

**Meta-analysis of 4R Nitrogen Management on Direct Nitrous Oxide Emissions
from Cropland in the Canadian Prairies and Northern Great Plain USA**

by
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A Thesis

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ABSTRACT

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Agricultural soils are a major source of direct and indirect emissions of the greenhouse gas nitrous oxide (N_2O). The 4R nutrient stewardship framework, involving using the right source at the right time, rate, and place, can significantly reduce N_2O emissions. Here a meta-analysis of reported studies conducted in Western Canada and Northern Great Plains of USA with similar climatic conditions (Köppen Dfb, warm summer humid continental climate) compared total emissions of N_2O ($\Sigma\text{N}_2\text{O}$, $\text{kg N}_2\text{O-N- ha}^{-1}$) for fertilizer sources (conventional fertilizers versus Enhanced Efficiency Fertilizers- EEFs), placement (broadcast versus band), timing of application (spring versus fall), and application rate. The results show that compared to conventional granular urea, the use of nitrification inhibitors, dual inhibitors (Super-U), and polymer-coated urea (PCU) significantly reduced $\Sigma\text{N}_2\text{O}$ by 35%, 48%, and 16%, respectively. Urease inhibitors had no effect on $\Sigma\text{N}_2\text{O}$. Products containing nitrification inhibitors with UAN significantly reduced $\Sigma\text{N}_2\text{O}$ by 17%. Overall, the use of nitrification inhibitors reduced the fertilizer-induced N_2O emissions by 67% from urea alone and by 30% from UAN alone. Compared to broadcast-incorporation, banding generally tended to decrease $\Sigma\text{N}_2\text{O}$ by 4%. Among banding depths, deep banding (> 6 cm) tended to decrease $\Sigma\text{N}_2\text{O}$ by 16% whereas shallow banding (< 6 cm) tended to increase $\Sigma\text{N}_2\text{O}$ by 5%. In case of banding positions, side banding and midrow banding tended to decrease $\Sigma\text{N}_2\text{O}$ by 2% and 4% respectively. Whereas compared to surface application, banding resulted in an increase of $\Sigma\text{N}_2\text{O}$ by 14%. Across banding depths, deep and shallow banding tended to increase $\Sigma\text{N}_2\text{O}$ by 3% and 20%, respectively. Among banding positions, side banding tended to decrease $\Sigma\text{N}_2\text{O}$ by 11% whereas

midrow banding showed a considerable increase in $\Sigma\text{N}_2\text{O}$ by 40%. The fall application of fertilizer significantly reduced $\Sigma\text{N}_2\text{O}$ compared with spring application under specific soil conditions (i.e., $\text{pH} < 7$, and silt soil) but the overall impact was not statistically significant. Total and fertilizer-induced N_2O emissions exhibited increasing trend with the increase in nitrogen (N) input. Based on the analysis we conclude that adopting the 4Rs can greatly reduce N_2O emissions among the reviewed and sorted datasets.

Keywords: N_2O emissions, meta-analysis, emission factor, EEFs, 4Rs.

FOREWORD

This thesis has been developed in adherence with the manuscript guidelines established by the University of Manitoba's Department of Soil Science. The thesis has three chapters. Chapter 1 provides background information about N₂O emissions, factors affecting N₂O production, meta-analysis and literature review of the 4R framework i.e, right source, time, place and rate. Chapter 2 is the key research chapter focusing on the meta-analysis of 4Rs impact on mitigation of N₂O emissions. Chapter 2 was structured as a manuscript for publication in the Canadian Journal of Soil Science. Chapter 3 is an overall synthesis chapter providing summary of the study findings and the best practices that can be adopted by the farmers. Supplementary materials are provided in the appendices section.

CONTRIBUTIONS

I started my MSc. program in the Winter of 2022. Initially, I started my coursework online, and by mid of March, I was able to travel to Canada and henceforth was able to join my classes in person. Literature search was initiated soon after finishing the first semester of course work, followed by data calculations and statistical analyses (using RStudio). I prepared and analyzed the data set with the help of Drs. Gao and Tenuta, who also edited this thesis. I shared the findings of this study at the Manitoba Agronomists Conference (December 2022 and, 2023), Canadian Society of Soil Science Conference (June 2023) and Manitoba Society of Soil Science Conference (February 2023 and, 2024).

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LIST OF ABBREVIATIONS

AA	Anhydrous ammonia
CH₄	Methane
CO₂	Carbon dioxide
CSA	Carbon Savings Account
CI	Confidence interval
DCD	Dicyandiamide
DMPP	3,4-dimethylpyrazole phosphate
DMPSA	3,4- dimethylpyrazole succinic acid
NBPT	N-(n-butyl) thiophosphoric triamide
ESN	Environmentally smart nitrogen
EEFs	Enhanced efficiency fertilizers
EF	Emission Factor
GHG	Greenhouse gas
IPCC	Intergovernmental panel on climate change
N	Nitrogen
N₂O	Nitrous oxide
N₂	Dinitrogen
NO	Nitric oxide
NO₃⁻	Nitrate

NO₂⁻	Nitrite
NH₂OH	Hydroxylamine
NH₃	Ammonia
NH₄⁺	Ammonium
NI	Nitrification inhibitor
PCU	Polymer coated urea
PPT	Precipitation
SOC	Soil organic carbon
UAN	Urea ammonium nitrate
UI	Urease inhibitor
WFPS	Water filled pore space

Chapter 1. Introduction

1.1 Contribution of agriculture to N₂O emission

Nitrogen (N) is essential for optimal plant growth, different plant structures and metabolic activities. It is required in greater amounts than any other mineral nutrients. It is also a source of nitrates in groundwater and ammonia (NH₃) and nitrous oxide (N₂O) emissions in the nitrogen cycle. The plant available N (NO₃⁻, NH₄⁺) is usually low in re-cropped fields, therefore, a large amount of N inputs through synthetic fertilizer or organic manure is typically required to meet crop needs and achieve higher yields. However, generally, only 50% of applied fertilizer can be used by crops in the year of application, and the rest is lost in various ways, such as leaching and gaseous emissions (Yan et al., 2014).

Global climate systems have undergone an unusual transformation since the 1950s. Over the last three decades, surface temperatures on land and in the ocean have risen by almost 0.85°C (Pachauri et al., 2014). The primary cause of climate change is the increasing concentration of greenhouse gases such as methane (CH₄), carbon dioxide (CO₂) and N₂O in the atmosphere (IPCC, 2014). Infrared light is absorbed by these greenhouse gases (GHGs), releasing longwave radiation back to the earth's surface. Consequently, more energy is trapped on the earth as atmospheric concentrations of GHG increase. Thus, higher land and ocean surface temperatures are a result from increased radiation trapped on the earth's atmosphere (IPCC, 2014).

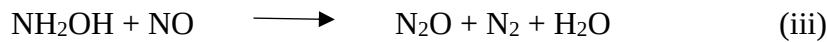
Nitrous oxide is a potent greenhouse gas with a global warming potential of ~300 times that of CO₂ and is responsible for stratospheric ozone depletion (IPCC, 2013). It can remain active in the atmosphere for nearly 120 years (USEPA, 2012). Agriculture plays a crucial role in N₂O

emissions and is responsible for two-thirds of all anthropogenic N₂O emissions worldwide (Lu et al., 2022). The application of animal manures and synthetic N fertilizers is considered one of the major contributors to N₂O emissions from agriculture. The Canadian Prairies, which encompass the provinces of Alberta, Saskatchewan, and Manitoba, renowned for their expansive agricultural landscapes, account for nearly 80% of all N fertilizers used in Canada with a corresponding 71% of anthropogenic N₂O emissions from the agricultural sector (Environment Canada, 2013; Statistics Canada, 2014). Canada has committed to reduce GHG emissions by 30% from 2005 levels by 2030. Therefore, it is essential to comprehend the issue of GHG emissions and take the necessary steps to mitigate them (Environment and Climate Change Canada, 2017).

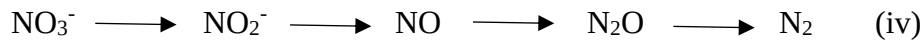
In Manitoba, 29% of the GHG emissions come from agriculture and 37% from the transportation sector, the two largest emissions sources. Due to the adoption of the province's emissions reduction programs, carbon tax signals and increasing environmental awareness, a 900 kt reduction was seen in Manitoba's emissions from 2018 through 2020 (Manitoba Environment and Climate Change, 2020). Mitigation efforts also involve a combination of optimizing nitrogen management practices, adopting the 4R nutrient stewardship framework i.e., the use of enhanced efficiency fertilizers (EEFs), the right method of placement, the right time of application of fertilizers, the right rate and implementing environmentally friendly policies. Manitoba developed a Carbon Savings Account (CSA) to ensure continuous emission reduction within the province. CSA is calculated as the sum of all emissions reductions over five years cumulatively. Manitoba aimed to reduce emissions by 1Mt throughout the 2018-2022 CSA period and brought down the emissions by 200 kt of CO₂ equivalent. Various programs, including Efficiency Manitoba and Efficient Trucking, were launched during this period, and they will continue to help in the future as well (Manitoba Environment and Climate Change, 2020).

1.2 Soil and environmental factors that affect N₂O production

Direct N₂O emissions are produced mainly by biological processes of nitrification and denitrification in the soil (Fig. 1). The primary step in nitrification is the biological oxidation of ammonia (NH₃) to nitrite (NO₂⁻) by aerobic ammonia-oxidizing archaea and ammonia-oxidizing bacteria. During this step, the ammonia monooxygenase enzyme converts NH₃ to hydroxylamine (NH₂OH) proceeded by oxidation of NH₂OH to NO₂ in the presence of hydroxylamine oxidoreductase. Further NO₂⁻ is oxidized to NO₃⁻ in the presence of nitrite oxidoreductase, as shown in the equations below (Wood et al., 2023). The initial phase of ammonia oxidation is carried out by *Nitrosomonas* and *Nitroso coccus* bacteria and archaea like *Nitrosopumilus* and *Nitrososphaera*. The second step of oxidation of NO₂⁻ to NO₃⁻ is carried out by *Nitrobacter* or *Nitrospira* (Aryal et al., 2022).



Denitrification is a microbial process in the nitrogen cycle where NO₃⁻ is reduced and ultimately converted into dinitrogen gas (N₂). During this process, nitric oxide (NO) and N₂O are produced as by-products, as shown in the equation below. This is an anaerobic process primarily carried out by heterotrophic bacteria like *Para coccus* and *Pseudomonas* and some autotrophic denitrifiers like *Thiobacillus* (Aryal et al., 2022). Nitrification and denitrification processes are regulated by soil temperature, carbon availability, soil moisture, and soil pH (Granli et al., 1994).



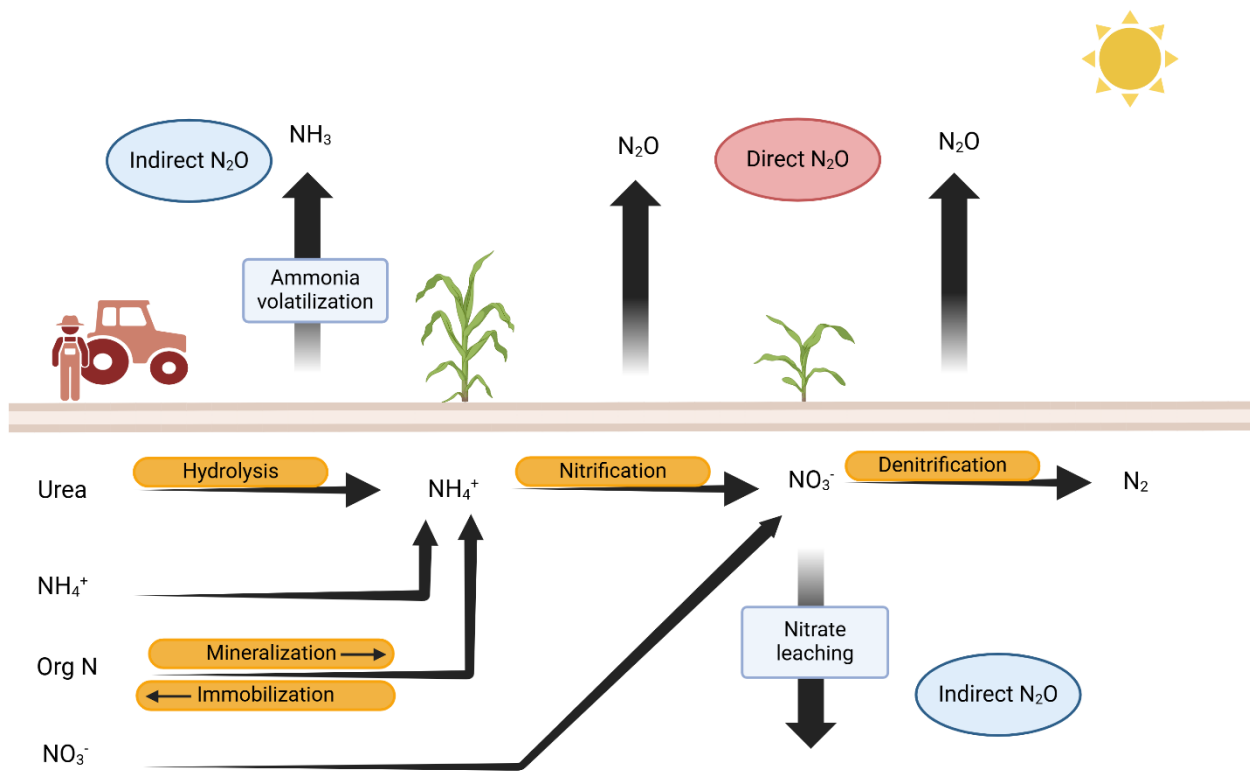


Figure 1.1 The nitrogen cycle (Source: Aryal et al., 2022; Modified with BioRender.com)

Soil temperature: Temperature significantly impacts biogeochemical processes, particularly those involving bacteria. Soil temperature affects N mineralization and soil availability in terrestrial ecosystems by altering microbial growth. In cold climates, the microbial activity is restricted, thereby leading to low N mineralization rates and decreased N supply in plants (Geng et al., 2017). With the increase in soil temperature, the processes of nitrification and denitrification also show an increase with the peak N_2O production to occur at approximately $35^\circ C$ (Subbarao et al., 2006; Aryal et al., 2022). Due to global warming, the rise in temperature might affect the microbial activity and soil characteristics, which could further impact N_2O emission. For example, Wang et al. (2021) observed a peak in the nitrification rates at a temperature of $30-40^\circ C$ with the

highest production rates occurring around 45°C, and Cheng et al. (2020) reported a 54% increase in N₂O emissions in coastal wetlands due to warming effect. Thus, temperature is crucial in controlling biogeochemical cycles that impact the overall nitrogen cycle.

Carbon availability: The presence of soil carbon serves as a source of energy for the microorganisms, which helps raise the microbial activity of nitrifiers and denitrifiers to facilitate the oxidation of ammonium and reduction of nitrate (Signor et al., 2013). Generally, the occurrence of soil nitrification and denitrification processes increases with increased SOC (Butterbach et al., 2013). A study by Tenuta et al. (2011) reported an increase in denitrification activity and N₂O emissions due to high soluble carbon and organic matter in the soil. Similarly, another study conducted in China (Chen et al., 2014) found that N₂O emissions increased with increasing soil carbon.

Soil moisture: Soil moisture affects the availability of oxygen and occurrence of anerobic conditions. N₂O emissions are high during seasons with increased precipitation and high soil water content. This observation has been confirmed by a study conducted in New Zealand on a silt clay loam soil (Choudhary et al., 2001). Another study in Australia (Schwenke et al., 2016) measured N₂O emissions to be five times higher during the wet season than dry season. Generally, N₂O is released at a higher rate when water-filled pore space (WFPS) is greater than 60%. At this moisture level, the soil pore water displaces oxygen, leading to anaerobic conditions that are conducive to the production of N₂O through denitrification (Wang et al., 2021). Under these circumstances, facultative anaerobic bacteria convert NO₃⁻ to NO₂⁻, N₂O and finally to N₂. Nonetheless, the ideal WFPS for nitrification and denitrification depends on soil texture (Weier et al., 1993).

Soil pH: Another factor that affects the denitrification rate and significantly impacts microbial processes responsible for N₂O emission is soil pH. Denitrification rates typically rise with rising

pH, with maximum rates observed between 7 to 7.5 pH in most of the conducted studies (Kesik et al., 2006; Aryal et al., 2022). One such research (Su et al., 2019), focusing on the impact of pH on biologically driven N₂O emissions, found that at pH 6.5 to 8, the net N₂O emission rate increased by seven times but declined somewhat at pH 8.5. In contrast, other studies showed reduced N₂O flux/denitrification rate in acidic soils (Yamulki et al., 1997; Sun et al., 2012; Saleh et al., 2009). Over time, the use of fertilizers, increased leaching rate, and organic matter build-up have all contributed to an increase in soil acidity. Therefore, soil pH is a significant component that impacts denitrification rates and ultimately, the N₂O emission rate.

The indirect sources of N₂O emission from agricultural soils include ammonia volatilization, leaching and run-off. Ammonia volatilization is the release of NH₃ gas into the atmosphere. Still, most of this ammonia comes back to the earth's surface through wet and dry deposition, thereby resulting in eutrophication and acidification of water bodies. The release of ammonia gas is favored by the application of N fertilizers, manures, mineralization of organic matter and high pH soils. Around 50% of ammonia volatilization comes from the agricultural sector. Runoff and leaching of fertilizers occur due to excessive irrigation or rainfall. The reactive nitrogen in fertilizers either gets washed away into water bodies or leaches into the groundwater, which increases nitrogen levels in those areas, thereby causing greater N₂O emissions (Ussiri et al., 2012).

1.3 Meta-analysis

Meta-analysis is a systematic synthesis of the results of different individual studies (Hedges et al., 1992). Meta-analysis seeks to aggregate findings from earlier research projects quantitatively and integrates results from the chosen studies into a single numerical estimate using statistical techniques to determine the overall effect. The term "effect size" is a standardized measure of the magnitude and direction of a relationship or difference between variables, enabling comparison

across studies regardless of their scales of measurement (Harrer et al., 2022). In meta-analysis, effect sizes are crucial as they summarize study results into comparable metrics such as mean differences, odds ratios, correlations, or standardized mean differences. These values, paired with their standard errors, form the foundation of pooled analyses in meta-analytical studies. This way it offers a standardized way to aggregate and compare results from different studies.

The majority of national GHG inventories have been built using a N₂O emission factor (EF) technique that uses the total input of N to soil and its subsequent availability as a reliable predictor of N₂O fluxes (Shcherbak et al., 2014). The N₂O emission factor is the percentage of N-fertilizer applied and transformed into fertilizer-induced N₂O emissions. The IPCC Tier 1 protocol uses EF of 1%, meaning almost 1% of the applied N fertilizer is emitted as N₂O directly from the soil. Global research is ongoing on the 4R Nutrient Stewardship framework, which includes the use of N fertilizer at the right rate, placement, source, and timing to reduce N₂O emissions and increase crop productivity (Snyder et al., 2009; Venterea et al., 2016). In Canada, “right source” is counted as an option for lowering N₂O emissions in the Nitrous Oxide Emission Reduction Protocol (Alberta Environment, 2011). The use of nitrification inhibitors is also recommended by the IPCC as an effective mitigation option for N₂O emissions from agriculture (IPCC, 2014).

Many meta-analyses investigated how 4R management of N fertilizer can affect N₂O emissions from crop production systems. However, these meta-analyses were limited regarding regional scope, temporal scale, and management factors. For instance, the global meta-analysis carried out by Liu et al. (2023) did not consider the timing of fertilizer applications and N₂O loss due to the unavailability of data. Akiyama et al. (2010) were unable to consider the timing and placement method of fertilization that could have affected N₂O emissions. Another meta-analysis study by Shcherbak et al. (2014) studied the impact of one of the 4Rs, the rate of N fertilizer, on

N₂O emissions, whereas other factors were not considered. Furthermore, previous research on the efficacy of EEFs in lowering N₂O emissions found varying results depending on the native properties of various EEFs, as well as various soil, environmental and management factors. In the case of the relationship between N rate and direct N₂O emissions, Kim et al. (2013) did a global meta-analysis of 26 datasets and reported a non-linear relationship for 18 datasets and a linear relationship for 4 datasets, suggesting further comprehensive analysis with more data availability are needed to examine the response of N₂O emissions to N input rates. So, our study will focus on covering this research gap and help to determine the relationship. Cold climates are often underrepresented in the scientific literature compared to temperate regions, as most of the prior conducted meta-studies had a global focus rather than focusing on a region with a specific climate. Therefore, we proposed an updated meta-analysis to consider 4R practices together and their impact on N₂O emission, specifically in cold climate regions.

This study will focus on quantifying the 4Rs' impact on the mitigation of N₂O emissions from agricultural crop production systems across Western Canada and the regions with similar climatic conditions. Specifically, we collect all studies from the “Dfb” climate conditions, as defined by the Köppen climate classification system (Kottek et al., 2006). The “Dfb” is specifically associated with a warm summer continental or hemi-boreal climate, consistent precipitation throughout the year, and a warm summer season. Different letters of the climate classification represent different meanings, as follows:

- **D:** This letter represents a warm summer continental or hemi-boreal climate.
- **f:** This letter indicates that the climate has significant precipitation throughout the year, with no dry season.

- **b:** This letter designates that the climate has a warm summer, where the average temperature of the warmest month is above 10°C (50°F).

Areas with this climate type often experience distinct seasons, with warm to hot summers and cold winters. This meta-analysis aims to offer comprehensive guidance for optimizing fertilizer management to maximize both economic and environmental benefits under the unique conditions of the Canadian Prairies.

1.4 Source

For crop production in the Canadian Prairies, the main nitrogen sources are urea and anhydrous ammonia (AA) (Gao et al., 2015; Tenuta et al., 2000). After application of urea to soil, it undergoes rapid hydrolysis by urease enzyme, producing ammonium (NH_4^+) and ammonia (NH_3). If the soil moisture and temperature conditions are favourable, ammonium and ammonia will undergo nitrification within 2 to 4 weeks, ultimately leading to N_2O production (Gao et al., 2015). In the Prairies, the two most common methods of applying urea are banding and broadcast incorporation. For annual crops, side banding (placement of fertilizer in a narrow band to the side of the seed) or midrow banding (placement of fertilizer between every second row below the seed) is recommended, because studies have proven banding of N fertilizer to be more efficient than broadcast-incorporation (Gao et al., 2015; Grant et al., 2008; Lemke et al., 2009). Another common source used in Western Canada is AA, which declined from 19.6% of N fertilizer used for canola production in 2022 to 14.2% in 2023 (Statistics Canada, 2024). It is usually applied in the fall due to drier soil conditions, greater availability for farmers' time window, and lower retail price than at spring planting. In Manitoba, it is advisable to band fall applied AA and postpone application until the soil temperature falls below 5°C (MAFRD, 2007; Tenuta et al., 2016). On average, 4,240 metric tonnes of urea, 4,481 metric tonnes of AA, 1,441 metric tonnes of UAN, 610 metric tonnes

of ammonium nitrate/calcium nitrate, 1,242 metric tonnes of ammonium sulphate, and 22,258 metric tonnes of potash were used annually in Canada between 2019 and 2023 (Statistics Canada, 2024).

Use of EEFs is an option that could be used in minimizing N losses. Stabilized and polymer-coated fertilizers are the two common categories of EEFs. One commonly used polymer-coated urea is Environmentally Smart Nitrogen (ESN, 44-0-0), produced by Nutrien Ag. It has a semipermeable coating, which allows water to diffuse and slowly solubilize urea-N in the soil (Trenkel et al., 2010). Thus, the N release from ESN highly depends on soil moisture and temperature conditions. For the stabilized EEFs, fertilizers are treated with chemical additives, such as nitrification and/or urease inhibitors, which can restrict the enzyme activity of N-cycling microbes (Ruser et al., 2015). Specifically, the presence of nitrification inhibitors such as dicyandiamide (DCD), 2-chloro-6-[trichloromethyl] pyridine (nitrapyrin), and 3,4-dimethylpyrazole phosphate (DMPP), can reduce the activity of the ammonium monooxygenase enzyme responsible for conversion of NH_3 to NH_2OH , thereby delaying the oxidation of ammonium (NH_4^+) to NO_2^- , up-to 4 to 7 weeks (Nelson et al., 2001). Super-U (46-0-0) is a commercially available stabilized urea product that contains a urease inhibitor, N-(n-butyl) thiophosphoric triamide (NBPT), and a nitrification inhibitor, DCD, in the formulation. These EEFs are designed so that the plant N demand is matched by the N release from the applied fertilizer products. The main advantage of using such formulations is that during the early growing season of the crop, when the crop uptake is comparatively slow, it helps lower the amount of available N, which results in fewer N losses.

A study conducted in Alberta (Li et al., 2012) showed that the use of ESN reduced N₂O emissions by 15–20% in comparison with urea in barley (*Hordeum vulgare* L.) and canola (*Brassica napus* L.). Another study conducted on maize (*Zea mays* L.) in Illinois showed greater N₂O emissions with the application of Urea (by 44%) and AA (by 73%) as compared to ESN (Fernández et al., 2015). In Colorado, applying ESN and Super-U at the rate of 202 kg N ha⁻¹ reduced N₂O emissions by 26% and 51%, respectively, compared to granular urea (Halvorson et al., 2013). Another study by Halvorson et al. (2014) reported that the use of ESN and Super-U reduced N₂O emissions by 42% and 46%, respectively, compared to urea in maize-based rotation systems. At another maize (*Zea mays* L.) site in Minnesota, a study reported that the application of Super-U and ESN at a rate of 180 kg ha⁻¹ reduced N₂O emissions by 70% and 53% compared to urea, respectively (Maharjan et al., 2013). In Manitoba, the use of ESN for canola and wheat reduced the N₂O emission factor by almost half compared to urea, still the use of Super-U was ineffective, likely due to high soil organic carbon at the study site (Asgedom et al., 2014). In Colorado, Delgado et al. (1996) reported that the application of DCD in barley reduced emissions of N₂O by 82%. Compared to conventional urea, using eNtrench and Super-U reduced N₂O emissions from spring wheat production by 54% and 43% respectively, across six site years in Manitoba (Wood et al., 2023). Combined, all these studies suggest that using EEFs can slow the release or conversion of N transformations in soils that may be less susceptible to N₂O emissions.

In the fall season, solid or liquid manures are also applied to some regions in the Northern Great Plains and Canadian Prairies to allow for the mineralization process in spring or early summer. Around 1.7 million ha of agricultural land in Canada receives livestock solid manures (Statistics Canada, 2011). The release of N after manure application is a slow process compared to synthetic fertilizer application, which results in less inorganic N in soil that is susceptible to

conversion into N₂O (VanderZaag et al., 2011). However, adding manure also increases carbon availability to soil microbes, and thus enhances N₂O production through nitrification and denitrification processes. Previous studies investigating the impact of manure application on soil N₂O emissions have revealed different results depending on various factors, including the type and amount of manure, soil properties, climatic conditions, and management practices.

A worldwide meta-analysis of 182 studies reported that the use of nitrification inhibitors effectively reduced N₂O emissions on average by 49% (Fan et al., 2022) with the effectiveness being influenced by soil, climate, and management practices. However, the analysis did not consider the timing of fertilizer application due to limited availability of comprehensive data in the majority of the reviewed studies. Another meta-analysis of 35 studies indicated that nitrification inhibitors and polymer-coated fertilizers significantly reduced N₂O emissions by 38% and 35%, respectively, as compared to conventional fertilizers (Akiyama et al., 2010). However, the studies included in this analysis failed to provide sufficient information regarding the method and timing of fertilizer application that could affect N₂O emissions. Also, using a meta-analysis of 43 studies, Thapa et al. (2016) reported that the use of nitrification inhibitors and double inhibitors significantly reduced N₂O emissions by 38% and 30%, respectively. Thapa et al. (2016) also reported that the addition of nitrification inhibitors significantly increased the yield of cereal crops by 7.1%. The limiting factor of this analysis was that almost 63% of the studies included did not report standard deviation, or standard errors. To cover this research gap, our analysis will consider different fertilizer application methods (band, broadcast) and timing (fall, spring).

1.5 Placement

The placement of N fertilizer is an integral part of 4R nutrient management. The choice of fertilizer placement is influenced by different factors such as soil texture, soil moisture, crop, application equipment and interaction with other 4R components, especially source. The placement method may have varying effects on residual nitrogen from year to year, based on soil-climatic factors that affect crop N uptake, N release, and N loss (Halvorson et al., 2013). Granular urea is usually applied by banding in the Northern Great Plains of Canada. Banding of N fertilizer can potentially increase nitrogen use efficiency and lower N₂O emissions than broadcast-incorporation, so side-banding or mid-row banding is generally recommended (Grant et al., 2008). The impact of the depth of nitrogen fertilizer placement on N₂O emissions is contingent upon the specific soil-climatic conditions and management practices. For example, Kessel et al. (2013) reported that in a no-till system, nitrification and denitrification rates usually diminish in deeper soils, primarily because of reduced substrate supply and microbial activity compared to the near-surface layers. Thus, placing fertilizer N at deeper levels(>5cm) usually reduces overall N₂O emissions (Chapuis-Lardy *et al.*, 2007). Steusloff et al. (2019) also reported that deep band placement of urea plus nitrification inhibitor had 54% lower N₂O emissions than urea broadcast-incorporation.

Surface application of fertilizers (urea, UAN, manure) poses a considerable risk of volatilization loss, an indirect source of N₂O emissions, especially on alkaline soils and high-temperature conditions. The majority of N volatilization occurs within the initial seven to fourteen days following the application of a top-dress fertilizer, provided the moisture conditions are favourable to initiate the conversion of urea to ammonia. However, the losses may persist longer depending on the prevailing conditions. In an Ontario study, averaged 3-year data showed that

ammonia losses were reduced by 99% from injected UAN treatment as compared to broadcasted urea, even though there was no difference in corn yield (Woodley et al., 2020).

In a field trial with spring wheat in Manitoba, Gao et al. (2015) reported that midrow band of Super-U and ESN reduced N₂O emissions by 47% on an average compared to broadcast-incorporated urea. In Saskatchewan, a 3-year experiment was conducted at four sites out of which two sites reported lower N₂O emissions with single side-band urea compared to broadcast-incorporated urea (Hultgreen et al., 2003). In a study with corn, Nash et al. (2012) reported greater N₂O emissions from no-till/surface broadcast urea compared with strip-till/subsurface single side-banded urea when N was applied at 140 kg N ha⁻¹ at planting. However, the above studies did not compare different banding depths. A recent published study conducted in Manitoba compared the banding depths in reducing N₂O emissions across six site-years (Tenuta et al., 2023). It reported that deep banding of urea application lowers N₂O emissions compared with shallow banding of urea. Additionally, it also found an increase in N₂O emissions across wet site-years, especially when urea was shallow banded. Liu et al. (2023) recently conducted a global meta-analysis to examine the effects of N fertilizer application depth on crop yield and nitrogen uptake, and reported that N application at 10-15 cm depth was the most effective as it increased the crop yield by 11.6% and nitrogen uptake by 26.2%. The limiting factor of this study was not considering fertilization timing and nitrogen losses (such as N₂O emissions, ammonia volatilization, leaching and run-off). Therefore, an updated comprehensive analysis of published studies is required to examine the impact of banding depths in reducing N₂O emissions.

1.6 Time

Applying N fertilizers at the right time has a great potential of reducing N₂O emissions. In the Northern Great Plains of Canada, it is a common practice to apply AA in the fall due to lower retail

cost and the presence of dry soil conditions as compared to spring application. However, nitrification can take place before winter freeze-up, so in Manitoba, it is recommended to band AA and postpone its application until soil temperatures fall below 5°C (MAFRD, 2007). Application of fertilizer when the soil is cool results in less N₂O emissions than high soil temperatures in spring. Through a 2-year study conducted at TGAS-MAN in Manitoba, Tenuta et al. (2016) monitored N₂O fluxes using a flux-gradient micrometeorological method. They reported that late fall application reduced N₂O emissions by 33% as compared to spring pre-plant application. Another study in Alberta showed that nitrification inhibitors, DMPP and nitrapyrin, with fall injection of liquid manures significantly reduced N₂O emissions by 81% and 58%, respectively, compared to spring application (Lin et al., 2017).

Crop productivity and nitrogen use efficiency can also be highly influenced by the timing of N fertilizer. A field study conducted for 2.5 years in Alberta reported that during the first year, N₂O emissions were 36% greater for the spring application of N fertilizers as compared to fall application (Thilakarathna et al., 2020), which is attributed to the majority of rainfall occurring after spring application of N fertilizer. Also, applying EEFs in spring increased the grain yield by 11% and doubled the nitrogen use efficiency. However, in the second year N₂O emissions were significantly greater for fall-applied N fertilizer than for spring because most of the annual emissions were associated with soil thawing. Another study in Alberta reported that delaying the application of N-fertilizer (urea) in the fall not only increases the efficiency of the source but increases the barley yield as well (Malhi et al., 1990). Studies conducted in poorly drained field conditions reported that the application of EEFs can promote crop yields as compared to conventional fertilizers (Thapa et al., 2016). In Manitoba, a 2-year study was carried out to know the impact of application date and urease and nitrification inhibitors on the efficacy of fall-banded

N fertilizer source. In the initial year of the study, the application of early fall-banded N along with urease and nitrification inhibitors increased the wheat grain yield as compared to without the use of inhibitors (Tiessen et al., 2005). A meta-analysis was conducted to study the impact of nitrapyrin application on maize nitrogen use efficiency, grain yield and plant N uptake. The results showed the positive impact of nitrapyrin on grain yield and plant N uptake, but this impact was not seen for nitrogen use efficiency (Burzaco et al., 2014). However, this research was limited to maize crops with all the N fertilizers applied in spring. Thus, more meta-studies need to be conducted that compare different timings of N fertilizer application, considering different crop types and evaluating N losses. So, to cover this gap our meta-study will be conducted in Western Canada to know the impact of the timing of N fertilizer on N₂O emissions.

1.7 Rate

Determining the right rate of fertilizer to maximize crop yield and minimize environmental losses can depend on different factors such as soil nutrient availability, moisture availability, soil type, crop type, producers' preference, and fertilizer price. The total amount of N added to the soil and its subsequent accessibility, is a reliable indicator of N₂O emissions. This information has been utilized in the development of most national GHG inventories, employing a method known as the N₂O EF approach (Eggleston et al., 2006). The IPCC Tier 1 methodology uses EF of 1%, meaning for every 100 kg of N input, approximately 1 kg of N in N₂O is directly emitted from the soil. An EF of 1% assumes a linear relationship between N input and N₂O emissions without considering any limitations that might occur, such as when the amount of soil inorganic N surpasses the needs of the crop (Shcherbak et al., 2014). Earlier findings indicated a linear relationship between the rise in N input and the subsequent increase in direct N₂O emissions across different agricultural systems (Bouwman et al., 1996; Dobbie et al., 1999). Nevertheless, there is an increasing number

of evidence/studies suggesting that N_2O emission in response to N input follows a non-linear or exponential pattern (McSwiney et al., 2005; Zebarth et al., 2008; Kim et al., 2010; Hoben et al., 2011; Signor et al., 2013).

A meta-analysis of 40 field sites in China associated with plastic-shed vegetable production revealed both exponential and linear relationship between N input rate and N_2O emissions (Ni et al., 2021). This meta-study was limited to one country and was unable to consider the method of N placement and timing of N fertilizer. Another global meta-analysis of 78 published studies reported an exponential increase in EF with increasing N-fertilizer rates, but this study lacked information about EF for different fertilizer types (Shcherbak et al., 2014). So additional studies are required in different climate zones with various N fertilizers used and considering N application timing. Kim et al. (2013) conducted a worldwide meta-analysis with 26 published datasets, out of which 18 datasets showed a non-linear relationship (hyperbolic or exponential) between N_2O emission and N rate, whereas 4 datasets exhibited a linear relationship. Due to the unavailability of data, this study could not explain the relationship fully and suggested more studies to be conducted. Therefore, our study of N_2O emissions from various N sources will try to reveal more about the relationship between N_2O emissions and N fertilizer rate across the cropping systems in Canadian Prairies and those regions with similar climates.

1.8 Objectives

Developing mitigation protocols requires an understanding of how agricultural management techniques affect N₂O emissions, so we proposed a meta-analysis study of 4R nitrogen management and its impact on N₂O emissions. This thesis aims to quantify the impact of N fertilizer application's source, place, rate and timing on direct N₂O emissions from crop production systems in cold climates. To attain this, a comprehensive meta-analysis is conducted by creating a database from relevant research and from regions with climatic conditions similar to the Canadian Prairies. Our research objectives are:

- 1) to determine the efficacy of different fertilizer sources (sole or double inhibitors, polymer-coated products) in reducing N₂O emission compared to conventional fertilizers;
- 2) to compare the impact of fall versus spring application timing on N₂O emissions;
- 3) to examine the different placement methods and depths impact on N₂O emissions;
- 4) to determine whether there is a linear or non-linear relationship between N application rates and N₂O emissions;
- 5) to identify key soil and environmental factors determining the benefits of 4R practices on mitigation of N₂O emissions.

1.9 Hypotheses

It was hypothesized that:

- 1) Compared to conventional fertilizers, using nitrification inhibitor-based EEFs would significantly reduce cumulative N_2O emissions, due to the inhibition of transformation from ammonia to nitrate and ultimately slowing down nitrification rates. Similarly, using urease inhibitors is anticipated to slow down the hydrolysis of urea, resulting in a significant reduction in N losses. Polymer-coated urea (PCU) would also reduce N_2O emissions by better matching crop N needs.
- 2) Applying N fertilizer in the fall before freeze-up would reduce N_2O emissions rather than in the spring by reducing emissions in the early growing season (Tenuta et al., 2016).
- 3) Compared to broadcast incorporation, banding of N fertilizers would reduce N_2O emissions by minimizing contact between the fertilizer and soil. Deep banding would significantly reduce N_2O emissions as compared to shallow banding, likely due to the consumption of N_2O during upward diffusion in soils.
- 4) I anticipate a non-linear relationship between N_2O emissions and N input rate, as a higher percentage of N inputs may be susceptible to N_2O loss when N rates surpass crop requirements.

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Chapter 2. 4R Nitrogen Management Practices and Nitrous Oxide Emission Reductions in the Canadian Prairies and Similar Climate Regions: A Meta-analysis

2.1 Abstract

Nitrous oxide (N_2O) emissions from agricultural soils are predominantly attributed to fertilizer nitrogen (N) inputs and contribute significantly to climate change. The 4R nutrient management framework of using the right source, place, time, and rate of N fertilizer has emerged as a mitigation option for N_2O emissions. Many field studies have examined the potential of 4Rs in reducing N_2O emissions from agricultural lands in cold climate regions, whereas a comprehensive analysis in a larger geographic context is lacking. We conducted a meta-analysis of field studies consisting of 21 studies from the Canadian Prairies and 18 from North Great Plains in the USA (39 studies with 452 paired observations). We evaluated the effectiveness of enhanced efficiency fertilizers (nitrification inhibitors, urease inhibitors, polymer-coated urea, dual inhibitors), method of placement (band, broadcast-incorporation and surface), time of fertilizer application (fall and spring) and different rates of N fertilizer across regions with humid continental (Köppen Dfb) climate. Total N_2O emissions across the growing season from each study were considered. The results indicated that compared to conventional urea, use of nitrification inhibitors, polymer-coated urea, and dual inhibitors (Super-U) significantly reduced cumulative N_2O emissions ($\Sigma\text{N}_2\text{O}$ kg N-ha⁻¹) by 35%, 16%, and 48%, respectively. In contrast, use of urease inhibitors did not show a significant impact on N_2O emissions. Compared to UAN, the use of nitrification inhibitors significantly reduced N_2O by 17%. It was observed that fertilizer-induced N_2O emissions were reduced by 67% from urea and by 30% from UAN, with the use of nitrification inhibitors. Banding of fertilizers generally resulted in 4% lower N_2O emissions as compared to broadcast-

incorporation, with the effectiveness being influenced by position and depth of banding. Side banding and midrow banding tended to decrease N₂O emissions by 2% and 4% respectively. Deep banding tended to decrease N₂O emissions by 16% whereas shallow banding tended to increase N₂O emissions by 5%. However, compared to surface application of fertilizer, banding increased N₂O emissions by 14%. Deep and shallow banding showed an increase of 3% and 20% respectively, and midrow banding indicated a significant increase of 40%. Contrastingly, side banding indicated decrease in N₂O emissions by 11%. Compared to spring application, fall application of fertilizer did not affect N₂O emissions across all studies but emissions were 27% lower with fall application on acidic and silt soils. Total and fertilizer-induced N₂O emissions increased significantly with N addition rates, highlighting the importance of avoiding excessive fertilizer application beyond crop needs. This regional-scale assessment demonstrates that optimizing the 4R strategy can effectively reduce N₂O emissions from agricultural production in cold climates. Specifically, use of the nitrification inhibitor based enhanced efficiency N fertilizers is the most effective approach for N₂O mitigation.

Keywords: N₂O emissions, meta-analysis, emission factor, EEFs, 4Rs.

2.2 Introduction

Climate change has emerged as a major problem worldwide. Globally, its evidence can be seen, such as escalation in surface temperature, elevation of sea level, and reduction of snow cover (Shakoor et al., 2011). Over the years, the effects of climate change are expected to continue. The agricultural sector is highly susceptible to the impacts of climate change as the frequency of extreme weather conditions and shifts in precipitation and temperature patterns directly affect crop yield, water availability and livestock productivity. Climate change also contributes to the emission of greenhouse gases (GHG), primarily methane (CH_4), nitrous oxide (N_2O), and carbon dioxide (CO_2), which worsen the greenhouse effect and amplify global warming. In Canada, agriculture is responsible for almost 71% of N_2O emissions, primarily associated with nitrogen fertilizers use, including conventional fertilizers and organic sources (Environment Canada, 2013). To prevent the most severe consequences of climate change, the Government of Canada has committed to decrease GHG emissions by 40%-45% below 2005 levels by 2030 and achieve net zero emission by 2050 (Government of Canada, 2021). Therefore, there is a pressing need for targeted strategies and technologies to mitigate N_2O emissions from Canadian agriculture, ensuring sustainable food production while reducing the sector's environmental footprint.

Implementing the principles of 4R nutrient stewardship, namely, right source, placement, time, and rate, offers a strategic approach to mitigate N_2O emissions in agricultural systems. This approach enhances nutrient use efficiency and crop productivity with minimizing GHG emissions, contributing positively to climate change mitigation efforts. The use of enhanced efficiency fertilizer products is an effective way to reduce N_2O emissions. Enhanced efficiency fertilizers such as nitrification inhibitors (NIs), urease inhibitors (UIs), dual inhibitors, and polymer-coated urea (PCU), are designed to improve nutrient uptake by crops while minimizing losses to the

environment. They modify the behavior of nutrients in the soil, making them more available to plants and reducing their susceptibility to loss through emissions, volatilization, run-off, and leaching. Nitrification inhibitors can slow the conversion of ammonium (NH_4^+) into nitrite (NO_2^-) by inhibiting the activity of two groups of microorganisms: ammonia-oxidizing bacteria (AOB) and ammonia-oxidizing archaea (AOA). By keeping N in the ammonium form for longer periods, NIs help to reduce N losses in the nitrate form, such as leaching and denitrification. Commonly used NIs include dicyandiamide (DCD), nitrapyrin, eNtrench, and 3,4-dimethylpyrazole phosphate (DMPP), frequently incorporated into conventional fertilizer products. Urease inhibitors disrupt the enzymatic function of urease, which is responsible for catalyzing the hydrolysis of urea, thereby slowing down the conversion of urea to ammonia. The most widely used UIs include N-(n-butyl) thiophosphoric triamide (NBPT), the active ingredient for commercially available EEF products such as Agrotain Plus and LIMUS. Application of dual inhibitors (combined action of NI and UI), such as Super-U, inhibit both nitrifying bacteria and urease enzyme activity resulting in lower N_2O emissions. Many studies across the Canadian Prairies and Northern Great Plain USA showed the benefits of NI-based EEFs in reducing N_2O emissions from various cropping systems (Hyatt et al., 2010; Graham et al., 2018; Gao et al., 2015; Thilakarathna et al., 2020; Thilakarathna et al., 2023; Tenuta et al., 2023; Oleson et al., 2023; Wood et al., 2023).

Polymer-coated urea is a controlled-release N fertilizer where urea granules are coated with a polymer layer. This coating serves as a barrier that regulates the release of N into the soil over an extended period, providing a more gradual and sustained supply of N to plants. A typical commercially available product is Environmental Smart Nitrogen (ESN) produced by Nutrien. The release of nitrogen from PCU is greatly influenced by soil temperature and moisture. Initially, the

presence of sufficient soil moisture hydrates the PCU granule and causes nitrogen within the granule to dissolve but, due to the presence of polymer coating, granule remains intact. As soil temperature rises, nitrogen diffuses out of the granule and become available for crop uptake. This technique synchronizes the release of nitrogen with the crop requirement, thereby minimizing N losses through nitrification and denitrification processes (Gao et al., 2015; Wood et al., 2023). Several field experiments showed reduction in N₂O emissions from the use of PCU in comparison with conventional urea (Li et al., 2012; Gao et al., 2015; Gao et al., 2017; Thilakarathna et al., 2020; Oleson et al., 2023). Utilization of EEFs has been suggested by various studies to offer agronomic and environmental advantages as compared to conventional N fertilizers. Overall, EEFs play a valuable role in improving nitrogen management in agriculture, thereby optimizing nutrient use efficiency and reducing environmental impacts.

Based on the importance of EEFs in minimizing environmental impacts, it is essential to consider the widespread adoption of placement methods as well. Approximately 75-90% of grain producers in Canadian Prairies side or midrow band nitrogen fertilizers as it is considered the most environmental efficient placement method under the Prairie conditions (Gao et al., 2015). Nitrogen fertilizers are generally required at high rates and could induce toxicity of NH₃, NO₂⁻, and salts to seedlings if they are placed in the seedrow. Therefore, banding of fertilizer is typically recommended to minimize such toxicity risks. However, excessive deep application of fertilizer might result in inefficient root uptake, reduced effectiveness and risk of leaching and immobilization. Based on the position of the band, side banding of N fertilizer (banded 2.5 to 8.0 cm to the side and/or 2.5 to 8.0 cm below the seed) or midrow banding (2.5 to 8.0 cm below the seed between every second seed row) is generally recommended for annual crops (Gao et al., 2015). Also based on the band's depth, N fertilizer can either be deep banded (more than 6 cm

deep) or shallow banded (less than 6 cm deep). Several studies have been carried out to determine the placement effect on N₂O emissions. Some of them reported that compared to broadcast, banding increased N₂O emissions (Halvorson et al., 2013; Engel et al., 2010; Maharjan et al., 2013), whereas others showed that N₂O emissions are reduced by banding of fertilizer (Liu et al., 2006; Gao et al., 2015; Gao et al., 2017). The reduced N₂O emissions associated with banding could be attributed to the decreased contact between the soil and the fertilizer, thus potentially resulting in lower rates of nitrification and denitrification.

Some recent studies proved that the response of N₂O emissions to banding is influenced by the depth of banding, soil properties and other environmental factors. For example, a study conducted in Manitoba by Tenuta et al. (2023) reported that shallow banding of urea increased N₂O emissions compared to deep banding across six site-years. Also, in dry site-years a reduction in N₂O emissions was reported when conventional urea was subsurface banded in comparison with broadcast-incorporation whereas in case of high rainfall an increase in emissions was noted, specifically when urea was shallow banded. To assess the impact of shallow banding on N₂O emissions in relation to soil texture, two field experiments were conducted on clay and sandy soils of Manitoba. It was found that deep and shallow banded urea applications had more increase in N₂O emissions compared with broadcast urea. The clay soils reported almost 3 times higher N₂O emissions compared with emissions from the sandy soil (Tenuta, 2023). Similar results of increase in N₂O emissions were found when urea was shallow banded compared to deep banded urea in another field experiment conducted in Manitoba (Tenuta, 2022). However, a comprehensive analysis is required to know the most effective depth of bands in reducing N₂O emissions.

The timing of fertilizer application could also significantly affect N₂O emissions. Fall application is common in the Prairies for several reasons 1) lower price, 2) more time window for

farmers' practice, 3) cool soil conditions, and 4) increased seed bed preservation (Tenuta et al., 2016; Wood et al., 2023). From a two-year field trial on a clay soil in Red River Valley of Manitoba, Tenuta et al. (2016) concluded that late fall application reduced N₂O emissions by approximately 50% than in spring application. However, that study focused on one nitrogen fertilizer, anhydrous ammonia (82-0-0), so the results might differ for other sources. Also in Manitoba, a study by Wood et al. (2018) reported lower N₂O emissions from fall-applied EEFs. Similarly, other field studies reported higher N₂O emissions in early spring than in fall applications (Lin et al., 2017; Thies et al., 2020). In contrast, some studies reported lower N₂O emissions by applying N fertilizer in spring, likely due to spring application minimized the risks of N₂O losses through the post-harvest and early spring-thaw periods (Hao et al., 2001; Grant et al., 2004; Soon et al., 2011). These studies suggest that the impact of fall vs. spring application timing on N₂O emissions are highly associated with soil environmental factors such as moisture, temperature and fertilizer management factors such as sources or placement of fertilizers. Therefore, there is a need for a comprehensive analysis to provide more detailed information about the impact of soil and other environmental conditions on the reduction of N₂O emissions from fall and spring-applied fertilizers.

Additionally, N fertilizer rates also significantly influence N₂O emissions. Previous studies reported that N₂O emissions from agricultural lands increased linearly (Bouwman et al., 1996; Dobbie et al., 1999) or non-linearly (McSwiney et al., 2005; Zebarth et al., 2008; Kim et al., 2010; Hoben et al., 2011; Signor et al., 2013) with increasing fertilizer N rates. The IPCC Tier 1 methodology adopted a linear relationship between N input rates and N₂O emissions, suggesting a default value of 1% of applied N emitted as N₂O (IPCC, 2006). In contrast, other studies reported a nonlinear, exponential relationship between N input rates and N₂O emissions (Zebarth et al.,

2008; Hoben et al., 2011; Cardenas et al., 2010; Kim et al., 2013; Shcherbak et al., 2014), mainly attributed to the increased percentage of N₂O emissions at excessive N input surpassing crop requirements. This uncertainty suggests that the specific response can vary based on climatic conditions, soil properties, crop type, and nitrogen fertilizer management factors. One objective of this meta-analysis is to provide a quantitative response of N₂O emissions to varying fertilizer nitrogen rates across the humid continental climatic region.

In recent years, many field experiments have been conducted across the Canadian Prairies and regions with similar climates to evaluate the efficacy of EEF products, method of placement, time of application and rate of N fertilizer in reducing N₂O emissions. However, it is a challenge to conclude the best practise because of the variation in the performance of 4Rs across different soil types and field management factors. Therefore, we conducted this meta-analysis to provide an update on the 4Rs strategy across warm summer humid continental (Dfb) climatic regions. The overall objective of this study was to quantify the benefit of 4R practices in mitigating N₂O emission from agricultural production systems in regions with similar climates as the Canadian Prairies. Specifically, we aim to answer the following questions:

- 1) To what extent do EEFs (nitrification/urease/dual inhibitors, polymer-coated urea) reduce N₂O emissions?
- 2) How does nitrogen fertilizer placement (band vs. broadcast, side vs. midrow banded, shallow vs. deep banded) affect N₂O emissions?
- 3) Does fall application result in higher N₂O emissions than spring application?
- 4) How do N₂O emissions change with increased fertilizer nitrogen rate?
- 5) Do soil, environmental, and crop factors (i.e., soil texture, soil pH, soil organic carbon, precipitation, crop type) alter the effect of 4R practices on N₂O emission reductions?

2.3 Materials and Methods

2.3.1 Data collection

A detailed systematic literature search was conducted using the Web of Science, Research Gate and Google Scholar databases, using the following keywords and their combinations “nitrification inhibitors”, “urease inhibitors”, “double inhibitors”, “nitrous oxide emissions”, “urea”, “enhanced-efficiency fertilizer” or “polymer coated urea”, “N fertilization rate”, “timing of fertilizer”, “method of placement”, “nitrous oxide emission factor”. The research was primarily conducted for the Canadian Prairie Provinces of Alberta (AB), Saskatchewan (SK), and Manitoba (MB). We also included research from the Northern Great Plains of the USA in the states of Colorado (CO), Iowa (IA), Idaho (ID), Illinois (IL), Indiana (IN), Minnesota (MN), Montana (MT), North Dakota (ND), and South Dakota (SD). Studies were selected based on Köppen Dfb climate classification (The Köppen-Geiger climate classification consists of five main climate groups: tropical (A), arid (B), temperate (C), continental (D) and polar (E) (Kottek et al., 2006). It is classified based on seasonal precipitation and temperature patterns. Dfb refers to warm summer humid continental climate. If a study encompassed multiple experiments conducted at different locations and soil types, we treated them as separate observations. The period for measuring cumulative N₂O (kg N₂O-N ha⁻¹) emissions in different studies encompassed a growing season and only direct N₂O emissions were considered. To prevent bias, each study was reviewed to see if it matched the following criteria:

- (i) Only field experiments were included, and greenhouse and laboratory-based studies were excluded.
- (ii) Field trials of experiments had a minimum of three replicate treatment plots included.

(iii) Experiments were conducted in warm summer humid continental climatic region as defined by Köppen Dfb.

Overall, a meta-dataset was established with a total of 442 observations. The dataset included date reference or source, province or state, latitude and longitude of study sites, soil texture, clay content, soil pH, soil organic carbon (SOC), average precipitation (including irrigation water) and air temperature for the study period, crop, standard deviation and standard error of treatment means, standard deviation and standard error of comparison or control treatment, N-addition rate, fertilizer source, inhibitor type (nitrification, urease and double inhibitor), cumulative growing season N₂O emission of treatment, cumulative emission of comparison or control treatment, year, emission factor (kg N₂O-N kg⁻¹ added N), number of treatment replicates for a trial, timing of fertilizer application, method of fertilizer placement. Data were extracted from those studies in which the application of fertilizers with varying sources, rates, placement methods and timings were used. Soil characteristics (soil texture, clay content, pH, SOC), geographical location (latitude, longitude) and climate variables (air temperature and precipitation) were obtained directly from the publications.

All primary data were derived from the text, appendices, figures, tables and supplementary tables/figures from each individual publication. When data were given in graphic format, Web plot digitizer (v3 exe) was used to extract data (Li et al., 2021). The dataset was sub-divided to find out the effect of different variables on N₂O emissions such as: precipitation into two groups: greater than 350 mm precipitation and less than 350 mm precipitation and soil organic carbon as: higher than 30 g kg⁻¹ and lower than 30 g kg⁻¹. In addition, studies were subdivided into three soil pH categories: acidic (<7), neutral (7-8) and alkaline (>8). Soil texture was a categorical variable and independent moderator, grouped into three major classes sand (sandy loam, sandy clay loam,

loamy fine sand, fine loam), silt (silt clay, silt clay loam, silt loam,) and clay (clay loam, heavy clay) according to USDA (1999). If soil texture was not reported, it was acquired using the location information or the amount of clay content present per USDA (1999). Data not reported in the study were obtained by contacting the respective authors.

2.3.2 Data analysis

The effect of source, placement, and timing of nitrogen application cumulative N₂O emission was estimated using the natural logarithm of the response ratio (*lnRR*) as effect size (Kuang et al., 2021).

$$\ln RR = \ln \left(\frac{x_{ti}}{x_{ci}} \right) = \ln(x_{ti}) - \ln(x_{ci})$$

Where x_{ti} and x_{ci} are the mean values of cumulative N₂O emissions (kg N₂O-N ha⁻¹) for the treatment group and comparison or control of the i^{th} observation, respectively. For the source variable, the treatments were application of EEFs with conventional N fertilizers as the control (urea, UAN). For the time variable, the treatment was fall application with spring application as the control. For the method of placement, treatment was banding (deep band, shallow band, side band, midrow band) while broadcasting (surface broadcast and broadcast-incorporation) was used as the control.

Further, the variance of effect size was calculated as:

$$v = \frac{SD_{ti}^2}{x_{ti}^2 \times n_{ti}} + \frac{SD_{ci}^2}{x_{ci}^2 \times n_{ci}}$$

Where SD_{ti}^2 and SD_{ci}^2 are the standard deviations of mean values of cumulative N₂O emissions for the treatment group (x_{ti}) and comparison or control (x_{ci}) of the i^{th} observation, n_{ti} and n_{ci} represent

the number of replicates for treatment and control of the i^{th} observation, respectively. Standard deviations were considered as most of the studies generally reported it.

Soil organic matter was converted to SOC using a conversion factor of 0.58 (Pribyl et al., 2010). Missing standard deviation values in the dataset were estimated using “metagear” package in R (Bracken et al., 1992; Kuang et al., 2021). If the standard deviation (SD) was not reported, it was calculated using the formula:

$$SD = SE \times \sqrt{n},$$

where n is the sample size and SE is the standard error.

For each study, the total variance was considered as the sum of between-study and within-study variance $v^* = v_b + v_w$. Between study variance was estimated using the restricted maximum likelihood method (REML, Veroniki et al., 2016). A nonparametric weighting function was used to weigh every study individually (Kuang et al., 2021; Hedges et al., 1999). The weighting factor was calculated as the inverse of pooled variance ($w = 1/v^*$). If a study had multiple observations, the weight was adjusted by the total number of observations from that study. Thus, the final weight was calculated as:

$$w^* = \frac{w}{e} = \frac{1}{e(v_b + v_w)} \text{ where, } e \text{ is the effect size.}$$

Then, weighted effect size was calculated as:

$$e^* = w^* \times e$$

Further, the mean effect size was calculated as:

$$\text{Mean effect size} = \sum e^* / \sum w^*$$

We used a mixed effect model with “metafor” and “metaforest” packages in R Version 4.2.2 (R Core Team, 2020) to analyze the impact of source, method of placement and timing of

fertilizer application on N₂O emissions. The fixed factors include crop type, precipitation levels, soil organic carbon, soil pH and soil texture. The random factors include year of N₂O emission and study sites. Since, some studies contributed more than one effect size, each “observation” was treated as a random factor to deal with within-study non-independence in observations (Yin et al., 2023). The effect was considered significant if the 95% confidence intervals of the response variable did not overlap with zero. Additionally, a mixed-effect analysis was conducted to determine the relationship between N₂O emissions and continuous (mean seasonal precipitation, SOC, pH) and categorical (soil texture, inhibitors, crop) factors. The association between the effect size of N₂O emissions and both continuous and categorical moderators was deemed significant at $p < 0.05$. Publication bias was assessed using the Egger’s regression test and Funnel plots method (Egger et al., 1997).

Furthermore, a random forest analysis was conducted, for only those datasets which showed an overall significant impact, using the R package, rfPermute, to assess the significance and contribution of each factor influencing the response of N₂O emissions to 4R nitrogen management. The considered factors consisted of crop, SOC, mean air temperature for the study period, mean precipitation for the study period, soil texture, and soil pH. For generating the forest trees, three essential parameters were required including (a) the number of trees to be generated in the forest; (b) the minimum number of observations at the tree’s terminal nodes; and (c) the number of variables to be chosen and assessed for the optimal split during the tree-growing process. The forest was configured to generate 1,000 trees as a greater numerical value will lead to more reliable estimations of variable significance (Reese et al., 2014). The square root of the variable count was designated as the parameter for node splitting, and the minimum number of observations at the terminal nodes was established as 5 (Ren et al., 2019). This analysis produces numerous trees but

ultimately yields a singular prediction characterized by low variance and low bias. Random forest analysis uses permutation importance to determine which variables most significantly affect target variables, and it ranks the importance of predictors in explaining the variation in effect size.

2.4 Results

The dataset used for analysis were comprised of conventional urea, nitrification inhibitor, dual inhibitor, urease inhibitor, polymer coated urea and urea ammonium nitrate as the main sources. The nitrification inhibitors included DMPSA, and Nitrapyrin; urease inhibitors include LIMUS, and Agrotain; dual inhibitors include Super-U having a nitrification inhibitor (DCD) and an urease inhibitor (NBPT). The timing of fertilizer application included fall and spring. The different methods of fertilizer placement included deep banding, shallow banding, midrow banding, side banding, broadcast-incorporation and broadcast. The major crops included in the dataset were wheat, corn, canola, potato, and barley.

The application of nitrification inhibitors with urea, had total 48 observations out of which 5 observations included the use of DMPSA, and 43 observations included Nitrapyrin. The use of dual inhibitor and PCU with urea resulted in 77 observations and 116 observations, respectively. For urease inhibitor in the urea analysis, there were a total of 24 observations, out of which in 21 observations the fertilizer was banded (midrow, deep) whereas in the remaining 3 observations the fertilizer was surface applied. The UAN analysis section had 22 observations with NI (Agrotain Plus, Nitrapyrin, Nfusion) products. Furthermore, the banding of fertilizer versus broadcast-incorporation included 47 observations with further sub-divisions: deep banding with 20 observations, shallow banding with 27 observations among banding depths, and side banding with 23 observations, midrow banding with 24 observations among banding positions. However,

banding versus surface application of fertilizer resulted in only 15 observations with further classification resulting in 7 observations for deep banding, 8 observations for shallow banding for banding depths, whereas 6 observations for side banding, 9 observations for midrow banding for banding positions. For the time of fertilizer application (fall versus spring), it included 108 observations. It should be noted that some categories in the dataset had some missing values so the number of observations would not add up to the total number of observations for the specific dataset.

2.4.1 Effect of EEFs on reduction of N₂O emissions

Nitrification Inhibitors with Urea

Compared to conventional urea alone, the use of urea together with nitrification inhibitors (DMPSA, Nitrapyrin) significantly ($p=0.01$) reduced N₂O emission by 35% ($\pm 21\%$, 95% confidence interval) (Fig 2.1). Regarding crop type, NIs significantly reduced N₂O emissions by 45% ($\pm 28\%$) in wheat production systems but did not show a significant effect in potato and canola production. NIs were effective when precipitation was greater than 350 mm, with a significant reduction of 36% ($\pm 22\%$). Similarly, when precipitation was less than 350 mm, a significant reduction of 53% ($\pm 22\%$) was observed. Amongst the soil properties, NIs were effective and significantly reduced N₂O emissions by 40% ($\pm 34\%$) when SOC was greater than 30 g kg⁻¹ and by 31% ($\pm 28\%$) when SOC was less than 30 g kg⁻¹. In addition, a significant ($p=0.01$) reduction of approximately 41% ($\pm 34\%$) was observed when soil pH was between 7 to 8. Regarding soil texture, NIs significantly reduced N₂O emissions by 44% ($\pm 32\%$) in clay soils. However, the effectiveness of NIs in reducing N₂O emissions was insignificant when pH was less than 7 and greater than 8, and when soil texture was silt and sand.

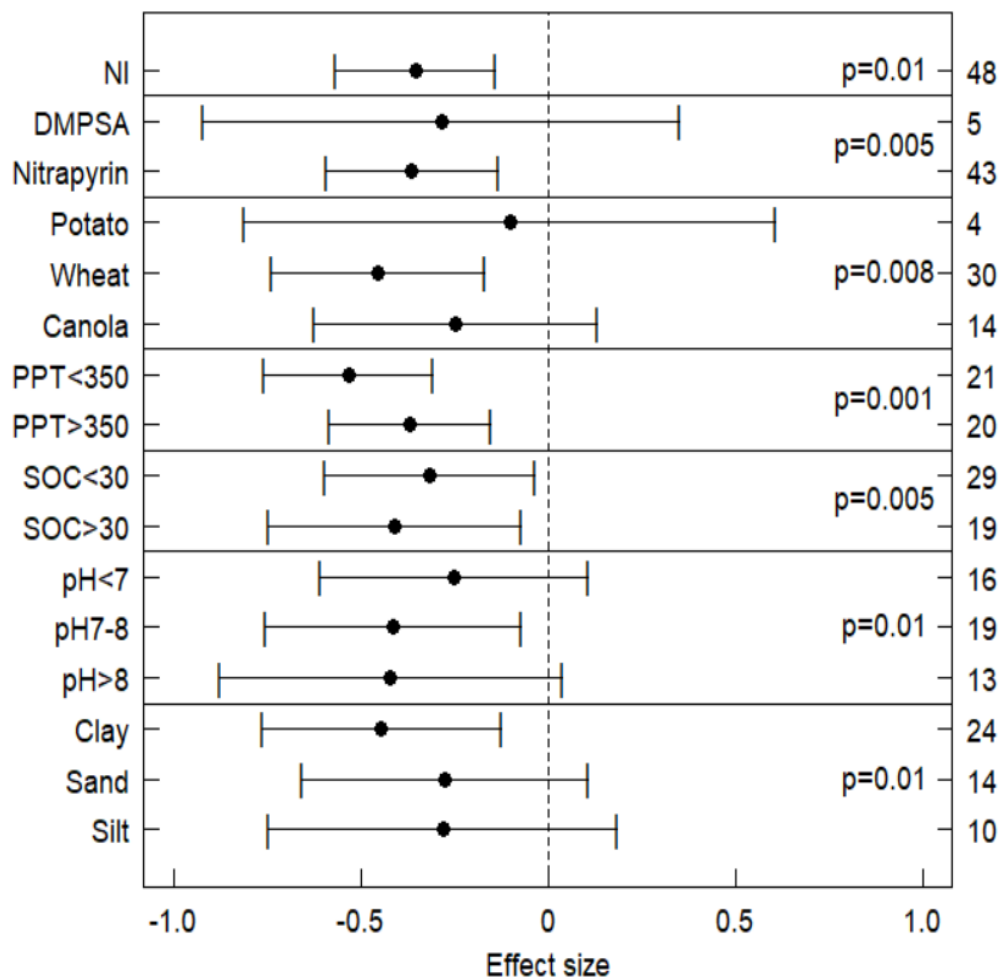


Figure 2.1 Effect of nitrification inhibitors on N₂O emission reduction from conventional urea application as influenced by soil, environmental and crop factors. The figure displays the means of the effect size along with their corresponding 95% confidence intervals. Number of observations for each variable are shown on the right axis. The effect was considered statistically significant ($p < 0.05$) if the 95% confidence interval of the effect size did not overlap with zero.

The random forest analysis showed that SOC, mean seasonal precipitation, soil pH and crop type were the most significant factors that contributed, 24%, 19%, 12% and 12% respectively,

to the variation of NIs impact on N₂O emission reduction (Fig 2.2). Contrastingly, the contribution of mean seasonal air temperature and soil texture was not significant.

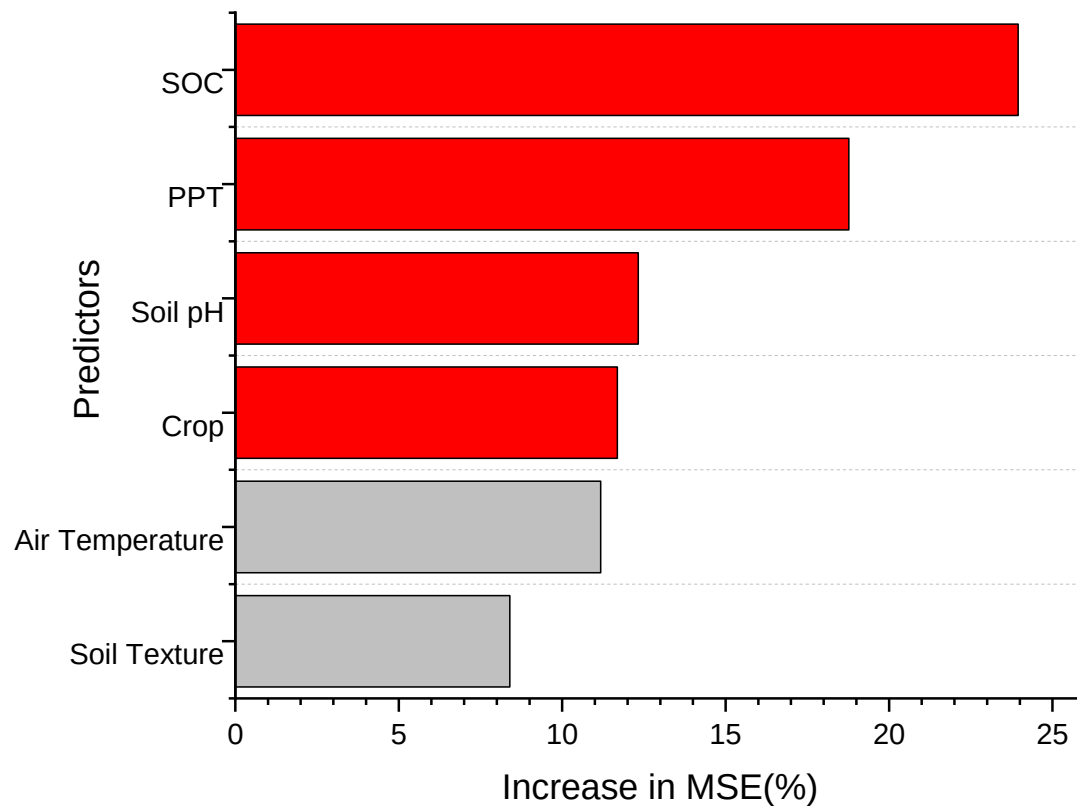


Figure 2.2 Random Forest analysis identifying the main predictors of N₂O emission reduction in response to addition of nitrification inhibitors. Mean squared errors (MSE %) show the importance of main predictors. The red bars reflect the predictors with significant ($p < 0.05$) contributions.

Dual Inhibitor with Urea

The use of the dual inhibitor, Super-U (DCD+NBPT), significantly ($p = 0.001$) reduced N₂O emissions by 48% ($\pm 10\%$, 95% confidence interval) compared to the conventional urea, across all studies (Fig 2.3). The only exception was for potato, where Super-U did not show a significant

impact on N₂O emission. In contrast, Super-U significantly ($p<0.005$) reduced N₂O emissions by 64% ($\pm 21\%$) in canola, by 66% ($\pm 20\%$) in corn, and by 48% ($\pm 13\%$) in wheat. Irrespective of the considered environmental and soil factors including mean seasonal precipitation, SOC, soil pH and soil texture, Super-U consistently and significantly reduced N₂O emissions by 37%-57%.

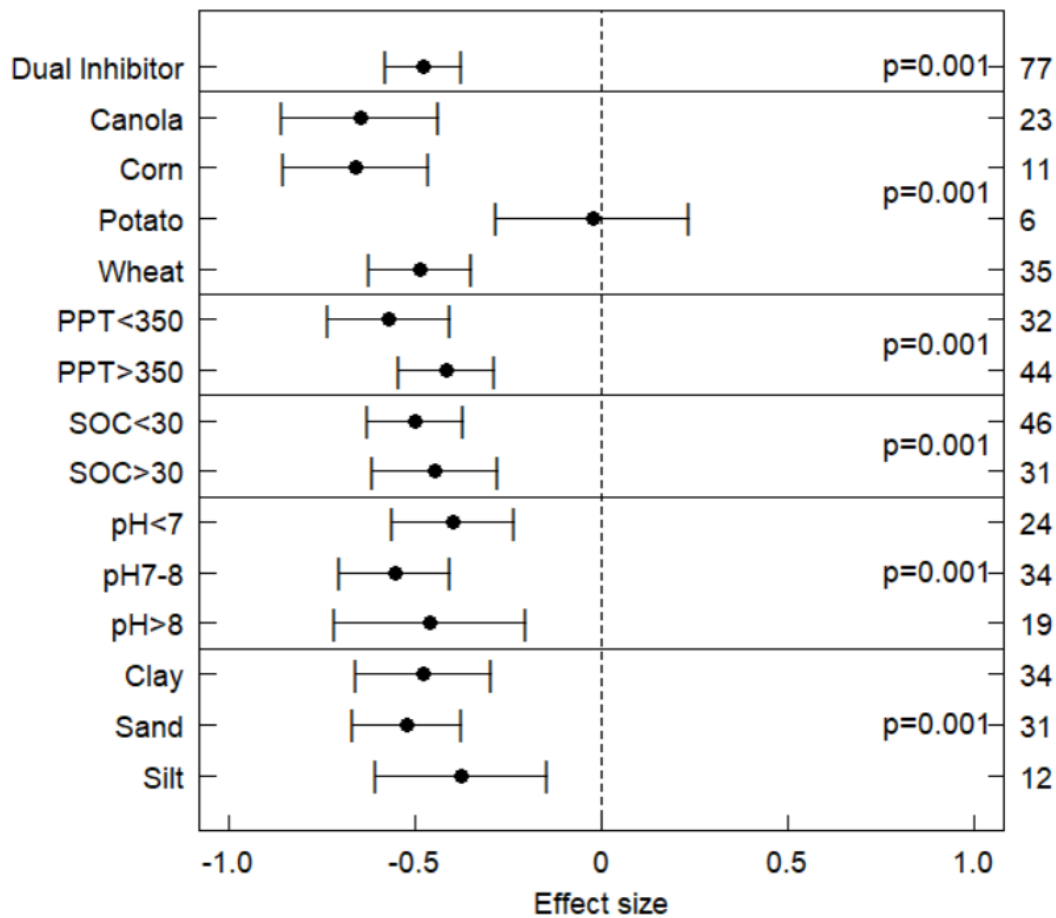


Figure 2.3 Effect of the addition of the dual inhibitor, Super-U, on N₂O emission reduction from conventional urea application as influenced by soil, environmental and crop factors. The figure displays the means of the effect size along with their corresponding 95% confidence intervals. Number of observations for each variable are shown on the right axis. The effect was considered statistically significant ($p<0.05$) if the 95% confidence interval of the effect size did not overlap with zero.

The random forest analysis showed that all tested variables including SOC, mean seasonal air temperature, soil texture, and soil pH were significant contributors to the effectiveness of Super-U in reducing N₂O emission, accounting for 19%, 17%, 17%, and 13%, respectively (Fig 2.4). Mean seasonal precipitation and crop type did not show a significant role.

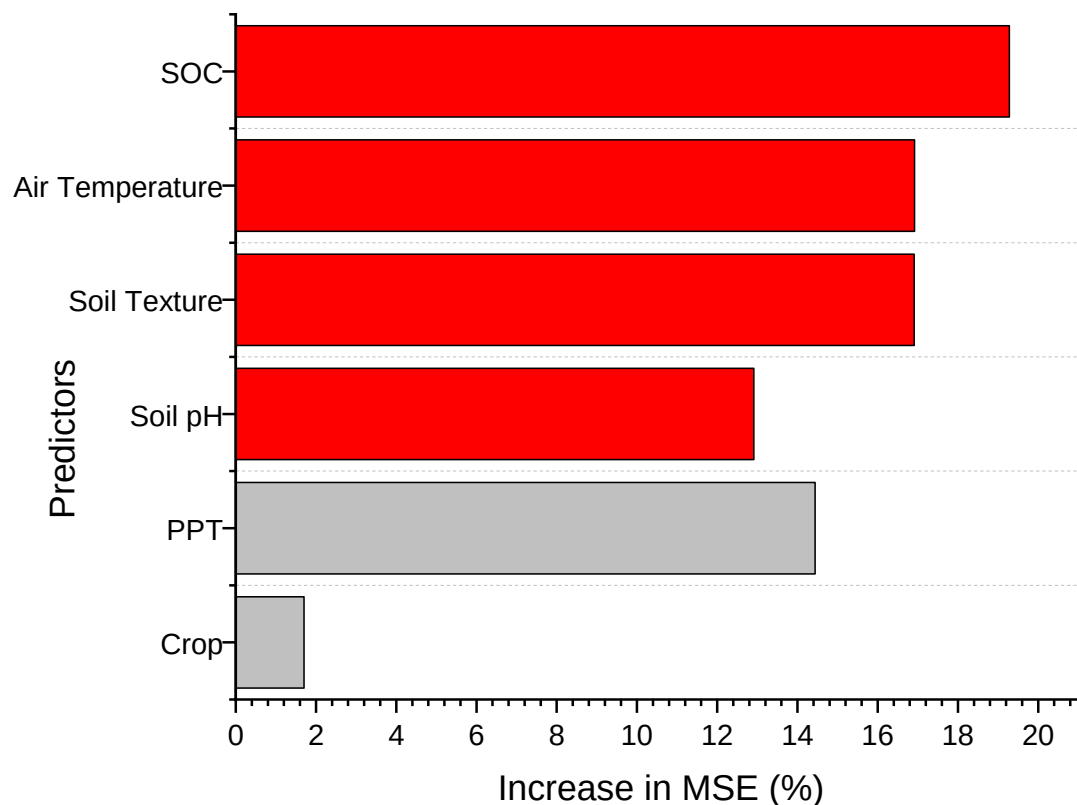


Figure 2.4 Random Forest analysis identifying the main predictors of N₂O emission reduction in response to the addition of dual inhibitor, Super-U (DCD + NBPT). Mean squared errors (MSE %) show the importance of main predictors. The red bars reflect the predictors with significant ($p < 0.05$) contributions.

Urease Inhibitors with Urea

The addition of urease inhibitors to urea did not significantly affect N₂O emissions (Fig 2.5). The use of Agrotain numerically increased emissions by 11%, but the difference was not statistically significant. In contrast, the application of LIMUS numerically decreased emissions by 17%. None of the considered factors showed a significant impact on N₂O emissions in response to UI applications.

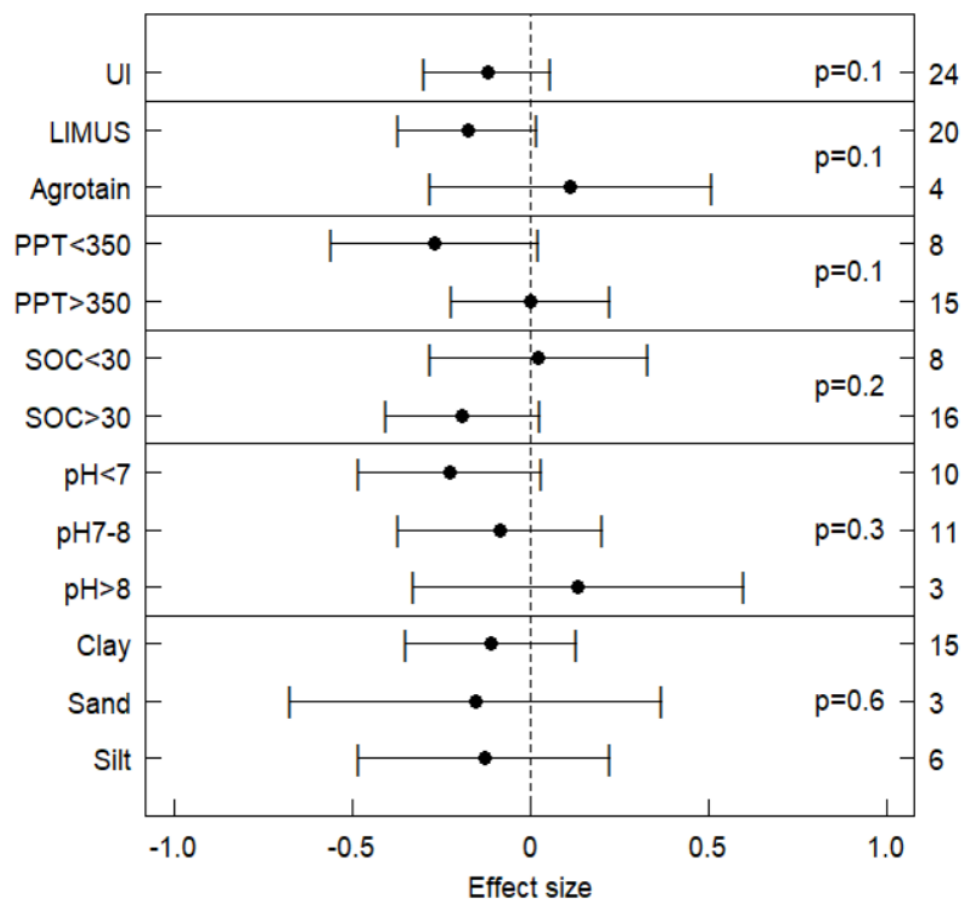


Figure 2.5 Effect of urease inhibitors on N₂O emission reduction from conventional urea application as influenced by soil, environmental and crop factors. The figure displays the means of the effect size along with their corresponding 95% confidence intervals. Number of observations

for each variable are shown on the right axis. The effect was considered statistically significant ($p < 0.05$) if the 95% confidence interval of the effect size did not overlap with zero.

Polymer Coated Urea

Across all the 116 observations included in the analysis, PCU significantly reduced N_2O emissions by 16% ($\pm 9\%$, 95% confidence interval) compared to conventional urea (Fig 2.6). For crop types, corn showed a significant ($p = 0.001$) reduction in N_2O emissions by 46% ($\pm 22\%$). Barley, canola, potato, and wheat also showed a trend of reduction, even though the differences were not statistically significant. Considering environmental conditions, PCU significantly ($p = 0.007$) reduced N_2O emissions by 18% ($\pm 14\%$) and 16% ($\pm 11\%$) when precipitation was less and more than 350 mm, respectively. For soil properties, PCU significantly ($p = 0.001$) reduced N_2O emissions by 23% ($\pm 11\%$) when SOC was less than 30 g kg^{-1} whereas the reduction was not significant when SOC was more than 30 g kg^{-1} . Additionally, the effectiveness of PCU on N_2O reduction was significant when soil pH was between 7-8 and soil texture was sand.

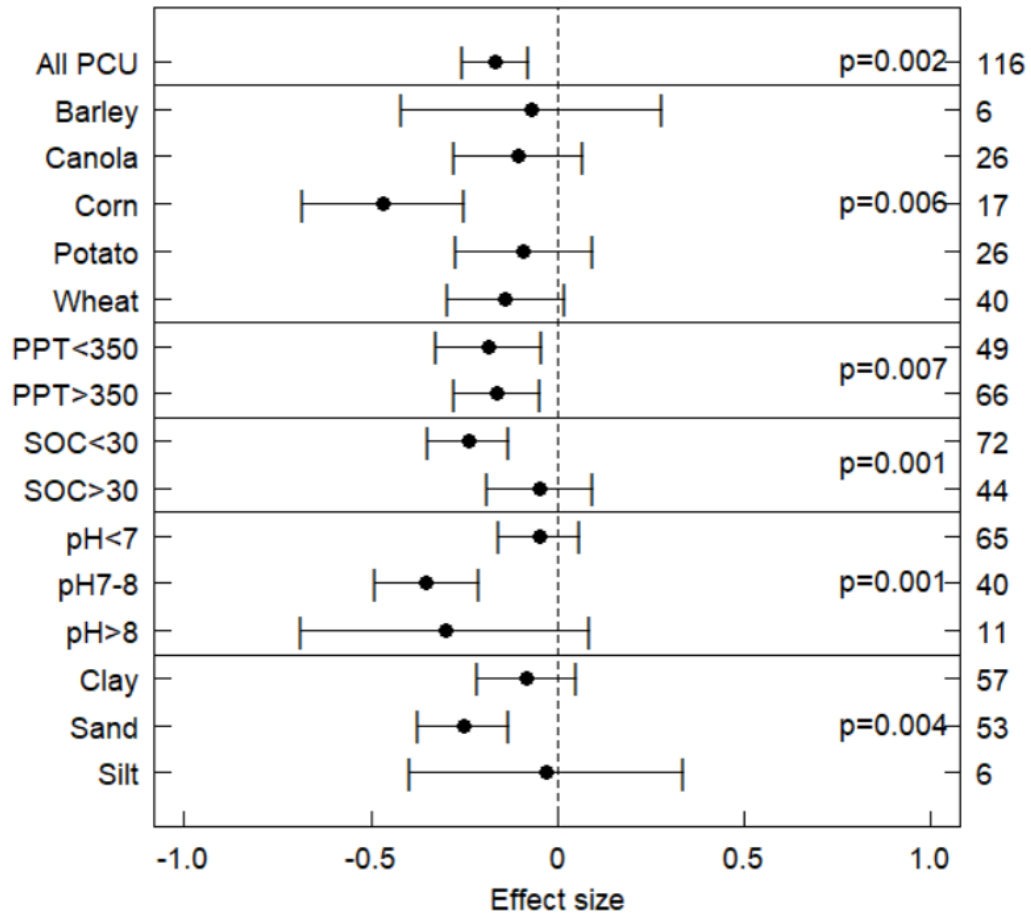


Figure 2.6 Effect of polymer coated urea on N_2O emission reduction from conventional urea application as influenced by soil, environmental and crop factors. The figure displays the means of the effect size along with their corresponding 95% confidence intervals. Number of observations for each variable are shown on the right axis. The effect was considered statistically significant ($p < 0.05$) if the 95% confidence interval of the effect size did not overlap with zero.

The random forest analysis showed that crop type, and soil texture were the most significant factors, contributing to the effectiveness of PCU on N_2O emission reduction, accounting for 12%, and 10%, respectively (Fig 2.7). In contrast, SOC, soil pH, mean seasonal air temperature and mean seasonal precipitation did not have a significant impact.

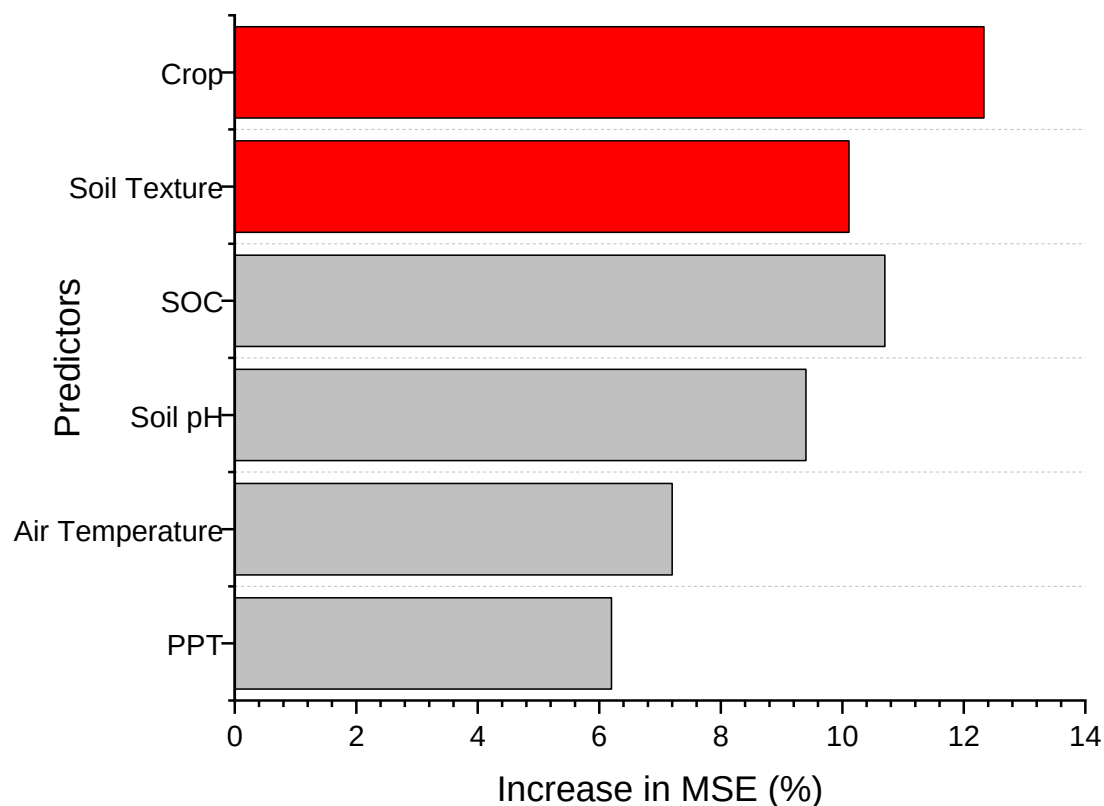


Figure 2.7 Random Forest analysis identifying the main predictors of N₂O emission reduction in response to addition of polymer coated urea. Mean squared errors (MSE %) show the importance of main predictors. The red bars reflect the predictors with significant ($p < 0.05$) contributions.

Products containing Nitrification Inhibitor with UAN

An analysis of the impact of products containing nitrification inhibitor along with UAN on N₂O emissions was conducted across different soil and environmental factors. The use of such products significantly ($p = 0.03$) reduced emissions by 17% ($\pm 17\%$, 95% confidence interval) across certain agronomic and environmental factors (Fig 2.8). When considering different crop production systems, a significant ($p = 0.03$) reduction of 18% ($\pm 18\%$) was observed for corn whereas no

significant impact was observed for wheat. Mean seasonal precipitation did not significantly affect the impact of nitrification inhibitors on N₂O emissions from UAN application. Among different soil properties, use of nitrification inhibitors significantly ($p=0.005$) reduced N₂O emissions by 39% ($\pm 22\%$) when SOC was less than 30 g kg⁻¹ but did not show any impact when SOC was higher. When soil pH was between 7-8, significant ($p=0.01$) reduction of 28% ($\pm 22\%$) was observed with no impact observed when the pH was less than 7 and greater than 8. Additionally, nitrification inhibitors significantly ($p=0.03$) reduced N₂O emissions by 18% ($\pm 18\%$) when soil texture was sand.

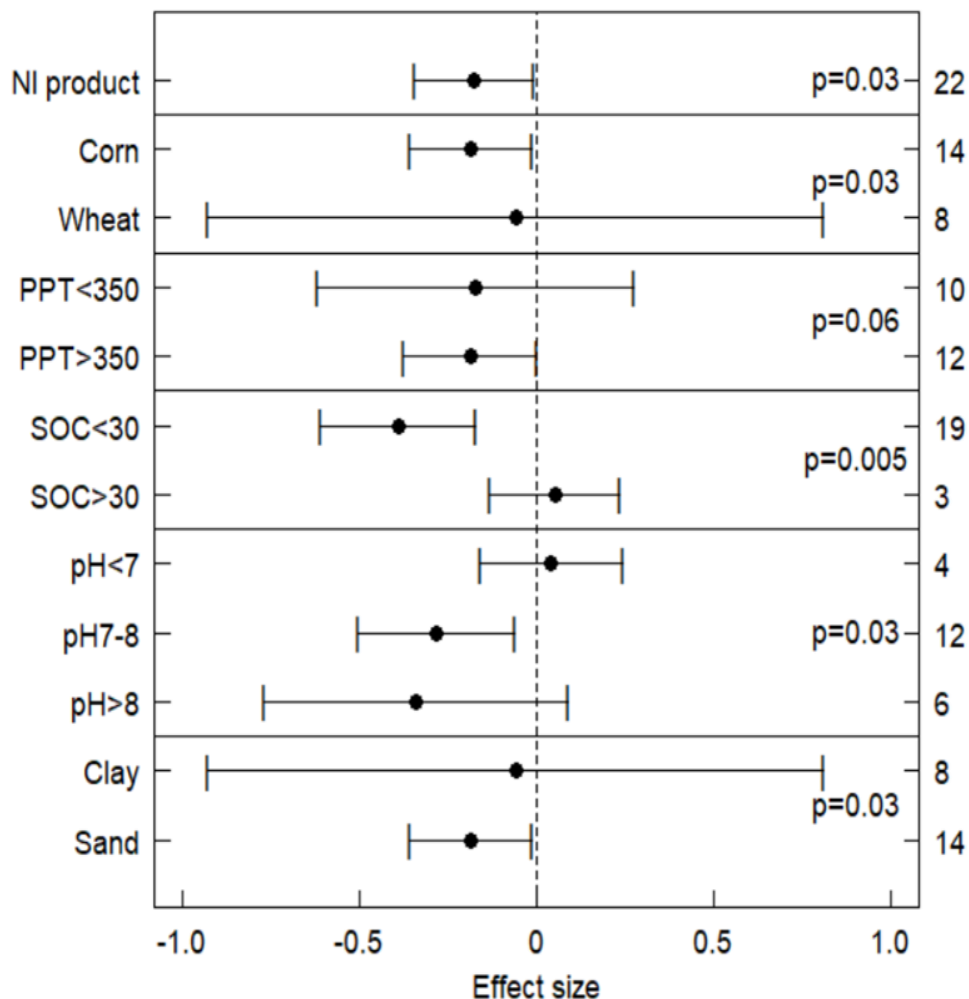


Figure 2.8 Effect of addition of nitrification inhibitor containing products on N₂O emission reduction from urea ammonium nitrate application. The figure displays the means of the effect size along with their corresponding 95% confidence intervals. Number of observations for each variable are shown on the right axis. The effect was considered statistically significant ($p < 0.05$) if the 95% confidence overlap of the effect size did not intersect with zero.

The random forest analysis showed that air temperature, and SOC were the most significant factors, contributing to the effectiveness of nitrification inhibitors on N₂O emission reduction, accounting for 13%, and 12%, respectively (Fig 2.9). In contrast, PPT, soil pH, soil texture, and crop type did not have a significant impact.

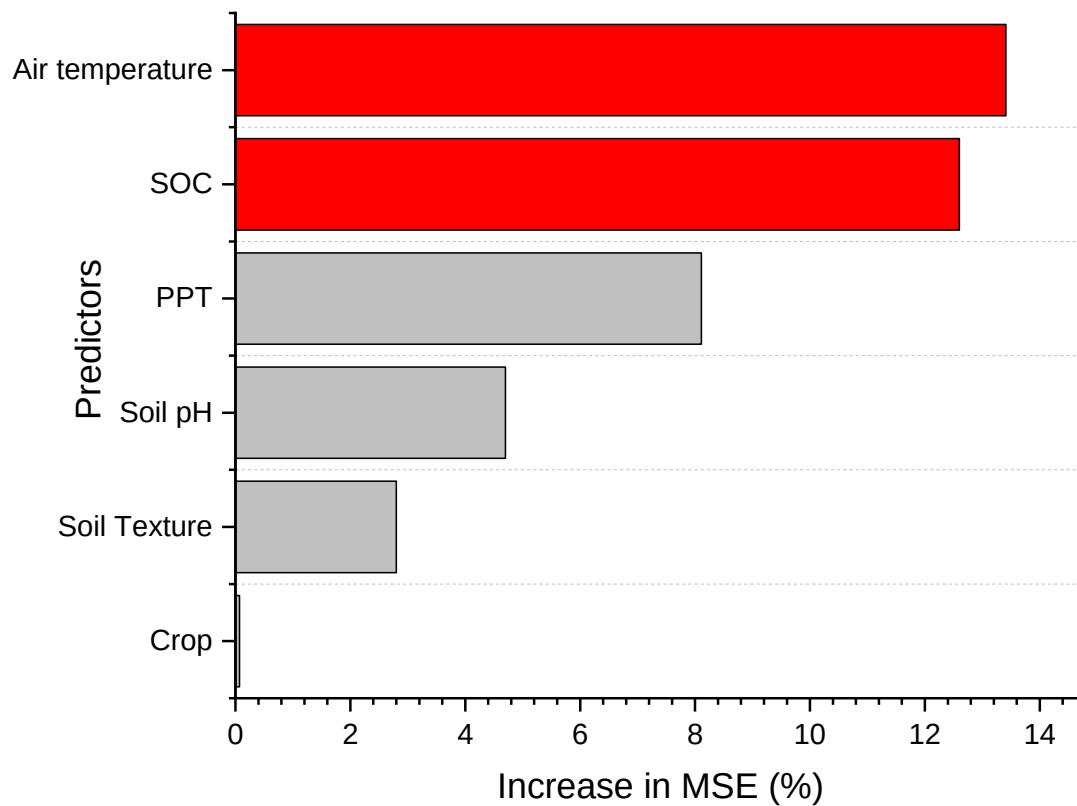


Figure 2.9 Random Forest analysis identifying the main predictors of N₂O emission reduction in response to addition of products containing nitrification inhibitors. Mean squared errors (MSE %) show the importance of main predictors. The red bars reflect the predictors with significant ($p < 0.05$) contributions.

2.4.2 Effect of method of fertilizer placement on N₂O emission reduction

Across all 47 paired observations, banding of fertilizer tended to decrease N₂O emissions by 4% ($\pm 19\%$, 95% confidence interval) as compared to broadcast-incorporation (Fig 2.10). When different banding depths were compared, deep banding (fertilizer was placed more than 6 cm deep) tended to decrease N₂O emissions by 16% ($\pm 29\%$), whereas shallow banding (fertilizer was placed

less than 6 cm deep) tended to increase N₂O emissions by 5% ($\pm 15\%$), but this difference was not statistically significant. When different banding positions were compared, both side banding and midrow banding tended to reduce N₂O emissions by 2% ($\pm 28\%$) and 4% ($\pm 28\%$) respectively, with the impact being non-significant. In case of certain factors like precipitation greater than 350 mm, and soil pH greater than 7, a trend of increasing N₂O emissions by 3-65% was observed. However, other environmental, and soil factors showed a trend of reduction in N₂O emissions by 3-22%.

When comparing different methods of banding with surface application of fertilizer, an increase of 14% ($\pm 17\%$) in N₂O emissions was observed, but this difference was non-significant (Fig 2.11). Across different banding depths, both deep and shallow banding tended to increase N₂O emissions by 3% ($\pm 19\%$) and 20% ($\pm 23\%$), respectively. Among different banding positions, side banding tended to reduce N₂O emissions by 11% ($\pm 18\%$) whereas midrow banding significantly increased N₂O emissions by 40% ($\pm 21\%$). In the canola production system, precipitation less than 350 mm, SOC greater than 30 g kg⁻¹, and clay textured soil, a significant increase in N₂O emissions by 40% ($\pm 21\%$), 20% ($\pm 19\%$), 72% ($\pm 42\%$), and 72% ($\pm 42\%$) was observed whereas in case of precipitation greater than 350 mm, a decreasing trend of N₂O emissions by 16% ($\pm 40\%$) was seen. Other soil factors, like SOC less than 30 g kg⁻¹, alkaline and acidic soil pH, and sandy soils showed an increasing trend with the impact being non-significant.

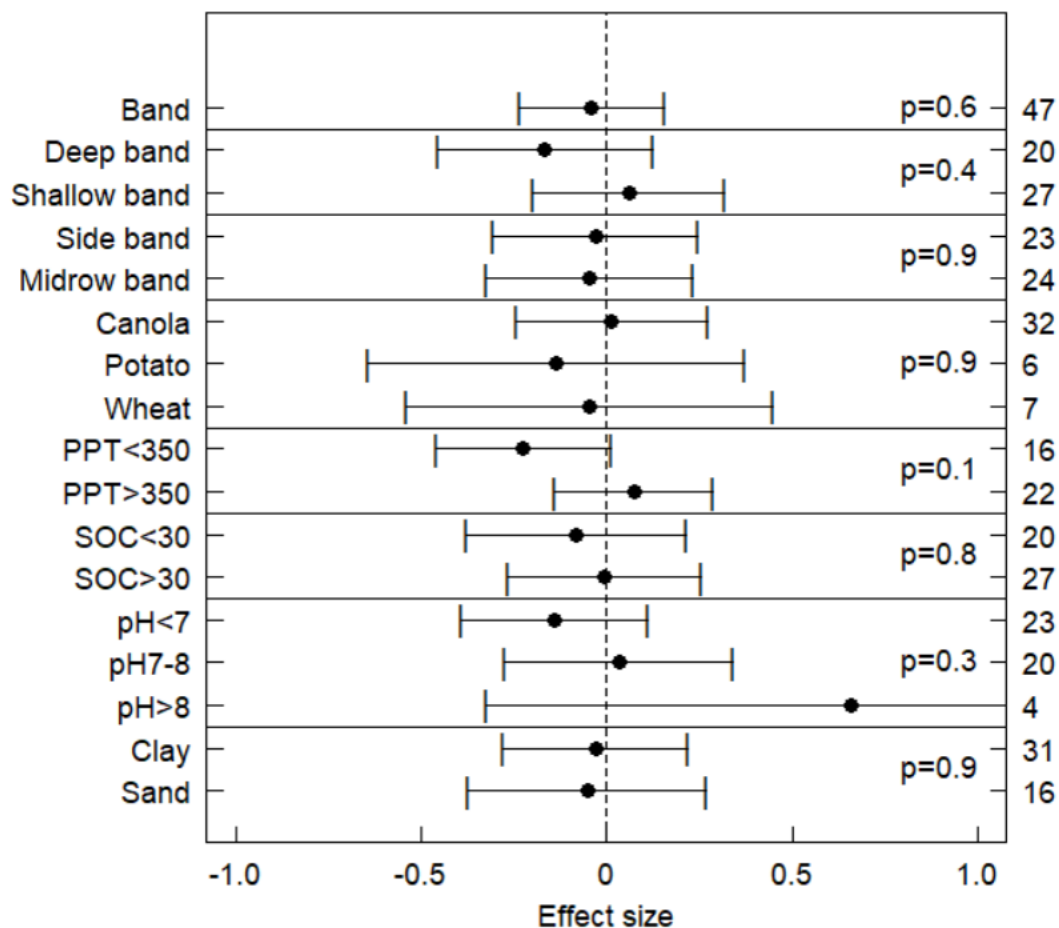


Figure 2.10 Effect of banding of fertilizer versus broadcast-incorporation on N₂O emission reduction as influenced by soil, environmental and crop factors. The figure displays the means of the effect size along with their corresponding 95% confidence intervals. Number of observations for each variable are shown on the right axis. The effect was considered statistically significant ($p < 0.05$) if the 95% confidence interval of the effect size did not overlap with zero.

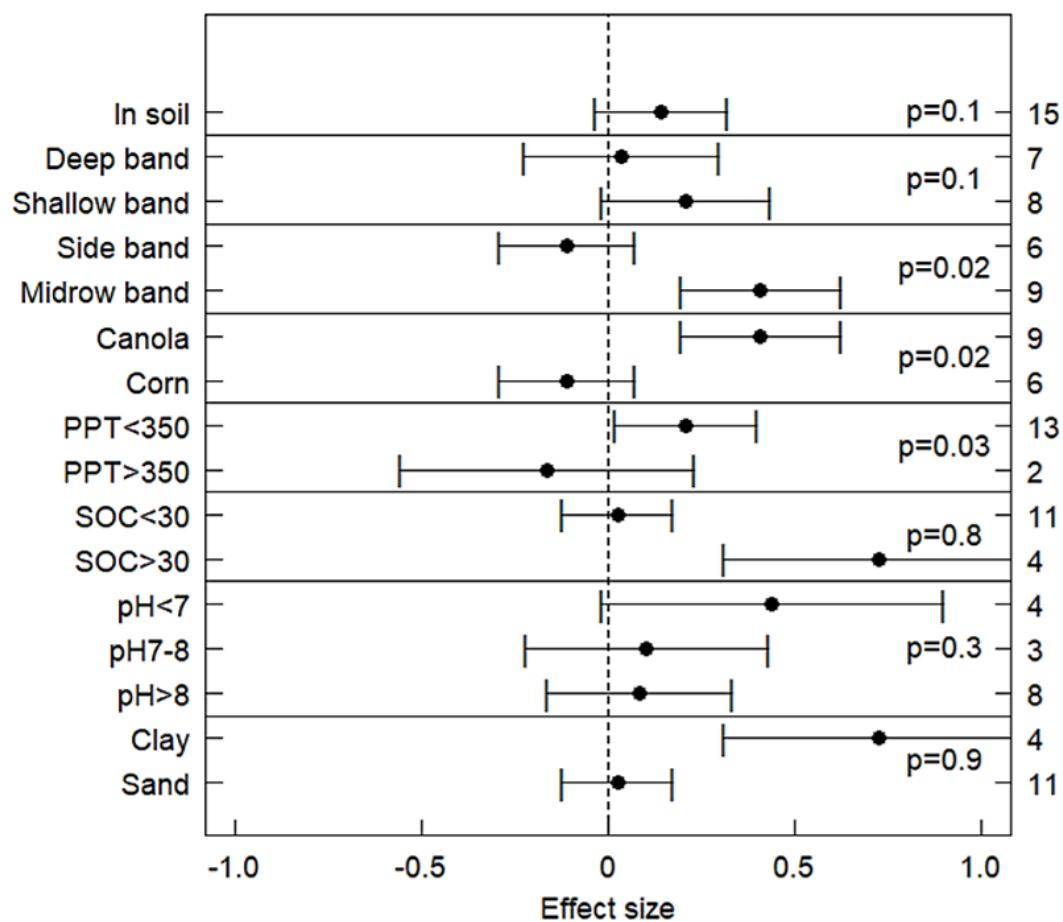


Figure 2.11 Effect of banding of fertilizer versus surface application on N₂O emission reduction as influenced by soil, environmental and crop factors. The figure displays the means of the effect size along with their corresponding 95% confidence intervals. Number of observations for each variable are shown on the right axis. The effect was considered statistically significant ($p < 0.05$) if the 95% confidence interval of the effect size did not overlap with zero.

2.4.3 Effect of time of fertilizer application on N₂O emission reduction

Compared to spring application, fall application generally resulted in comparable N₂O emissions whereas the impact was significantly affected by soil pH and soil texture (Fig 2.12). Specifically, fall application significantly reduced N₂O emissions than spring application by 16% ($\pm 16\%$, 95% confidence interval) at soil pH <7. In contrast, for alkaline soils with pH >7, fall application resulted in 23% ($\pm 30\%$) higher N₂O emissions. Fertilizer timing impact on N₂O emissions was also affected by soil texture where fall application resulted in 37% ($\pm 23\%$) significantly lower N₂O emissions for silt soils but not for clay or sandy soils. It is important to note that only 7 out of 99 observations were from sandy soils, which could bias the results towards clay soils. Other factors including crop type, precipitation and SOC did not show a significant impact.

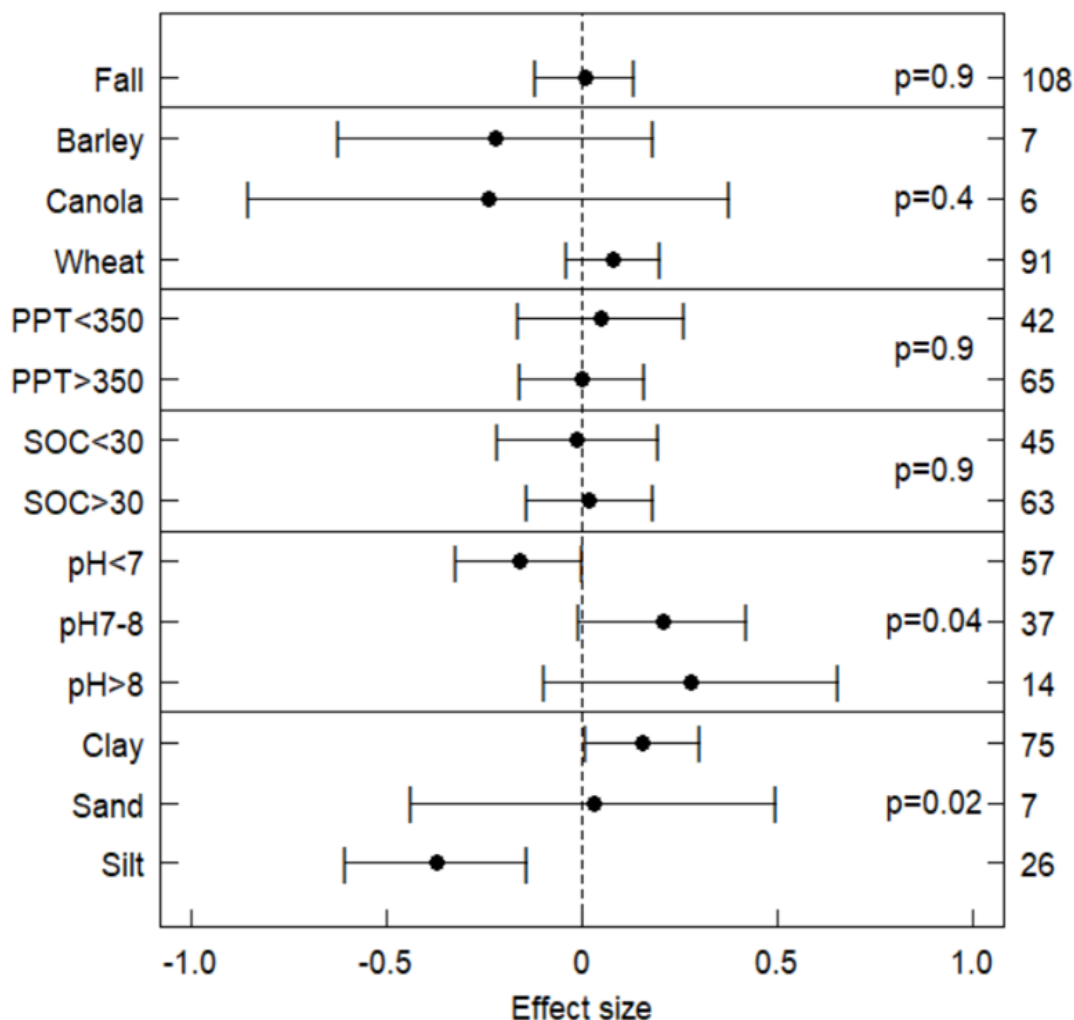


Figure 2.12 Effect of time of fertilizer application on N₂O emission reduction as influenced by soil, environmental and crop factors. The figure displays the means of the effect size along with their corresponding 95% confidence intervals. Number of observations for each variable are shown on the right axis. The effect was considered statistically significant ($p < 0.05$) if the 95% confidence interval of the effect size did not overlap with zero.

2.4.4 Effect of N fertilizer application rate on N₂O emission

On examining the dataset with 672 observations, we found a non-linear dependency of fertilizer-induced and soil background cumulative N₂O emissions on N rate (Fig 2.13). The N input range

in the dataset was up-to 285 kg N ha⁻¹ (with both conventional and EEFs as source) and N₂O emissions increased up-to 50 kg N₂O-N ha⁻¹. For the overall dataset, cumulative N₂O emissions showed an increasing trend with increasing N rate. We also noted that the relationship was highly driven by some extremely high emissions observed in a study which used three different cultivars of potato in an irrigated production system on the sandy loam soils of North Dakota.

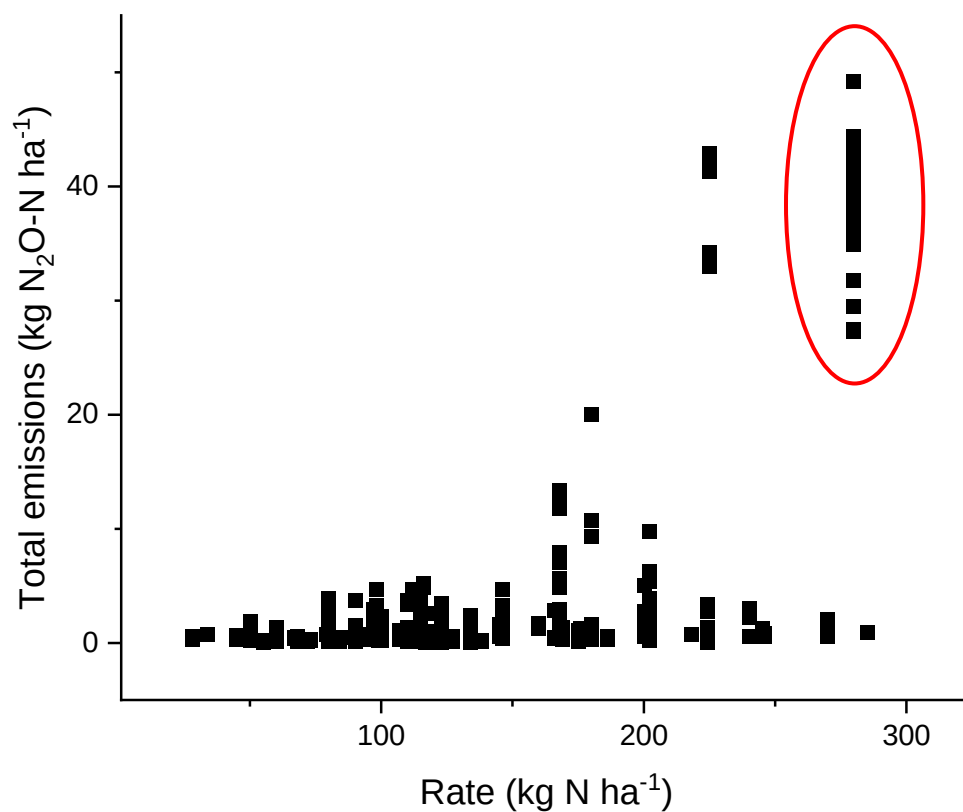


Figure 2.13 Increasing trend of fertilizer-induced and soil background cumulative N₂O emissions with N input rates across all studies. (The highlighted part shows highest emissions observed from a single study).

The dataset with 672 observations was sub-divided into three rate categories, 0-100 kg N ha⁻¹, 101-200 kg N ha⁻¹, and 201-300 kg N ha⁻¹ respectively, and plotted along with the cumulative N₂O emissions (Fig 2.14). It is clear from the figure that the highest emissions up to 50 kg N₂O-N ha⁻¹ were from a study which had greater than 200 kg ha⁻¹ of N rate, whereas the emissions were well below 20 kg N₂O-N ha⁻¹, when less than 200 kg ha⁻¹ of fertilizer rate was used.

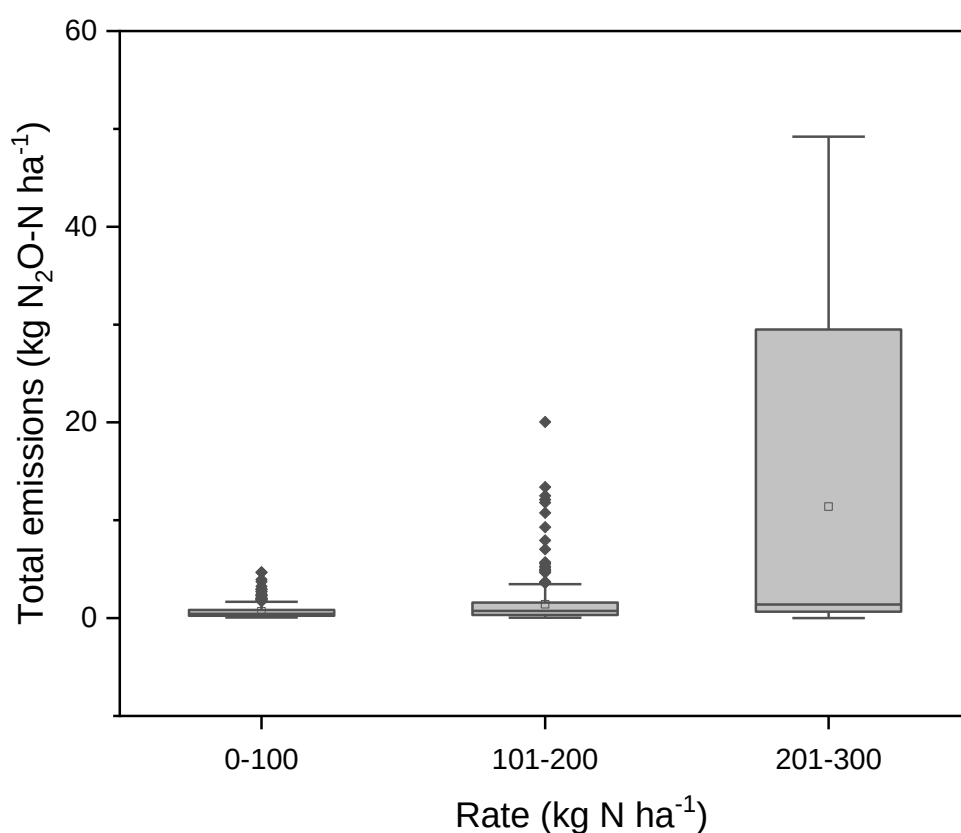


Figure 2.14 The figure displaying three different N fertilizer rate groups and the respective fertilizer-induced and soil background cumulative N₂O emissions.

For the overall dataset, fertilizer-induced cumulative N₂O emissions showed an increasing trend with increasing N rate (Fig 2.15). The N input range in the dataset was up-to 285 kg N ha⁻¹ and

N_2O emissions increased up-to $28 \text{ kg N}_2\text{O-N ha}^{-1}$. The negative emissions shown in the figure were from a study in which the control had higher emissions as compared to the treatment.

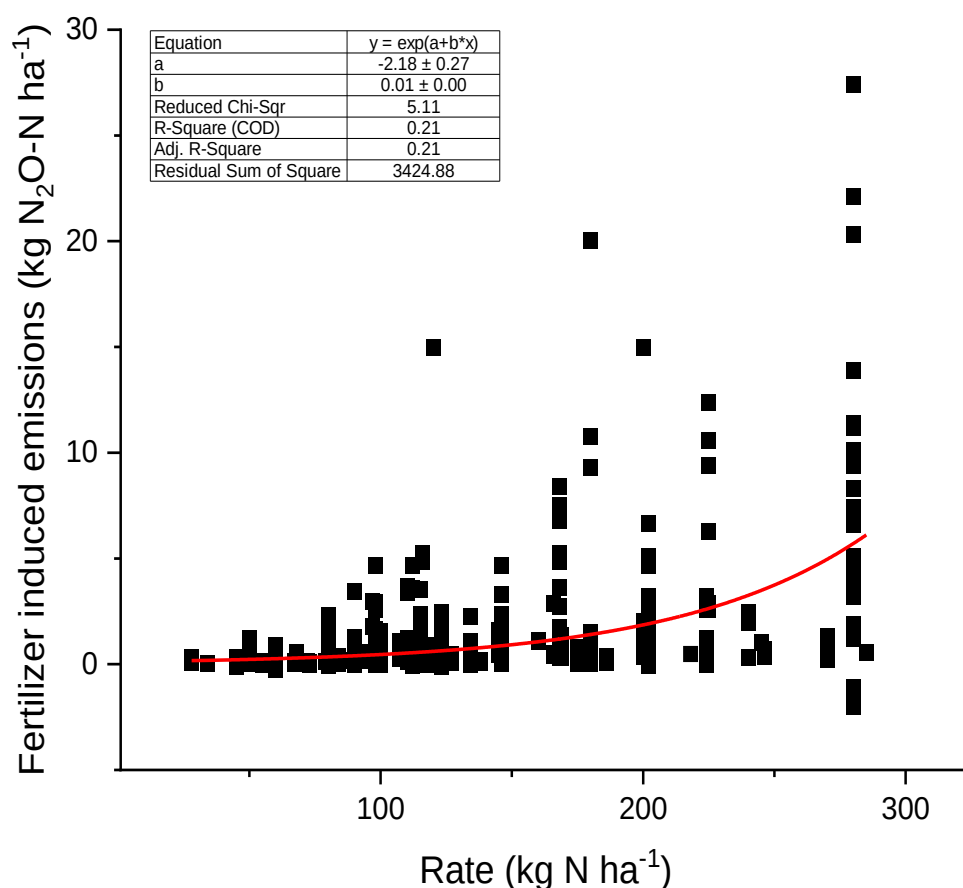


Figure 2.15 Increasing trend of fertilizer-induced cumulative N_2O emissions with N input rates (Exponential-fit model) across all studies.

Upon plotting the collected 672 fertilizer-induced cumulative N_2O emissions against N application rate (Fig 2.16), the highest emissions were found up to $28 \text{ kg N}_2\text{O-N ha}^{-1}$ and majority of the high emissions were from the study that used greater than 200 kg ha^{-1} of N rate whereas the emissions were below $20 \text{ kg N}_2\text{O-N ha}^{-1}$, when less than 200 kg ha^{-1} of fertilizer rate was used.

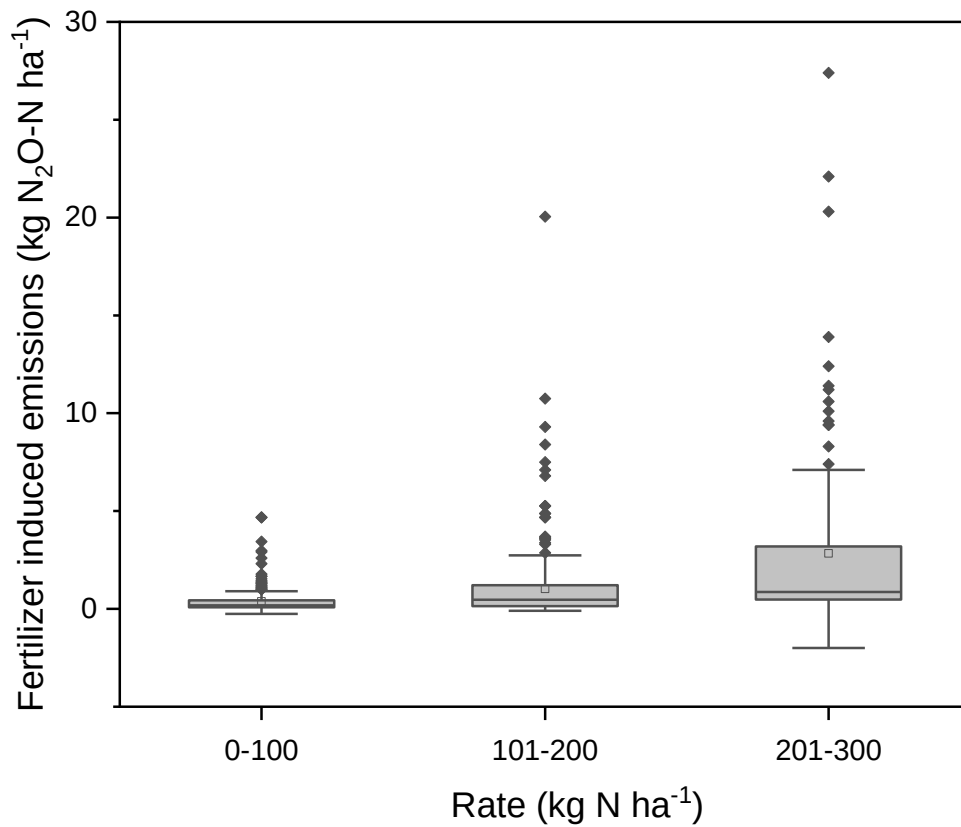


Figure 2.16 The figure displaying three different N fertilizer rate groups and the respective fertilizer-induced cumulative N₂O emissions.

2.5 Discussion

This study is distinct as it is the first to evaluate all the 4Rs and their impact on N₂O emission reduction from croplands across Canadian Prairies and those regions with similar climate conditions. This region typically experiences warm summer continental (Köppen Dfb) type of climate (Kottek et al., 2006). In the Canadian Prairies Chernozemic type of soil is prevalent, which is usually rich in organic matter and beneficial for agricultural practices (Pennock et al., 2011). Wheat and canola are the two main crops grown in the Prairies, accounting for almost 80% of N

fertilizer usage in the region (Tenuta et al., 2016). This use of synthetic fertilizers results in higher N losses, including N₂O emissions, ammonia volatilization, nitrate leaching and run-off. Although some individual studies in this region have evaluated the impact of a single 4R component (such as source) or its combination (such as time and source; placement and source) on N₂O emissions, more research is needed to determine the best combination of 4R practices in reducing N₂O emissions, specifically in cold climate regions.

2.5.1 Effect of EEFs

Inhibitors-incorporated products

The global meta-study conducted by Akiyama et al. (2010) and Thapa et al. (2016) estimated a 38% reduction in N₂O emissions with the use of nitrification inhibitors compared to conventional N fertilizers. Similarly, our meta-analysis based on 48 observations (9 studies) in cold climatic regions showed that the use of NIs (DMPSA, Nitrapyrin) effectively reduced N₂O emissions by 35% compared to conventional urea (Fig 2.1). Among these 48 observations, 44 observations were collected from the Black Soil Zones in Canadian Prairies and 4 observations from silt soils of Minnesota. It should be noted that due to the limited number of paired observations (43 for Nitrapyrin and 5 for DMPSA), we were not able to compare the effectiveness of each individual type of nitrification inhibitor across different environmental and soil factors. In other meta-studies, DCD was reported to reduce N₂O emissions by 30% while DMPP and nitrapyrin reduced emissions by 50% (Wolt et al., 2004; Akiyama et al., 2010). Thapa et al. (2016) concluded that DMPP, DCD and nitrapyrin were all effective in reducing N₂O emissions.

Urea ammonium nitrate is a liquid fertilizer which serves as a source of crop nutrition. Previous study has shown that surface application of UAN increases losses through ammonia

volatilization whereas banding UAN at more than 6 inches depth helps in lowering volatilization losses (Woodley et al., 2020). In this meta-analysis we evaluated the effectiveness of Agrotain Plus, Nfusion and Nitrapyrin on the reduction of N₂O emissions compared with UAN. The use of products containing NIs significantly reduced N₂O emissions from UAN by 17% (Fig 2.8). However, the limited number of studies (7 studies with 22 observations) prevented separate analysis of each inhibitor across different soil and environmental factors. Therefore, more field studies are required in cold regions to summarize the effect of liquid fertilizers along with the use of nitrification inhibitors. A study conducted on the loamy soils of Germany also proved that using NIs significantly reduced cumulative N₂O emissions by 42% compared to UAN application alone (Wang et al., 2020). Another study conducted on the clayey soils of Colorado showed 35% reduction in N₂O emissions with the use of product containing NI compared with UAN (Halvorson et al., 2010). Thus, NIs are generally effective in suppressing the activity of ammonia-oxidizing organisms in the soil, and thus slowing down the nitrification process.

Our results clearly showed that the effectiveness of NIs was affected by soil and environmental factors such as precipitation, SOC, soil pH and soil texture. NIs were more effective in alkaline soils, potentially due to improved retention of NIs and higher susceptibility to the nitrifier population in high pH soils compared to low pH soils (Yan et al., 2012; Feng et al., 2016). NIs were also more effective irrespective of the precipitation levels (more or less than 350 mm), in consistency with the results of previous findings (Chen et al., 2010; Lin et al., 2020; Pokharel et al., 2021; Fan et al., 2022). The oxygen availability in the soil is controlled by the moisture level, which in turn affects whether the primary pathway of N₂O production is aerobic nitrification or anaerobic denitrification (Wu et al., 2013). An increased moisture level near saturation would promote denitrification, leading to an increase in N₂O emissions (Butterbach et al., 2013). The use

of NIs could restrict the rate of nitrate production thereby inhibiting denitrification (Di et al., 2016). Further, NIs significantly reduced N₂O emissions more in fine than coarse textured soils. The reason could be that fine textured soils have greater cation exchange capacity and greater ability for NH₄⁺ adsorption, thereby reducing N₂O emissions and these results align with the previous conducted studies (Thapa et al., 2016). For soils with less organic carbon content, the application of NIs primarily target the activity of ammonia-oxidizing enzyme slowing down the conversion to nitrate thereby inhibiting the process of denitrification and less N₂O emissions (Bouwman et al., 2002).

The application of dual inhibitors (combined application of NI and UI) was more effective in reducing N₂O emissions compared to using NIs or UIs alone. The simultaneous use of NI and UI not only delays the breakdown of urea into NH₄⁺ but also prevents the conversion of NH₄⁺ into nitrate. This results in increased availability and a longer retention of NH₄⁺ in the soil. Thus, more nitrogen remains available for plant uptake leading to improved crop productivity or nitrogen use efficiency of crops and reduced requirement for nitrogen fertilizers (Thapa et al., 2016). In this study, Super-U (DCD + NBPT) was analyzed as a dual inhibitor as it is the most widely used inhibitor-based EEFs across the Canadian Prairies. Our results showed a 48% reduction in N₂O emissions across all the studies, in consistency with previous studies by Thapa et al. (2016), which reported a 38% reduction and Fan et al. (2022), which reported a 31% reduction. This indicate that dual inhibitors can be applied in various agricultural systems, offering flexibility and adaptability to different cropping practice. Also, a positive impact was seen on the yield of crops, being in consistency with the results from another studies (Thilakarathna et al., 2020; Tenuta et al., 2023). Thus, these are suitable for widespread adoption by farmers as their application offer multiple benefits for agricultural productivity and environment sustainability.

Urease inhibitors delay the transformation of urea into NH_4^+ , thereby decreasing the concentration of NH_4^+ in the soil solution and mitigating the potential for ammonia volatilization (Watson et al., 2005; Akiyama et al., 2010). In conjunction with the plant uptake, decrease in concentration of NH_4^+ can lead to a reduction in the amount of nitrogen potentially undergoing nitrification and denitrification. Being consistent with a previous meta-analysis (Akiyama et al., 2010), our analysis also indicated that overall use of UIs did not reduce N_2O emissions as compared to urea alone. The reason behind this could be that unlike nitrification, the hydrolysis of urea is not directly associated with N_2O emissions. The application of UIs specifically targets urea hydrolysis and therefore does not have a direct impact on N_2O emissions. However, UIs have the potential to reduce indirect N_2O emissions by reducing ammonia volatilization. In contrast to our results, based on 5 studies collected globally, Thapa et al. (2016) concluded that use of UIs significantly reduced N_2O emissions by 36% in corn systems, 28% in coarse textured soils, 32% in irrigated field conditions, and 19% in split application of N fertilizer. Another meta study reported 13% reduction in N_2O emission by use of UIs (Fan et al., 2022). This difference in result could be due to the global focus of the previous studies compared to regional focus of the current study. Since these conclusions were based on limited number of studies, more field studies need to be conducted to know the impact of UIs.

Regarding UIs, my analysis focused on two types (LIMUS and Agrotain), with LIMUS showing a 17% reduction in N_2O emissions, although this was not statistically significant. LIMUS contains two active ingredients, NBPT and NPPT, which makes it 40% more effective and it can block the activity of broader variety of urease enzymes. When SOC was higher than 30 g kg^{-1} , UI tended to decrease emissions by 19%, likely because soils with high SOC content exhibit improved structure and decreased occurrences of moist and anaerobic conditions. This could lead to

reduction in emissions of N_2O (Johannes et al., 2017). The efficacy of UI was more pronounced in acidic to neutral soils. The primary mechanism behind regulation of UI efficacy in alkaline soils is by affecting NH_3 volatilization (Rochette et al., 2013, Abalos et al., 2014). The increased NH_3 -N loss in high pH soils may indirectly reduce N_2O -N loss by decreasing the amount of inorganic nitrogen in the soil. This, in turn, limits the effectiveness of UI in mitigating NH_3 emissions but enhance its effectiveness in mitigating N_2O emissions (Fan et al., 2022). Compared to fine textured soils, coarse textured soil showed a greater reduction with UIs as these soils are well drained and have high aeration which facilitates nitrification process.

Polymer coated urea

PCU is a type of controlled-release fertilizers, which are designed to release nutrients gradually over an extend period, thereby providing a more consistent and sustained supply of nutrients to plants. The rate of release can be regulated by altering both the composition and thickness of the coating. PCUs have the potential to maximize nitrogen use efficiency and minimize nutrient losses through leaching, volatilization, run-off and N_2O emissions by synchronizing the N-release with the plant demand (Shaviv et al., 2001; Akiyama et al., 2010). In cases where nitrogen release from PCUs does not match with the plant demand, it can result in higher environmental losses and lower nitrogen use efficiency (Akiyama et al., 2010). A 2-year study on the Canadian Prairies demonstrated significant decrease in N_2O emissions from PCU at one of the two sites where conventional and zero tillage methods were used for growing canola and barley (Soon et al., 2011). In a Manitoba study on potato, Gao et al. (2017) reported 18% less emissions from ESN than conventional urea when both were band-applied at 200 kg N ha^{-1} . Also in Manitoba with spring wheat, Gao et al. (2015) showed that midrow banded ESN effectively reduced N_2O emissions by 47% compared to broadcast-incorporated urea in a wet year with warm early season conditions

but did not play a role in a dry year. Thapa et al. (2016) reported that PCU reduced N₂O emissions by 19%, aligning with this meta study that indicated a 16% reduction in emissions compared to conventional urea. Similarly, Akiyama et al. (2010) reported a 35% N₂O emission reduction with the application of PCUs. These studies consistently demonstrate a benefit of PCUs in reducing N₂O emissions at a regional or global scale, whereas the effectiveness or magnitude of reduction is highly dependent on various environmental and management factors.

Our analysis also indicated that PCU significantly reduced N₂O emissions by 46% in corn production system. Compared to other test crops such as wheat and canola, corn generally has a high N requirement, necessitating a high rate of N application. As a result, use of PCU was more effective to reduce the potentially higher N₂O emissions from corn systems. In case of less precipitation, PCU showed low emissions due to the prevalence of dry soil conditions. Use of PCU significantly mitigated N₂O emissions by 34% in neutral to alkaline soils. This decrease in emissions can be attributed to the fact that alkaline soil pH promotes loss of nitrate which intensifies the availability of N for nitrification and denitrification process (Kyveryga et al., 2004; Feng et al., 2016). A significant reduction of 24% was observed in coarse soils, whereas in fine and medium soils no significant reduction was observed. This was different from the results by Feng et al. (2016) who reported that PCUs were more effective with fine-textured soils. A field study suggested that clay soil with high cation exchange capacity exhibit greater adsorption of NH₄⁺ compared to sandy soil which ultimately hinders the release of nitrogen from PCU (Jarecki et al., 2008). This means that sandy soils have a reduced ability to hold ammonium, allowing the controlled-release mechanism of PCUs to function more effectively. Higher effectiveness with sandy soils could be also related to that sandy soils tend to warm up and cool down more rapidly

than fine-textured soils, which can enhance the diffusion of N from PCUs, aligning better with plant uptake.

2.5.2 Effect of method of placement

Banding fertilizer application is a common agricultural practice that involves placing fertilizer in concentrated bands rather than broadcasting it uniformly across a field. In the Canadian Prairies, it is advisable to apply N fertilizer in concentrated bands (at least 8 cm deep) as this method helps to decrease ammonia volatilization, enhances root access to nitrogen, improves crop nitrogen use efficiency and slows down the conversion of NH_4^+ to NO_3^- (Tenuta et al., 2023). Despite this, a portion of farmers in Western Canada are shifting towards surface application of urea due to the pressure of completing field operation in a stipulated time. Applying fertilizer on the surface increases the likelihood of nitrogen loss by ammonia volatilization, which occurs when urea hydrolysis raises pH levels and leads to higher concentration of gaseous ammonia near the granules.

Studies that have proved that deep application of fertilizer is more beneficial in reducing N_2O emissions. According to Gao et al. (2015) at two sites in Manitoba, applying N fertilizer at a depth of 2.5-7.5 cm through side banding or midrow banding showed decrease in N_2O emissions as compared to broadcast-incorporation. Also, deep injection (10-15 cm) of UAN resulted in less N_2O emissions in comparison with shallow injection (5 cm) (Liu et al., 2006). A six-site year study on clayey soils in Manitoba reported an increase in N_2O emissions with shallow placement of urea, specifically at those site years which experienced more rainfall (Tenuta et al., 2023). In Manitoba, as per Tenuta et al. (2022), shallow banding of urea had high N_2O emissions compared to deep placement. Another study in Manitoba reported decline in N_2O emissions when banding of PCU was adopted rather than broadcast method of application (Gao et al., 2017). In contrast, there are

few studies that suggest deep application (more than 15 cm deep) can have some disadvantages such as higher production cost for farmers, increased energy consumption and adverse impact on the quality of seedbed (Kargbo et al., 2016; Zhu et al., 2019; Liu et al., 2023).

In the current meta-analysis, the dataset was classified into two broad categories of method of placement: band and broadcast. Further, the data was sub-divided into deep band (more than 6 cm), and shallow band (less than 6 cm) depending on the banding depth and side band, midrow band depending on the banding position. On comparing banding with broadcast-incorporation (Fig 2.10), the results showed that deep banding, side banding, and midrow banding tended to decrease emissions whereas shallow banding tended to increase emissions, being consistent with the results of other field studies (Gao et al., 2015; Tenuta et al., 2022; Tenuta et al., 2023). However, when different methods of banding were compared with surface application of fertilizer, it resulted in an increase of N₂O emissions (Fig 2.11). This may be due to the fact that banding creates variations in soil moisture and temperature, which further increases nitrification and denitrification rates thereby contributing to high N₂O emissions. In contrast, surface application does not create major changes in moisture and temperature levels and lowers the likelihood of conditions that promote N₂O emissions. This difference in the results could also be attributed to different fertilizer sources and N rates used in different studies. Further, the differing effect within banding could be attributed to a higher nitrogen rate per unit area. The increase in N₂O emissions could be related to the high concentration of N fertilizers in the band (Engel et al., 2010). When urea is deep banded it allows for the interconversion of ammonia (gaseous form) into ammonium (NH₄⁺) which is a non-volatile ion that can then be absorbed by negatively charged soil particles leading to reduction in N loss (Tenuta et al., 2022). Apart from these there could be many different reasons behind reduced N₂O emissions with banding. Initially, banding could have led to reduced soil contact with urea, thereby

slowing down the activity of urease (Nash et al., 2012). Further, a high concentration of NH_3 and NH_4^+ along with a specific pH level can impede the process of nitrification by exerting harmful effects on nitrifying bacteria (Russell et al., 2002). Banding also enhances the uptake of fertilizer N by the crop, potentially reducing N_2O emissions. Additionally, banding can enhance the consumption of N_2O during the vertical movement of the gas towards the soil surface (Gao et al., 2014).

2.5.3 Effect of fertilizer application time

The timing of fertilizer application, whether in the fall or spring, can substantially influence N_2O emissions from agricultural soils. In the Canadian Prairies, fall N fertilizer application is frequently practiced by farmers to take advantage of the lower fertilizer costs and more time windows in fall relative to spring, as well as to preserve the quality of spring seedbeds (Williamson et al., 2011). Several experiments conducted in cold regions with frozen soils over winter have proved that fall application of fertilizers helped to reduce N_2O emissions (Parkin et al., 2010; Tenuta et al., 2016; Lin et al., 2017; Thies et al., 2020; Wood et al., 2023). Contrastingly, some studies have shown different results. For example, Soon et al. (2011) performed a field study in Alberta and Saskatchewan to test the impact of PCU in reducing N_2O emissions, and found that N_2O emissions were 1.5 times lower with spring application compared to fall application at the Saskatchewan site. Similarly, Hao et al. (2001) reported higher N_2O emissions from fall applied N fertilizer from a two-year field study in Alberta. In one of the studies in Manitoba, it was found that there was no noticeable variation in emissions when comparing the application of fall and spring banded AA (Burton et al., 2008).

The results from the current analysis showed that fall application of fertilizers tended to decrease N_2O emissions as compared to spring application, although the differences were not

statistically significant. When various environmental conditions were considered, significant reduction in N₂O emissions was observed only under two conditions, namely, acidic soils and silt containing soils. In acidic soils, the activity of nitrifying bacteria is inhibited, reducing nitrate availability for subsequent nitrification, and ultimately lowering N₂O emissions. In silt containing soils, the fine particles provide better aeration and retain more water than coarse textured soils but do not retain water as tightly as clay soils. This retention capacity helps maintain aerobic conditions thereby reducing N₂O emissions. Also, silt soils have lower microbial activity resulting in a reduced rate of nitrification and lower N₂O emissions. There was no publication bias found in the dataset, but the results might still be biased by the dominance of data from a particular soil or environmental factor.

2.5.4 Effect of N application rate

Upon analysing the collected datasets, it was discovered that the direct N₂O emission (total emissions and fertilizer-induced emissions) exhibited an increasing trend in response to N input rates. It should be noted that an exponential or linear model was not applied to the total N₂O emissions dataset due to lack of homogeneity in variance at high N rates (Fig. 2.13). The highest cumulative N₂O emissions ranged between 27-50 kg N₂O-N ha⁻¹ and all these emissions were contributed by one study which was conducted on the sandy soils of North Dakota. This study compared N₂O emissions from three different varieties of potato in an irrigated system, suggesting that irrigation accelerates N₂O emissions through denitrification. Therefore, these emissions served as an outlier in the analysis making the dataset unevenly distributed and unfit for model fitting. Whereas an exponential model was fitted to the fertilizer-induced N₂O emissions (Fig. 2.15), the analysis showed that 21% of the variability in N₂O emissions is explained by the model. The dataset with linear fit model is shown in the supplementary figure S1 (Appendix C).

Previous studies reported varying patterns of N₂O emissions in response to N rates, with some studies reporting linear (Bouwman et al., 1996; Dobbie et al., 1999; Kim et al., 2013; Ni et al., 2021), and others reporting nonlinear increase (McSwiney et al., 2005; Zebarth et al., 2008; Ma et al., 2010; Kim et al., 2010; Hoben et al., 2011; Signor et al., 2013; Kim et al., 2013; Shcherbak et al., 2014; Ni et al., 2021). These findings were demonstrated from both individual field experiments and global scale meta-analysis. In Canadian Prairies, linear increase in N₂O emission and N rate was observed (Gao et al., 2013) whereas other study suggested non-linear relationship between N rate and N₂O emission (Grant et al., 2006).

Across all studies in the current meta-analysis, we noticed that linear relationships are more common when N rates are equal to or below the crop's requirements, whereas the nonlinear relationships occur at N rates surpassing crop needs. The primary reason behind this might be an excessive supply of nitrogen surpassing the demands of the plants (Bouwman et al., 2002; Kim et al., 2013). This surplus of nitrogen in the soil would simultaneously cause a decrease in plant nitrogen uptake efficiency. Consequently, this surplus nitrogen would remain in the soil as residual nitrogen, serving as a substrate for further N₂O emissions (Zebarth et al., 2008; Kim et al., 2013). Overall, such increase of N₂O emissions at N rates greater than crop needs suggest that it is particularly important to recommend appropriate fertilizer rate based on soil test and crop N needs. From the perspective of assessing regional or national GHG inventory in Canada, this study suggest that fertilizer N rate should be considered as an important attribute when developing a climate zone or crop-specific (Tier II) or a model-based (Tier III) methodology. Instead, using an IPCC default (Tier I) value of 1% emission factor without considering the non-linear increase of N₂O emissions at rates greater than N needs may result in an underestimation of the overall emissions.

2.6 Conclusion

Source: This recent study has confirmed that incorporation of EEFs is an effective mitigation option for reducing N₂O emissions. The degree of effectiveness varies depending on crop type, soil properties (pH, SOC, soil texture) and environmental conditions (precipitation). Nitrification inhibitors effectively reduced N₂O emissions but their effectiveness was notably pronounced in wet conditions, soils with low organic carbon content, neutral to alkaline soils, and both in fine and coarse texture soils. Overall, NIs are more efficient compared to urease inhibitors as they directly inhibit the generation of N₂O by inhibiting the process of nitrification and the formation of nitrate, which serves as a precursor to N₂O. PCU significantly reduced N₂O emissions irrespective of the precipitation conditions, soils with low organic carbon content, neutral to alkaline soils, and coarse texture soils. Application of dual inhibitors was effective across almost all the factors. The superior potential of dual inhibitors as compared to PCU in reducing N₂O emissions implies that the inhibition of nitrification and urea hydrolysis is more effective than the slow-release mechanism of PCU (Maharjan et al., 2014, Ghosh et al., 2019). Ultimately, the most effective approach in reducing N₂O emissions can include best management practices such as incorporating nitrification inhibitors, dual inhibitors, and controlled release fertilizers. Thus, optimal management practices should consider site-specific environmental conditions for different types of inhibitors, which are crucial to maximize their mitigation potential of gaseous N loss.

Placement: Based on the present analysis, it is advisable to apply nitrogen fertilizer deep (more than 6 cm) into the soil while shallow application is not recommended, and side banding is more appropriate rather than adopting midrow banding for lowering N₂O emissions. Across different factors the difference was not statistically significant, but the impact was affected by crop type,

precipitation, and SOC. Thus, additional research is required to better understand the impact of method of placement on N₂O emissions, especially in cold regions.

Time: The current study showed that the overall impact of fertilizer application timing was not significant, but fall application decreased emissions over spring application under specific soil pH, and soil texture conditions (soil pH lower than 7, and silt texture soil). The results indicate that specific management practices can effectively lower N₂O emissions and support the idea that postponing N application until the soil temperature below 5°C can slow down the nitrification process and reduce losses. Future studies should investigate the impact of fall application on yield-scaled N₂O emissions, accounting how application timing affects crop productivity.

Rate: This meta-analysis found that across all studies, direct N₂O emissions increased with increasing N rates. The non-linear trend indicate that a higher percentage of N fertilizer is emitted to N₂O when application rates exceed crop needs. These results suggest that optimizing N application rate based on soil test is a crucial component in the 4R N management strategies. It should be also noted that the relationship between N input and N₂O emissions in the current meta-analysis is subject to uncertainty and potential bias due to data limitations, such as variability in soil types, climate conditions, and management practices across different studies. These limitations can lead to inconsistencies and gaps in the data, making it challenging to draw definitive conclusions and necessitating further research to refine our understanding and improve predictive models.

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Chapter 3. Synthesis

3.1 Study Findings and Recommendations

To meet the increasing food demand, agriculture heavily relies on conventional fertilizers, which significantly contribute to climate change. Synthetic fertilizers play a significant role in agriculture due to their affordability and ease of application. However, inappropriate management, particularly applying at excessive rates, can lead to substantial N losses. This thesis provides a comprehensive meta-analysis of field studies conducted in the Canadian Prairies and regions with similar climates, and demonstrated that using nitrification inhibitors, dual inhibitors (Super-U), and polymer-coated urea significantly reduced N₂O emissions by 35%, 48% and 16% respectively, compared to conventional N fertilizers. It is interesting to note that use of PCU significantly reduced N₂O emissions in Western Canada. Among the banding depths and positions, shallow banding showed a tendency to increase N₂O emissions by 5% and midrow banding significantly increased N₂O emissions by 40% compared to surface application of fertilizer. Application timing, and use of urease inhibitors alone had a non-significant impact on N₂O emissions. Enhanced efficiency fertilizers exhibited diverse impact on N₂O emissions depending on soil, environmental and management properties. Overall, EEFs that used both nitrification and urease inhibitors had the largest reductions in emissions.

Based on the current analysis, deep application of N fertilizer is advised while shallow banding is not recommended for lowering N₂O emissions. Late fall application did not result in higher N₂O emissions compared to spring application due to the generally cold conditions in the region. Thus, it can be an effective alternative application time, being cost-effective and less labor-intensive than spring application. The analysis also revealed a potential increase of N₂O emissions

with increasing N application rates, although the relationship was driven by several individual studies with high N inputs in the wheat, potato, canola and corn cropping systems. The results suggest that optimizing N rate, by considering soil N supply, crop needs, as well as incorporation of the other 3 Rs (source, placement, timing) are crucial for N₂O reduction for agricultural systems in the Prairies.

Canada's federal government aims to reduce national GHG emissions by 40%-45% relative to 2005 levels by 2030, on the path to net zero emissions by 2050. For fertilizer related emissions, Canada has set a national target of 30% below 2020 levels by 2030. Our analysis clearly indicates that incorporation of nitrification inhibitors can reduce N₂O emissions from croplands across Prairies by 35% from urea and by 17% from UAN. One of the previously conducted meta-analyses had also shown similar results that integration of nitrification inhibitors reduces total N₂O emissions by 38% in comparison with conventional N fertilizers (Thapa et al., 2016). Likewise, another meta-analysis conducted worldwide with 182 studies showed that nitrification inhibitors effectively reduced total N₂O emissions by 49% (Fan et al., 2022). It should be noted that such reductions refer to total N₂O emissions from both applied synthetic fertilizers and soil native background emissions. Without accounting for the background emissions, the use of nitrification inhibitors can be more promising and reduce the fertilizer-induced emissions by 67% from urea and by 30% from UAN. A worldwide meta-analysis by Yin et al. (2023), based on 88 peer-reviewed papers and with 1437 observations, concluded that nitrification inhibitors are responsible for the mitigation of fertilizer-induced N₂O emissions. Similarly, another global meta-analysis with 2068 observations extracted from 144 studies found that fertilizer-induced N₂O emissions are highly impacted by the associated N functional genes (You et al., 2022). Therefore, this analysis

highlights the importance of a better nitrogen management plan through employing the 4R Nutrient Stewardship, which can make a significant contribution to the national GHG reduction target.

3.2 Study Limitations and Future Considerations

Meta-analysis proves to be a valuable approach capable of synthesizing/summarizing the results of individual field studies across different field management practices and environments. Our analysis was limited to field experimental data, excluding controlled environmental studies such as incubation experiments. It is important to note that the results from controlled studies cannot be directly compared with those from field studies. The duration of measurement periods can also influence the outcome of the analysis. The studies included in the present analysis assessed N₂O emissions throughout the growing season, but the impact of EEFs may persist beyond this timeframe. Thus, future research should consider extending N₂O flux measurements throughout the whole year to cover the non-growing season. Specifically, under cold climates, freeze-thaw cycles significantly influence N₂O emissions through mechanisms such as enhanced anaerobiosis, substrates availability, and retention and release of N₂O trapped underneath the ice layer; along with changes in the composition and functioning of denitrifying microorganisms (Risk et al., 2013; Nemeth et al., 2014). Previous studies have demonstrated that factors such as soil temperature, soil moisture, duration of freeze-up of soil, depth of soil, and concentration of nitrate influence the extent of N₂O emissions during spring thaw (Wagner et al., 2008; Tenuta et al., 2011; Wood et al., 2023), with these emissions accounting for more than 50% of the annual total (Wagner et al., 2017). Application of fertilizer in late fall does not cause immediate N₂O emissions during winter but it leads to an increase in emissions in the subsequent spring thaw. Contrastingly, the application of fertilizer before planting in the spring, followed by rainfall, results in high N₂O emissions as compared to late fall. Overall, the addition of fertilizer in late fall before freeze-up results in

minimal N₂O emissions during winters and post-application fall periods at places where soil and air conditions are below freezing (Tenuta et al., 2016). While analysing the dataset it was found that amongst the cold regions there are quite few published literatures comparing timing (fall vs. spring) of N fertilizers, along with the use of inhibitors, and their impact on N₂O emissions. Thus, more research is required to perform future meta-analysis and come-up with better management strategies in reducing environmental pollution coming from the agricultural sector.

The analysis in this thesis focused on direct N₂O emissions, excluding indirect emissions associated with N losses such as nitrate leaching, ammonia volatilization, run-off, and erosion. In agricultural systems, ammonia volatilization is a significant pathway of fertilizer N loss, not only representing agronomic and economic losses for farmers, but also resulting in serious environmental issues such as indirect N₂O emissions. A global meta-analysis of 824 observations on the impact of 4Rs on NH₃ volatilization concluded that controlled release fertilizers, UIs, and deep placement of fertilizers significantly reduced ammonia volatilization by 68%, 54%, and 55% respectively (Pan et al., 2016). In contrast, the use of NIs resulted in significant 36% increase of ammonia volatilization (Pan et al., 2016; Wu et al., 2021). Nitrate leaching is another environmental concern as it leads to eutrophication of water bodies. Unfortunately, there is scarcity of published studies on nitrate leaching despite its significant environmental impact. Therefore, it is suggested that more experiments are conducted focusing on indirect N₂O emissions.

The present study did not analyze organic source of fertilizers such as manure and compost due to limited data availability. Thus, further field experiments are needed to assess the effectiveness of organic fertilizers across cold climate regions. Some of the studies included in this analysis did not report standard deviation, standard error, clay content, sample size, etc. In future studies, it is imperative to clearly report these measures of variability, along with the relevant

environmental variables. Having this information will facilitate data analysis and help in formulating the best management decision.

I conducted a basic pairwise meta-analysis, without analyzing the interaction among the treatments (net meta-analysis) due to the availability of data. Additionally, the current meta-analysis study did not include crop yields and nitrogen use efficiency, which are important factors as they are directly associated with farmer's profitability. From this perspective, yield-based N₂O emissions intensity, which refers to the amount of N₂O emissions produced per unit of crop yield, is crucial for combining the environmental impact of agricultural practices with crop productivity. Therefore, future research should focus on yield-based emissions intensity to better identify practices that maximize productivity while minimizing environmental harm. This approach not only promotes more efficient use of fertilizers and better soil management but also supports efforts to meet global food demands sustainably.

3.3 References

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Appendix A: Dataset used in the meta-analysis

Supplemental Table 1. Dataset used for assessment of the effectiveness of nitrification inhibitors versus conventional urea

No.	Reference	Treatment	Emission (kg N ₂ O-N ha ⁻¹)	Control	Emission (kg N ₂ O-N ha ⁻¹)	Effect size	Variance
1	Thilakarantha et al. 2023	DMPSA	0.778	Urea	0.623	0.22	0.03
2	Thilakarantha et al. 2023	DMPSA	0.252	Urea	0.279	-0.10	0.03
3	Thilakarantha et al. 2023	DMPSA	0.085	Urea	0.087	-0.02	0.03
4	Thilakarantha et al. 2023	DMPSA	0.154	Urea	0.256	-0.51	0.03
5	Wood et al. 2023	Nitrapyrin	0.9	Urea	2.47	-1.01	0.11
6	Wood et al. 2023	Nitrapyrin	1.04	Urea	1.67	-0.47	0.11
7	Wood et al. 2023	Nitrapyrin	0.29	Urea	0.62	-0.76	0.29
8	Wood et al. 2023	Nitrapyrin	0.4	Urea	1.06	-0.97	0.10
9	Wood et al. 2023	Nitrapyrin	0.64	Urea	0.97	-0.42	0.08
10	Wood et al. 2023	Nitrapyrin	0.47	Urea	1.15	-0.89	0.03
11	Wood et al. 2023	Nitrapyrin	0.36	Urea	0.54	-0.41	0.07
12	Wood et al. 2023	Nitrapyrin	0.31	Urea	0.7	-0.81	0.35
13	Wood et al. 2023	Nitrapyrin	0.12	Urea	0.33	-1.01	0.14
14	Wood et al. 2023	Nitrapyrin	0.08	Urea	0.24	-1.10	0.01
15	Wood et al. 2023	Nitrapyrin	2.64	Urea	1.31	0.70	0.13
16	Wood et al. 2023	Nitrapyrin	0.56	Urea	0.53	0.06	0.03
17	Thilakarathna et al. 2020	Nitrapyrin	0.535	Urea	0.393	0.31	0.03
18	Thilakarathna et al. 2020	Nitrapyrin	0.478	Urea	0.63	-0.28	0.03
19	Thilakarathna et al. 2020	Nitrapyrin	0.292	Urea	0.278	0.05	0.03
20	Thilakarathna et al. 2020	Nitrapyrin	0.428	Urea	0.232	0.61	0.03
21	Thapa et al. 2017	Nitrapyrin	1.07	Urea	2.07	-0.66	0.06
22	Thapa et al. 2017	Nitrapyrin	1.02	Urea	2.4	-0.86	0.06
23	Owens et al. 2019	Nitrapyrin	0.11	Urea	0.17	-0.44	0.80
24	Owens et al. 2019	Nitrapyrin	0.16	Urea	0.16	0.00	0.46
25	Owens et al. 2019	Nitrapyrin	0.18	Urea	0.21	-0.15	0.77
26	Owens et al. 2019	Nitrapyrin	0.13	Urea	0.18	-0.33	0.07
27	Thapa et al. 2015	Nitrapyrin	0.57	Urea	0.67	-0.16	0.10
28	Thapa et al. 2015	Nitrapyrin	0.6	Urea	1.16	-0.66	0.17

29	Owens et al. 2019	Nitrapyrin	0.15	Urea	0.15	0.00	0.45
30	Owens et al. 2019	Nitrapyrin	0.23	Urea	0.17	0.30	0.89
31	Tenuta et al. 2023	DMP5A	0.12	Urea	0.33	-1.01	0.03
32	Tenuta et al. 2023	Nitrapyrin	0.19	Urea	0.33	-0.55	0.03
33	Tenuta et al. 2022	Nitrapyrin	0.14	Urea	0.51	-1.29	0.03
34	Tenuta et al. 2022	Nitrapyrin	0.18	Urea	0.36	-0.69	0.03
35	Tenuta et al. 2022	Nitrapyrin	0.34	Urea	0.07	1.58	0.03
36	Tenuta et al. 2022	Nitrapyrin	0.09	Urea	0.08	0.12	0.03
37	Tenuta et al. 2022	Nitrapyrin	0.31	Urea	0.76	-0.90	0.03
38	Tenuta et al. 2022	Nitrapyrin	0.25	Urea	0.02	2.53	0.03
39	Tenuta et al. 2022	Nitrapyrin	0.14	Urea	0.24	-0.54	0.03
40	Tenuta et al. 2022	Nitrapyrin	0.29	Urea	0.53	-0.60	0.03
41	Tenuta et al. 2022	Nitrapyrin	0.29	Urea	0.46	-0.46	0.03
42	Tenuta et al. 2022	Nitrapyrin	0.05	Urea	0.13	-0.96	0.03
43	Tenuta et al. 2022	Nitrapyrin	0.11	Urea	0.17	-0.44	0.03
44	Tenuta et al. 2022	Nitrapyrin	0.14	Urea	0.18	-0.25	0.03
45	Ogilvie et al. 2022	Nitrapyrin	2.02	Urea	3.01	-0.40	0.03
46	Ogilvie et al. 2022	Nitrapyrin	0.73	Urea	1.95	-0.98	0.03
47	Ogilvie et al. 2022	Nitrapyrin	0.75	Urea	3.26	-1.47	0.03
48	Ogilvie et al. 2022	Nitrapyrin	1.01	Urea	1.98	-0.67	0.03

Supplemental Table 2. Dataset used for assessment of the effectiveness of dual inhibitors versus conventional urea

No.	Reference	Treatment	Emission (kg N ₂ O-N ha ⁻¹)	Control	Emission (kg N ₂ O-N ha ⁻¹)	Effect size	Variance
1	Wood et al. 2023	Super-U	1.61	Urea	2.47	-0.43	0.03
2	Wood et al. 2023	Super-U	0.55	Urea	1.67	-1.11	0.21
3	Wood et al. 2023	Super-U	0.35	Urea	0.62	-0.57	0.06
4	Wood et al. 2023	Super-U	0.37	Urea	1.06	-1.05	0.11
5	Wood et al. 2023	Super-U	0.59	Urea	0.97	-0.50	0.03
6	Wood et al. 2023	Super-U	0.75	Urea	1.15	-0.43	0.08
7	Wood et al. 2023	Super-U	0.48	Urea	0.54	-0.12	0.11
8	Wood et al. 2023	Super-U	0.32	Urea	0.7	-0.78	0.44
9	Wood et al. 2023	Super-U	0.2	Urea	0.33	-0.50	0.14
10	Wood et al. 2023	Super-U	0.14	Urea	0.24	-0.54	0.09
11	Wood et al. 2023	Super-U	1.15	Urea	1.31	-0.13	0.12
12	Wood et al. 2023	Super-U	0.51	Urea	0.53	-0.04	0.00
13	Gao et al. 2019	Super-U	0.8	Urea	1.36	-0.53	0.30
14	Gao et al. 2019	Super-U	0.47	Urea	1.1	-0.85	0.31
15	Gao et al. 2019	Super-U	0.44	Urea	0.93	-0.75	0.20
16	Gao et al. 2019	Super-U	0.67	Urea	0.56	0.18	0.61
17	Gao et al. 2019	Super-U	0.56	Urea	0.72	-0.25	0.43
18	Gao et al. 2019	Super-U	0.32	Urea	0.3	0.06	0.30
19	Gao et al. 2019	Super-U	0.87	Urea	1.18	-0.30	0.38
20	Gao et al. 2019	Super-U	0.87	Urea	3.72	-1.45	0.36

21	Gao et al. 2019	Super-U	1.09	Urea	1.57	-0.36	0.60
22	Gao et al. 2019	Super-U	0.13	Urea	0.22	-0.53	0.10
23	Gao et al. 2019	Super-U	0.14	Urea	0.19	-0.31	0.28
24	Gao et al. 2019	Super-U	0.13	Urea	0.16	-0.21	0.34
25	Gao et al. 2019	Super-U	0.35	Urea	0.52	-0.40	1.25
26	Gao et al. 2019	Super-U	0.66	Urea	1.13	-0.54	0.47
27	Gao et al. 2019	Super-U	0.66	Urea	0.95	-0.36	0.61
28	Gao et al. 2019	Super-U	0.55	Urea	0.67	-0.20	0.45
29	Gao et al. 2019	Super-U	0.55	Urea	1.66	-1.10	0.33
30	Gao et al. 2019	Super-U	0.68	Urea	1.32	-0.66	0.23
31	Gao et al. 2015	Super-U	1.64	Urea	2.04	-0.22	0.00
32	Gao et al. 2015	Super-U	0.31	Urea	0.58	-0.63	0.00
33	Gao et al. 2015	Super-U	0.18	Urea	0.51	-1.04	0.00
34	Gao et al. 2015	Super-U	0.25	Urea	0.25	0.00	0.00
35	Thilakarathna et al. 2020	Super-U	0.264	Urea	0.393	-0.40	0.00
36	Thilakarathna et al. 2020	Super-U	0.528	Urea	0.63	-0.18	0.00
37	Thilakarathna et al. 2020	Super-U	0.24	Urea	0.278	-0.15	0.00
38	Thilakarathna et al. 2020	Super-U	0.233	Urea	0.232	0.00	0.00
39	Oleson et al. 2023	Super-U	0.23	Urea	0.465	-0.70	0.00
40	Oleson et al. 2023	Super-U	0.189	Urea	0.29	-0.43	0.00
41	Oleson et al. 2023	Super-U	0.494	Urea	1.3	-0.97	0.00
42	Ghosh et al. 2019	Super-U	35.2	Urea	39.8	-0.12	0.00
43	Ghosh et al. 2019	Super-U	39.6	Urea	37.3	0.06	0.00

44	Ghosh et al. 2019	Super-U	39.8	Urea	40.6	-0.02	0.00
45	Ghosh et al. 2019	Super-U	49.2	Urea	43.9	0.11	0.00
46	Ghosh et al. 2019	Super-U	34.9	Urea	39.1	-0.11	0.00
47	Ghosh et al. 2019	Super-U	27.5	Urea	29.5	-0.07	0.00
48	Thapa et al. 2017	Super-U	0.99	Urea	2.07	-0.74	0.04
49	Thapa et al. 2017	Super-U	1.57	Urea	2.4	-0.42	0.04
50	Owens et al. 2019	Super-U	0.23	Urea	0.15	0.43	0.17
51	Owens et al. 2019	Super-U	0.31	Urea	0.17	0.60	0.61
52	Owens et al. 2019	Super-U	0.16	Urea	0.17	-0.06	0.81
53	Owens et al. 2019	Super-U	0.15	Urea	0.15	0.00	NA
54	Owens et al. 2019	Super-U	0.19	Urea	0.16	0.17	0.58
55	Owens et al. 2019	Super-U	0.17	Urea	0.21	-0.21	0.47
56	Owens et al. 2019	Super-U	0.19	Urea	0.18	0.05	0.15
57	Owens et al. 2019	Super-U	0.18	Urea	0.17	0.06	1.63
58	Thapa et al. 2015	Super-U	0.36	Urea	0.67	-0.62	0.11
59	Thapa et al. 2015	Super-U	0.55	Urea	1.16	-0.75	0.12
60	Halvorson et al. 2010	Super-U	0.334	Urea	0.865	-0.95	0.00
61	Halvorson et al. 2010	Super-U	0.529	Urea	0.805	-0.42	0.00
62	Halvorson et al. 2011	Super-U	0.972	Urea	1.698	-0.56	0.00
63	Halvorson et al. 2011	Super-U	0.631	Urea	1.726	-1.01	0.00
64	Halvorson et al. 2012	Super-U	1.017	Urea	1.841	-0.59	0.00
65	Halvorson et al. 2012	Super-U	0.653	Urea	1.267	-0.66	0.00
66	Dungan et al. 2017	Super-U	0.28	Urea	0.59	-0.75	0.00

67	Dungan et al. 2017	Super-U	0.43	Urea	0.44	-0.02	0.00
68	Parkin et al. 2014	Super-U	2.92	Urea	2.88	0.01	0.07
69	Tenuta et al. 2023	Super-U	0.13	Urea	0.21	-0.48	0.00
70	Tenuta et al. 2023	Super-U	0.13	Urea	0.38	-1.07	0.00
71	Tenuta et al. 2023	Super-U	0.16	Urea	0.38	-0.86	0.00
72	Tenuta et al. 2023	Super-U	0.13	Urea	0.33	-0.93	0.00
73	Tenuta et al. 2023	Super-U	0.13	Urea	0.21	-0.48	0.00
74	Ogilvie et al. 2022	Super-U	1.74	Urea	3.01	-0.55	0.00
75	Ogilvie et al. 2022	Super-U	0.86	Urea	1.95	-0.82	0.00
76	Ogilvie et al. 2022	Super-U	0.58	Urea	3.26	-1.73	0.00
77	Ogilvie et al. 2022	Super-U	0.91	Urea	1.98	-0.78	0.00

Supplemental Table 3. Dataset used for assessment of the effectiveness of urease inhibitors versus conventional urea

No.	Reference	Treatment	Emission (kg N ₂ O- N ha ⁻¹)	Control	Emission (kg N ₂ O- N ha ⁻¹)	Effect size	Variance
1	Wood et al. 2023	LIMUS	3.63	Urea	2.47	0.39	0.09
2	Wood et al. 2023	LIMUS	1.32	Urea	1.67	-0.24	0.17
3	Wood et al. 2023	LIMUS	0.85	Urea	0.62	0.32	0.09
4	Wood et al. 2023	LIMUS	0.66	Urea	1.06	-0.47	0.11
5	Wood et al. 2023	LIMUS	0.68	Urea	0.97	-0.36	0.06
6	Wood et al. 2023	LIMUS	1.11	Urea	1.15	-0.04	0.04
7	Wood et al. 2023	LIMUS	0.51	Urea	0.54	-0.06	0.07
8	Wood et al. 2023	LIMUS	0.54	Urea	0.7	-0.26	0.34
9	Wood et al. 2023	LIMUS	0.28	Urea	0.33	-0.16	0.13
10	Wood et al. 2023	LIMUS	0.17	Urea	0.24	-0.34	0.02
11	Wood et al. 2023	LIMUS	1.08	Urea	1.31	-0.19	0.13
12	Wood et al. 2023	LIMUS	0.48	Urea	0.53	-0.10	0.02
13	Thilakarathna et al. 2020	LIMUS	0.259	Urea	0.393	-0.42	0.02
14	Thilakarathna et al. 2020	LIMUS	0.407	Urea	0.63	-0.44	0.02
15	Thilakarathna et al. 2020	LIMUS	0.242	Urea	0.278	-0.14	0.02
16	Thilakarathna et al. 2020	LIMUS	0.413	Urea	0.232	0.58	0.02
17	Burton et al. 2008	Agrotain	0.69	Urea	0.48	0.36	0.02
18	Burton et al. 2008	Agrotain	0.58	Urea	0.61	-0.05	0.02
19	Burton et al. 2008	Agrotain	0.23	Urea	0.21	0.09	0.02
20	Tenuta et al. 2023	Agrotain	0.22	Urea	0.21	0.05	0.02

21	Ogilvie et al. 2022	LIMUS	3.43	Urea	3.01	0.13	0.02
22	Ogilvie et al. 2022	LIMUS	2.67	Urea	1.95	0.31	0.02
23	Ogilvie et al. 2022	LIMUS	0.84	Urea	3.26	-1.36	0.02
24	Ogilvie et al. 2022	LIMUS	1.14	Urea	1.98	-0.55	0.02

Supplemental Table 4. Dataset used for assessment of the effectiveness of PCU versus conventional urea

No.	Reference	Treatment	Emission (kg N ₂ O-N ha ⁻¹)	Control	Emission (kg N ₂ O-N ha ⁻¹)	Effect size	Variance
1	Halvorson et al. 2010	PCU	0.632	Urea	0.865	-0.31	0.00
2	Halvorson et al. 2010	PCU	0.519	Urea	0.805	-0.44	0.00
3	Wood et al. 2023	PCU	2.14	Urea	2.47	-0.14	0.07
4	Wood et al. 2023	PCU	2.13	Urea	1.67	0.24	0.08
5	Wood et al. 2023	PCU	0.44	Urea	0.62	-0.34	0.09
6	Wood et al. 2023	PCU	0.51	Urea	1.06	-0.73	0.09
7	Wood et al. 2023	PCU	0.97	Urea	0.97	0.00	0.08
8	Wood et al. 2023	PCU	0.93	Urea	1.15	-0.21	0.04
9	Wood et al. 2023	PCU	0.45	Urea	0.54	-0.18	0.09
10	Wood et al. 2023	PCU	0.31	Urea	0.7	-0.81	0.44
11	Wood et al. 2023	PCU	0.25	Urea	0.33	-0.28	0.13
12	Wood et al. 2023	PCU	0.18	Urea	0.24	-0.29	0.01
13	Wood et al. 2023	PCU	2.36	Urea	1.31	0.59	0.29
14	Wood et al. 2023	PCU	0.67	Urea	0.53	0.23	0.00
15	Gao et al. 2015	PCU	1.67	Urea	2.04	-0.20	0.00
16	Gao et al. 2015	PCU	0.26	Urea	0.58	-0.80	0.00
17	Gao et al. 2015	PCU	0.39	Urea	0.51	-0.27	0.00
18	Gao et al. 2015	PCU	0.16	Urea	0.25	-0.45	0.00
19	Gao et al. 2017	PCU	1.57	Urea	2.39	-0.42	0.30
20	Gao et al. 2017	PCU	2.03	Urea	2.39	-0.16	0.15

21	Gao et al. 2017	PCU	2.32	Urea	2.8	-0.19	0.43
22	Gao et al. 2017	PCU	2.59	Urea	2.8	-0.08	0.18
23	Gao et al. 2017	PCU	1.2	Urea	0.49	0.90	0.00
24	Gao et al. 2017	PCU	0.52	Urea	0.73	-0.34	0.17
25	Gao et al. 2017	PCU	0.53	Urea	0.63	-0.17	0.27
26	Gao et al. 2017	PCU	0.35	Urea	0.73	-0.74	0.15
27	Gao et al. 2017	PCU	1.15	Urea	0.63	0.60	0.16
28	Gao et al. 2017	PCU	0.43	Urea	0.77	-0.58	0.00
29	Thilakarathna et al. 2020	PCU	0.299	Urea	0.393	-0.27	0.00
30	Thilakarathna et al. 2020	PCU	0.365	Urea	0.63	-0.55	0.00
31	Thilakarathna et al. 2020	PCU	0.293	Urea	0.278	0.05	0.00
32	Thilakarathna et al. 2020	PCU	0.506	Urea	0.232	0.78	0.00
33	Oleson et al. 2023	PCU	NA	Urea	0.465	NA	NA
34	Oleson et al. 2023	PCU	0.157	Urea	0.29	-0.61	0.00
35	Oleson et al. 2023	PCU	0.548	Urea	1.3	-0.86	0.00
36	Ghosh et al. 2019	PCU	39.8	Urea	39.8	0.00	0.00
37	Ghosh et al. 2019	PCU	42.2	Urea	37.3	0.12	0.00
38	Ghosh et al. 2019	PCU	42.8	Urea	40.6	0.05	0.00
39	Ghosh et al. 2019	PCU	42.1	Urea	43.9	-0.04	0.00
40	Ghosh et al. 2019	PCU	42.2	Urea	39.1	0.08	0.00
41	Ghosh et al. 2019	PCU	31.8	Urea	29.5	0.08	0.00
42	Li et al. 2012	PCU	0.32	Urea	0.47	-0.38	0.00
43	Li et al. 2012	PCU	0.25	Urea	0.47	-0.63	0.00
44	Li et al. 2012	PCU	0.16	Urea	0.56	-1.25	0.00
45	Li et al. 2012	PCU	0.21	Urea	0.56	-0.98	0.00

46	Li et al. 2012	PCU	0.32	Urea	0.46	-0.36	0.00
47	Li et al. 2012	PCU	0.36	Urea	0.46	-0.25	0.00
48	Li et al. 2012	PCU	0.55	Urea	0.44	0.22	0.00
49	Li et al. 2012	PCU	0.4	Urea	0.44	-0.10	0.00
50	Li et al. 2012	PCU	2.97	Urea	1.77	0.52	0.00
51	Li et al. 2012	PCU	2.86	Urea	1.77	0.48	0.00
52	Li et al. 2012	PCU	0.4	Urea	0.44	-0.10	0.00
53	Li et al. 2012	PCU	0.51	Urea	0.44	0.15	0.00
54	Li et al. 2012	PCU	0.15	Urea	0.22	-0.38	0.00
55	Li et al. 2012	PCU	1.37	Urea	0.22	1.83	0.00
56	Li et al. 2012	PCU	0.47	Urea	0.55	-0.16	0.00
57	Li et al. 2012	PCU	0.8	Urea	0.55	0.37	0.00
58	Li et al. 2012	PCU	0.15	Urea	0.21	-0.34	0.00
59	Li et al. 2012	PCU	0.33	Urea	0.21	0.45	0.00
60	Halvorson et al. 2010	PCU	0.646	Urea	0.865	-0.29	0.00
61	Halvorson et al. 2010	PCU	0.462	Urea	0.805	-0.56	0.00
62	Parkin et al. 2014	PCU	2.88	Urea	2.88	0.00	0.04
63	Parkin et al. 2014	PCU	2.59	Urea	2.88	-0.11	0.04
64	Halvorson et al. 2011	PCU	0.856	Urea	1.698	-0.68	0.00
65	Halvorson et al. 2011	PCU	0.716	Urea	1.698	-0.86	0.00
66	Halvorson et al. 2011	PCU	1.439	Urea	1.726	-0.18	0.00
67	Halvorson et al. 2011	PCU	1.028	Urea	1.726	-0.52	0.00
68	Halvorson et al. 2012	PCU	1.365	Urea	1.841	-0.30	0.00
69	Halvorson et al. 2012	PCU	0.666	Urea	1.841	-1.02	0.00
70	Halvorson et al. 2012	PCU	1.346	Urea	1.267	0.06	0.00
71	Halvorson et al. 2012	PCU	0.674	Urea	1.267	-0.63	0.00
72	Thilakarantha et al. 2023	PCU	0.745	Urea	0.623	0.18	0.00
73	Thilakarantha et al. 2023	PCU	0.296	Urea	0.279	0.06	0.00
74	Thilakarantha et al. 2023	PCU	0.143	Urea	0.087	0.50	0.00

75	Thilakarantha et al. 2023	PCU	0.19	Urea	0.256	-0.30	0.00
76	Burton et al. 2008	PCU	2.4	Urea	2.74	-0.13	0.00
77	Burton et al. 2008	PCU	1.07	Urea	0.72	0.40	0.00
78	Burton et al. 2008	PCU	0.97	Urea	1.77	-0.60	0.00
79	Owens et al. 2019	PCU	0.32	Urea	0.15	0.76	0.94
80	Owens et al. 2019	PCU	0.1	Urea	0.17	-0.53	0.71
81	Owens et al. 2019	PCU	0.12	Urea	0.15	-0.22	4.99
82	Owens et al. 2019	PCU	0.2	Urea	0.16	0.22	0.44
83	Owens et al. 2019	PCU	0.18	Urea	0.18	0.00	0.37
84	Owens et al. 2019	PCU	0.16	Urea	0.17	-0.06	1.15
85	Owens et al. 2019	PCU	0.23	Urea	0.17	0.30	1.00
86	Owens et al. 2019	PCU	0.17	Urea	0.21	-0.21	0.47
87	Hyatt et al. 2010	PCU	0.58	Urea	0.9	-0.44	0.00
88	Hyatt et al. 2010	PCU	0.6	Urea	0.9	-0.41	0.00
89	Hyatt et al. 2010	PCU	1	Urea	2.1	-0.74	0.00
90	Hyatt et al. 2010	PCU	1.8	Urea	2.1	-0.15	0.00
91	Hyatt et al. 2010	PCU	0.9	Urea	1.2	-0.29	0.00
92	Hyatt et al. 2010	PCU	0.9	Urea	1.2	-0.29	0.00
93	Soon et al. 2011	PCU	0.676	Urea	0.5	0.30	0.00
94	Soon et al. 2011	PCU	0.46	Urea	0.616	-0.29	0.00
95	Soon et al. 2011	PCU	0.679	Urea	1.22	-0.59	0.00
96	Soon et al. 2011	PCU	1.09	Urea	1.37	-0.23	0.00
97	Soon et al. 2011	PCU	0.683	Urea	0.922	-0.30	0.00

98	Soon et al. 2011	PCU	0.837	Urea	1.31	-0.45	0.00
99	Soon et al. 2011	PCU	1.44	Urea	1.91	-0.28	0.00
100	Soon et al. 2011	PCU	NA	Urea	NA	NA	NA
101	Soon et al. 2011	PCU	1.18	Urea	1.31	-0.10	0.00
102	Soon et al. 2011	PCU	0.119	Urea	0.128	-0.07	0.00
103	Soon et al. 2011	PCU	0.058	Urea	0.139	-0.87	0.00
104	Soon et al. 2011	PCU	0.203	Urea	0.17	0.18	0.00
105	Soon et al. 2011	PCU	0.226	Urea	0.267	-0.17	0.00
106	Soon et al. 2011	PCU	0.259	Urea	0.096	0.99	0.00
107	Soon et al. 2011	PCU	0.149	Urea	0.197	-0.28	0.00
108	An et al. 2020	PCU	0.22	Urea	0.21	0.05	0.00
109	An et al. 2020	PCU	0.545	Urea	0.484	0.12	0.00
110	An et al. 2020	PCU	0.834	Urea	0.952	-0.13	0.00
111	Tenuta et al. 2023	PCU	0.26	Urea	0.38	-0.38	0.00
112	Tenuta et al. 2023	PCU	0.14	Urea	0.21	-0.41	0.00
113	Ogilvie et al. 2022	PCU	2.67	Urea	3.01	-0.12	0.00
114	Ogilvie et al. 2022	PCU	1.91	Urea	1.95	-0.02	0.00
115	Ogilvie et al. 2022	PCU	2.02	Urea	3.26	-0.48	0.00
116	Ogilvie et al. 2022	PCU	2.35	Urea	1.98	0.17	0.00

Supplemental Table 5. Dataset used for assessment of the effectiveness of nitrification inhibitor containing products versus conventional UAN

No.	Reference	Treatment	Emission (kg N ₂ O- N ha ⁻¹)	Control	Emission (kg N ₂ O- N ha ⁻¹)	Effect size	Variance
1	Oleson et al. 2023	Agrotain Plus	0.26	UAN	0.25	0.06	0.12
2	Oleson et al. 2023	Agrotain Plus	0.18	UAN	0.26	-0.37	0.12
3	Oleson et al. 2023	Agrotain Plus	0.20	UAN	0.32	-0.49	0.12
4	Halvorson et al. 2011	Agrotain Plus	0.35	UAN	0.77	-0.78	0.16
5	Halvorson et al. 2011	Agrotain Plus	0.67	UAN	1.21	-0.60	0.16
6	Halvorson et al. 2011	Nfusion	0.47	UAN	0.77	-0.49	0.16
7	Halvorson et al. 2011	Nfusion	1.00	UAN	1.21	-0.19	0.16
8	Halvorson et al. 2010	Agrotain Plus	0.53	UAN	0.72	-0.30	0.16
9	Halvorson et al. 2010	Agrotain Plus	0.26	UAN	0.50	-0.65	0.16
10	Halvorson et al. 2012	Agrotain Plus	0.60	UAN	0.91	-0.42	0.16
11	Halvorson et al. 2012	Agrotain Plus	0.58	UAN	0.93	-0.47	0.16
12	Parkin et al. 2014	Agrotain Plus	5.70	UAN	5.55	0.03	0.02
13	Parkin et al. 2014	Agrotain Plus	13.40	UAN	12.50	0.07	0.03
14	Parkin et al. 2014	Agrotain Plus	2.36	UAN	2.16	0.09	0.05
15	An et al. 2020	Agrotain Plus	0.24	UAN	0.17	0.35	1.14
16	An et al. 2020	Agrotain Plus	0.44	UAN	0.72	-0.49	5.55
17	An et al. 2020	Agrotain Plus	1.05	UAN	1.31	-0.22	3.35
18	An et al. 2020	Nitrapyrin	0.12	UAN	0.17	-0.32	0.88
19	An et al. 2020	Nitrapyrin	0.95	UAN	0.72	0.27	4.03
20	An et al. 2020	Nitrapyrin	0.51	UAN	1.31	-0.94	4.62
21	Owens et al. 2019	Nitrapyrin	0.14	UAN	0.12	0.15	4.67

22	Owens et al. 2019	Nitrapyrin	0.14	UAN	0.14	0.00	0.49
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Supplemental Table 6. Dataset used for assessment of the effectiveness of band (shallow/deep; side/midrow) versus broadcast-incorporation of fertilizer

No .	Reference	Treatment (Shallow/Deep)	Treatment (Side/Midrow)	Emission (kg N ₂ O-N ha ⁻¹)	Control	Emission (kg N ₂ O-N ha ⁻¹)	Effect size	Variance
1	Gao et al. 2017	Shallow	Side	1.57	Broadcast -Inc.	2.32	-0.39	0.48
2	Gao et al. 2017	Shallow	Side	2.03	Broadcast -Inc.	2.59	-0.24	0.09
3	Gao et al. 2017	Shallow	Side	2.39	Broadcast -Inc.	2.80	-0.16	0.24
4	Gao et al. 2017	Shallow	Side	0.52	Broadcast -Inc.	0.35	0.40	0.20
5	Gao et al. 2017	Shallow	Side	0.53	Broadcast -Inc.	1.15	-0.77	0.27
6	Gao et al. 2017	Shallow	Side	0.73	Broadcast -Inc.	0.63	0.15	0.15
7	Gao et al. 2015	Shallow	Side	2.41	Broadcast -Inc.	2.70	-0.11	0.19
8	Gao et al. 2015	Deep	Midrow	2.04	Broadcast -Inc.	2.70	-0.28	0.19
9	Gao et al. 2015	Shallow	Side	0.69	Broadcast -Inc.	0.94	-0.31	0.19
10	Gao et al. 2015	Deep	Midrow	0.58	Broadcast -Inc.	0.94	-0.48	0.19
11	Gao et al. 2015	Shallow	Side	0.18	Broadcast -Inc.	0.30	-0.51	0.19
12	Gao et al. 2015	Deep	Midrow	0.51	Broadcast -Inc.	0.30	0.53	0.19
13	Gao et al. 2015	Shallow	Side	0.26	Broadcast -Inc.	0.20	0.26	0.19
14	Gao et al. 2015	Deep	Midrow	0.25	Broadcast -Inc.	0.20	0.22	0.19
15	Tenuta et al. 2019	Shallow	Side	4.68	Broadcast -Inc.	3.38	0.33	0
16	Tenuta et al. 2023	Shallow	Side	1.10	Broadcast -Inc.	1.36	-0.21	0.44
17	Tenuta et al. 2023	Deep	Midrow	0.93	Broadcast -Inc.	1.36	-0.38	0.34
18	Tenuta et al. 2023	Shallow	Side	0.47	Broadcast -Inc.	0.80	-0.53	0.17
19	Tenuta et al. 2023	Deep	Midrow	0.44	Broadcast -Inc.	0.80	-0.60	0.16

20	Tenuta et al. 2023	Shallow	Side	0.72	Broadcast -Inc.	0.56	0.25	0.66
21	Tenuta et al. 2023	Deep	Midrow	0.30	Broadcast -Inc.	0.56	-0.62	0.57
22	Tenuta et al. 2023	Shallow	Side	0.56	Broadcast -Inc.	0.67	-0.18	0.38
23	Tenuta et al. 2023	Deep	Midrow	0.32	Broadcast -Inc.	0.67	-0.74	0.34
24	Tenuta et al. 2023	Shallow	Side	3.72	Broadcast -Inc.	1.18	1.15	0.50
25	Tenuta et al. 2023	Deep	Midrow	1.57	Broadcast -Inc.	1.18	0.29	0.79
26	Tenuta et al. 2023	Shallow	Side	0.87	Broadcast -Inc.	0.87	0.00	0.24
27	Tenuta et al. 2023	Deep	Midrow	1.09	Broadcast -Inc.	0.87	0.23	0.20
28	Tenuta et al. 2023	Shallow	Side	0.19	Broadcast -Inc.	0.22	-0.15	0.17
29	Tenuta et al. 2023	Deep	Midrow	0.16	Broadcast -Inc.	0.22	-0.32	0.32
30	Tenuta et al. 2023	Shallow	Side	0.14	Broadcast -Inc.	0.13	0.07	0.21
31	Tenuta et al. 2023	Deep	Midrow	0.13	Broadcast -Inc.	0.13	0.00	0.12
32	Tenuta et al. 2023	Shallow	Side	1.13	Broadcast -Inc.	0.52	0.78	1.05
33	Tenuta et al. 2023	Deep	Midrow	0.95	Broadcast -Inc.	0.52	0.60	1.13
34	Tenuta et al. 2023	Shallow	Side	0.66	Broadcast -Inc.	0.35	0.63	0.68
35	Tenuta et al. 2023	Deep	Midrow	0.66	Broadcast -Inc.	0.35	0.63	0.74
36	Tenuta et al. 2023	Shallow	Side	1.66	Broadcast -Inc.	0.67	0.91	0.37
37	Tenuta et al. 2023	Deep	Midrow	1.32	Broadcast -Inc.	0.67	0.68	0.37
38	Tenuta et al. 2023	Shallow	Side	0.55	Broadcast -Inc.	0.55	0.00	0.41
39	Tenuta et al. 2023	Deep	Midrow	0.68	Broadcast -Inc.	0.55	0.21	0.31
40	Tenuta et al. 2022	Shallow	Midrow	0.36	Broadcast -Inc.	0.51	-0.35	0.93
41	Tenuta et al. 2022	Shallow	Midrow	0.18	Broadcast -Inc.	0.14	0.25	0.65
42	Tenuta et al. 2022	Deep	Midrow	0.07	Broadcast -Inc.	0.51	-1.99	0.43

43	Tenuta et al. 2022	Deep	Midrow	0.34	Broadcast -Inc.	0.14	0.89	0.34
44	Tenuta et al. 2022	Shallow	Midrow	0.76	Broadcast -Inc.	0.08	2.25	0.58
45	Tenuta et al. 2022	Shallow	Midrow	0.31	Broadcast -Inc.	0.09	1.24	0.49
46	Tenuta et al. 2022	Deep	Midrow	0.02	Broadcast -Inc.	0.08	-1.39	0.08
47	Tenuta et al. 2022	Deep	Midrow	0.25	Broadcast -Inc.	0.09	1.02	0.42

Supplemental Table 7. Dataset used for assessment of the effectiveness of band (side, midrow) versus surface placement of fertilizer

No.	Reference	Treatment (Shallow/Deep)	Treatment (Side/Midrow)	Emission (kg N ₂ O-N ha ⁻¹)	Control	Emission (kg N ₂ O-N ha ⁻¹)	Effect size	Variance
1	Oleson et al. 2023	Shallow	Side	0.30	Surface	0.25	0.19	0.05
2	Oleson et al. 2023	Deep	Side	0.22	Surface	0.25	-0.13	0.05
3	Oleson et al. 2023	Shallow	Side	0.24	Surface	0.26	-0.07	0.05
4	Oleson et al. 2023	Deep	Side	0.20	Surface	0.26	-0.26	0.05
5	Oleson et al. 2023	Shallow	Side	0.31	Surface	0.32	-0.05	0.05
6	Oleson et al. 2023	Deep	Side	0.23	Surface	0.32	-0.35	0.05
7	Tenuta et al. 2023	Shallow	Midrow	0.16	Surface	0.13	0.21	0.03
8	Tenuta et al. 2022	Shallow	Midrow	0.53	Surface	0.24	0.79	0.21
9	Tenuta et al. 2022	Shallow	Midrow	0.29	Surface	0.14	0.73	0.17
10	Tenuta et al. 2022	Deep	Midrow	0.46	Surface	0.24	0.65	0.17
11	Tenuta et al. 2022	Deep	Midrow	0.29	Surface	0.14	0.73	0.17
12	Tenuta et al. 2022	Shallow	Midrow	0.17	Surface	0.13	0.27	0.09
13	Tenuta et al. 2022	Shallow	Midrow	0.11	Surface	0.05	0.79	0.38
14	Tenuta et al. 2022	Deep	Midrow	0.18	Surface	0.13	0.33	0.11
15	Tenuta et al. 2022	Deep	Midrow	0.14	Surface	0.05	1.03	0.47

Supplemental Table 8. Dataset used for assessment of the effectiveness of fall versus spring application

No.	Reference	Treatment	Emission (kg N ₂ O- N ha ⁻¹)	Control	Emission (kg N ₂ O- N ha ⁻¹)	Effect size	Variance
1	Thies et al. 2020	Fall	0.261	Spring	0.293	-0.12	0.02
2	Thies et al. 2020	Fall	0.086	Spring	0.169	-0.68	0.02
3	Thies et al. 2020	Fall	0.005	Spring	0.103	-3.03	0.02
4	Tenuta et al. 2016	Fall	3.6	Spring	9.3	-0.95	0.02
5	Wood et al. 2023	Fall	2.47	Spring	1.67	0.39	0.09
6	Wood et al. 2023	Fall	0.9	Spring	1.04	-0.14	0.13
7	Wood et al. 2023	Fall	3.63	Spring	1.32	1.01	0.18
8	Wood et al. 2023	Fall	1.61	Spring	0.55	1.07	0.16
9	Wood et al. 2023	Fall	2.14	Spring	2.13	0.00	0.06
10	Wood et al. 2023	Fall	2	Spring	1.36	0.39	0.11
11	Wood et al. 2023	Fall	1.6	Spring	2.19	-0.31	0.09
12	Wood et al. 2023	Fall	0.62	Spring	1.06	-0.54	0.10
13	Wood et al. 2023	Fall	0.29	Spring	0.4	-0.32	0.30
14	Wood et al. 2023	Fall	0.85	Spring	0.66	0.25	0.11
15	Wood et al. 2023	Fall	0.35	Spring	0.37	-0.06	0.08
16	Wood et al. 2023	Fall	0.44	Spring	0.51	-0.15	0.08
17	Wood et al. 2023	Fall	0.53	Spring	0.78	-0.39	0.04
18	Wood et al. 2023	Fall	0.49	Spring	0.8	-0.49	0.13
19	Wood et al. 2023	Fall	0.97	Spring	1.15	-0.17	0.03
20	Wood et al. 2023	Fall	0.64	Spring	0.47	0.31	0.08

21	Wood et al. 2023	Fall	0.68	Spring	1.11	-0.49	0.06
22	Wood et al. 2023	Fall	0.59	Spring	0.75	-0.24	0.07
23	Wood et al. 2023	Fall	0.97	Spring	0.93	0.04	0.09
24	Wood et al. 2023	Fall	1.83	Spring	1.67	0.09	0.27
25	Wood et al. 2023	Fall	1.07	Spring	1.6	-0.40	0.09
26	Wood et al. 2023	Fall	0.54	Spring	0.7	-0.26	0.38
27	Wood et al. 2023	Fall	0.36	Spring	0.31	0.15	0.04
28	Wood et al. 2023	Fall	0.51	Spring	0.54	-0.06	0.03
29	Wood et al. 2023	Fall	0.48	Spring	0.32	0.41	0.17
30	Wood et al. 2023	Fall	0.45	Spring	0.31	0.37	0.15
31	Wood et al. 2023	Fall	0.83	Spring	0.78	0.06	0.08
32	Wood et al. 2023	Fall	0.51	Spring	1.09	-0.76	0.17
33	Wood et al. 2023	Fall	0.33	Spring	0.24	0.32	0.11
34	Wood et al. 2023	Fall	0.12	Spring	0.08	0.41	0.05
35	Wood et al. 2023	Fall	0.28	Spring	0.17	0.50	0.05
36	Wood et al. 2023	Fall	0.2	Spring	0.14	0.36	0.12
37	Wood et al. 2023	Fall	0.25	Spring	0.18	0.33	0.04
38	Wood et al. 2023	Fall	0.23	Spring	0.8	-1.25	0.01
39	Wood et al. 2023	Fall	0.3	Spring	0.41	-0.31	0.15
40	Wood et al. 2023	Fall	1.31	Spring	0.53	0.90	0.12
41	Wood et al. 2023	Fall	2.64	Spring	0.56	1.55	0.02
42	Wood et al. 2023	Fall	1.08	Spring	0.48	0.81	0.02
43	Wood et al. 2023	Fall	1.15	Spring	0.51	0.81	0.01

44	Wood et al. 2023	Fall	2.36	Spring	0.67	1.26	0.17
45	Wood et al. 2023	Fall	0.88	Spring	0.52	0.53	8.08
46	Wood et al. 2023	Fall	0.88	Spring	0.52	0.53	0.02
47	Thilakarathna et al. 2020	Fall	0.393	Spring	0.63	-0.47	0.02
48	Thilakarathna et al. 2020	Fall	0.317	Spring	1.08	-1.23	0.02
49	Thilakarathna et al. 2020	Fall	0.299	Spring	0.365	-0.20	0.02
50	Thilakarathna et al. 2020	Fall	0.264	Spring	0.528	-0.69	0.02
51	Thilakarathna et al. 2020	Fall	0.259	Spring	0.407	-0.45	0.02
52	Thilakarathna et al. 2020	Fall	0.535	Spring	0.478	0.11	0.02
53	Thilakarathna et al. 2020	Fall	0.353	Spring	0.27	0.27	0.02
54	Thilakarathna et al. 2020	Fall	0.278	Spring	0.232	0.18	0.02
55	Thilakarathna et al. 2020	Fall	0.287	Spring	0.327	-0.13	0.02
56	Thilakarathna et al. 2020	Fall	0.293	Spring	0.506	-0.55	0.02
57	Thilakarathna et al. 2020	Fall	0.24	Spring	0.233	0.03	0.02
58	Thilakarathna et al. 2020	Fall	0.242	Spring	0.413	-0.53	0.02
59	Thilakarathna et al. 2020	Fall	0.292	Spring	0.428	-0.38	0.02
60	Thilakarathna et al. 2020	Fall	0.18	Spring	0.455	-0.93	0.02
61	Burton et al. 2008	Fall	1.93	Spring	2.74	-0.35	0.02
62	Burton et al. 2008	Fall	1.74	Spring	1.19	0.38	0.02
63	Burton et al. 2008	Fall	1.47	Spring	1.77	-0.19	0.02
64	Burton et al. 2008	Fall	0.55	Spring	0.38	0.37	0.02
65	Burton et al. 2008	Fall	0.55	Spring	0.72	-0.27	0.02
66	Burton et al. 2008	Fall	1.16	Spring	0.72	0.48	0.02

67	Burton et al. 2008	Fall	1.25	Spring	0.64	0.67	0.02
68	Burton et al. 2008	Fall	0.26	Spring	0.26	0.00	0.02
69	Burton et al. 2008	Fall	0.29	Spring	0.21	0.32	0.02
70	Dungan et al. 2017	Fall	0.66	Spring	0.59	0.11	0.02
71	Dungan et al. 2017	Fall	0.52	Spring	0.44	0.17	0.02
72	Soon et al. 2011	Fall	0.616	Spring	0.5	0.21	0.02
73	Soon et al. 2011	Fall	0.46	Spring	0.676	-0.38	0.02
74	Soon et al. 2011	Fall	0.708	Spring	1.22	-0.54	0.02
75	Soon et al. 2011	Fall	0.922	Spring	1.37	-0.40	0.02
76	Soon et al. 2011	Fall	0.683	Spring	1.09	-0.47	0.02
77	Soon et al. 2011	Fall	1.05	Spring	1.31	-0.22	0.02
78	Soon et al. 2011	Fall	NA	Spring	1.91	NA	NA
79	Soon et al. 2011	Fall	NA	Spring	1.44	NA	NA
80	Soon et al. 2011	Fall	NA	Spring	1.31	NA	NA
81	Soon et al. 2011	Fall	0.139	Spring	0.128	0.08	0.02
82	Soon et al. 2011	Fall	0.058	Spring	0.119	-0.72	0.02
83	Soon et al. 2011	Fall	0.124	Spring	0.17	-0.32	0.02
84	Soon et al. 2011	Fall	0.096	Spring	0.267	-1.02	0.02
85	Soon et al. 2011	Fall	0.259	Spring	0.226	0.14	0.02
86	Soon et al. 2011	Fall	0.254	Spring	0.197	0.25	0.02
87	Owens et al. 2019	Fall	0.17	Spring	0.17	0.00	1.30
88	Owens et al. 2019	Fall	0.23	Spring	0.1	0.83	0.53
89	Owens et al. 2019	Fall	0.31	Spring	0.16	0.66	0.25

90	Owens et al. 2019	Fall	0.23	Spring	0.11	0.74	0.51
91	Owens et al. 2019	Fall	0.21	Spring	0.18	0.15	0.50
92	Owens et al. 2019	Fall	0.17	Spring	0.18	-0.06	0.33
93	Owens et al. 2019	Fall	0.17	Spring	0.19	-0.11	0.12
94	Owens et al. 2019	Fall	0.18	Spring	0.13	0.33	0.34
95	Ogilvie et al. 2022	Fall	3.01	Spring	3.26	-0.08	0.02
96	Ogilvie et al. 2022	Fall	2.67	Spring	2.02	0.28	0.02
97	Ogilvie et al. 2022	Fall	1.74	Spring	0.58	1.10	0.02
98	Ogilvie et al. 2022	Fall	2.02	Spring	0.75	0.99	0.02
99	Ogilvie et al. 2022	Fall	3.43	Spring	0.84	1.41	0.02
100	Ogilvie et al. 2022	Fall	3.09	Spring	2.95	0.05	0.02
101	Ogilvie et al. 2022	Fall	3.47	Spring	1.18	1.08	0.02
102	Ogilvie et al. 2022	Fall	1.95	Spring	1.98	-0.02	0.02
103	Ogilvie et al. 2022	Fall	1.91	Spring	2.35	-0.21	0.02
104	Ogilvie et al. 2022	Fall	0.86	Spring	0.91	-0.06	0.02
105	Ogilvie et al. 2022	Fall	0.73	Spring	1.01	-0.32	0.02
106	Ogilvie et al. 2022	Fall	2.67	Spring	1.14	0.85	0.02
107	Ogilvie et al. 2022	Fall	1.24	Spring	1.28	-0.03	0.02
108	Ogilvie et al. 2022	Fall	1.87	Spring	1.22	0.43	0.02

Appendix B: Summary of the studies included in the meta-analysis.

Reference	Location	EEFs	Rate (kg N-ha⁻¹)	Placement	Time
Wood et al. 2023	Manitoba	Nitrapyrin, LIMUS, Super-U, PCU	90, 100, 115, 123,	Band	Fall, Spring
Tenuta et al. 2016	Manitoba	NA	112, 180	Band	Fall, Spring
Tenuta et al. 2023	Manitoba	Super-U	90, 95, 107, 110, 145	Band, Broadcast	Fall
Gao et al. 2015	Manitoba	ESN, Super-U	80	Band, Broadcast-Inc.	Spring
Thilakarantha et al. 2023	Alberta	DMPSA, PCU	99, 117, 123, 138	Broadcast-Inc.	Spring
Gao et al. 2017	Manitoba	PCU	100, 180, 200	Band, Broadcast-Inc.	Spring
Thilakarantha et al. 2020	Alberta	Super-U, PCU, Nitrapyrin	100	Band	Fall, Spring
Gao et al. 2013	Manitoba	NA	80, 160, 240	Broadcast-Inc.	Spring
Oleson et al. 2023	Manitoba	Super-U, PCU, Agrotain, Agrotain Plus	112	Band, Broadcast-Inc.	Spring
Ghosh et al. 2019	North Dakota	Super-U, PCU	225, 280	Broadcast-Inc.	Spring
Burton et al. 2008	Manitoba	PCU	80	Band, Broadcast	Fall, Spring
Thapa et al. 2017	Minnesota	Super-U, Nitrapyrin	146, 168	Broadcast	Spring

Graham et al. 2018	Illinois	PCU, Super-U, Nitrapyrin	202	Band, Broadcast	Spring
Liu et al. 2005	Colorado	NA	134, 224	Band	Spring
Glenn et al. 2012	Manitoba	NA	120, 200	Band	Spring
Omonode et al. 2015	Indiana	NA	145, 202	Band	Spring
An et al. 2020	Alberta	PCU, Nitrapyrin, Agrotain	146, 175, 176	Band, Broadcast	Spring
Owens et al. 2019	Manitoba	Nitrapyrin, PCU, Super-U	72, 84	Band, Broadcast	Fall, Spring
Thies et al. 2020	South Dakota	NA	224	Broadcast	Fall, Spring
Sainju et al. 2012	North Dakota	NA	28, 34, 45, 73, 79, 90	Band, Broadcast	Spring
Tenuta et al. 2019	Manitoba	NA	98, 110, 112, 146, 168, 180	Band, Broadcast-Inc.	Spring
Thapa et al. 2015	Minnesota	Super-U, Nitrapyrin	146, 168	Broadcast	Spring
Dusenbury et al. 2008	Montana	NA	50, 85, 175, 218, 240, 245, 285	Band, Broadcast	Fall, Spring
Li et al. 2012	Alberta	PCU	68, 97, 110, 116, 166, 169	Band	Spring
Malhi et al. 2006, 2007	Saskatchewan	NA	120	Band	Spring
Venterea et al. 2010	Minnesota	NA	146	Band, Broadcast-Inc.	Spring

Halvorson et al. 2010	Colorado	PCU, Super-U, Agrotain Plus	202, 246	Band	Spring
Halvorson et al. 2011	Colorado	PCU, Super-U, Nfusion, Agrotain Plus	202	Band	Spring
Halvorson et al. 2012	Colorado	PCU, Super-U, Agrotain Plus	202	Band	Spring
Dungan et al. 2017	Idaho	Super-U	67, 168, 186	Broadcast-Inc.	Fall, Spring
Adelekun et al. 2021	Manitoba	NA	80, 180	Broadcast-Inc.	Spring
Fujinuma et al. 2011	Minnesota	NA	180	Band, Broadcast-Inc.	Spring
Hyatt et al. 2010	Minnesota	PCU	270	Band, Broadcast-Inc.	Spring
Parkin et al. 2014	Iowa	PCU, Super-U, Agrotain Plus	168	Broadcast	Spring
Soon et al. 2011	Saskatchewan	PCU	50, 55, 60	Band	Fall, Spring
Engel et al. 2010	Montana	NA	100, 200	Band, Broadcast	Spring
Tenuta et al. 2023	Manitoba	PCU, Super-U, DMPSA, Nitrapyrin, Agrotain	95, 96, 112, 124, 125	Band, Broadcast	Spring
Tenuta et al. 2022	Manitoba	Nitrapyrin	118, 127	Band, Broadcast	Spring
Ogilvie et al. 2022	Saskatchewan	PCU, Super-U, LIMUS, Nitrapyrin	98, 123	Band	Fall, Spring

Appendix C: Increasing trend of fertilizer-induced cumulative N₂O emissions with N input rates
(Linear-fit model) across all studies.

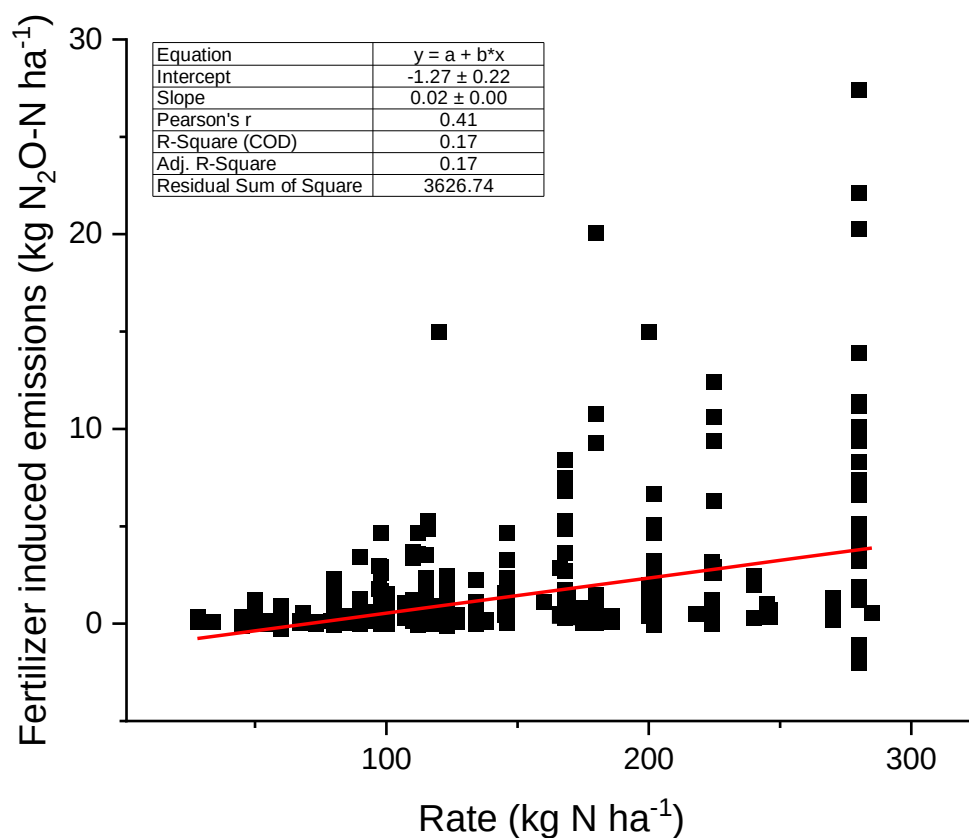


Figure S1: Increasing trend of fertilizer-induced cumulative N₂O emissions with N input rates
 (Linear-fit model) across all studies.