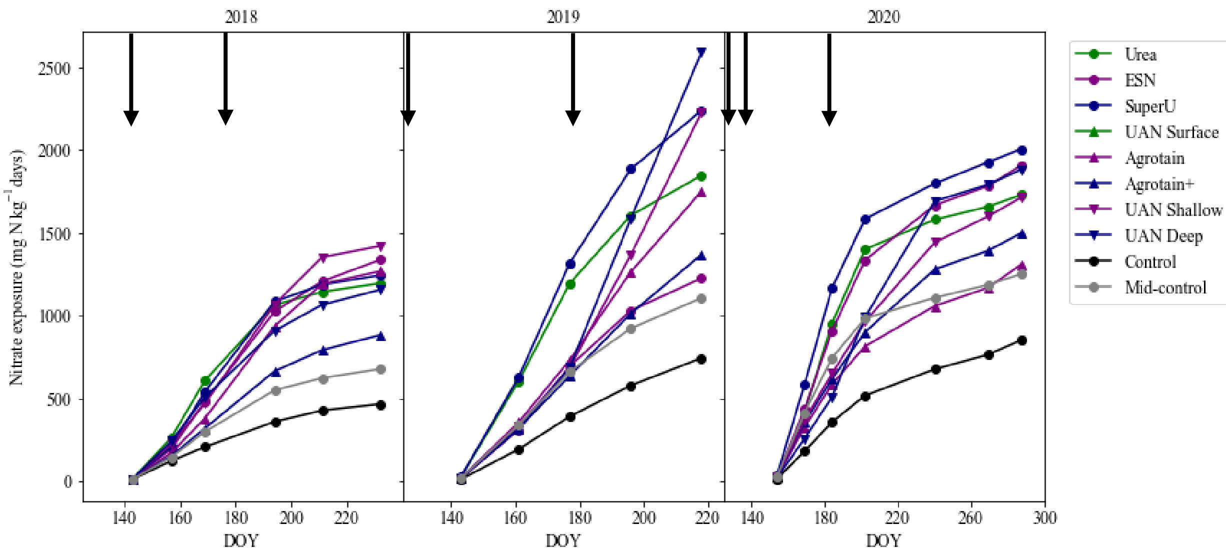



Figure 3.12: Cumulative nitrate exposure for all treatments and site-years (Post-harvest sampling date was cut out for 2018/19). Black arrows represent the time of N application.

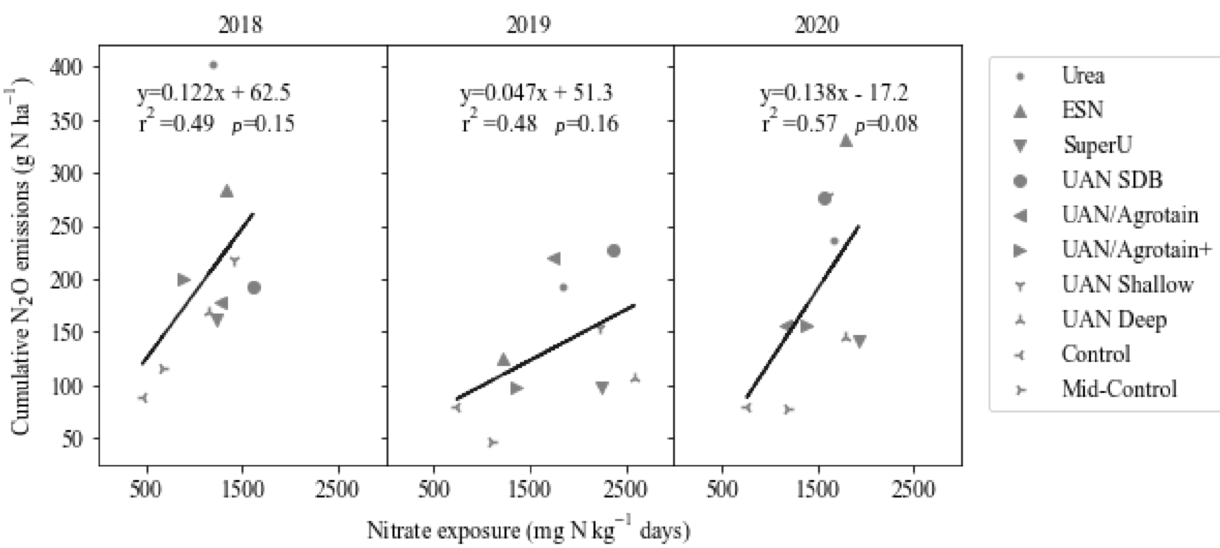



Figure 3.13: Relationships of nitrate exposure and cumulative $N_2O$ emissions for all treatments and site-years (2018–2020).

## 3.5 Discussion

### 3.5.1 At-Planting Sources

As noted by Tenuta *et al.* (2019), the majority of growing season $N_2O$ emissions typically occur during spring thaw and after N fertilization in heavy clay soils of Manitoba. This study shows a similar $N_2O$ response after fertilization in each growing season and suggests that EEF's such as ESN and SuperU have great potential to reduce early season $N_2O$ emissions in sandy soils outside the Red River Valley. The effectiveness of ESN and SuperU at reducing N loss is dependent on meteorological and soil conditions from year to year (Li *et al*. 2018). Drought conditions persisted for the majority of each growing season in this study, with the majority of months in each growing season having less than normal amounts of precipitation. As shown in figure 3.2, the wet spring of 2020 had the greatest volumetric moisture content readings (30% volumetric moisture content) and coincided with mean daily $N_2O$ fluxes for urea more than an order of magnitude greater than the drier years in the present study**.** It was under these conditions that ESN and SuperU had 58% and 32% lower area-scaled emissions compared to urea, respectively.

Results from this study demonstrate how $N_2O$ emissions resulting from applications of urea, ESN/urea, and SuperU during the growing season depend on environmental conditions at-planting, particularly soil-moisture and precipitation in this soil-climatic context (Thapa *et al*. 2016, Sahota 2020). Higher volumetric moisture content granted a greater potential for $N_2O$ production in 2020 and ESN/SuperU treatments were more efficient at reducing $N_2O$ emissions early in the growing season. SuperU significantly reduced $N_2O$ emissions across site-years ($P$ $<0.1$). Despite the differences in magnitude of $N_2O$ production, similar responses were observed in each site-year; Urea consistently had the greatest area-scaled $N_2O$ emissions, EF and EI among at-planting sources of N.

The observed $N_2O$ fluxes in this study were relatively low compared to other studies in Manitoba, which is expected during dry years (Tenuta *et al.* 2019, Thapa *et al.* 2016). Corn has a high risk for water deficit in Manitoba and the moisture supplied during spring thaw contributes a great amount of moisture to soils in this region. Soil moisture storage is also of great importance since these soils are imperfectly drained with interbedded layers of silt and clay that provide crops with moisture and nutrients in dry years (Boyd 2007). Emissions after planting/fertilization had a great effect on area-scaled $N_2O$, particularly in 2020. Due to high soil moisture conditions and a greater magnitude of $N_2O$ production in 2020, EEF's were more effective at reducing $N_2O$ emissions compared to other site-years. However, urea consistently had the greatest peak emissions during each site-year.

Contrastingly, other researchers have observed increased, or similar $N_2O$ fluxes by using ESN and SuperU compared to urea; such high variability in the effectiveness of EEF's to reduce $N_2O$ emissions in coarse textured soils and rainfed corn is expected, since the breakdown and crop uptake of fertilizer granules is dependent on many environmental factors such as temperature and soil moisture throughout each growing season (Sistani *et al.* 2011, Asegedom *et al.* 2014, Thapa *et al.* 2016). Urea consistently had greater area-scaled emissions and therefore had greater EF and EI compared to enhanced efficiency fertilizers. The effects on yield and nitrogen use efficiency between at-planting sources were also impacted by changes in soil moisture and meteorological conditions between site-years, as discussed in Chapter 2.

We observed contrasting soil and meteorological conditions from 2018–2020 in Manitoba; ESN and SuperU consistently reduced area-scaled $N_2O$ emissions, EF, and EI compared to urea. The amount of $N_2O$ flux associated with other peak emissions throughout the growing season will differ depending on soil N pools and meteorological conditions, thus influencing area-scaled emissions differently (Parkin and Hatfield 2014).

There were notable differences in cumulative $NH_3$ volatilization loss for each site-year, with greatest fluxes ranking ESN > Urea > SuperU in 2018 and 2019; Urea > SuperU > ESN in 2020. ESN had greater fluxes of $NH_3$ in 2018 and 2019, however ESN mitigated $NH_3$ losses in 2020; the observed differences in volatilization losses were likely caused by wet-dry soil conditions and microbial access to N. In this study. ESN had a slowed release of $NH_4^+$ and $NO_3^-$ at 0–15.24cm soil depth in 2020, thereby reducing volatilization losses in wet soil conditions. SuperU appeared to have similar volatilization losses to urea in each site-year; the use of nitrification inhibitors in combination with NBPT or other urease inhibitors may offset the benefits toward reduced $NH_3$ volatilization by retaining N in the ammoniacal form (Canterella *et al*. 2018). Afshar *et al*. (2018) found that SuperU reduced volatilization losses by 45% compared to urea in a dryland soil, suggesting that SuperU provides a wider timeframe for N to enter the soil with timely precipitation or incorporation. During a dry year, Jantalia *et al.* (2012) found ESN had the greatest $NH_3$ emissions in a semi-arid climate and clay loam soil. The authors also noted a gradual release of N throughout the season. Similarly, in this study, ESN slowed the release of N in 2018 and 2019, showing greater volatilization and peak $N_2O$ losses later in the growing season. The rate of N release from fertilizers granules is highly dependent on temperature and moisture conditions, and may be prolonged in dry climates; other researchers have suggested a blend of ESN and urea to allow for a more controlled release of N (Sahota 2020). This strategy appeared to reduce $NH_3$ volatilization losses in 2020 compared to urea. The results from the present study suggest that EEF's, such as Super and ESN, are most effective at reducing growing season $N_2O$ and/or $NH_3$ emissions with higher levels of moisture at planting/fertilization, such as in 2020.

SuperU and ESN had greater soil N concentrations than urea for the majority of each growing season which may promote increased yield, N uptake and/or residual N. Many researchers have observed yield benefits in warm, wet conditions (Noellsch *et al*. 2009, Halvorson and Bartolo 2014) while others have found reductions in gaseous emissions and/or leaching by using ESN and SuperU (Maharjan and Venterea 2013, Thapa *et al.* 2016, Drury *et al.* (2017), Lam *et al.* 2017). Regardless of the effects of EEF's on crop productivity and N uptake in a given growing season, ESN and SuperU consistently reduced area-scaled $N_2O$ emissions, EF, and EI, thereby serving as reliable options to reduce $N_2O$ emissions during the growing season.

### 3.5.2 In-Season Sources

For in-season application of N to corn in sandy soils of Manitoba, these results support past research to show how area-scaled $N_2O$ emissions, EF, and EI were reduced by mixing UAN with Agrotain or AgrotainPlus. AgrotainPlus consistently had the lowest $N_2O$ emissions in each site year due to the combination or urease and nitrification inhibitors NBPT and DCD in this product (Lam *et al*. 2017). Despite such dry conditions that were experienced for the majority of each site-year, precipitation events of at least 5mm occurred within a few days of in-season N application, incorporating N into the root zone and limiting volatilization loss (Afshar *et al.* 2018, Woodley *et al.* 2018). In 2018, in-season application occurred on June 26$^{th}$ (DOY 177) before 29.7 mm precipitation on June 29$^{th}$ (DOY 180); in 2019, fertilizer was applied on June 28$^{th}$ (DOY 179) before 5.2mm precipitation on June 29$^{th}$ (DOY 180); in 2020, fertilizer was applied June 30th (DOY 182) prior to 24.2mm precipitation the same day. There was likely a greater opportunity for volatilization losses in 2018 due to a longer time period between fertilization and a precipitation event; UAN surface had notably greater volatilization losses in 2018 compared to Agrotain and AgrotainPlus.

These qualitative observations suggest that reduced N loss by volatilization may allow for increased losses through $N_2O$ emissions and/or greater soil N concentrations later in the growing season. In this study, Agrotain had the lowest $N_2O$ emissions among in-season sources in 2018 while Agrotain also had the lowest $NH_3$ losses in 2018, this likely contributed to high soil N concentrations after fertilization (Thapa *et al.* 2016). It is difficult for growers in rainfed systems to use EEF's at their own discretion, given such great variability in soil moisture storage and precipitation from year to year. Dosimeter readings in 2018 suggest that in-season application without UI may result in substantial volatilization losses, particularly in coarse, calcareous soils (Nadler and Bullock 2011, Lasisi *et al.* 2019). More notable differences in $NH_3$ losses may have been observed in the absence of timely precipitation after N application and may have influenced $N_2O$ losses between treatments (Lam *et al.* 2017). Timing of precipitation after N fertilization can greatly influence volatilization loss and the retention of soil N pools available for $N_2O$ production (Lam *et al.* 2017, Woodley *et al.* 2018). In 2019, Agrotain had the greatest area-scaled emissions, showing the potential trade-off of pollutants when urease inhibitors are used alone (Lam *et al*. 2017). Results from this study show AgrotainPlus significantly lowered area-scaled $N_2O$ compared to UAN Surface across site-years ($P < 0.05$). EI of UAN Surface was also significantly greater than Agrotain and AgrotainPlus in 2020 ($P<0.05$) .

### 3.5.3 In-Season Placements

In each site-year, deep placement of UAN had the lowest cumulative $N_2O$ emissions compared to other placements of UAN. Similar to in-season N sources, timely rain events limited the amount of $NH_3$ volatilization following in-season application. Furthermore, different amounts of volatilization loss can influence $N_2O$ emissions throughout growing season(s) and the ability to detect significant differences between treatments (Woodley *et al.* 2020).

UAN Surface had higher volatilization losses in 2018 compared to other site-years due to a three day time period between N fertilization and a major precipitation event. In 2018, it was clear that shallow and deep placement prevented volatilization losses throughout qualitative observations. Furthermore, UAN Surface had lower area-scaled emissions compared to Agrotain (urease inhibitor) in this site-year. This scenario further outlines the trade-off of pollutants that can occur with various management practices (Lam *et al.* 2017). Greater placement depth combined with precipitation events directly after fertilization can promote downward N movement and increase soil contact of ammoniacal N (Rochette *et al.* 2013). This explains why UAN Shallow had the greatest N concentrations from 0–15.24cm depth after fertilization in 2018, as surface placement appeared to have lost more N through volatilization while deep placement likely promoted downward movement of N to deeper soil layers.

In 2019, site variability caused volatilization losses of UAN Deep to be greater than other treatments prior to in-season application; $NH_3$ losses were greater for UAN Shallow after in-season application. Cumulative $N_2O$ emissions were also greater for UAN Surface and UAN Shallow with greater peak emissions on July 15$^{th}$ (DOY 196). However, Figure 3.10 shows that UAN Deep had the greatest soil inorganic-N concentrations in 2019 (DOY 196), implying that deep placement reduced net emissions through increased $N_2O$ consumption (Chapuis-Lardy *et al.*

2007). Similarly, UAN Deep had the lowest cumulative $N_2O$ and $NH_3$ losses in 2020 and the greatest N concentrations on DOY 201 after fertilization. An explanation may be that deep placement of UAN may give more opportunity for $N_2O$ consumption, decreasing effluxes to the atmosphere compared to surface placement as $N_2O$ gases must travel a further distance to reach the soil-atmosphere interface (Chapuis-Lardy *et al.* 2007).

Although we did not find significant differences in area-scaled $N_2O$ between placement depths included in this study, deep banding had the lowest area-scaled $N_2O$ emissions in each site-year and had the greatest soil inorganic N concentrations after fertilization in 2019 and 2020. Many researchers have observed yield benefits with deep banding due to decreased volatilization losses, however, others have found that deep banding can increase $N_2O$ emissions in tilled soils when organic rich top soil is moved into deeper soil horizons (Eagle *et al*. 2017). The effects of various 4R management practices on gaseous emissions, nitrogen use efficiency, and yield is highly variable in space and time. For example, during years that have low volatilization losses and greater soil N retention due to timely precipitation, there is greater substrate availability for nitrification, denitrification, and $N_2O$ production later in the growing season. Thus, the responses of $NH_3$ volatilization and $N_2O$ production by placement depth are highly dependent on soil and environmental conditions, particularly during in-season application. In dry conditions, no-till management systems implemented for more than ten years have demonstrated reduced $N_2O$ emissions when fertilizer N is placed > 5cm below the surface due the distribution of organic matter in no-till soils (Kessel *et al*. 2013); it is clear that management also plays a role in the response of $N_2O$ emissions to various placement depths of UAN. Among the placement depths included in this study, deep placement consistently had the lowest area-scaled $N_2O$ emissions, EF, and EI fluxes in each site-year, as all sites have implemented no-till for several years.

Reduced $N_2O$ production combined with greater $N_2O$ consumption likely resulted in lower net fluxes to the atmosphere with deep placement of UAN.

### 3.5.4 At-Planting Vs. In-Season Conventional Sources

Results from this study show that in-season applications consistently reduced area-scaled $N_2O$ emissions, EF, and EI compared to urea applied at-planting; Urea had significantly greater EF compared to UAN in 2018. There is a greater opportunity for $N_2O$ production when applying the full recommended N rate at-planting, when there is high soil moisture after spring thaw; there is a relatively high risk of moisture stress for corn grown in Manitoba and this reduces the potential for $N_2O$ production through nitrification and denitrification when N is applied in split applications (Davidson 2000, Nadler and Bullock 2011). Due to more consistent water availability and greater substrate supply at-planting, urea consistently had greater daily emissions after fertilization in each site-year, resulting in greater area-scaled $N_2O$ emissions, EF, and EI compared to UAN applied in-season. Split-applications typically offer better synchrony between crop N supply and demand, therefor soil N pools are kept low and the potential for $N_2O$ production is reduced.

Although there is great potential for split applications to reduce $N_2O$ emissions in Manitoba, split applications may result in lower nitrogen use efficiency, greater residual soil N and greater $N_2O$ emissions in certain situations, depending on soil and meteorological conditions (Clark 2020). For example, decreased crop N uptake during dry years may result in a greater amount of residual N that is left susceptible to produce $N_2O$ emissions during the next growing season. As such, farmers must adapt in-season N rates based on crop and meteorological conditions each year. When farmers are able to apply in-season N prior to light precipitation event(s) and minimize volatilization losses, in-season applications are a reliable method for reducing $N_2O$ emissions and potentially increasing yield/N uptake (Clark 2020).

### 3.5.5 Soil Nitrate Intensity

As shown by Asgedom *et al.* (2014), soil $NO_3^-$ intensity can offer an explanation for cumulative $N_2O$ emissions for various N treatments in Manitoba. Theoretically, the N treatments that have the greatest soil $NO_3^-$ concentrations throughout each growing season will reflect greater cumulative $N_2O$ emissions compared to other treatments. However, meteorological conditions and/or the effects of enhanced efficiency fertilizers may have affected the relationship of cumulative $N_2O$ emissions and $NO_3^-$ intensity in this context. We did not find significant relationships between nitrate exposure and cumulative $N_2O$ emissions in either site-year, however the relationship was strongest in 2020 ($r^2$ 0.57=, $P$=0.08). Control treatments had the lowest nitrate exposure in each site-year while there was a lack of consistency between fertilized treatments. This led to inconsistencies regarding the ordination of treatments along linear regression lines. The use of inhibitor and slow release products may have blurred the relationship between soil inorganic-N pools and cumulative $N_2O$ emissions, a relationship that is also unclear in dry conditions. For example, SuperU consistently had high $NO_3^-$ exposure compared to other treatments but also had some of the lowest cumulative $N_2O$ emissions throughout site years. This implies that cumulative $N_2O$ emissions were controlled more dominantly by factors other than N availability for nitrification and denitrification processes. Peak $N_2O$ emissions coincided with rain events throughout each growing season due to persistent dry conditions, therefore cumulative $N_2O$ emissions were likely more dependent on soil and meteorological conditions that influence microbial access to N and subsequent $N_2O$ production, rather than the supply of soil N. Stronger relationships between $NO_3^-$ intensity and $N_2O$ emissions may have been observed in wetter soil conditions, such as the relationships found by Asgedom *et al.* (2014) in clay soils of the Red River Valley**.**

### 3.6 Conclusion

Overall, the results of this study agree with the findings of past research on $N_2O$ emissions resulting from 4R management options, however the responses that we observed for each-site year appeared to be highly related to soil moisture and precipitation events throughout the growing season. Results from this research show the potential for EEF's to decrease $N_2O$ emissions at planting, particularly with moist soil conditions; SuperU and ESN consistently had lower $N_2O$ fluxes, EF, and EI compared to urea. Additionally, the use of urease and nitrification inhibitor products combined (AgrotainPlus) consistently had the lowest area-scaled $N_2O$ emissions, EF, and EI among in-season N sources; AgrotainPlus had significantly lower area-scaled $N_2O$ emissions, EF, and EI compared to UAN Surface. The use of urease inhibitors alone with UAN may result in greater cumulative fluxes of $N_2O$ compared to UAN without a urease or nitrification inhibitor (Lam *et al*. 2017), however this type of response was only observed in 2019. UAN Deep consistently had the lowest cumulative $N_2O$ flux among in-season placements, however no significant differences were observed between fertilized treatments.

Enhanced efficiency fertilizer such as controlled-release (ESN) and double inhibitors (SpuerU, AgrotainPlus) products are effective tools for the mitigation of $N_2O$ emissions for at-planting or in-season application. However, agronomic benefits are most likely to be observed in wet conditions that promote N loss and are conducive to high corn productivity. In-season application of UAN also consistently reduced cumulative $N_2O$ emissions and lowered EF and EI compared to urea applied at-planting.

This research aims to give corn growers a number of 4R field-tested options for reducing $N_2O$ emissions in Manitoba while maintaining or improving crop productivity. Further field studies investigating $N_2O$ emissions resulting from EEF's and placement depth in Manitoba soils will improve the understanding of how different 4R management practices can be used to reduce $N_2O$ emissions in various soil-cropping contexts. The magnitude of $N_2O$ flux resulting from various 4R practices is dependent on environmental conditions from year to year, however this study shows how the use of EEF's at-planting, EEF's applied in-season, deep placement of UAN, and split-application of N numerically reduced area-scaled $N_2O$ emissions, EF, and EI very consistently compared to conventional fertilizers. These practices are viable options for reducing $N_2O$ emissions by 30% while maintaining crop productivity in this soil-cropping context.

## 3.7 References

Afshar, R. K., R. Lin, Y. A. Mohammed, and C. Chen. "Agronomic Effects of Urease and Nitrification Inhibitors on Ammonia Volatilization and Nitrogen Utilization in a Dryland Farming System: Field and Laboratory Investigation." *Journal of Cleaner Production 172* (2018): 4130–39. https://doi.org/10.1016/j.jclepro.2017.01.105.

Akiyama, H., X. Yan, and K. Yagi. "Evaluation of Effectiveness of Enhanced-Efficiency Fertilizers as Mitigation Options for N2O and NO Emissions from Agricultural Soils: Meta-Analysis." *Global Change Biology 16*, no. 6 (2010): 1837–46. https://doi.org/10.1111/j.1365-2486.2009.02031.x.

Alonso-Ayuso, M., J. L. Gabriel, and M. Quemada. “Nitrogen Use Efficiency and Residual Effect of Fertilizers with Nitrification Inhibitors.” *European Journal of Agronomy 80* (2016): 1–8.

An, H., J. Owens, J. Stoeckli, X. Hao, B. Beres, and Y. Li. “Nitrous Oxide Emissions Following Split Fertilizer Application on Winter Wheat Grown on Mollisols of Southern Alberta, Canada.” *Geoderma Regional 21* (2020): e00272.

Asgedom, H., M. Tenuta, D. N. Flaten, and X. Gao.“Nitrous Oxide Emissions from a Clay Soil Receiving Granular Urea Formulations and Dairy Manure” *Agronomy Journal 106,* no. 2 (2014): 732–744.

Awale, R., and A. Chatterjee. “Enhanced Efficiency Nitrogen Products Influence Ammonia Volatilization and Nitrous Oxide Emission from Two Contrasting Soils.” *Agronomy Journal 109,* no. 1 (2017): 47–57. https://doi.org/10.2134/agronj2016.04.0219.

Bouwmeester, R. J. B., P. L. G. Vlek, J. M. Stumpe “Effect of Environmental Factors on Ammonia Volatilization from a Urea-Fertilized Soil” *Soil Science Society of America Journal 49,* no.2 (1985): 376–381. https://acsess-onlinelibrary-wiley-com.uml.idm.oclc.org/doi/abs/10.2136/sssaj1985.03615995004900020021x.

Boyd, M. “Early Postglacial History of the Southeastern Assiniboine Delta, Glacial Lake Agassiz Basin.” *Journal of Paleolimnology 37,* no. 3 (2007): 313–29. https://doi.org/10.1007/s10933-006-9044-3.

Cantarella, H., R. Otto, J. R. Soares, and A. G. D. B. Silva. “Agronomic Efficiency of NBPT as a Urease Inhibitor: A Review.” *Journal of Advanced Research 13* (2018): 19–27. https://doi.org/10.1016/j.jare.2018.05.008.

Chapuis-Lardy, L., N. Wrage, A. Metay, J. Chotte, and M. Bernoux. "Soils, a Sink for N2O? A Review." *Global Change Biology 13*, no. 1 (2007): 1–17. https://doi.org/10.1111/j.1365-2486.2006.01280.x.

Clark, J. "When to Use a Single or Split Application of Nitrogen Fertilizer in Corn." *Crops & Soils* 53, no. 5 (2020): 20–24. https://doi.org/10.1002/crso.20070.

Conrad, R., W. Seiler, and G. Bunse. "Factors Influencing the Loss of Fertilizer Nitrogen into the Atmosphere as N2O." *Journal of Geophysical Research: Oceans 88*, no. C11 (1983): 6709–18. https://doi.org/10.1029/JC088iC11p06709.

Davidson, E. A., M. Keller, H. E. Erickson, L. V. Verchot, and E. Veldkamp. "Testing a Conceptual Model of Soil Emissions of Nitrous and Nitric Oxides" *BioScience 50*, no.8 (2000): 667–80. https://academic.oup.com/bioscience/article/50/8/667/243260?login=true.

Dell, C. J., K. Hun, R. B. Bryant, J. P. Schmidt. "Nitrous Oxide Emissions with Enhanced Efficiency Nitrogen Fertilizers in a Rainfed System" *Agronomy Journal 106*, no. 2 (2014): 723–31. https://acsess-onlinelibrary-wiley-com.uml.idm.oclc.org/doi/full/10.2134/agronj2013.0108.

Di Capua, F., F. Pirozzi, P. N. L. Lens, and G. Esposito. "Electron Donors for Autotrophic Denitrification." *Chemical Engineering Journal 362* (2019): 922–37. https://doi.org/10.1016/j.cej.2019.01.069.

Drury, C. F., X. Yang, W. D. Reynolds, W. Calder, T. O. Oloya, and A. L. Woodley. "Combining Urease and Nitrification Inhibitors with Incorporation Reduces Ammonia and Nitrous Oxide Emissions and Increases Corn Yields." *Journal of Environmental Quality 46*, no. 5 (2017): 939–49.

Eagle, A. J., L. P. Olander, K. L. Locklier, J. B Heffernan, and E. S. Bernhardt. "Fertilizer Management and Environmental Factors Drive $N_2O$ and $NO_3$ Losses in Corn: A Meta-Analysis" *Soil Science Society of America Journal 81*, no. 5 (2017): 1191–1202.

Ernst, J. W., and H. F. Massey. "The Effects of Several Factors on Volatilization of Ammonia Formed from Urea in the Soil" *Soil Science Society of America Journal 24,* no.2 (1960): 87–90.

Ferguson, R. B., D. E. Kissel, J. K. Koelliker, and W. Basel. "Ammonia Volatilization from Surface-Applied Urea: Effect of Hydrogen Ion Buffering Capacity." *Soil Science Society of America Journal 48*, no. 3 (1984): 578–82. https://doi.org/10.2136/sssaj1984.03615995004800030022x.

Fillery, I. R. P., J. R. Simpson, and S. K. D. Datta, "Influence of Field Environment and Fertilizer Management on Ammonia Loss from Flooded Rice." *Soil Science Society of America Journal 48,* no.4 (1984): 914–20. https://acsess-onlinelibrary-wiley-com.uml.idm.oclc.org/doi/abs/10.2136/sssaj1984.03615995004800040043x.

Fixen, P. E. "A Brief Account of the Genesis of 4R Nutrient Stewardship." *Agronomy Journal 112,* no.5 (2020): 4511–18. https://doi.org/10.1002/agj2.20315.

Gao, X., H. Asgedom, M. Tenuta, and D. N. Flaten. "Enhanced Efficiency Urea Sources and Placement Effects on Nitrous Oxide Emissions." *Agronomy Journal 107,* no. 1 (2015): 265–77.

Halvorson, A. D., and M. E. Bartolo "Nitrogen Source and Rate Effects on Irrigated Corn Yields and Nitrogen-Use Efficiency." *Agronomy Journal 106,* no. 2 (2014): 681–93.

Hink, L., G. W. Nicol, and J. I. Prosser. "Archaea Produce Lower Yields of $N_2O$ than Bacteria during Aerobic Ammonia Oxidation in Soil," *Environmental Microbiology 19,* no. 12 (2017): 48294837. https://sfamjournals.onlinelibrary.wiley.com/doi/epdf/10.1111/1462-2920.13282.

Højberg O., N. P. Revsbech, and J. M. Tiedje. “Denitrification in Soil Aggregates Analyzed with Microsensors for Nitrous Oxide and Oxygen” *Soil Science Society of America Journal 58*, no. 6 (1994): 1691–1698. https://acsess-onlinelibrary-wiley-com.uml.idm.oclc.org/doi/abs/10.2136/sssaj1994.03615995005800060016x.

Jantalia, C. P., A. D. Halvorson, R. F. Follett, B. J. R. Alves, J. C. Polidoro, and S. Urquiaga. “Nitrogen Source Effects on Ammonia Volatilization as Measured with Semi-Static Chambers.” *Agronomy Journal 104*, no. 6 (2012): 1595–1603. https://doi.org/10.2134/agronj2012.0210.

Johnston, A. M., and T. W. Bruulsema. “4R Nutrient Stewardship for Improved Nutrient Use Efficiency.” *Procedia Engineering 83*, (2014): 365–70. https://doi.org/10.1016/j.proeng.2014.09.029.

Kessel, C. V., R. Venterea, J. Six, M. A. Adviento-Borbe, B. Linquist, and K. J. V. Groenigen. “Climate, Duration, and N Placement Determine $N_2O$ Emissions in Reduced Tillage Systems: A Meta-Analysis.” *Global Change Biology 19*, no. 1 (2013): 33–44.

Khalil, K., B. Mary, and P. Renault. “Nitrous Oxide Production by Nitrification and Denitrification in Soil Aggregates as Affected by $O_2$ Concentration” *Soil Biology and Biochemistry 36*, no. 4 (2004): 687–699. https://www.sciencedirect.com/science/article/abs/pii/S0038071704000355.

Lam, S. K., H. Suter, A. R. Mosier, and D. Chen. “Using Nitrification Inhibitors to Mitigate Agricultural N2O Emission: A Double-Edged Sword?” *Global Change Biology 23*, no. 2 (2017): 485–89.

Lasisi, A. A., O. O. Akinremi, and D. Kumaragamage. “Efficacy of a New N-(n-Butyl) Thiophosphoric Triamide Formulation in Reducing Ammonia Volatilization from Urea-Based

Fertilizers." *Canadian Journal of Soil Science 99,* no. 4 (2019): 395–405. https://doi.org/10.1139/cjss-2018-0072.

Lehtovirta-Morley, L. E. "Ammonia Oxidation: Ecology, Physiology, Biochemistry and Why They Must All Come Together." *FEMS Microbiology Letters 365,* no. 9 (2018). https://doi.org/10.1093/femsle/fny058.

Li, T., W. Zhang, J. Yin, D. Chadwick, D. Norse, Y. Lu, X. Liu, X. Chen, F. Zhang, D. Powlson, Z. Dou. "Enhanced-Efficiency Fertilizers Are Not a Panacea for Resolving the Nitrogen Problem." *Global Change Biology 24*, no. 2 (2018): e511–521. https://doi.org/10.1111/gcb.13918.

Liu, L., X. Zhang, W. Xu, X. Liu, Y. Li, J. Wei, Z. Wang, and X. Lu. "Ammonia Volatilization as the Major Nitrogen Loss Pathway in Dryland Agro-Ecosystems." *Environmental Pollution 265* (2020): 114862. https://doi.org/10.1016/j.envpol.2020.114862.

Maharjan, B., and R. T. Venterea. "Nitrite Intensity Explains N Management Effects on N2O Emissions in Maize." *Soil Biology and Biochemistry 66* (2013): 229–38. https://doi.org/10.1016/j.soilbio.2013.07.015.

Maynard, D. G., Kalra, Y. P., and Crumbaugh, J. A. "Nitrate and exchangeable ammonium nitrogen." *Soil sampling and methods of analysis 1* (1993): 25-38.

Myhre, G., Shindell, D., and Pongratz, J. "Anthropogenic and natural climate forcing." *Climate Change* (2013).

Nadler, A. J., and P. R. Bullock. "Long-Term Changes in Heat and Moisture Related to Corn Production on the Canadian Prairies." *Climatic Change 104*, no. 2 (2011): 339–52. https://doi.org/10.1007/s10584-010-9881-y.

Nash, P. R., P. P. Motavalli, and K. A. Nelson. "Nitrous Oxide Emissions from Claypan Soils Due to Nitrogen Fertilizer Source and Tillage/Fertilizer Placement Practices." *Soil Science Society of America Journal 76*, no. 3 (2012): 983–93.

Noellsch, A. J., P. P. Motavalli, K. A. Nelson, and N. R. Kitchen. "Corn Response to Conventional and Slow-Release Nitrogen Fertilizers across a Claypan Landscape." *Agronomy Journal 101*, no. 3 (2009): 607–14. https://doi.org/10.2134/agronj2008.0067x.

O'Sullivan, C. A., S. A. Wakelin, I. R. P. Fillery, and M. M. Roper. "Factors Affecting Ammonia-Oxidising Microorganisms and Potential Nitrification Rates in Southern Australian Agricultural Soils." *Soil Research 51*, no. 3 (2013): 240–52. https://doi.org/10.1071/SR13039.

Omara, P., L. Aula, F. Oyebiyi, and W. R. Raun. "World Cereal Nitrogen Use Efficiency Trends: Review and Current Knowledge." *Agrosystems, Geosciences & Environment 2*, no. 1 (2019):1–8. https://doi.org/10.2134/age2018.10.0045.

Pan, B., S. K. Lam, A. Mosier, Y. Luo, and D. Chen. "Ammonia Volatilization from Synthetic Fertilizers and Its Mitigation Strategies: A Global Synthesis." *Agriculture, Ecosystems & Environment 232* (2016): 283–89. https://doi.org/10.1016/j.agee.2016.08.019.

Parkin, T. B., and J. L. Hatfield. "Enhanced Efficiency Fertilizers: Effect on Nitrous Oxide Emissions in Iowa." *Agronomy Journal 106*, no. 2 (2014): 694–702. https://doi.org/10.2134/agronj2013.0219.

Pawlick, A. A., C. Wagner-Riddle, G. W. Parkin, and A. A. Berg. "Assessment of Nitrification and Urease Inhibitors on Nitrate Leaching in Corn (Zea Mays L.)." *Canadian Journal of Soil Science 99*, no. 1 (2019): 80–91.

Placella, S. A., and M. K. Firestone. “Transcriptional Response of Nitrifying Communities to Wetting of Dry Soil.” *Applied and Environmental Microbiology 79*, no. 10 (2013): 3294–3302. https://doi.org/10.1128/AEM.00404-13.

Prather, M. J., J. Hsu, N. M. DeLuca, C. H. Jackman, L. D. Oman, A. R. Douglass, E. L. Fleming, S. E. Strahan, S. D. Steenrod, O. A. Søvde, I. S. A Isaksen, L. Froidevaux, and B. Funke.“Measuring and Modeling the Lifetime of Nitrous Oxide Including Its Variability.” *Journal of Geophysical Research: Atmospheres 120*, no. 11 (2015): 5693–5705. https://doi.org/10.1002/2015JD023267.

Qiao, C., L. Liu, S. Hu, J. E. Compton, T. L. Greaver, and Q. Li. “How Inhibiting Nitrification Affects Nitrogen Cycle and Reduces Environmental Impacts of Anthropogenic Nitrogen Input.” *Global Change Biology 21*, no. 3 (2015): 1249–57. https://doi.org/10.1111/gcb.12802.

Rochette, P., D. A. Angers, M. H. Chantigny, M. Gasser, J. D. MacDonald, D. E. Pelster and N. Bertrand. “Ammonia Volatilization and Nitrogen Retention: How Deep to Incorporate Urea?” *Journal of Environmental Quality 42*, no. 6 (2013): 1635–42. https://doi.org/10.2134/jeq2013.05.0192.

Rodríguez, D. “Greenhouse gas emissions of agriculture: A comparative analysis.” *Environmental Chemistry and Recent Pollution Control Approaches* (2019): 21-40.

Sahota, T. S. “Environmentally Smart Nitrogen (ESN)—Potential for Improving Modern Crop Production and N-Use Efficiency.” *Journal of Agricultural Science and Technology 10*, no. 6 (2020): 327–340. Schepers, James Stuart, and William Raun. *Nitrogen in Agricultural Systems*. ASA-CSSA-SSSA, 2008.

Sahrawat, K. L. “Factors Affecting Nitrification in Soils.” *Communications in Soil Science and Plant Analysis 39*, no. 9–10 (2008): 1436–46.

Schepers, J. S., and W. Raun. "Nitrogen in Agricultural Systems." ASA-CSSA-SSSA, (2008).

Schimel, J. P. "Life in Dry Soils: Effects of Drought on Soil Microbial Communities and Processes." *Annual Review of Ecology, Evolution, and Systematics 49*, no. 1 (2018): 409–32. https://doi.org/10.1146/annurev-ecolsys-110617-062614.

Sistani, K. R., M. Jn-Baptiste, N. Lovanh, and K. L. Cook. "Atmospheric Emissions of Nitrous Oxide, Methane, and Carbon Dioxide from Different Nitrogen Fertilizers." *Journal of Environmental Quality 40*, no. 6 (2011): 1797–1805. https://doi.org/10.2134/jeq2011.0197.

Smil, V. "Global Population and the Nitrogen Cycle." *Scientific American 277*, no. 1 (1997): 76–81.

Tenuta, M., B. D. Amiro, X. Gao, C. Wagner-Riddle, and M. Gervais. "Agricultural Management Practices and Environmental Drivers of Nitrous Oxide Emissions over a Decade for an Annual and an Annual-Perennial Crop Rotation." *Agricultural and Forest Meteorology 276–277* (2019): 107636.

Thapa R., A. Chatterjee, R. Awale, D. A. McGranahan, and A. Daigh. "Effect of Enhanced Efficiency Fertilizers on Nitrous Oxide Emissions and Crop Yields: A Meta-analysis" *Soil Science Society of America Journal 80*, no. 5 (2016): 1121–1134. https://acsess.onlinelibrary.wiley.com/doi/abs/10.2136/sssaj2016.06.0179.

Tian, H., R. Xu, J. G. Canadell, R. L. Thompson, W. Winiwarter, P. Suntharalingam, E. A. Davidson, P. Ciais, R. B. Jackson, G. Janssens-Maenhout, M. J. Prather, P. Regnier, N. Pan, S. Pan, G. P. Peters, H. Shi, F. N. Tubiello, S. Zaehle, F. Zhou, A. Arneth, G. Battaglia, S. Berthet, L. Bopp, A. F. Bouwman, E. T. Buitenhuis, J. Chang, M. P. Chipperfield, S. R. S. Dangal, E. Dlugokencky, J. W. Elkins, B. D. Eyre, B. Fu, B. Hall, A. Ito, F. Joos, P. B. Krummel, A. Landolfi, G. G. Laruelle, R. Lauerwald, W. Li, S. Lienert, T. Maavara, M. MacLeod, D. B.

Millet, S. Olin, P. K. Patra, R. G. Prinn, P. A Raymond, D. J. Ruiz, G. R. V. D. Werf, N. Vuichard, J. Wang, R. F. Weiss, K. C Wells, C. Wilson, J. Yang, and Y. Yao "A Comprehensive Quantification of Global Nitrous Oxide Sources and Sinks." *Nature 586,* no. 7828 (2020): 248–56. https://doi.org/10.1038/s41586-020-2780-0.

Upadhyay, L. S. B., "Urease Inhibitors: A Review." *IJBT 11*. No. 4 (2012): 381–388. http://nopr.niscair.res.in/handle/123456789/15679.

Van Andel, M., J. S. Warland, P.D. Zwart, B.J. V. Heyst, and J.D. Lauzon. "Development of a Simple and Affordable Method of Measuring Ammonia Volatilization from Land Applied Manures." *Canadian Journal of Soil Science 97*, no. 4 (2017): 541–51.

Wang, Y., L. Ma, Y. Mao, X. Jiang, Y. Xia, K. Yu, B. Li, and T. Zhang. "Comammox in Drinking Water Systems." *Water Research 116,* (2017): 332–41. https://doi.org/10.1016/j.watres.2017.03.042.

Ward, B. "Chapter 5 – Nitrification in marine systems and nitrogen in the marine environment." (2008) :199-261.

Westphal, M, M. Tenuta, and M. H. Entz. "Nitrous Oxide Emissions with Organic Crop Production Depends on Fall Soil Moisture." *Agriculture, Ecosystems & Environment 254,* (2018): 41–49. https://doi.org/10.1016/j.agee.2017.11.005.

Wood, M., M. Tenuta., and D. Flaten. "Nitrogen Application Timing and Source to Reduce Nitrous Oxide Emissions and Improve Spring Wheat Production with Enhanced Efficiency Fertilizers." *SSSA International Soils Meeting* (2019). ASA-CSSA-SSSA.

Woodley, A. L., C. F. Drury, X. M. Yang, W. D. Reynolds, W. Calder, and T. O. Oloya. "Streaming Urea Ammonium Nitrate with or without Enhanced Efficiency Products Impacted

Corn Yields, Ammonia, and Nitrous Oxide Emissions." *Agronomy Journal 110*, no. 2 (2018): 444–54.

Woodley, A. L., C. F. Drury, X. Y. Yang, L. A. Phillips, D. W. Reynolds, W. Calder, and T. O. Oloya. "Ammonia Volatilization, Nitrous Oxide Emissions, and Corn Yields as Influenced by Nitrogen Placement and Enhanced Efficiency Fertilizers." *Soil Science Society of America Journal 84*, no. 4 (2020): 1327–41.

# 4. Synthesis

## 4.1 Project Accomplishments

Manitoba accounted for approximately 8.4% of total Canadian corn production in 2020, this proportion has increased from 3.6% in 2011 (Government of Manitoba 2020). Nitrogen fertilizer is an important input for corn to reach full growth potential and deliver high yield. In 2016, commercial fertilizers were applied to 70.4 million acres in Canada, compared to 61.6 million in 2011 (Statistics Canada 2017)). The trend of increasing inputs to agricultural land imposes great risk towards the environment and the socioeconomic livelihood of farming communities in Canada and around the world; by investigating ways of applying and using N fertilizer more efficiently, agroecosystems and global food production will eventually become more sustainable.

Previous studies have shown the potential of the 4R's to reduce $N_2O$ emissions from various soil types and environmental conditions in Manitoba. Wood (2019) showed that eNTrench and SuperU were most effective at reducing emissions compared to urea during years with normal or above-normal precipitation. Gao *et al.* (2015) showed that ESN and SuperU were effective at reducing $N_2O$ emissions in contrasting soil types. However, there is still a lack of studies that investigate multiple sets of 4R management practices in the same site-year(s). To my knowledge, there is no study in Manitoba that has investigated $N_2O$ emissions and agronomic performance of ten different N management options simultaneously, at a field scale. This project had a total of 144 plots in each site-year; 40 of which were used to monitor $N_2O$ fluxes at the recommended rate of 112 kg N $ha^{-1}$. Yield and NUE were evaluated at 56, 84, 112, and 168 kg N $ha^{-1}$. In this study, we observed contrasting meteorological conditions in Spring of 2020 compared to other site-years, which offers farmers in Manitoba a better perspective of how various 4R management practices can interact with soil-moisture conditions to influence environmental losses of N and nitrogen use efficiency of grain corn in this region.

Over three site-years, the objectives of this thesis were to evaluate the agronomic capability and environmental sustainability between 1) broadcast-incorporated N sources applied at-planting (Urea, ESN/Urea, SuperU); 2) N sources applied at the V4 stage as surface dribble band (UAN, UAN/Agrotain, UAN/AgrotainPlus); 3) Placement depth of UAN applied at the V4 stage (Surface dribble band, 1.5" depth, 3" depth). In chapter 2, we compared yield, AE, NRE, and residual inorganic N after corn harvest; in chapter 3, we used the static-vented chamber method to compare cumulative $N_2O$ emissions, emission factors, and emission intensities between each treatment within our objectives, while giving a qualitative assessment of $NH_3$ volatilization. Comparisons of various 4R practices are needed to assess national greenhouse gas budgets from year to year. Growing season $N_2O$ emissions were successfully monitored for three consecutive years while plant and soil samples were taken for agronomic assessments. The objectives of this thesis encompass both the agronomic and environmental benefits that result from various 4R management strategies; this study includes sites with very similar soil characteristics as well as years with contrasting environmental conditions at-planting.

Area-scaled $N_2O$ emissions were relatively low compared to other studies done in Manitoba (Tenuta *et al.* 2019), however, EEF's applied at-planting show great potential to reduce early season $N_2O$ emissions, particularly with high soil moisture at-planting; Urea had the greatest area-scaled $N_2O$ fluxes in each site-year and was significantly greater than SuperU across site-years ($P$<0.1). These results show that enhanced efficiency fertilizers, particularly SuperU, consistently reduced $N_2O$ emissions in this soil-climatic context. Li *et al.* (2018)

performed a meta-analysis on the efficacy of various inhibitor products in different soil-climatic conditions and only observed improvements toward, yield, NUE, or N losses in regions with rainfall >800mm/year. Similarly, we observed a much greater magnitude of $N_2O$ loss in 2020 when soil moisture was high compared to other site-years and the potential for EEF's to improve yield/NUE was greater. Results from this study show the potential that farmers have to manage N applications depending on soil moisture conditions from year to year. EEF's are very reliable in warm, wet temperatures and in irrigated systems (Li *et al.* 2018**)**, however corn growers in rainfed systems must carefully manage these products in order to reduce N losses and improve crop productivity. This calls for improved accessibility and reduced costs for EEF products particularly in this region of the world. In dry years, yield and NUE results were not consistent among N rates while ESN/Urea and SuperU tended to increase yield and NUE in 2020; furthermore, ESN and SuperU very consistently had greater residual N in each site-year. Enhanced efficiency fertilizers can aid in reducing N inputs during the next growing season(s), however greater soil N concentrations may result in greater spring emissions of $N_2O$ (Tenuta *et al*. 2019).

This research also highlights the benefits of mid-season application in Manitoba, as growers have the option to use UAN/AgrotainPlus to further reduce $N_2O$ emissions compared to urea applied at-planting; AgrotainPlus was the only treatment with area-scaled emissions that were not significantly different from the control (0 kg N) and had significantly lower emissions compared to UAN Surface. AgrotainPlus boosted yield, NUE in 2019 and 2020, however the results for residual N were not consistent.

Deep banding consistently had the lowest $N_2O$ emissions but this treatment was not significantly different from UAN Surface or UAN Shallow. The results for yield, NUE, and residual N were highly variable, likely due to the timing and intensity of precipitation events that greatly control the dominant pathways of N losses each year. For example, less volatilization and more leaching losses are likely to be observed when notable precipitation event(s) occur on the same day of N application, particularly in sandy soils; we qualitatively observed reductions in $NH_3$ volatilization by shallow and deep banding in 2018. Overall, this project assessed several 4R management practices that can be used to reduce $N_2O$ emissions and/or improve crop productivity in Manitoba.

### 4.2 Surprises

This project was originally designed to calculate the economically optimal rate of N, however the potential for N loss was relatively low in this study (Tenuta *et al.* 2019). As a result, the relationships between grain yield and N rate were not quadratic and gave unreasonably high estimations of the EONR for each treatment group (56, 84, 112, 168 kg N $ha^{-1}$ for each N source or placement). In wet soil conditions, there is greater potential for N loss, particularly with conventional fertilizers, therefore crops can take advantage of increased soil N retention of EEF's applied at-planting or in-season.

The trends observed for $N_2O$ fluxes in this study were very much as expected, however, the magnitude of flux was relatively low compared to other field studies (Tenuta *et al.* 2019). EEF's consistently had the lowest area-scaled emissions across site-years for both at-planting and mid-season applications of N; slowed release and delayed microbial access to N clearly reduced losses and increases residual soil N.

### 4.3 Challenges And Improvements

This project required vast amounts of labour for gas sampling operations, soil sampling, biomass harvesting, sample management, and analysis. The main disadvantage of including such a large number of treatments in the experimental design for this study was that only 4 replicates could be included per treatment. $N_2O$ emissions are highly variable in space and time, thus including more replicates per treatment would give greater statistical power and less risk for Type I error. Static-vented chambers are cheap and effective tools to compare N fluxes of various treatments, however this method may overlook flux events between sampling dates and only captures fluxes from small areas of a field. Automated chambers would give a more detailed perspective of $N_2O$ flux events, however the cost would be unfeasible due to the size of this experiment and the large number of treatments. Chamber methods may also overlook microsites that produce large amounts of $N_2O$ compared to other areas, known as $N_2O$ hotspots. Mason *et al.* (2017) estimated 40% of total $N_2O$ is emitted from hotspots that have different characteristics from the majority of the landscape; such as differences in landscape type, soil temperature, respiration rates, soil porosity, and/or water content (Nicolini *et al.* 2013) Hotspots may increase the variability between replicates and increase the risk for type I error, alternatively they may not be captured by static-vented chambers and cause an underestimation of $N_2O$ flux. To further compare the various management practices included in this study, such as at-planting sources of N, eddy-covariance towers could be used to capture fluxes from larger areas of the landscape while giving a greater temporal resolution for $N_2O$ fluxes throughout the growing season. Eddy-covariance techniques would also allow for precise measurement of spring-thaw $N_2O$ fluxes; residual N tended to be greater for EEF's compared to conventional fertilizers and could have greater fluxes of $N_2O$ the following spring (Wood 2019, Tenuta *et al*. 2019).

### 4.4 Future Work

This project only focused on the effects of various N treatments during the growing season; due to greater amounts of residual inorganic N after harvest, future work should investigate losses and agronomic benefits during the following growing season(s). The quantification of $N_2O$ emissions, $NH_3$ volatilization, and $NO_3^-$ leaching over multiple growing seasons would give a better perspective of how we can adapt to soil-climatic conditions to achieve the best economic and environmental outcomes in different situations. The scientific community must gain a better perspective of how various nitrogen rates, sources, application timings, and placement depths perform in various soil-climatic contexts in order to find solutions for meeting on-farm goals of farmers and enable them to adopt and manage various 4R practices on their farms from year to year.

### 4.5 Recommendations For Growers And Policy Makers

When farmers apply the full recommended rate of N in spring, the results of this study suggest that SuperU and ESN are more effective at reducing $N_2O$ emissions during years with relatively high soil moisture. If possible, farmers should gauge their need for enhanced efficiency fertilizers based on meteorological and soil moisture conditions each year. For example, ESN and SuperU are more likely to increase NUE and reduce environmental losses during years with high amounts of fall, winter, and/or spring precipitation. These fertilizers may not be as effective at attaining these goals in dry conditions (Drury *et al*. 2012). Drier than normal conditions in 2018 and 2019 gave little risk for N loss through gaseous emission or leaching, thus, crops were more limited by moisture than by N; Wetter soil conditions in 2020 gave more opportunity for EEF's to improve N retention and give agronomic benefits. Across site-years, SuperU and/or ESN consistently had greater residual N compared to urea at each application rate, similar to a study conducted by Wood (2019) in red spring wheat of Manitoba.

Across site-years and N rates, results for yield and N uptake were not consistent. Other research has shown that EEF's such as ESN can be detrimental to yield in dry conditions, due to the prolonged release of N from polymer coated fertilizer granules (Sahota 2020). However, the ESN treatment in this study was 30% urea, thus providing early season N to the crop while mitigating N losses during the growing season. Policy makers may need to provide greater incentives for the use of EEF's, such as reduced costs, for small-scale producers to use this technology each year and ensure that the public is informed on how to use them properly in order to realize crop and/or environmental benefits. In the current study, ESN provided both environmental and agronomic benefits during a year with high soil moisture from antecedent rainfall; moreover, ESN and SuperU consistently had greater residual N after harvest. With more inorganic N leftover in the soil, input costs can potentially be reduced the following growing season(s). The EEF's in this study consistently lowered growing season $N_2O$ emissions, however there is a low probability for these fertilizer treatments to give agronomic benefits in this context, due to the high risk of moisture deficit for corn crops in Manitoba (Nadler and Bullock 2011). This research shows that farmers must have the ability to access different types of N fertilizer and easily adapt to their soil-climatic conditions each year for similar input costs.

For mid-season applications of UAN (V4 stage), AgrotainPlus should be used for the reduction of both $NH_3$ volatilization and $N_2O$ emissions; each N treatment in this experiment had significantly greater cumulative $N_2O$ emissions compared to the control, excluding AgrotainPlus.

AgrotainPlus significantly reduced $N_2O$ compared to UAN Surface and also boosted yield in some situations (not significantly). However, UAN Surface consistently had the greatest NRE among mid-season sources at each N rate in each site-year. If N is applied directly before precipitation events and there is minimal opportunity for N loss, UAN will likely have greater N uptake than EEF's. More immediate urea hydrolysis and nitrification by conventional UAN would allow for $NO_3^-$ movement to deeper soil layers where root systems have developed to access water; more diverse N species for crop N uptake accompanied by a wider spatial distribution of N among soil depths likely promoted N uptake. It is difficult for growers to predict which mid-season application will give the greatest economic benefit in rainfed systems, however this study shows that AgrotainPlus consistently reduced $N_2O$ emissions; EEF's should definitely be used in warm, wet conditions, however we observed similar responses with very dry conditions throughout the study period (Li *et al.* 2018). The magnitude of $N_2O$ reduction is dependent on the magnitude of gas production and consumption in each site-year.

For mid-season placements of UAN (V4 stage), deep placement depth consistently had the lowest cumulative $N_2O$ emissions, however this was not significant. Deep placement tended to have the lowest yield, AE, and NRE, particularly during a wet year. Precipitation events occurred soon after mid-season application in each year of this study, thus, deep banding of N was not effective at reducing N losses by volatilization and promoted downward movement of N. In 2018, we observed the highest volatilization loss by UAN surface throughout each site-year and treatment due to delayed precipitation after mid-season application; deep banding agronomically outperformed shallow and deep banding at 112 and 168 kg N $ha^{-1}$ in 2018, however was not statistically significant. In this context, deep banding should be used only when there is a high risk for volatilization loss, such as in dry soil conditions and at high application rates.

The results of this study show how reductions of seasonal $N_2O$ emissions are not always accompanied by agronomic benefits in the form of yield or N uptake during the same growing season (Asgedom *et al.* 2014). However there is great potential for EEF's to achieve environmental and economic goals simultaneously in this region. Corn growers in this region must carefully manage soil N pools with accurate soil nitrogen tests and careful selection of management from year to year to boost farm profitability and reduce environmental losses. It is important for policy makers to ensure the proper supply, cost, and accessibility of various N sources for farmers to use in rainfed systems.

### 4.6 References

Asgedom, H., M. Tenuta, D. N. Flaten, X. Gao, and E. Kebreab. "Nitrous Oxide Emissions from a Clay Soil Receiving Granular Urea Formulations and Dairy Manure." *Agronomy Journal 106,* no. 2 (2014): 732–44. https://doi.org/10.2134/agronj2013.0096.

Drury, C. F., W. D. Reynolds, X. M. Yang, N. B. Mclaughlin, T. W. Welacky, W. Calder, C. A. Grant."Nitrogen Source, Application Time, and Tillage Effects on Soil Nitrous Oxide Emissions and Corn Grain Yields." *Soil Science Society of America Journal 76,* no.4 (2012): 1268–1279. https://acsess.onlinelibrary.wiley.com/doi/abs/10.2136/sssaj2011.0249.

Gao, X., H. Asgedom, M. Tenuta, and D. N. Flaten. "Enhanced Efficiency Urea Sources and Placement Effects on Nitrous Oxide Emissions." *Agronomy Journal 107*, no. 1 (2015): 265–77.

Government of Manitoba "Estimates of Field Crop Production 2020." (2020) [Online] Available: https://www.gov.mb.ca/agriculture/markets-and-statistics/crop-statistics/pubs/estimates-of-production-2020.pdf#:~:text=With%20the%20spring%20pandemic%20lockdown%20in%20March%202020%2C,3.6%20per%20cent%2010%20years%20ago%20in%202011.

Li, T., W. Zhang, J. Yin, D. Chadwick, D. Norse, Y. Lu, X. Liu., X. Chen, F. Zhang, D. Powlson, and Z. Dou. "Enhanced-Efficiency Fertilizers Are Not a Panacea for Resolving the Nitrogen Problem." *Global Change Biology 24*, no. 2 (2018): e511–21. https://doi.org/10.1111/gcb.13918.

Nadler, A. J., and Paul R. Bullock. "Long-Term Changes in Heat and Moisture Related to Corn Production on the Canadian Prairies." *Climatic Change 104*, no. 2 (2011): 339–52. https://doi.org/10.1007/s10584-010-9881-y.

Nicolini, G., S. Castalidi, G. Fratini, and R. Valentini. 2013. A Literature Overview of Micrometeorological $CH_4$ and $N_2O$ Flux Measurements in Terrestrial Ecosystems. *Atmosphere and environment 81*, (2013):311-319. https://doi: 10.1016/j.agrformet.2012.11.009

Mason, C. W., C. R. Stoof, B. K. Richards,S. Das, C. L. Goodale, T. S. Steenhuis. "Hotspots of Nitrous Oxide Emission in Fertilized and Unfertilized Perennial Grasses." *Soil Science Society of America Journal 81*, no. 3 (2017): 450–458. https://acsess.onlinelibrary.wiley.com/doi/abs/10.2136/sssaj2016.08.0249.

Sahota, T. S. "Environmentally Smart Nitrogen (ESN)—Potential for Improving Modern Crop Production and N-Use Efficiency." *Journal of Agricultural Science and Technology B 10*, no. 6 (2020). https://doi.org/10.17265/2161-6264/2020.06.002.

Statistics Canada "Seeding Decisions Harvest opportunities for Canadian Farmers." (2017) [Online] Available: https://www150.statcan.gc.ca/n1/pub/95-640-x/2016001/article/14813-eng.htm.

Tenuta, M., B. D. Amiro, X. Gao, C. Wagner-Riddle, and M. Gervais. "Agricultural Management Practices and Environmental Drivers of Nitrous Oxide Emissions over a Decade for an Annual and an Annual-Perennial Crop Rotation." *Agricultural and Forest Meteorology 276,* (2019): 107636. https://doi.org/10.1016/j.agrformet.2019.107636.

Wood, M. " Right Source and Right Time: Reducing Nitrous Oxide Emissions with Enhanced Efficiency Fertilizers." *The University of Manitoba*, (2019). https://mspace.lib.umanitoba.ca/bitstream/handle/1993/33681/Wood_Matthew.pdf?sequence=1&isAllowed=y

## Appendices

Table 2.A1**:** Means and ±1 standard error for corn grain yield (15% moisture) in 2018. At each rate, mean comparisons were made between Urea, ESN, and SuperU (abc); UAN Surface, Agrotain, and AgrotainPlus (ABC); UAN Surface, UAN Shallow, and UAN Deep (xyz). For each set of comparisons, different letters indicate significant differences using Fischer's protected LSD (*P* <0.05). 2018 ESN left out.

| | | Grain Yield (Mg ha$^{-1}$) | | | |
|---|---|---|---|---|---|
| N Rate (kg ha$^{-1}$) | 0 | 56 | 84 | 112 | 168 |
| Control | 5.21±0.48 | | | | |
| Urea | | 8.86±0.59 | 8.24±0.51 | 10.1±0.70 | 9.47±0.55 |
| ESN | | - | - | - | - |
| SuperU | | 8.15±0.57 | 8.84±0.67 | 8.84±0.58 | 10.1±0.80 |
| UAN Surface | | 7.11±0.83 | 7.16±0.58 | 8.37±1.15 | 8.78±0.98 |
| UAN/Agrotain | | 6.93±0.42 | 7.76±0.61 | 6.96±0.68 | 7.89±0.83 |
| UAN/Agrotain+ | | 7.17±0.87 | 6.93±0.44 | 7.60±0.55 | 8.87±0.54 |
| UAN Surface | | 7.11±0.83 | 7.16±0.58 | 8.37±1.15 | 8.78±0.98 |
| UAN Shallow | | 6.43±0.46 | 6.71±0.50 | 8.05±0.76 | 8.22±0.48 |
| UAN Deep | | 6.45±0.42 | 6.62±0.70 | 8.32±0.34 | 9.21±0.46 |
| Anova | | | | | |
| Planting sources | | 0.2700 | 0.3754 | 0.1325 | 0.1533 |
| Season sources | | 0.9461 | 0.0563 | 0.3189 | 0.4041 |
| Season placements | | 0.4635 | 0.7967 | 0.9412 | 0.4289 |
| All treatments | | | | | |

Table 2.A2**:** Means and ±1 standard error for corn grain yield (15% moisture) in 2019. At each rate, mean comparisons were made between Urea, ESN, and SuperU (abc); UAN Surface, Agrotain, and AgrotainPlus (ABC); UAN Surface, UAN Shallow, and UAN Deep (xyz). For each set of comparisons, different letters indicate significant differences using Fischer's protected LSD (*P* <0.05).

| | Grain Yield (Mg $ha^{-1}$) | | | | |
|---|---|---|---|---|---|
| N Rate (kg $ha^{-1}$) | 0 | 56 | 84 | 112 | 168 |
| Urea | 6.00±0.59 | 7.31±1.50 | 8.90±0.64 | 8.82±0.77 | 9.88±0.78 |
| ESN | | 7.63±0.79 | 7.70±1.10 | 8.60±0.59 | 8.76±1.13 |
| SuperU | | 7.40±0.69 | 7.74±0.83 | 6.88±0.99 | 8.73±1.02 |
| UAN Surface | | 8.00±1.72 | 10.2±1.30 | 7.27±1.46 | 8.30±1.03 |
| UAN/Agrotain | | 7.40±0.60 | 8.10±0.63 | 8.83±0.77 | 9.86±0.96 |
| UAN/Agrotain+ | | 6.68±0.95 | 8.44±0.76 | 8.97±1.35 | 8.96±1.33 |
| UAN Surface | | 8.00±1.72 | 10.2±1.30 | 7.27±1.46 | 8.30±1.03 |
| UAN Shallow | | 7.17±0.78 | 7.96±0.97 | 7.71±1.06 | 8.91±0.56 |
| UAN Deep | | 6.38±0.26 | 7.53±0.36 | 8.14±0.49 | 7.68±0.65 |
| Anova | | | | | |
| Planting sources | | 0.5704 | 0.4428 | 0.1304 | 0.6686 |
| Season sources | | 0.3828 | 0.1916 | 0.1413 | 0.3552 |
| Season placements | | 0.5841 | 0.0739 | 0.8524 | 0.4529 |
| All treatments | | | | | |

Table 2.A3**:** Means and ±1 standard error for corn grain yield (15% moisture) in 2020. At each applied rate, mean comparisons were made between Urea, ESN, and SuperU (abc); UAN Surface, Agrotain, and AgrotainPlus (ABC); UAN Surface, UAN Shallow, and UAN Deep (xyz). For each set of comparisons, different letters indicate significant differences using Fischer's protected LSD (*P* <0.05).

| | Grain Yield (Mg ha$^{-1}$) | | | | |
|---|---|---|---|---|---|
| N Rate (kg ha$^{-1}$) | 0 | 56 | 84 | 112 | 168 |
| Treatment | | | | | |
| Control | 2.35±0.19 | | | | |
| Urea | | 5.51±0.71 | 4.81±0.43 b | 5.63±0.44 | 7.39±0.52 |
| ESN | | 5.00±0.49 | 6.71±0.35 a | 6.70±0.51 | 9.75±1.00 |
| SuperU | | 5.37±0.52 | 6.37±0.17 a | 5.46±0.52 | 7.92±1.02 |
| UAN Surface | | 5.43±0.58 | 6.13±0.54 | 6.86±0.33 | 8.41±0.48 |
| UAN/Agrotain | | 5.55±0.57 | 5.90±0.46 | 6.69±0.54 | 7.95±0.62 |
| UAN/Agrotain+ | | 5.17±0.33 | 6.24±0.38 | 7.70±0.29 | 8.28±0.34 |
| UAN Surface | | 5.43±0.58 | 6.13±0.54 | 6.86±0.33 | 8.41±0.48 |
| UAN Shallow | | 5.32±0.46 | 6.84±0.21 | 7.32±0.48 | 8.75±0.67 |
| UAN Deep | | 4.99±0.48 | 5.65±0.53 | 5.91±0.51 | 7.70±0.47 |
| Anova | | | | | |
| Planting sources | | 0.8230 | 0.0151 | 0.1674 | 0.0834 |
| Season sources | | 0.7889 | 0.8694 | 0.2392 | 0.7808 |
| Season placements | | 0.6644 | 0.0807 | 0.0564 | 0.4351 |
| All treatments | | | | | |

Table 2.A4**:** Means and ±1 standard error for corn agronomic efficiency (15% moisture) in 2018. At each rate, mean comparisons were made between Urea, ESN, and SuperU (abc); UAN Surface, Agrotain, and AgrotainPlus (ABC); UAN Surface, UAN Shallow, and UAN Deep (xyz). For each set of comparisons, different letters indicate significant differences using Fischer's protected LSD ($P$ <0.05).

| | Agronomic efficiency (kg kg$^{-1}$) | | | |
|---|---|---|---|---|
| N Rate (kg ha$^{-1}$) | 56 | 84 | 112 | 168 |
| Treatment | | | | |
| Urea | 66±6 | 36±2 | 44±3 | 26±2 |
| ESN | - | - | - | - |
| SuperU | 53±8 | 43±7 | 32±3 | 29±3 |
| UAN Surface | 34±7 | 23±1 | 28±7 | 21±3 |
| UAN/Agrotain | 31±10 | 31±6 | 16±3 | 16±3 |
| UAN/Agrotain+ | 35±11 | 21±2 | 21±6 | 22±4 |
| UAN Surface | 34±7 | 23±1 | 28±7 | 21±3 |
| UAN Shallow | 22±8 | 18±8 | 26±8 | 18±3 |
| UAN Deep | 22±10 | 17±7 | 28±4 | 24±2 |
| Anova | | | | |
| Planting sources | 0.2616 | 0.3962 | 0.0822 | 0.1282 |
| Season sources | 0.9393 | 0.0543 | 0.3285 | 0.4296 |
| Season placements | 0.4591 | 0.7430 | 0.9443 | 0.4530 |
| All treatments | | | | |

Table 2.A5: Means and ±1 standard error for corn agronomic efficiency (15% moisture) in 2019. At each rate, mean comparisons were made between Urea, ESN, and SuperU (abc); UAN Surface, Agrotain, and AgrotainPlus (ABC); UAN Surface, UAN Shallow, and UAN Deep (xyz). For each set of comparisons, different letters indicate significant differences using Fischer's protected LSD (*P* <0.05).

| | Agronomic efficiency (kg kg$^{-1}$) | | | |
|---|---|---|---|---|
| N Rate (kg ha$^{-1}$) | 56 | 84 | 112 | 168 |
| Treatment | | | | |
| Urea | 31±20 | 39±8 | 29±8 | 26±4 |
| ESN | 46±16 | 31±6 | 32±1 | 22±4 |
| SuperU | 32±12 | 25±9 | 12±6 | 19±8 |
| UAN Surface | 43±23 | 55±13 | 15±11 | 16±6 |
| UAN/Agrotain | 32±6 | 30±3 | 29±2 | 26±3 |
| UAN/Agrotain+ | 20±12 | 34±5 | 30±8 | 20±5 |
| UAN Surface | 43±23 | 55±13 | 15±11 | 16±6 |
| UAN Shallow | 28±13 | 28±8 | 19±6 | 20±4 |
| UAN Deep | 14±17 | 24±9 | 23±9 | 12±4 |
| Anova | | | | |
| Planting sources | 0.5424 | 0.4501 | 0.1096 | 0.7348 |
| Season sources | 0.3870 | 0.1497 | 0.1245 | 0.3362 |
| Season placements | 0.5613 | 0.0812 | 0.8499 | 0.4323 |
| All treatments | | | | |

Table 2.A6**:** Means and ±1 standard error for corn agronomic efficiency (15% moisture) in 2020. At each rate, mean comparisons were made between Urea, ESN, and SuperU (abc); UAN Surface, Agrotain, and AgrotainPlus (ABC); UAN Surface, UAN Shallow, and UAN Deep (xyz). For each set of comparisons, different letters indicate significant differences using Fischer's protected LSD (*P* <0.05).

| | Agronomic efficiency (kg $kg^{-1}$) | | | |
|---|---|---|---|---|
| N Rate (kg $ha^{-1}$) | 56 | 84 | 112 | 168 |
| Treatment | | | | |
| Urea | 49±11 | 25±4b | 25±4 | 24±5 |
| ESN | 49±6 | 46±10a | 33±5 | 33±8 |
| SuperU | 52±10 | 44±7a | 24±5 | 29±7 |
| UAN Surface | 50±8 | 42±8 | 34±6 | 31±7 |
| UAN/Agrotain | 53±9 | 39±6 | 35±8 | 28±6 |
| UAN/Agrotain+ | 44±6 | 41±8 | 40±8 | 31±6 |
| UAN Surface | 50±8 | 42±8 | 34±6 | 31±7 |
| UAN Shallow | 51±8 | 48±8 | 35±6 | 32±7 |
| UAN Deep | 40±3 | 35±5 | 27±3 | 29±6 |
| Anova | | | | |
| Planting sources | 0.9697 | 0.0414 | 0.3055 | 0.1836 |
| Season sources | 0.6258 | 0.9044 | 0.5288 | 0.6857 |
| Season placements | 0.3250 | 0.1471 | 0.2086 | 0.7964 |
| All treatments | | | | |

Table 2.A7: Means and ±1 standard error for corn apparent N recovery efficiency (0% moisture) in 2018. At each rate, mean comparisons were made between Urea, ESN, and SuperU (abc); UAN Surface, Agrotain, and AgrotainPlus (ABC); UAN Surface, UAN Shallow, and UAN Deep (xyz). For each set of comparisons, different letters indicate significant differences using Fischer's protected LSD (*P* <0.05).

| | Apparent N recovery efficiency (% N applied) | | | |
|---|---|---|---|---|
| N Rate (kg ha$^{-1}$) | 56 | 84 | 112 | 168 |
| Treatment | | | | |
| Urea | 96±12 | 57±7 | 81±9 | 48±6 |
| ESN | - | - | - | - |
| SuperU | 90±13 | 80±16 | 64±10 | 68±7 |
| UAN Surface | 55±21 | 42±3 | 53±14 | 45±7 |
| UAN/Agrotain | 31±10 | 31±5 | 16±6 | 16±5 |
| UAN/Agrotain+ | 35±27 | 21±8 | 21±8 | 22±9 |
| UAN Surface | 55±21 | 42±3 | 53±14 | 45±7 |
| UAN Shallow | 35±13 | 34±15 | 45±13 | 38±6 |
| UAN Deep | 29±20 | 24±13 | 52±13 | 56±5 |
| Anova | | | | |
| Planting sources | 0.7579 | 0.2813 | 0.2505 | 0.0945 |
| Season sources | 0.5990 | 0.3431 | 0.2741 | 0.5043 |
| Season placements | 0.5892 | 0.5823 | 0.8860 | 0.1611 |
| All treatments | | | | |

Table 2.A8: Means and ±1 standard error for corn apparent N recovery efficiency (0% moisture) in 2019. At each rate, mean comparisons were made between Urea, ESN, and SuperU (abc); UAN Surface, Agrotain, and AgrotainPlus (ABC); UAN Surface, UAN Shallow, and UAN Deep (xyz). For each set of comparisons, different letters indicate significant differences using Fischer's protected LSD ($P$ <0.05).

| | Apparent N recovery efficiency (%) | | | |
|---|---|---|---|---|
| N Rate (kg ha$^{-1}$) | 56 | 84 | 112 | 168 |
| Treatment | | | | |
| Urea | 49±23 | 58±4 | 50±9 | 44±6 |
| ESN | 72±24 | 57±14 | 55±9 | 41±9 |
| SuperU | 69±7 | 55±9 | 45±5 | 45±10 |
| UAN Surface | 100±28 A | 100±18 A | 47±12 | 43±6 |
| UAN/Agrotain | 32±12 B | 30±8 B | 29±6 | 26±9 |
| UAN/Agrotain+ | 20±17 B | 34±8 B | 30±13 | 20±10 |
| UAN Surface | 100±28 | 100±18 | 47±12 | 43±6 |
| UAN Shallow | 56±27 | 54±16 | 47±8 | 35±5 |
| UAN Deep | 30±24 | 55±15 | 54±15 | 37±7 |
| Anova | | | | |
| Planting sources | 0.5320 | 0.9614 | 0.7043 | 0.9720 |
| Season sources | 0.0249 | 0.0379 | 0.8225 | 0.9270 |
| Season placements | 0.2364 | 0.1521 | 0.9002 | 0.6471 |
| All treatments | | | | |

Table 2.A9: Means and ±1 standard error for corn apparent N recovery efficiency (0% moisture) in 2020. At each rate, mean comparisons were made between Urea, ESN, and SuperU (abc); UAN Surface, Agrotain, and AgrotainPlus (ABC); UAN Surface, UAN Shallow, and UAN Deep (xyz). For each set of comparisons, different letters indicate significant differences using Fischer's protected LSD (*P* <0.05).

| | Apparent N recovery efficiency (%) | | | |
|---|---|---|---|---|
| N Rate (kg ha$^{-1}$) | 56 | 84 | 112 | 168 |
| Treatment | | | | |
| Urea | 90±24 | 42±9 a | 52±12 | 42±6 |
| ESN | 63±7 | 76±9 b | 62±4 | 73±9 |
| SuperU | 78±13 | 69±4 b | 49±7 | 57±9 |
| UAN Surface | 86±11 | 67±6 | 60±5 | 58±6 |
| UAN/Agrotain | 53±11 | 39±4 | 35±12 | 28±6 |
| UAN/Agrotain+ | 44±14 | 41±11 | 40±5 | 31±6 |
| UAN Surface | 86±11 | 67±6 xy | 60±5 | 58±6 |
| UAN Shallow | 78±9 | 83±3 x | 77±8 | 65±6 |
| UAN Deep | 67±15 | 57±6 y | 53±5 | 59±4 |
| Anova | | | | |
| Planting sources | 0.5542 | 0.0234 | 0.4927 | 0.0846 |
| Season sources | 0.3498 | 0.4366 | 0.3097 | 0.9399 |
| Season placements | 0.5691 | 0.0371 | 0.8860 | 0.1611 |
| All treatments | | | | |

Table 2.A10: Means and ±1 standard error for total residual N to 4’ depth (kg N $ha^{-1}$) in 2018. At each rate, mean comparisons were made between Urea, ESN, and SuperU (abc); UAN Surface, Agrotain, and AgrotainPlus (ABC); UAN Surface, UAN Shallow, and UAN Deep (xyz). For each set of comparisons, different letters indicate significant differences using Fischer’s protected LSD ($P < 0.05$). Total residual N for the control was 65±9 kg N $ha^{-1}$.

| | Total residual N to 4’ (kg N $ha^{-1}$) | | | |
|---|---|---|---|---|
| N Rate (kg $ha^{-1}$) | 56 | 84 | 112 | 168 |
| Treatment | | | | |
| Urea | 73±2 a | 83±15 | 91±5 | 81±10 |
| ESN | - | - | - | - |
| SuperU | 61±3 b | 71±8 | 95±11 | 124±20 |
| UAN Surface | 57±17 | 78±22 | 70±6 | 86±16 |
| UAN/Agrotain | 64±15 | 76±9 | 91±6 | 105±12 |
| UAN/Agrotain+ | 55±8 | 74±3 | 82±7 | 129±33 |
| UAN Surface | 57±17 | 78±22 | 70±6 | 86±16 |
| UAN Shallow | 62±8 | 67±11 | 85±10 | 101±13 |
| UAN Deep | 67±8 | 56±10 | 104±13 | 107±16 |
| Anova | | | | |
| Planting sources | 0.0130 | 0.2511 | 0.6180 | 0.1579 |
| Season sources | 0.8896 | 0.9836 | 0.1422 | 0.4454 |
| Season placements | 0.7854 | 0.6208 | 0.0736 | 0.5968 |
| All treatments | | | | |

Table 2.A11: Means and ±1 standard error for total residual N to 4' depth (kg N ha$^{-1}$) in 2019. At each rate, mean comparisons were made between Urea, ESN, and SuperU (abc); UAN Surface, Agrotain, and AgrotainPlus (ABC); UAN Surface, UAN Shallow, and UAN Deep (xyz). For each set of comparisons, different letters indicate significant differences using Fischer's protected LSD ($P$ <0.05). Total residual N for the control was 32±4 kg N ha$^{-1}$.

| | Total residual N to 4' (kg N ha$^{-1}$) | | | |
|---|---|---|---|---|
| N Rate (kg ha$^{-1}$) | 56 | 84 | 112 | 168 |
| Treatment | | | | |
| Urea | 29±4 | 37±9 | 45±16 | 77±11 |
| ESN | 45±3 | 54±11 | 71±12 | 109±25 |
| SuperU | 58±21 | 60±16 | 83±21 | 95±20 |
| UAN Surface | 67±22 | 57±12 | 59±13 | 92±21 |
| UAN/Agrotain | 30±7 | 40±9 | 58±29 | 66±18 |
| UAN/Agrotain+ | 38±10 | 51±14 | 60±9 | 125±30 |
| UAN Surface | 67±22 | 57±12 | 59±13 y | 92±21 |
| UAN Shallow | 62±8 | 72±15 | 135±34 x | 131±30 |
| UAN Deep | 34±7 | 41±6 | 63±16 y | 121±32 |
| Anova | | | | |
| Planting sources | 0.2320 | 0.3282 | 0.2183 | 0.3491 |
| Season sources | 0.1985 | 0.3079 | 0.9936 | 0.2912 |
| Season placements | 0.1730 | 0.1394 | 0.0160 | 0.3283 |
| All treatments | | | | |

Table 2.A12: Means and ±1 standard error for total residual N to 4’ depth (kg N ha$^{-1}$) in 2020. At each rate, mean comparisons were made between Urea, ESN, and SuperU (abc); UAN Surface, Agrotain, and AgrotainPlus (ABC); UAN Surface, UAN Shallow, and UAN Deep (xyz). For each set of comparisons, different letters indicate significant differences using Fischer’s protected LSD ($P$ <0.05). Total residual N for the control was 24±5 kg N ha$^{-1}$.

| | Total residual N (kg N ha$^{-1}$) | | | |
|---|---|---|---|---|
| N Rate (kg ha$^{-1}$) | 56 | 84 | 112 | 168 |
| Treatment | | | | |
| Urea | 22±5 | 20±6 | 22±4 | 21±4 |
| ESN | 29±5 | 25±4 | 39±7 | 43±7 |
| SuperU | 24±5 | 26±6 | 20±5 | 28±6 |
| UAN Surface | 35±17 | 42±18 | 37±9 | 68±23 |
| UAN/Agrotain | 20±2 | 30±3 | 37±3 | 86±25 |
| UAN/Agrotain+ | 30±7 | 38±7 | 41±12 | 57±17 |
| UAN Surface | 35±17 | 42±18 | 37±9 | 68±23 |
| UAN Shallow | 27±2 | 26±3 | 32±3 | 44±9 |
| UAN Deep | 27±4 | 26±6 | 25±1 | 38±7 |
| Anova | | | | |
| Planting sources | 0.5867 | 0.7343 | 0.0728 | 0.0895 |
| Season sources | 0.6358 | 0.7597 | 0.9397 | 0.6679 |
| Season placements | 0.8122 | 0.5503 | 0.3018 | 0.3618 |
| All treatments | | | | |

Table 2.A13: Means and ±1 standard error for residual N to 2’ depth (kg N $ha^{-1}$) in 2018. At each rate, mean comparisons were made between Urea, ESN, and SuperU (abc); UAN Surface, Agrotain, and AgrotainPlus (ABC); UAN Surface, UAN Shallow, and UAN Deep (xyz). For each set of comparisons, different letters indicate significant differences using Fischer’s protected LSD ($P$ <0.05). Mean root-zone extractable N for the control was 28±3 kg N $ha^{-1}$.

| | Root-zone residual N (kg N $ha^{-1}$) | | | |
|---|---|---|---|---|
| N Rate (kg $ha^{-1}$) | 56 | 84 | 112 | 168 |
| Treatment | | | | |
| Urea | 26±4 | 31±5 | 42±2 | 40±9 |
| ESN | - | - | - | - |
| SuperU | 32±4 | 31±2 | 49±5 | 68±19 |
| UAN Surface | 26±5 | 41±5 | 39±3 | 56±15 |
| UAN/Agrotain | 32±5 | 35±4 | 43±4 | 59±12 |
| UAN/Agrotain+ | 30±5 | 40±4 | 39±2 | 87±32 |
| UAN Surface | 26±5 | 41±5 | 39±3 | 56±15 |
| UAN Shallow | 25±4 | 27±2 | 33±3 | 42±7 |
| UAN Deep | 26±5 | 29±5 | 42±3 | 43±10 |
| Anova | | | | |
| Planting sources | 0.2596 | 0.9768 | 0.2722 | 0.2280 |
| Season sources | 0.5893 | 0.5659 | 0.5788 | 0.5568 |
| Season placements | 0.9778 | 0.0982 | 0.1768 | 0.6415 |
| All treatments | | | | |

Table 2.A14: Means and ±1 standard error for residual N to 2' depth (kg N ha$^{-1}$) in 2019. At each rate, mean comparisons were made between Urea, ESN, and SuperU (abc); UAN Surface, Agrotain, and AgrotainPlus (ABC); UAN Surface, UAN Shallow, and UAN Deep (xyz). For each set of comparisons, different letters indicate significant differences using Fischer's protected LSD ($P$ <0.05). Mean root-zone extractable N for the control was 21±2 kg N ha$^{-1}$.

| | Root-zone residual N (kg N ha$^{-1}$) | | | |
|---|---|---|---|---|
| N Rate (kg ha$^{-1}$) | 56 | 84 | 112 | 168 |
| Treatment | | | | |
| Urea | 22±2 | 25±2 | 27±2 | 33±3 |
| ESN | 27±2 | 31±5 | 34±2 | 58±8 |
| SuperU | 29±4 | 28±4 | 43±6 | 44±11 |
| UAN Surface | 30±5 | 34±8 | 38±7 | 55±16 |
| UAN/Agrotain | 24±1 | 28±2 | 39±14 | 46±13 |
| UAN/Agrotain+ | 21±2 | 25±7 | 32±4 | 66±18 |
| UAN Surface | 30±5 | 34±8 | 38±7 | 55±16 |
| UAN Shallow | 24±3 | 30±5 | 47±15 | 65±15 |
| UAN Deep | 23±2 | 25±4 | 34±1 | 63±16 |
| Anova | | | | |
| Planting sources | 0.1623 | 0.5146 | 0.0710 | 0.1772 |
| Season sources | 0.0708 | 0.4430 | 0.8628 | 0.7041 |
| Season placements | 0.3403 | 0.5465 | 0.6165 | 0.8682 |
| All treatments | | | | |

Table 2.A15: Means and ±1 standard error for residual N to 2' depth (kg N ha$^{-1}$) in 2020. At each rate, mean comparisons were made between Urea, ESN, and SuperU (abc); UAN Surface, Agrotain, and AgrotainPlus (ABC); UAN Surface, UAN Shallow, and UAN Deep (xyz). For each set of comparisons, different letters indicate significant differences using Fischer's protected LSD ($P$ <0.05). Mean root-zone extractable N for the control was 15±2 kg N ha$^{-1}$.

| | Root-zone residual N (kg N ha$^{-1}$) | | | |
|---|---|---|---|---|
| N Rate (kg ha$^{-1}$) | 56 | 84 | 112 | 168 |
| Treatment | | | | |
| Urea | 15±4 | 13±3 | 14±2 | 13±2 b |
| ESN | 19±4 | 15±2 | 24±5 | 31±6 a |
| SuperU | 15±1 | 15±1 | 14±1 | 18±3 b |
| UAN Surface | 18±5 | 15±3 | 19±3 | 42±11 |
| UAN/Agrotain | 16±1 | 21±1 | 25±3 | 54±17 |
| UAN/Agrotain+ | 16±3 | 20±3 | 20±6 | 32±10 |
| UAN Surface | 18±5 | 15±3 | 19±3 | 42±11 |
| UAN Shallow | 17±0.3 | 15±1 | 19±1 | 25±6 |
| UAN Deep | 13±1 | 15±1 | 14±1 | 25±4 |
| Anova | | | | |
| Planting sources | 0.5307 | 0.7539 | 0.1056 | 0.0242 |
| Season sources | 0.8912 | 0.2416 | 0.4747 | 0.5211 |
| Season placements | 0.3659 | 0.9687 | 0.2014 | 0.2677 |
| All treatments | | | | |

Table 2.A16: Means and ±1 standard error for yield, agronomic efficiency and apparent nitrogen recovery efficiency in 2018. Different letters indicate significant differences using Fischer's protected LSD (*P* =0.05).

| | N rate (kg N ha$^{-1}$) | 56 | 84 | 112 | 168 |
|---|---|---|---|---|---|
| | | | Yield (Mg ha$^{-1}$) | | |
| Urea | | 8.86±0.59a | 8.24±0.51a | 10.1±0.70a | 9.47±0.55 |
| UAN Surface | | 7.11±0.83b | 7.16±0.58b | 8.37±1.15b | 8.78±0.98 |
| Anova | | 0.0127 | 0.0011 | 0.0884 | 0.4105 |
| | | | AE (kg kg-N$^{-1}$) | | |
| Urea | | 66±6 | 36±2a | 44±3a | 26±2 |
| UAN Surface | | 34±7 | 23±1b | 28±7b | 21±3 |
| Anova | | 0.0133 | 0.0013 | 0.0872 | 0.3524 |
| | | | NRE (%) | | |
| Urea | | 96±12 | 57±7a | 81±9 | 48±6 |
| UAN Surface | | 55±21 | 42±3b | 53±14 | 45±7 |
| Anova | | 0.1327 | 0.0760 | 0.1023 | 0.7353 |

Table 2.A17: Means and ±1 standard error for yield, agronomic efficiency and apparent nitrogen recovery efficiency in 2019. Different letters indicate significant differences using Fischer's protected LSD (*P* =0.05).

| | N rate (kg N ha$^{-1}$) | 56 | 84 | 112 | 168 |
|---|---|---|---|---|---|
| | | | Yield (Mg ha$^{-1}$) | | |
| Urea | | 7.31±1.50b | 8.90±0.64 | 8.82±0.77 | 9.88±0.78a |
| UAN Surface | | 8.00±1.72a | 10.2±1.30 | 7.27±1.46 | 8.30±1.03b |
| Anova | | 0.0558 | 0.1957 | 0.1494 | 0.0335 |
| | | | AE (kg kg-N$^{-1}$) | | |
| Urea | | 31±20b | 39±8 | 29±8 | 26±4a |
| UAN Surface | | 43±23a | 55±13 | 15±11 | 16±6b |
| Anova | | 0.0627 | 0.1942 | 0.1572 | 0.0331 |
| | | | NRE (%) | | |
| Urea | | 49±23b | 58±4b | 50±9 | 44±6 |
| UAN Surface | | 100±28a | 100±18a | 47±12 | 43±6 |
| Anova | | 0.0120 | 0.0950 | 0.8552 | 0.8575 |

Table 2.A18: Means and ±1 standard error for yield, agronomic efficiency and apparent nitrogen recovery efficiency in 2020. Different letters indicate significant differences using Fischer's protected LSD (*P* =0.05).

| | N rate (kg N ha$^{-1}$) | 56 | 84 | 112 | 168 |
|---|---|---|---|---|---|
| | | | Yield (Mg ha$^{-1}$) | | |
| Urea | | 5.51±0.71 | 4.81±0.43 | 5.63±0.44b | 7.39±0.52 |
| UAN Surface | | 5.43±0.58 | 6.13±0.54 | 6.86±0.33a | 8.41±0.48 |
| Anova | | 0.8970 | 0.1498 | 0.0556 | 0.2036 |
| | | | AE (kg kg-N$^{-1}$) | | |
| Urea | | 49±11 | 25±4 | 25±4 | 24±5 |
| UAN Surface | | 50±8 | 42±8 | 34±6 | 31±7 |
| Anova | | 0.9633 | 0.1541 | 0.1330 | 0.1064 |
| | | | NRE (%) | | |
| Urea | | 90±24 | 42±9 | 52±12 | 42±6b |
| UAN Surface | | 86±11 | 67±6 | 60±5 | 58±6a |
| Anova | | 0.8715 | 0.1120 | 0.4158 | 0.0034 |

Table 2.A19: Quadratic model parameters and estimations for the economically optimal nitrogen rate of each at-planting treatment and block throughout three site-years. Corn Price kg$^{-1}$ 0.015116 (Price per bushel = 4.06).

| Treatment | a | b | c | Cost (lb) | Cost N/ Price bu$^{-1}$ | EONR (kg ha$^{-1}$) | EONR (No Premium) |
|---|---|---|---|---|---|---|---|
| Urea 1 | 56.34 | 1.2472 | -0.00394 | 0.49 | 0.1214 | 160 | 160 |
| Urea 2 | 32.33 | 1.0062 | -0.00229 | 0.49 | 0.1214 | 216 | 216 |
| Urea 3 | 42.37 | 1.0737 | -0.00314 | 0.49 | 0.1214 | 170 | 170 |
| Urea 4 | 43.09 | 0.8598 | -0.00162 | 0.49 | 0.1214 | 255 | 255 |
| ESN 1 | 60.93 | 0.9510 | -0.00242 | 0.66 | 0.1626 | 182 | 192 |
| ESN 2 | 38.03 | 0.9478 | -0.00258 | 0.66 | 0.1626 | 170 | 179 |
| ESN 3 | 45.03 | 1.1613 | -0.00333 | 0.66 | 0.1626 | 168 | 175 |
| ESN 4 | 35.19 | 1.0113 | -0.00212 | 0.66 | 0.1626 | 224 | 235 |
| SuperU 1 | 68.03 | 0.6598 | -0.00120 | 0.60 | 0.1481 | 238 | 251 |
| SuperU 2 | 44.77 | 0.7021 | -0.00048 | 0.60 | 0.1481 | 646 | 678 |
| SuperU 3 | 38.64 | 1.2819 | -0.00424 | 0.60 | 0.1481 | 150 | 154 |
| SuperU 4 | 43.41 | 0.9130 | -0.00273 | 0.60 | 0.1481 | 156 | 163 |

Table 2.A20: Quadratic model parameters and estimations for the economically optimal nitrogen rate of each at-planting treatment and block throughout three site-years. Corn Price $kg^{-1}$ 0.015116 (Price per bushel = 4.06).

| Treatment | a | b | c | Cost (lb) | Cost N/ Price $bu^{-1}$ | EONR ($kg\ ha^{-1}$) | EONR (No Premium) |
|---|---|---|---|---|---|---|---|
| UAN 1 | 45.21 | 1.4382 | -0.00468 | 0.5130 | 0.1265 | 156 | 156 |
| UAN 2 | 23.01 | 1.2291 | -0.00367 | 0.5130 | 0.1265 | 168 | 168 |
| UAN 3 | 39.17 | 1.1579 | -0.00325 | 0.5130 | 0.1265 | 178 | 178 |
| UAN 4 | 48.04 | 0.8090 | -0.00250 | 0.5130 | 0.1265 | 152 | 152 |
| Agrotain 1 | 55.88 | 1.0266 | -0.00265 | 0.5915 | 0.1457 | 185 | 191 |
| Agrotain 2 | 36.61 | 0.8050 | -0.00177 | 0.5915 | 0.1457 | 208 | 215 |
| Agrotain 3 | 47.18 | 0.8819 | -0.00214 | 0.5915 | 0.1457 | 192 | 198 |
| Agrotain 4 | 45.56 | 0.9290 | -0.00256 | 0.5915 | 0.1457 | 170 | 176 |
| Agrotain+ 1 | 55.76 | 1.0020 | -0.00268 | 0.6256 | 0.1541 | 177 | 183 |
| Agrotain+ 2 | 30.54 | 0.8610 | -0.00169 | 0.6256 | 0.1541 | 234 | 243 |
| Agrotain+ 3 | 43.44 | 1.0284 | -0.00211 | 0.6256 | 0.1541 | 231 | 240 |
| Agrotain+ 4 | 40.62 | 1.0323 | -0.00332 | 0.6256 | 0.1541 | 147 | 152 |

Table 2.A21: Quadratic model parameters and estimations for the economically optimal nitrogen rate of each in-season placements and block throughout three site-years. Corn Price $kg^{-1}$ 0.015116 (Price per bushel = 4.06).

| Treatment | a | b | c | Cost (lb) | Cost N/ Price $bu^{-1}$ | EONR ($kg\ ha^{-1}$) | EONR (No Premium) |
|---|---|---|---|---|---|---|---|
| UAN 1 | 45.21 | 1.4382 | -0.00468 | 0.513 | 0.1265 | 156 | na |
| UAN 2 | 23.02 | 1.2291 | -0.00367 | 0.513 | 0.1265 | 168 | na |
| UAN 3 | 39.17 | 1.1579 | -0.00325 | 0.513 | 0.1265 | 178 | na |
| UAN 4 | 48.04 | 0.8087 | -0.00250 | 0.513 | 0.1265 | 152 | na |
| Agrotain 1 | 64.35 | 0.6775 | -0.00134 | 0.513 | 0.1265 | 230 | na |
| Agrotain 2 | 35.13 | 0.8349 | -0.00177 | 0.513 | 0.1265 | 224 | na |
| Agrotain 3 | 38.85 | 1.2198 | -0.00371 | 0.513 | 0.1265 | 164 | na |
| Agrotain 4 | 41.86 | 0.9366 | -0.00222 | 0.513 | 0.1265 | 203 | na |
| Agrotain+ 1 | 81.87 | 0.1122 | -0.00132 | 0.513 | 0.1265 | 6 | na |
| Agrotain+ 2 | 24.17 | 1.1210 | -0.00293 | 0.513 | 0.1265 | 190 | na |
| Agrotain+ 3 | 47.57 | 0.8856 | -0.00244 | 0.513 | 0.1265 | 174 | na |
| Agrotain+ 4 | 44.61 | 0.9045 | -0.00270 | 0.513 | 0.1265 | 161 | na |

## Chapter 3 Appendices

Table 3.A1: Fertilizer treatments used for field experiments in each site-year, each including 4 randomized plots receiving N rates of 56, 84, 112, and 168 kg N $ha^{-1}$.

| Treatment | Source | Time | Placement |
|---|---|---|---|
| 1 | Urea | At-planting | Broadcast incorporated |
| 2 | ESN/Urea | At-planting | Broadcast incorporated |
| 3 | SuperU | At-planting | Broadcast incorporated |
| 4 | Urea + UAN | V4–V5 stage | Shallow side dribble |
| 5 | Urea + UAN/Agrotain | V4–V5 stage | Shallow side dribble |
| 6 | Urea + UAN/AgrotainPlus | V4–V5 stage | Shallow side dribble |
| 7 | Urea + UAN | V4–V5 stage | Shallow band (1 1/2 " depth) |
| 8 | Urea + UAN | V4–V5 stage | Deep band (3" depth) |
| 9 | None | None | None |
| 10 | Urea (35 kg $ha^{-1}$) | At-planting | Side band |

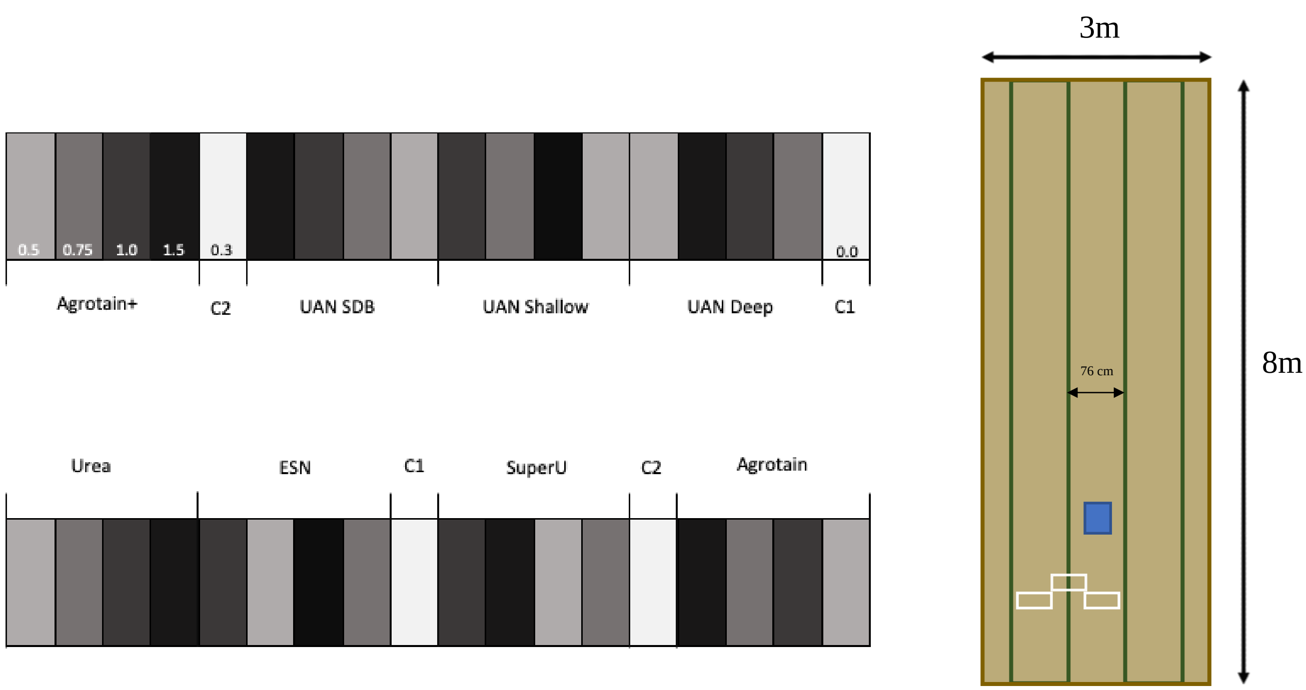



Figure 3.A1: Visualization for four-row corn plots containing $N_2O$ and $NH_3^+$ flux chambers (Control and 1.0x rate treatments) within one block of a randomized complete block design. C1 represents control plots receiving 0 kg N $ha^{-1}$ and C2 represents in-season control plots receiving 35 kg N $ha^{-1}$. Black lines separate 'main plots' of N sources that contain 'subplots' which were given either 0.5, 0.75, 1.0, or 1.5 times the recommended N rate. Note: The spacing between 'half blocks' are not to scale.

Table 3.A2: Soil parameters observed for pre-plant nutrient tests in each site-year. (0–60.96cm depth)

| Soil Parameter | 2018 | 2019 | 2020 |
|---|---|---|---|
| pH | 7.6 | 8.5 | 8.2 |
| EC (mS/cm) | 0.23 | 0.15 | 0.28 |
| Organic matter (%) | 2.1 | 3.7 | 2.5 |
| NO3-N (mg/kg) | 5.5 | 6.4 | 3.0 |
| PO4 – Olsen P (mg/kg) | 13 | 8.4 | 5.2 |
| K (mg/kg) | 140 | 54 | 150 |
| SO4-S (mg/kg) | 2.3 | 7.5 | 4 |
| Zn (mg/kg) | 0.99 | 0.55 | 0.7 |
| Cu (mg/kg) | 0.27 | 0.26 | 0.4 |

Table 3.A3: Area-scaled $N_2O$ emissions (g $N_2O$-N $ha^{-1}$) and standard errors for at-planting sources (abc), in-season sources (ABC) and in-season placements (xyz). ESN 2018 not included.

| Treatment | 2018 | 2019 | 2020 | All |
|---|---|---|---|---|
| Urea | 465±14a | 290±70 | 1300±855a | 685±295a |
| ESN | | 157±61 | 548±116a | 249±67ab |
| SuperU | 230±50ab | 189±41 | 494±223a | 304±81b |
| Control | 139±44b | 193±96 | 87±20b | 140±35c |
| | | | | |
| UAN Surface | 246±36 | 258±50 | 323±55A | 276±27A |
| Agrotain | 224±39 | 322±76 | 215±81AB | 254±39AB |
| AgrotainPlus | 261±53 | 178±66 | 198±89BC | 212±39B |
| Control | 139±44 | 193±96 | 87±20C | 140±35C |
| | | | | |
| UAN Surface | 246±36x | 258±50 | 323±55x | 276±27x |
| UAN Shallow | 297±43x | 240±45 | 307±88x | 282±34x |
| UAN Deep | 217±47x | 199±13 | 227±61x | 214±24x |
| Control | 139±44y | 193±96 | 87±20y | 140±35y |
| ANOVA Planting Source | 0.0762 | 0.3196 | 0.0191 | 0.0006 |
| Season Source | 0.1586 | 0.2907 | 0.0109 | 0.0029 |
| Season Placement | 0.0630 | 0.4978 | 0.0049 | 0.0002 |

Different letters indicate significant differences between fertilized treatments using a protected LSD method for post-hoc comparisons. (*P* <0.10). Log-normal distribution was used and data residuals were checked for normality and equal variance using the shapiro wilk statistic and visualization of scatter plots, respectively.

Table 3.A4: Area-scaled emission factors (% N applied) and standard errors for at-planting sources (abc), in-season sources (ABC) and in-season placements (xyz). ESN 2018 not included.

| Treatment | 2018 | 2019 | 2020 | All |
|---|---|---|---|---|
| Urea | 0.29±0.11 | 0.09±0.09 | 1.08±0.75 | 0.49±0.26 |
| ESN | | -0.03±0.05 | 0.41±0.09 | 0.19±0.06 |
| SuperU | 0.08±0.07 | 0.00±0.06 | 0.36±0.21 | 0.15±0.08 |
| | | | | |
| UAN Surface | 0.09±0.01 | 0.06±0.1 | 0.21±0.05 | 0.12±0.04 |
| Agrotain | 0.07±0.03 | 0.12±0.06 | 0.11±0.06 | 0.10±0.03 |
| AgrotainPlus | 0.11±0.08 | -0.01±0.08 | 0.10±0.07 | 0.06±0.04 |
| | | | | |
| UAN Surface | 0.09±0.01 | 0.06±0.1 | 0.21±0.05 | 0.12±0.04 |
| UAN Shallow | 0.14±0.06 | 0.04±0.07 | 0.20±0.07 | 0.13±0.04 |
| UAN Deep | 0.07±0.01 | 0.01±0.08 | 0.13±0.06 | 0.07±0.04 |
| | | | | |
| <u>ANOVA</u> | | | | |
| Planting Source | 0.7850 | 0.2751 | 0.5542 | 0.5033 |
| Season Source | 0.5627 | 0.7119 | 0.2409 | 0.1820 |
| Season Placement | 0.7402 | 0.4298 | 0.1996 | 0.1651 |

Different letters indicate significant differences between fertilized treatments using protected LSD method for post-hoc comparisons. ($P$<0.10) Log-normal distribution was used.

Table 3.A5: Mean yield-scaled $N_2O$ emissions (g $N_2O$-N $Mg^{-1}$) and standard errors for at-planting sources (abc), in-season sources (ABC) and in-season placements (xyz).

| Treatment | 2018 | 2019 | 2020 | All |
|---|---|---|---|---|
| Urea | 49±17 | 34±8 | 246±160 | 110±57a |
| ESN | | 18±6 | 84±19 | 48±10ab |
| SuperU | 26±5 | 29±5 | 100±45 | 51±17ab |
| Control | 27±13 | 34±17 | 36±18 | 32±9b |
| | | | | |
| UAN Surface | 33±9 | 36±4 | 48±10AC | 39±5 |
| Agrotain | 32±5 | 36±7 | 30±9BC | 33±4 |
| AgrotainPlus | 35±7 | 19±6 | 27±12BC | 27±5 |
| Control | 27±13 | 34±17 | 36±18C | 32±9 |
| | | | | |
| UAN Surface | 33±9 | 36±4 | 48±10 | 39±5 |
| UAN Shallow | 37±3 | 32±8 | 43±13 | 37±5 |
| UAN Deep | 26±5 | 25±2 | 42±14 | 31±5 |
| Control | 27±13 | 34±17 | 36±18 | 32±9 |
| | | | | |
| ANOVA | | | | |
| Planting Source | 0.3428 | 0.3708 | 0.3156 | 0.0866 |
| Season Source | 0.8649 | 0.3497 | 0.0278 | 0.1004 |
| Season Placement | 0.4858 | 0.8331 | 0.7341 | 0.4199 |

Different letters indicate significant differences between fertilized treatments using a protected LSD method for post-hoc comparisons. (*P* < 0.10). Log-normal distribution was used.

Table 3.A6: Area-scaled $N_2O$ emissions (g $N_2O$-N $ha^{-1}$) and standard errors for errors for urea applied at-planting and UAN applied as a split application at the V4 growth stage (abc).

| Treatment | 2018 | 2019 | 2020 | All |
|---|---|---|---|---|
| Urea | 465±14a | 290±70 | 1300±855a | 685±295a |
| UAN Surface | 246±36a | 258±50 | 323±55a | 276±27a |
| Control | 139±44b | 193±96 | 87±20b | 140±35b |
| | | | | |
| Anova | 0.0116 | 0.3911 | 0.0267 | 0.0003 |

Different letters indicate significant differences between fertilized treatments using a protected LSD method for post-hoc comparisons. (*P* = 0.10). Log-normal distribution was used.

Table 3.A7: Area-scaled emission factors and standard errors for urea applied at-planting and UAN applied as a split application at the V4 growth stage (abc).

| Treatment | 2018 | 2019 | 2020 | All |
|---|---|---|---|---|
| Urea | 0.29±0.11a | 0.09±0.09 | 1.08±0.75 | 0.49±0.26 |
| UAN Surface | 0.09±0.01b | 0.06±0.1 | 0.21±0.05 | 0.12±0.04 |
| Anova | 0.0510 | 0.6785 | 0.4082 | 0.1732 |

Different letters indicate significant differences between fertilized treatments using a protected LSD method for post-hoc comparisons. ($P$ < 0.10).

Table 3.A8: Yield-scaled $N_2O$ emissions (g $N_2O$-N $ha^{-1}$) and standard errors for urea applied at-planting and UAN applied as a split application at the V4 growth stage (abc).

| Treatment | 2018 | 2019 | 2020 | All |
|---|---|---|---|---|
| Urea | 49±17 | 34±8 | 246±160 | 110±57a |
| UAN Surface | 33±9 | 36±4 | 48±10 | 39±5ab |
| Control | 27±13 | 34±17 | 36±18 | 32±9b |
| Anova | 0.1017 | 0.5635 | 0.1777 | 0.0342 |

Different letters indicate significant differences between fertilized treatments using a protected LSD method for post-hoc comparisons. ($P$ < 0.10)