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Journal

Agronomy Journal, 106(2)

ISSN

0002-1962

Authors

Asgedom, Haben
Tenuta, Mario
Flaten, Donald N
[et al.](#)

Publication Date

2014-03-01

DOI

10.2134/agronj2013.0096

Peer reviewed

Nitrous Oxide Emissions from a Clay Soil Receiving Granular Urea Formulations and Dairy Manure

Haben Asgedom, Mario Tenuta,* Donald N. Flaten, Xiaopeng Gao, and Ermias Kebreab

ABSTRACT

Soil N₂O emissions vary with N source. A study was undertaken on a clay soil in the Red River Valley, Manitoba, Canada, to determine the effect of granular N fertilizers and dairy manure on N₂O emissions from a field cropped to rapeseed (*Brassica napus* L.) in 2009 and spring wheat (*Triticum aestivum* L.) in 2010. Treatments included an unamended control, granular urea, controlled-release urea (ESN), stabilized urea (SuperU), and solid dairy manure added at rates to achieve a total of 140 kg available N ha⁻¹ (product plus soil N test). The N fertilizers were broadcast and shallowly incorporated each spring before planting; the manure was broadcast incorporated the previous fall. Nitrous oxide emissions were monitored from planting to freeze in fall and during spring thaw in 2011 using static-vented chambers. In both years, N₂O emissions occurred within 4 to 5 wk of planting but not in fall after manure application. Area-scale cumulative N₂O emissions (Σ N₂O, kg N ha⁻¹) from planting to freeze were control < ESN = manure < urea = SuperU. Nitrous oxide emission factors were 0.017 kg N₂O-N kg⁻¹ available N added for urea and SuperU and 0.007 kg N₂O-N kg⁻¹ available N for ESN. Seventy-eight percent of the variation in Σ N₂O could be explained by NO₃⁻ intensity, an integration of soil NO₃⁻ concentrations during the study periods. Greater Σ N₂O were also associated with higher yields. These findings suggest that N release rates, as indicated by NO₃⁻ intensity and yield, determined N₂O emissions. The results highlight the challenge of meeting crop demand yet reducing N₂O emissions by selection of an N source.

IT IS WIDELY known that N inputs from synthetic fertilizers or manures increase NH₄⁺ and NO₃⁻ concentrations in the soil and consequently N₂O emissions (Rochette et al., 2008); however, synthetic fertilizer N products and manures differ in their capacity to induce N₂O emissions from soil (Bouwman et al., 2002; Tenuta and Beauchamp, 2003; VanderZaag et al., 2011). Hence, proper selection of the type of N applied, also known as the “right source,” is being examined to reduce N₂O emissions from agricultural soil (Halvorson et al., 2013). In the United States, the type of synthetic N fertilizer selected, the chemical form of N, and enhanced-efficiency formulations may mitigate 0.45 Mg CO₂ equivalents ha⁻¹ yr⁻¹ (Eagle et al., 2012). In Canada, the “right source” is included as a mitigation practice of N₂O emissions in the Nitrous Oxide Emission Reduction Protocol (Alberta Environment, 2011).

Urea is the main N source for crop production in the Canadian Prairies and Northern Great Plains. Commercially available enhanced-efficiency granular urea fertilizers allow better timing of N release, consistent with crop growth and N demand. Two products are SuperU, a stabilized granular urea product containing a urease inhibitor, *N*-(*n*-butyl) thiophosphoric triamide (NBPT), and a nitrification inhibitor, dicyandiamide (DCD),

and Environmentally Smart Nitrogen (ESN), controlled-release, polymer-coated urea granules (Trenkel, 2010).

Urea formulations such as ESN and SuperU are designed to synchronize N release from synthetic fertilizers to meet plant N demand (Trenkel, 2010). Such formulations can minimize the amount of available N during the early season when crop uptake is relatively slow and thus minimize the probability of N losses (Akiyama et al., 2010). In Canada, it is estimated that 1.7 million ha of agricultural land receives livestock solid manures (Statistics Canada, 2011). Release of N from manures containing straw bedding (solid manures) is usually slower than from synthetic fertilizers, with a consequence of perhaps less inorganic N in the soil being susceptible for transformation to N₂O (VanderZaag et al., 2011). In the Northern Great Plains and Canadian Prairies, solid manures are often applied in the fall such that mineralization of the material may occur in the spring or early summer following the frozen period of winter.

There have been relatively few studies that compared the magnitude of N₂O emissions associated with enhanced-efficiency N fertilizers and manures. Tenuta and Beauchamp (2003) reported that granular urea produced more N₂O than other granular N forms, NH₄⁺ and NO₃⁻ sources, added to clay loam soil. With urea being the most commonly used granular N fertilizer in the Canadian Prairies and Northern Great Plains, enhanced-efficiency urea products are being examined to mitigate emissions. The controlled-release fertilizer ESN reduced N₂O emissions by 42% compared with urea under no-till and strip-tillage conditions in corn (*Zea mays* L.)-based production systems in the Central Great Plains of Colorado

H. Asgedom, M. Tenuta, D.F. Flaten and X. Gao, Dep. of Soil Science, Univ. of Manitoba, Winnipeg, MB, Canada, R3T 2N2; and E. Kebreab, Dep. of Animal Science, Univ. of California, Davis, CA 95616. Received 26 Feb. 2013. *Corresponding author (mario.tenuta@ad.umanitoba.ca).

Published in Agron. J. 105:1–13 (2013)
doi:10.2134/agronj2013.0096

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Abbreviations: DCD, dicyandiamide; DOY, day of the year; EF, nitrous oxide emissions factor; EI, nitrous oxide emission intensity; NBPT, *N*-(*n*-butyl) thiophosphoric triamide; TGAS MAN, Trace Gas Manitoba.

(Halvorson et al., 2013). A meta-analysis of 35 field studies showed that the use of enhanced-efficiency N fertilizers sometimes reduced N₂O emissions compared with unformulated synthetic N sources (Akiyama et al., 2010). Li et al. (2012) recently showed that polymer-coated urea reduced N₂O emissions compared with conventional urea. Other studies, however, found more N₂O emissions from polymer-coated than from conventional urea (Sistani et al., 2011; Jiang et al., 2010; Zebarth et al., 2012) and that the effectiveness of stabilizers varied with soil properties (Kelliher et al., 2008), highlighting uncertainty in the effectiveness of enhanced-efficiency N fertilizer products to mitigate emissions. Nitrate intensity, sometimes referred as nitrate exposure, was introduced by Zebarth et al. (2008a, 2008b) and Burton et al. (2008a, 2008b) as an assessment of the magnitude and duration of soil NO₃⁻ and its potential impact on soil biology and the potential for NO₃⁻ loss to the environment. Nitrate intensity measurements in an enhanced-efficiency N fertilizer study could reflect a timely increase in the supply of soil mineral N and thus its relationship to N₂O emissions.

Studies of N₂O emissions from N sources applied to clay soils such as the Vertisols of the Red River Valley of Manitoba, Minnesota, and North Dakota are few. These soils are poorly drained, have very high clay and organic matter contents, and seem to release more N₂O than other areas of the Canadian Prairies and Northern Great Plains (Glenn et al., 2012). Thus, a field study was conducted with the objectives (i) to determine the effect of enhanced-efficiency N sources and a solid manure on N₂O emissions compared with conventional granular urea on a clay soil of the Red River Valley, Manitoba, and (ii) to determine if the amount and timing of N release from the products determined emissions.

MATERIALS AND METHODS

Site Description and Experimental Design

This study was conducted on plots established in 2008 in the Long-Term Manure and Crop Rotation Study at the National Centre for Livestock and the Environment, University of Manitoba, at Glenlea, MB (49°38'15" N, 97°9'25" W). The site is in the Red River Valley about 15 km south of the city of Winnipeg. The soil is mapped as the Red River association (Michalyna, 1975), a Gleysolic Humic Vertisol in the Canadian soil classification system and a Typic Humicryert in the U.S. system. The site is imperfectly drained. Before initiation of the experiment, 30 soil core samples (1.9-cm diameter) were composited for determination of soil characteristics (0–15 cm): clay texture (70% clay, 26% silt, and 4% sand), 7.0 pH, electrical conductivity of 0.32 dS m⁻¹, 21.0 g kg⁻¹ organic C content, and 1.0 Mg m⁻³ bulk density. Soil texture was determined by the pipette method (Loveland and Whalley, 1991). Soil pH and electrical conductivity were measured in a 1:2 soil/0.01 mol L⁻¹ CaCl₂ suspension. Soil organic C was determined using the dry combustion method (Carter, 1993). Soil bulk density was determined from core samples taken by driving a metal corer into the soil.

The experimental design was a complete randomized block with four replicates. Each plot was 20 by 20 m. The treatments were: no N addition (control), granular urea (46% N), a controlled release polymer-coated urea product (ESN, 44% N,

Table 1. Application date, application rate, and available N applied by the N sources in 2009 and 2010.

N source	Application date	Application rate	Available N applied
		kg ha ⁻¹	
		<u>2008</u>	
Control	–	–	23
Manure	19 Oct. (DOY† 293)	40,411‡	101
		<u>2009</u>	
Urea	29 May (DOY 149)	247	114
ESN	29 May	264	116
SuperU	29 May	264	121
Manure	20 Oct. (DOY 293)	44,901	137
		<u>2010</u>	
Urea	17 May (DOY 137)	271 (22)§	127
ESN	17 May	282	124
SuperU	18 May (DOY 138)	271	125
Manure	15 Oct. (DOY 288)	49,000	121

† Day of the year.

‡ As-is weight basis.

§ Amount of monoammonium phosphate added with seed in parentheses.

Agrium Advanced Technologies), a double-inhibitor stabilized urea product (SuperU, 46% N, Koch Fertilizer, LLC) and stockpiled solid dairy manure (6.0 g total N kg⁻¹, 4.2 g organic N kg⁻¹, 2.1 g total P kg⁻¹, 209 g dry matter kg⁻¹). The ESN product allows a controlled release of N with increasing moisture and temperature. The SuperU product contained two enzyme inhibitors to increase the soil residency of urea and NH₄⁺. During manufacturing, urease inhibitors (NBPT) and nitrification inhibitors (DCD) are distributed throughout the granule. The date of application as well as product rates and available-N applied for the N sources are provided in Table 1. The rate of addition of the N sources was based on provincial recommendations (Manitoba Soil Fertility Advisory Committee, 2004).

Application rates were calculated to supplement soil NO₃⁻ amounts determined to 60 cm the previous fall to meet 140 kg available-N ha⁻¹ and target yield goals. Plant-available N in the manure was estimated assuming that 25% of the organic N was available within 1 yr of application and 85% of NH₄⁺-N was available after volatilization loss (Prairie Provinces' Committee on Livestock Development and Manure Management, 2006). Manure was applied in the fall previous to each study year. The application rates of manure were 40,411, 44,901, and 49,000 kg ha⁻¹ in fall 2008, 2009, and 2010, providing available N of 101, 137, and 121 kg ha⁻¹, respectively. The reason for the fluctuation was that rates were set using average N content values for the manure from station records but the rates of available N applied were calculated from analysis of the applied manure. In both years, the N contents of the manure deviated from historical records.

Each plot received the same N source treatment in 2009 and 2010. The synthetic fertilizers were surface broadcast using a Valmar 1255 (Valmar Airflo) fertilizer spreader and incorporated to the 10-cm soil depth on 29 May 2009 (day of the year [DOY] 149) and 18 May 2010 (DOY 138) by shovels on 23-cm centers of an air seeder while sowing (5000HD, Flexi-Coil Ltd.). The shovels of the seeder at their widest were 23 cm, which allowed thorough shallow (5-cm) incorporation of the synthetic fertilizers. The manure was surface applied and incorporated to 15 cm

using a chisel cultivator (8T9002, Summers Manufacturing Co.) in the fall (19 Oct. 2008 [DOY 293], 20 Oct. 2009 [DOY 293], and 14 and 15 Oct. 2010 [DOY 287–288]).

In 2008 and before the current study, plots were sown to Legacy six-row malting barley (*Hordeum vulgare* L.). All plots were seeded on 23-cm rows to Red River 1826 Roundup Ready high-erucic-acid rapeseed in 2009 and Glenn spring feed wheat in 2010. The seeding rates were 6.7 kg ha⁻¹ for rapeseed and 134 kg ha⁻¹ for spring wheat. Harvest occurred on 8 Sept. 2009 (DOY 251) and 25 Aug. 2010 (DOY 237). Roundup Ultra 2 (glyphosate [*N*-(phosphonomethyl)glycine]) was applied post-planting to the rapeseed at 1.85 L ha⁻¹ (rate of product) to control weeds. In 2010, Curtail M (clopyralid [3,6-dichloro-2-pyridinecarboxylic acid] and MCPA-EHE [2-(4-chloro-2-methylphenoxy)acetic acid], 2 L ha⁻¹) and a tank mix of Curtail M (2 L ha⁻¹) and Horizon (clodinafop-propargyl [2-propynyl (2*R*)-2-[4-[(5-chloro-3-fluoro-2-pyridinyl)oxy]phenoxy]propanoate], 0.23 L ha⁻¹) were applied 3 June (DOY 154) and 14 June (DOY 165), respectively. The use of an herbicide resulted in light weed pressure in both years.

Nitrous Oxide Emissions

Nitrous oxide emissions were monitored using the static vented chamber technique with a polyvinyl chloride collar of 20.3-cm i.d. and 15-cm height (Tenuta et al., 2010). Collars were inserted 5 cm into the soil between rows and left open throughout the experiment periods, except during gas collection. Four collars were deployed in each plot. Lids of 23-cm diameter with a rubber gasket were made reflective using Al foil to reduce heat buildup during deployment and had vent tubes and a rubber septum for gas sampling. The lids were sealed to the collars using elastic rubber bands. Gas sampling was performed from planting through soil freeze between 30 May and 18 November (DOY 150–322) in 2009, between 19 May and 10 November (DOY 139–314) in 2010, and during the spring thaw of 2011 between 4 April and 6 May (DOY 94–126). The sampling interval was generally once or twice weekly, with a gap between 29 August and 22 October (DOY 241–295) in 2009 and 27 August and 7 October (DOY 239–280) in 2010 because of harvest and manure application activities. Gas samples (20 mL) were collected using disposable plastic syringes (Becton-Dickinson) at 0, 20, 40, and 60 min after lid placement on the collars. The gas samples were transferred to 12-mL twice-He-flushed and evacuated vials (Exetainer, Labco Ltd.). The vial tops were sealed with a thin layer of silicon sealant (Mastercraft, Canadian Tire Corp.). Fluxes were determined for a total of 25 events in 2009 and 22 in 2010. In 2011, there were six sample dates during the spring thaw. Gas samples were transported to the laboratory and stored at room temperature in darkness with other vials of 0.46 and 0.84 μL L⁻¹ N₂O standard gas (Welders Supplies) until analysis. Gas samples were analyzed for N₂O concentration using a gas chromatograph equipped with an electron capture detector (Varian CP-3800) and a Combi-PAL robotic sample introduction system. The chromatograph was calibrated using dilutions of pure N₂O gas (Welders Supplies). Gas sample analysis was repeated or the column reconditioned and calibration redone if quality control samples, placed every 10th position, showed >5% deviance from the expected concentration.

After 60 min of chamber deployment, the diffusive flux of N₂O from the soil surface might be reduced, resulting in a decrease in the rate of accumulation of headspace N₂O during chamber closure (Hutchinson and Mosier, 1981; Levy et al., 2011). Therefore, N₂O emission rates (ng N m⁻² min⁻¹) were calculated using the HMR package in the R computer language (Pedersen, 2011) considering linear or nonlinear best fits. The package recommends application of one of three regression approaches to estimate emission from the accumulation of N₂O during chamber deployment. A nonlinear model (Hutchinson and Livingston, 1993) is recommended if the accumulation of N₂O decreases with time. A linear model is recommended if the accumulation or dissipation of N₂O is consistent with time. An emission of zero is recommended in the absence of a clear trend in gas concentration with time. In the current study, we did not remove outlier concentration data from emission estimations or force negative emissions to zero. The application of the HMR package resulted in 29% of emissions being estimated using a nonlinear model and 71% using a linear model.

Area-scaled cumulative emissions (ΣN₂O kg N ha⁻¹) were determined from individual chambers for each whole growing season (May–November) by summation of daily estimates of N₂O emissions obtained by linear interpolation between sampling dates from 30 May to 18 Nov. 2009 (DOY 150–322) and from 19 May to 10 Nov. 2010 (DOY 139–314). Cumulative N₂O emissions during thaw (ΣN₂O_{thaw}) were estimated as the summation of daily estimates of N₂O emissions from 4 April to 6 May 2011 (DOY 94–126).

Whole growing season N₂O emission factors (EFs) for the synthetic fertilizer treatments, expressed as a percentage of N emitted as N₂O-N, was calculated as

$$EF = \frac{\Sigma N_2O_{N_{\text{source}}} - \Sigma N_2O_{\text{control}}}{\text{applied available } N_{N_{\text{source}}}} \times 100$$

where N₂O_{N_{source}} is the ΣN₂O (kg N ha⁻¹) for a synthetic N source treatment, N₂O_{Control} is the ΣN₂O (kg N ha⁻¹) of the control treatment, and applied available N_{N_{source}} (kg N ha⁻¹) is the application rate of N fertilizer. The EF for manure was not calculated because N₂O emissions following application in the fall had not been monitored.

Soil Analyses

Soil samples were collected six times in 2009 and four times in 2010 from just after planting to freeze. For each plot, 10, 3.8-cm-diameter soil cores were collected at 0 to 10 cm. The samples from the same plot were composited and kept at 4°C before drying at 30°C and then ground to pass a 2-mm mesh screen (Christy Turner Ltd.). The soils were extracted with 2 mol L⁻¹ KCl solution and analyzed for NH₄⁺-N colorimetrically using the Berthelot reaction and NO₃⁻-N colorimetrically using Cu–Cd reduction to NO₂⁻ and formation of a diazo compound using a Technicon Autoanalyzer II system. Ammonium, NO₃⁻, and N (NH₄⁺ plus NO₃⁻) intensities (mg N d kg⁻¹) were calculated in a similar way as ΣN₂O by summing daily estimates of the respective concentrations obtained by linear interpolation between sample dates from post-planting to freeze.

Yields and Plant Analyses

Aboveground plant material was collected at the harvest stage by clipping plants to 5 cm from the soil surface in two 0.25-m² quadrants. The plant material was dried at 48°C before dry-weight determination and grinding (Thomas Wiley Laboratory Mill Model 4). The rapeseed grain was separated by hand and the wheat grain was separated using a thresher (Bills Welding). Recovered grain and all other crop materials were analyzed for total N concentration (g kg⁻¹ dry material) using a LECO CNS-2000 Analyzer (LECO Corporation). Dry-weight grain yield (Mg ha⁻¹) and grain N concentration (g kg⁻¹) are reported. Grain N content (N_{gr} , kg N ha⁻¹) was estimated as the product of grain N concentration and dry-weight grain yield. Aboveground N content (N_{above} , kg N ha⁻¹) was estimated as the sum of the N content of non-grain material (the product of the N concentration [g kg⁻¹] of non-grain material and the dry weight of the non-grain material [Mg ha⁻¹]) and N_{gr} . Yield-scaled emissions as emission intensity (EI) for the synthetic fertilizer treatments were determined as ΣN_2O /yield (kg N Mg⁻¹). Emission intensity is a N₂O efficiency estimate considering crop yield.

Weather Conditions

Soil and air temperatures were measured during gas sampling periods using a Traceable Long-Stem Thermometer (Fisher Scientific Canada) at a depth of 2 cm next to each chamber and at 75 cm above the ground, respectively. Daily precipitation amounts were obtained from a weather station (Model T-200B Series precipitation gauge, Geonor Inc.) located at the Trace Gas Manitoba (TGAS-MAN) research site 1 km from the current study. Long-term mean air temperature and total precipitation May through October 1998 to 2007 for the study area were 14.1°C and 379 mm (Richardson International Airport, Winnipeg, Environment Canada). The 2009 study period was cooler (mean 13.1°C) than the long-term average, with normal precipitation (361 mm). The temperature in 2010 was normal (14.4°C), but precipitation was relatively high (649 mm).

Data Analysis and Statistics

The daily N₂O emission rate, cumulative N₂O emissions (ΣN_2O), ΣN_2O_{thaw} , yield, grain N concentration, N_{gr} , N_{above} , soil NH₄⁺-N and NO₃⁻-N concentrations, and EI were log₁₀- or power-transformed to ensure that the data were distributed normally. Variance analyses were then conducted on the transformed data using the Mixed Linear Model in IBM SPSS Statistics 19 (IBM Corporation). The statistical model considered treatment and year as fixed factors, with block and chambers-within-plots as random factors when considering ΣN_2O and ΣN_2O_{thaw} . Unless otherwise specified, all treatment mean comparisons used Fisher's LSD at the $\alpha = 0.05$ level. Mean values for untransformed data are reported. The associations of ΣN_2O with NH₄⁺, NO₃⁻, and N intensities and soil temperature, yield, N_{gr} , and N_{above} were determined by Pearson product moment correlation analysis for the whole growing season and also for the early season period (DOY 167–197 in 2009, DOY 147–175 in 2010) when the majority of N₂O emissions occurred. Linear regression analysis was used to relate NO₃⁻ intensities to ΣN_2O for the whole growing season and early season periods.

RESULTS

Nitrous Oxide Emissions

Nitrous oxide was emitted for several weeks following application of the synthetic fertilizer products (Fig. 1). In 2009, emissions reached a maximum 33 d after application, being 178, 154, and 108 g N d⁻¹ha⁻¹ for SuperU, Urea and ESN, respectively. In 2010, emissions reach a maximum approximately 15 d after application, being 153, 172, and 47 g N d⁻¹ha⁻¹ for SuperU, Urea and ESN, respectively. On the sampling dates when a fertilizer treatment effect was significant, emission rates were generally similar for Urea and SuperU but lower for ESN. The application of the manure in fall did not result in appreciable emissions of N₂O before freeze-up in 2009 and 2010. During this time, air and soil temperature declined to near 0°C compared to warm conditions following application of the N fertilizers in late spring (Fig. 2 and 3). However, emission for the manure treatment occurred during the same peak period as for the N fertilizers though rates of emission were comparatively small. Emissions from the control were also relatively small to the N sources with no distinct periods of high emission observed (Fig. 1).

The differing occurrence of emissions following planting for the study years coincided with large rain events. In 2009, a rain event on 27 and 28 June (DOY 178 and 179, Fig. 2) provided 73 mm which coincided with peak in emissions for all treatments a few days later. In 2010, a rain event on 29 and 30 May (DOY 149 and 150) resulted in 137 mm and an increase in emissions for about 2 wk afterward (Fig. 3). Rain events later in the growing season in both years did not elicit a response in N₂O emissions, for example, when 105 mm fell over 8 d starting Day 226 in 2009 (Fig. 2).

Area-scaled ΣN_2O tended to be highest for SuperU and urea in both years, intermediate for ESN and manure, and lowest for the control (Fig. 2 and 3). Over the study years, ΣN_2O was affected by N source but not by year (Table 2). Across the whole growing seasons, ΣN_2O were SuperU = Urea > ESN = manure > control. SuperU and Urea ΣN_2O averaged about 2.5 kg N₂O-N ha⁻¹ compared to half as much for ESN and manure while the control emitted slightly less than 0.5 kg of N₂O-N ha⁻¹. In 2011, ΣN_2O_{thaw} was negligible for all treatments except cumulative emissions in Urea treatment amounted to 0.14 kg of N₂O-N ha⁻¹ (Table 2).

The EF had the same relative response to N sources as ΣN_2O being SuperU = Urea > ESN (Table 2). The EF for SuperU and Urea was 1.7% of applied N and that for ESN was 0.7%. A significant treatment by year interaction for EF occurred because EFs for SuperU and Urea were higher in 2010 than 2009 (data not shown).

Soil Inorganic Nitrogen

There was no clear response in extractable NH₄⁺ as a result of the application of the N sources in 2009 (Fig. 4a). In 2010, concentrations of extractable NH₄⁺ for ESN tended to be greater than the other treatments (Fig. 4b). By the first soil sample occasion in 2009 and 2010, elevated NO₃⁻ concentrations for the urea products compared to the control indicated nitrification had taken place and likely accounted for the lack in response in extractable NH₄⁺ to the source additions (Fig. 4c and 4d). In early seasons of 2009 and 2010, Urea and SuperU had the greatest concentrations of NO₃⁻, followed

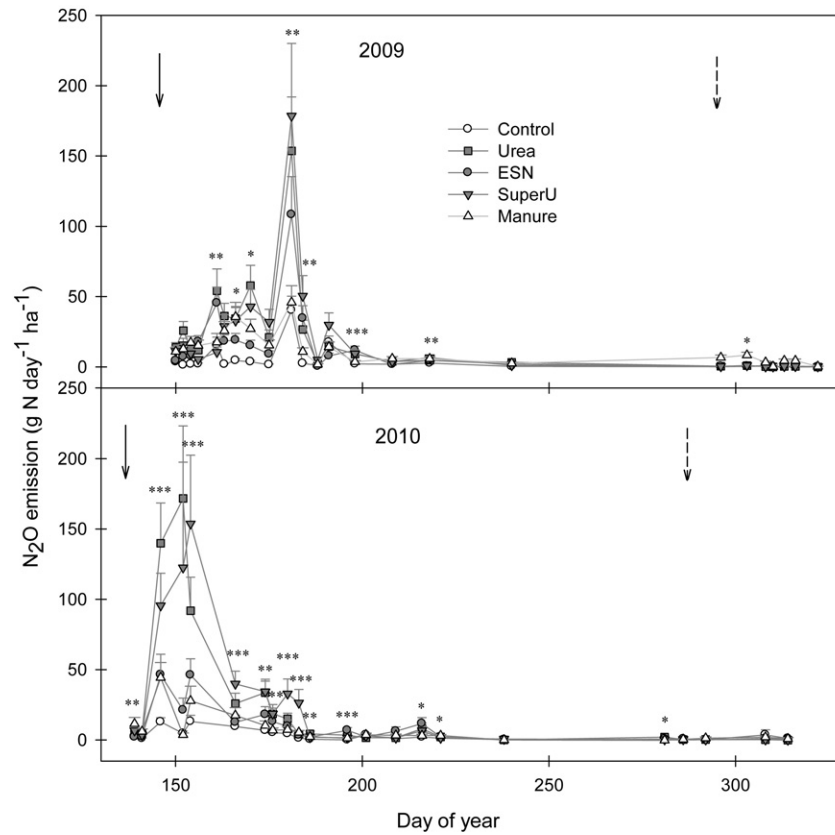


Fig. 1. Nitrous oxide emission rates from control, urea, ESN, SuperU, and solid dairy manure in 2009 and in 2010. Bars indicate one standard error of the mean ($n = 16$). Solid and dashed arrows indicate timing of synthetic fertilizer and manure applications, respectively. *, **, *** indicate differences between fertilizer treatments significant at $P < 0.05$, $P < 0.01$, $P < 0.001$, respectively.

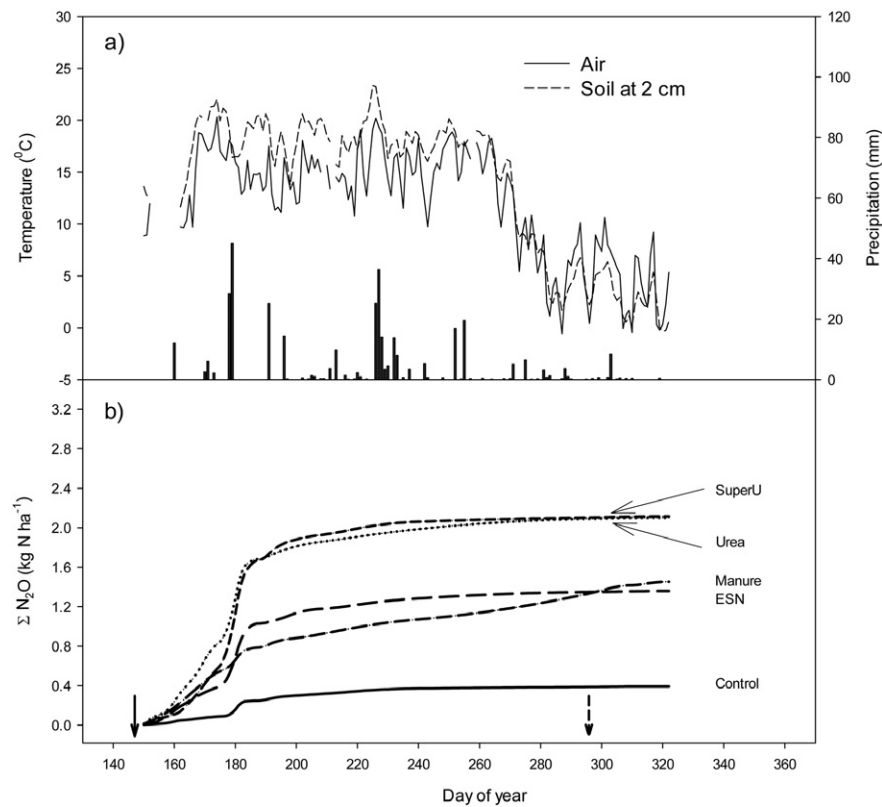


Fig. 2. (a) Soil temperature at 2 cm, air temperature, and precipitation and (b) cumulative N_2O emission (ΣN_2O) for control, urea, ESN, SuperU, and manure treatments in 2009. Mean values, $n = 16$. Solid and dashed arrows indicate timing of synthetic fertilizer and manure additions, respectively.

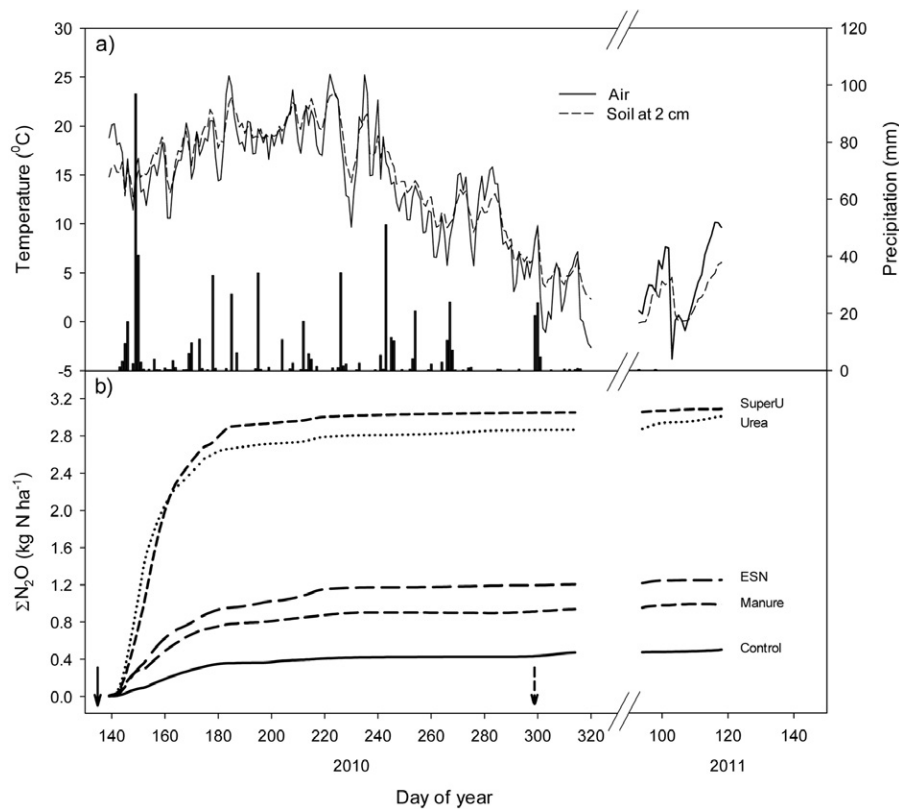


Fig. 3. (a) Soil temperature at 2 cm, air temperature, and precipitation and (b) cumulative N_2O emission (ΣN_2O) for control, urea, ESN, SuperU and manure treatments in 2010 and spring thaw in 2011. Mean values, $n = 16$. Solid and dashed arrows indicate timing of synthetic fertilizer and manure additions, respectively.

Table 2. Means and results of analysis of variance of cumulative N_2O emissions (ΣN_2O) across the whole growing season in 2009 and 2010 and during spring thaw in 2011. The N_2O emission factor (EF) during the 2009 and 2010 whole growing seasons is also shown ($n = 32$ for ΣN_2O and $n = 4$ for EF for fertilizer treatment; $n = 80$ for ΣN_2O and $n = 12$ for EF for year).

Treatment	ΣN_2O		EF 2009 and 2010
	2009 and 2010	Thaw 2011†	
	kg N_2O -N ha^{-1}		%
Control	0.43 ± 0.06 c‡	0.010 ± 0.003 b	
Urea	2.48 ± 0.34 a	0.142 ± 0.047 a	1.7 ± 0.3 a
ESN	1.28 ± 0.22 b	0.045 ± 0.015 b	0.7 ± 0.3 b
SuperU	2.58 ± 0.30 a	0.034 ± 0.016 b	1.7 ± 0.2a
Manure	1.19 ± 0.16 b	0.049 ± 0.015 b	–
2009	1.45 ± 0.16	–	1.4 ± 0.3
2010	1.71 ± 0.18	–	1.4 ± 0.3
2011	–	0.056	–
	ANOVA P value		
Treatment	<0.001	0.03	<0.001
Year	ns§	–	ns
Treatment × year	ns	–	<0.05

† Thaw 2011 included 4 Apr. to 6 May 2011.

‡ Means ± standard errors within a column followed by the same letter are not significantly different at $P > 0.05$.

§ ns, not significant at $P < 0.05$.

by ESN, then manure and lastly the control (Fig. 4c and 4d). Manure application in fall of 2009 but not fall 2010 resulted in increased NO_3^- in soil compared to other N sources for the last sample date of each year (Fig. 4c and 4d). Plant N uptake likely resulted in low NO_3^- concentrations (<5 mg N kg^{-1}) mid-season (Fig. 4c and 4d).

Crop Responses and Emission Intensities

The rapeseed yielded very well in 2009 (Table 3) for all N sources having exceeded the 1.0 Mg ha^{-1} 5-yr average for rapeseed in the area (Manitoba Management Plus Program, Manitoba Agricultural Services Corporation). Even the control yield matched the area average rapeseed yield. The high yield in the current study likely reflected that the variety used had a high yield potential, more similar to canola than rapeseed. In contrast, spring wheat yielded less than the 3.39 Mg ha^{-1} 5-yr average for all feed varieties in the area. In 2009, there was a general pattern for yield, grain N concentration, N_{gr} , and N_{above} to be greatest for the Urea treatment, smaller for ESN than other N sources and greater for all N sources, compared to the control. In 2010, the pattern for yield, N_{gr} , and N_{above} was for Urea and SuperU to be greatest, ESN to be the lowest of the N sources and the control the lowest of all treatments. Grain N concentration did not follow the pattern as concentrations were similar among N sources and all were greater than the control. Yield-based emission intensity, EI, was not significantly affected by the synthetic N treatments in 2009 with values ranging from 0.77 to 1.02 kg N Mg^{-1} (Table 3). In 2010, EI was significantly affected by the synthetic N sources with values for SuperU and Urea being greater than ESN and the control.

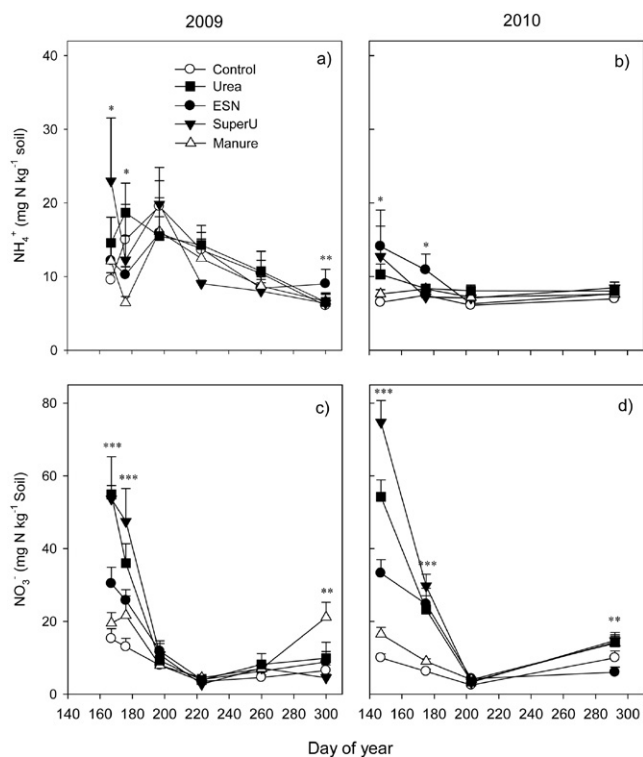


Fig. 4. Extractable soil NH_4^+ concentrations in (a) 2009 and (b) 2010 and extractable soil NO_3^- concentrations in (c) 2009 and (d) 2010 in the control, urea, ESN, SuperU, and manure treatments. Bars indicate standard error of the mean, $n = 4$. *, **, *** indicate differences between fertilizer treatments significant at $P < 0.05$, $P < 0.01$, $P < 0.001$, respectively.

Association of $\Sigma\text{N}_2\text{O}$ with Measured Variables

For the whole growing and early season periods of 2009, 2010 and across both years, NO_3^- intensity was most associated ($r = 0.87$ to 0.99) with $\Sigma\text{N}_2\text{O}$ of the treatments (Table 4). Inorganic N intensity was also highly correlated ($r = 0.87$ to 0.93) to $\Sigma\text{N}_2\text{O}$ estimates, but since NO_3^- concentrations were greater than NH_4^+ , this variable was largely influenced by NO_3^- . Yield, N_{gr} , and N_{above} were also significantly correlated to $\Sigma\text{N}_2\text{O}$ for the treatments in the early and whole growing season periods (Table 4).

Nitrate intensity was a very good predictor ($r^2 > 0.77$, $P < 0.01$) of $\Sigma\text{N}_2\text{O}$ for the treatments over the whole growing and early season periods (Fig. 5). Further, there was a consistent trend for ordination of treatments along the model's line of best fit using data from 2009, 2010, across both study years, and for the early and whole growing season periods (Fig. 5). Greater $\Sigma\text{N}_2\text{O}$ for Super U and Urea than other treatments occurred with high NO_3^- intensity values, ESN and manure were intermediate for $\Sigma\text{N}_2\text{O}$ and NO_3^- intensity while the control had the least emissions and lowest NO_3^- intensity values for the whole growing and early season periods.

DISCUSSION

Significantly decreasing greenhouse gas emissions from agriculture requires reducing the emissions of N_2O from N sources added to soil. Enhanced-efficiency N fertilizers such as controlled release and stabilized granular urea sometimes reduce N_2O emissions on an area-scaled basis (kg N ha^{-1}), depending on the formulation and cropping system (Akiyama

Table 3. Grain yield, grain N concentration, grain N uptake (N_{gr}), aboveground biomass N uptake (N_{above}), and N_2O emission intensity (EI) of high-erucic-acid rapeseed in 2009 and spring feed wheat in 2010 ($n = 4$).

Treatment	2009 rapeseed					2010 wheat				
	Yield	Grain N	N_{gr}	N_{above}	EI	Yield	Grain N	N_{gr}	N_{above}	EI
	Mg ha^{-1}	g kg^{-1}	kg N ha^{-1}	kg N ha^{-1}	kg N Mg^{-1}	Mg ha^{-1}	g kg^{-1}	kg N ha^{-1}	kg N ha^{-1}	kg N Mg^{-1}
Control	0.99 ± 0.28 c†	30.2 ± 1.0	30.9 ± 9.8 c	40.9 ± 11.7 c	0.38 ± 0.09	1.44 ± 0.22 d	22.0 ± 0.5 b	32.1 ± 5.3 d	40.1 ± 6.0 d	0.30 ± 0.07 b
Urea	2.66 ± 0.34 a	32.2 ± 2.7	88.2 ± 19.5 a	145.1 ± 46.2 a	0.77 ± 0.20	3.14 ± 0.29 a	24.7 ± 0.9 a	78.8 ± 10.1 a	105.4 ± 18.3 ab	0.90 ± 0.17 a
ESN	1.47 ± 0.27 bc	30.7 ± 1.9	44.7 ± 7.4 bc	65.0 ± 11.5 bc	1.02 ± 0.68	2.04 ± 0.18 c	24.0 ± 1.3 a	49.4 ± 6.4 c	68.9 ± 11.9 c	0.57 ± 0.11 b
SuperU	1.97 ± 0.27 ab	33.5 ± 2.1	73.7 ± 14.3 ab	97.9 ± 20.3 b	1.01 ± 0.08	3.09 ± 0.05 ab	25.5 ± 1.2 a	78.5 ± 3.3 a	115.9 ± 11.9 a	0.97 ± 0.14 a
Manure	2.09 ± 0.54 ab	31.2 ± 0.6	65.8 ± 17.8 b	91.9 ± 23.4 b	–	2.61 ± 0.03 b	24.5 ± 0.5 a	63.6 ± 1.6 b	91.1 ± 5.3 b	–
P value	0.01	ns	<0.01	<0.01	ns	<0.01	<0.05	<0.01	<0.01	<0.05

† Means \pm standard error within a column followed by the same letter are not significantly different at $P < 0.05$.

Table 4. Pearson product moment correlation coefficients (*r*) for the associations of cumulative N₂O emissions with NH₄⁺ intensity, NO₃⁻ intensity, total inorganic N intensity (N intensity), grain N uptake (N_{gr}), and total aboveground biomass N uptake (N_{above}) for the early and whole growing seasons in 2009 and 2010 individually and across both years (*n* = 5 for associations in separate years and *n* = 10 for associations across years).

Parameter	2009		2010		2009 and 2010	
	Early	Whole	Early	Whole	Early	Whole
NH ₄ ⁺ intensity	ns	ns	ns	ns	ns	ns
NO ₃ ⁻ intensity	0.95*	0.99**	0.94*	0.91*	0.88***	0.87***
N intensity	0.89*	0.93*	0.91*	0.88*	0.88***	0.88***
Yield	–	0.90*	–	0.88*	–	–
N _{gr}	–	0.94*	–	0.89*	–	–
N _{above}	–	ns	–	ns	–	–

* Significant at *P* < 0.05; ns, not significant.

** Significant at *P* < 0.01.

*** Significant at *P* < 0.001.

et al., 2010). Polymer-coated controlled release products have successfully reduced N₂O emissions from annual cropped land compared with conventional urea when placed on the soil surface (Halvorson et al., 2010a, 2010b, 2011; Venterea et al., 2011) or below the surface (Halvorson et al., 2011; Hyatt et al., 2010). Surface placement of stabilized granular urea products containing the inhibitors NBPT and/or DCD have reduced N₂O emissions from annual crop (Abalos et al., 2012; Ding et al., 2011; Halvorson et al., 2010a, 2010b, 2011; Jiang et al., 2010) and pasture (Zaman et al., 2008) soils. The current study advances our understanding of emissions from two commercially available enhanced-efficiency N fertilizers, a polymer-coated product, ESN, and a double inhibitor product, SuperU,

in relation to conventional granular urea and a solid manure. Most previous N₂O studies with these products have been conducted with placement on the soil surface, with or without irrigation soon after application to move the urea into the soil. In the current study, N sources were incorporated into a soil high in clay and organic matter; surprisingly, ESN but not SuperU emitted less N₂O than granular urea.

Ineffectiveness of SuperU to Reduce Nitrous Oxide Emissions

In the current study, SuperU was ineffective in reducing N₂O emissions. The temporal course of N₂O emissions was similar for SuperU and urea. Nitrogen release with SuperU was similar to that of urea, as evident in similar NO₃⁻ concentrations, NO₃⁻ intensities, yields, and N uptake for the products. Sistani et al. (2011) also found SuperU to be similar to urea for N₂O emissions, with no delay in the release of N to the soil as observed for ESN. Burton et al. (2008a) found that surface or band placement of urea with NBPT urease inhibitor alone did not reduce N₂O emissions compared with the same placement of granular urea on a clay loam soil near Brandon, MB.

The current study to our knowledge is the first to report N₂O emissions from SuperU incorporated into the soil. The soil at the study site is relatively high in organic C, at 21.0 g C kg⁻¹. Increasing soil organic C concentrations may reduce the effectiveness of the urease inhibitor NBPT (Bremner and Chai., 1986). The efficacy of the nitrification inhibitor DCD in SuperU is also restricted by increasing soil organic C concentrations. Jacinthe and Pichtel (1992) reported DCD to readily adsorb fulvic and humic acids through ionic bonding involving the protonated amino group of DCD to negatively charged functional groups

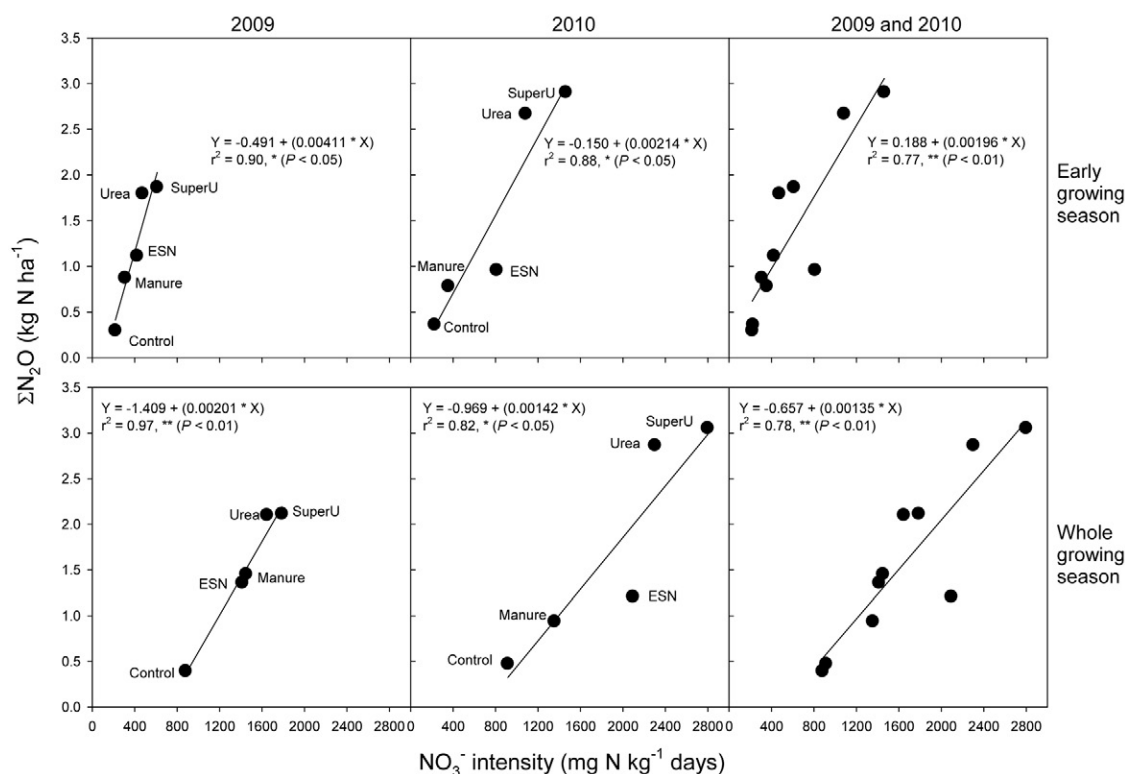


Fig. 5. The relationship between cumulative N₂O emissions (ΣN₂O) and NO₃⁻ intensity during the early and whole growing seasons in 2009 and in 2010.

of the organic acids. Dicyandiamide has also been reported to sorb to hydrophobic domains of soil organic matter (Zhang et al., 2004). Furthermore, Reddy (1964) showed that decomposition of DCD increased with soil organic C concentrations. In our experience with preventing nitrification in soil amended with a protein source of N, meat and bone meal, a soil with 21 g organic C kg⁻¹ required three times the addition rate of DCD to inhibit nitrification than those with 8.6 and 12 g organic C kg⁻¹ (Tenuta and Lazarovits, 2002a, 2002b). It is plausible that the high organic C content of the soil in the current study prevented the effectiveness of the inhibitors in SuperU. Tiessen et al. (2006), however, reported that SuperU effectively slowed the appearance of NO₃⁻ when applied in the fall to three fields in the Red River Valley of Manitoba with soil organic C concentrations similar to that of the current study. Soil temperature decreased following the fall application of SuperU in the study of Tiessen et al. (2006), whereas in the current study, it increased following application in the spring. Increasing temperature promotes DCD degradation by soil microorganisms (Kelliher et al., 2008), and reduced efficacy of NBPT may be responsible for the difference between the results of Tiessen et al. (2006) and the current study in the effectiveness of SuperU to prevent urea transformation to NO₃⁻. Also, Tiessen et al. (2006) mid-row-banded SuperU on 40-cm spacing, effectively concentrating the placement of SuperU's urea and inhibitors. Concentrating urea into fall subsurface bands from 15 to 60 cm decreased nitrification, with the inclusion of the nitrification inhibitors ATC (4-amino-1,2,4-triazole hydrochloride) or thiourea being of further benefit (Malhi and Nyborg, 1988). The role of band placement for limiting sorption and degradation reactions of the SuperU's inhibitors and reducing N₂O emissions remains to be explored but this practice could be of great practical significance because banding of N fertilizers is normal in the Red River Valley and the Canadian Prairies.

Importance of Early Growing Season Nitrogen Release

The N sources used in this study provided a range in N release abilities and transformation to NO₃⁻ that seems to have determined N₂O emissions and crop performance for the N sources. Early season NO₃⁻ accumulation before draw-down by crop uptake was in the order SuperU = urea > ESN = manure > control and of similar order for yield, N_{gr} , and N_{above} .

The early season appearance of NO₃⁻ also coincided with the period of vigorous N₂O emissions despite mid- to late-season rain events. As discussed above, the inhibitors in SuperU were ineffective in preventing hydrolysis and nitrification under the soil conditions of the current study. The dairy manure used in the study also had poor ability to supply inorganic N, as evident by the lowest early growing season concentrations of NO₃⁻, yield, and N uptake of all the N sources.

The apparent rate of nitrification as NO₃⁻ accumulation in the soil was important in determining soil N₂O loss during transformation of granular urea (Tenuta and Beauchamp, 2000). In the current study, NO₃⁻ intensities during both the early and whole growing season periods were equally strongly correlated to cumulative N₂O emissions. This is to be expected because both N₂O emissions and accumulation of NO₃⁻ occurred early in the season. Therefore, NO₃⁻ intensity in the

current study seemed to indicate the rate of release of NH₄⁺ from the N sources and subsequent nitrification. Emissions of N₂O are linked to nitrification through direct release of N₂O by nitrifying bacteria during oxidation of NH₄⁺ (Kool et al., 2011) and under microaerophilic conditions where reduction of generated NO₂⁻ to N₂O occurs via the nitrifier-denitrification process (Wrage et al., 2001; Kool et al., 2010, 2011). Nitrification can also be an indirect source of N₂O because NO₃⁻ is used as a terminal electron acceptor in denitrification under anaerobic conditions, referred to as nitrification-coupled denitrification (Nielsen et al., 1996; Arth et al., 1998). Nitrate can further determine N₂O emissions because an increased supply of terminal electron acceptor increases the N₂O/N₂ ratio of reduced N products in denitrification (Firestone, 1982; Cho et al., 1997). In the current and previous studies, N₂O emissions following the addition of synthetic N fertilizers and manures early in the season were linked to rainfall events (Glenn et al., 2012; Dunmola et al., 2010; Tenuta et al., 2010; Gao et al., 2013). Rainfall after application of the synthetic N sources probably displaced soil atmosphere and restricted gaseous diffusion in the clay soil of the current study, thereby lowering the availability of O₂ in the soil to stimulate denitrification. When the soils were dried and well aerated, nitrification probably became increasingly important as stimulated by the enhanced availability of NH₄⁺. Thus, N₂O emissions following the application of synthetic fertilizer could be due to nitrification or denitrification, while the current experimental design did not allow us to distinguish the two sources.

Cumulative Nitrous Oxide Emissions

Reports of N₂O emissions from cropping systems with soil characteristics of high clay and organic C contents and a humid climate such as in the Red River Valley of the eastern Canadian Prairies and northeastern Great Plains of the United States are few. Area-scaled ΣN₂O across the N sources in the current study ranged from 0.9 to 3.1 kg N ha⁻¹. About 20 km away, Burton et al. (2008a) reported whole-season emissions during 3 yr and across a variety of synthetic N source, timing, and placement treatments to range from 1.0 to 3.9 kg N ha⁻¹. At the TGAS MAN soil greenhouse gas study site 1 km from the current study, Glenn et al. (2012) reported whole-year emissions with granular urea incorporation for corn in 2006 and spring wheat in 2008 to be 5.5 and 4.3 kg N ha⁻¹, respectively. The flux-gradient technique for N₂O emission determinations was used by Glenn et al. (2012), so emissions were measured continuously throughout the entire year, perhaps explaining why emission estimates in that study were greater than those in the current study and the study of Burton et al. (2008a) using static vented chambers.

We monitored emissions during the spring thaw in 2011 to provide an estimate of whole-season emissions; however, N₂O emissions during and after soil thaw in March and April 2011 were negligible. The lack of emissions at this time was unexpected for this soil. From 2006 to 2010 at the TGAS MAN site, overwinter and spring thaw N₂O emissions averaged 23% of whole-year emissions (Stewart, 2011; Glenn et al., 2012). At the same site, overwinter and spring thaw emissions in 2011 amounted to 0.9 and 2.6 kg N ha⁻¹ for fields having received granular urea the previous spring and anhydrous NH₃ in the

fall of 2010, respectively. To the west 200 km, with slightly less precipitation than for the current study site but still within the Black soil zone of the Canadian Prairies, Dunmola et al. (2010) reported $\Sigma N_2O_{\text{thaw}}$ of 35% and 26% of whole-year emissions for spring wheat and flax (*Linum usitatissimum* L.), respectively, receiving urea– NH_4NO_3 fertilizer. Lower in the Red River Valley in Minnesota, where soil temperatures were also below zero, Phillips (2007) used the static chamber method and reported overwinter N_2O losses for two soybean [*Glycine max* (L.) Merr.] fields with pelletized dehydrated manure incorporated in the soil to be 0.6 and 1.6 kg N ha⁻¹. In the current study, sampling was undertaken using the static chamber method on 7 d during a 24-d period during the thaw of 2011 and thus may have missed peak N_2O emission events. In contrast, at the neighboring TGAS MAN site where substantial thaw emissions were observed, the flux gradient technique provided continuous monitoring of N_2O emissions (Glenn et al., 2012). These results suggest that capturing thaw emissions using the chamber method is a challenge to match sample occasions with short episodes of N_2O release.

Using an adjustment that overwinter and spring thaw N_2O emissions accounted for 23% of whole-year emissions (Stewart, 2011; Glenn et al., 2012), values for the synthetic N sources in the current study ranged from 1.1 to 3.8 kg N ha⁻¹. This range is similar to that reported for synthetic N sources at the nearby site studied by Burton et al. (2008a) but still less than that reported by Glenn et al. (2012) at TGAS MAN.

Nitrate Intensities

In the current study, both N_2O emissions and accumulation of NO_3^- occurred within 4 to 5 wk after planting, when crop uptake of N was relatively small. Still, N release evident as elevated NO_3^- concentrations in the soil during the early season determined crop yield and N uptake. This is not surprising because NO_3^- is the dominant source of N nutrition for crops because it is mobile in the soil and present at concentrations at which transpiration mass flow outweighs root interception and diffusion uptake of NH_4^+ and NO_3^- (Okajima and Taniyama, 1980; Barber, 1995). The crops grown in the current study are short-season crops and thus dependent on NO_3^- in the early season. Heard and Hay (2006) concluded from studies conducted on the Canadian Prairies that the majority of N uptake by canola (*Brassica napus* L. and *B. rapa* L.) and spring wheat was completed by the third week in June. Furthermore, N uptake in longer season crops such as corn, potato (*Solanum tuberosum* L.), soybean, and sunflower (*Helianthus annuus* L.) lagged behind that for canola and spring wheat by 3 wk. In the current study, the variation in NO_3^- concentration with N source was most evident up to the third week in June of each year, which coincided with the time when N_2O emissions basically ceased. For shorter season crops, enhanced-efficiency products applied at sowing may reduce N_2O emissions but also may not provide adequate N nutrition to a rapidly growing crop.

Similar to previous studies in New Brunswick (Burton et al., 2008b; Zebarth et al., 2008a), there was a strong concurrence between NO_3^- intensity and ΣN_2O in the current study. Burton et al. (2008b) reported that NO_3^- intensity explained the variation in cumulative N_2O emissions for growing seasons, row locations, and N fertility treatments of rainfed

potato. Zebarth et al. (2008a) reported that NO_3^- intensity was strongly related to ΣN_2O for barley. In the current study, NO_3^- intensity was consistently correlated to ΣN_2O for the treatments during the whole growing season and early season periods. Unlike in these studies, N_2O emissions occurred during a mid-growing-season rain event in the study by Venterea et al. (2011), when uptake by corn depressed NO_3^- concentrations. In the studies by Zebarth et al. (2008a) and Burton et al. (2008b), early season NO_3^- appearance coincided with N_2O emissions, as in the current study, with mid- and late-season rain events not eliciting emissions.

Dairy Manure

Less N release from the manure treatment resulted in less ΣN_2O relative to urea and SuperU in the current study. Nitrogen release was less from the manure treatment, as evident by lower concentrations of soil NO_3^- , NO_3^- intensity, yield, N_{gr} , and N_{above} relative to urea and SuperU. We followed provincial recommendations to set the dairy manure application rates. The provinces of Saskatchewan and Alberta use a similar approach of taking inorganic N content minus volatilization losses estimated from a look-up table plus 25% of organic N to be available within a year of addition to the soil. North Dakota and Minnesota estimate available N as a percentage of the total N content of manure by animal species and by method of application and timing of incorporation to account for volatilization of NH_3 . For the current study, available N estimated within 1 yr of application based on those neighboring states was 103, 129, and 125 kg N ha⁻¹ for the fall of 2008, 2009, and 2010 additions, respectively. Available N estimates from the manures were within 2 kg ha⁻¹ for the provinces and states for the first two applications. The manure used in the third application had lower NH_4^+ –N than the manure for the other applications, resulting in the recommended rates providing 12 kg available N ha⁻¹ less using the guidelines for North Dakota and Minnesota than those for Saskatchewan and Manitoba.

Clearly, N release from manure was insufficient to meet the N requirements of the short-season crops grown in the current study. Qian and Schoenau (2002) reported the organic C/N ratio to better reflect N release from cattle manures, with manures with total C/N ratios ranging from 13 to 15 and organic C/N ratios >15 resulting in limited N availability during 67 d in a growth chamber study. Our manure source had a total C/N ratio of 14 and organic C/N ratio of 18, perhaps explaining the poor release of N. Davis et al. (2012) pointed out that N mineralization rates from laboratory incubation studies are much lower than rates used by state and Canadian provincial extension services for field-applied beef and dairy manures and composts. As a result of these low rates of N mineralization, Mooleki et al. (2004) recommended high application rates (≥ 400 total N ha⁻¹) of solid manures or addition of supplemental N fertilizer to low application rates of solid manures to meet the N requirements of the short-season crops canola, spring wheat, and barley. Such practices for modifying solid manure application practices to meet crop demand for N would probably have resulted in higher emissions than in the current study.

The Canada Tier II Intergovernmental Panel on Climate Change (IPCC) protocol (Rochette et al., 2008) estimated N_2O emissions from manure applied to the soil as the product

of total manure N applied (kg N ha^{-1}), a regional factor for the ecodistrict ($0.008 \text{ kg N}_2\text{O-N kg}^{-1} \text{ N}$ for the Black soil zone), and a texture factor (1.0 for the Black soil zone). Area-scaled whole-year $\Sigma\text{N}_2\text{O}$ emissions estimated using the Tier II protocol was 2.3 kg N ha^{-1} compared with whole growing season $\Sigma\text{N}_2\text{O}$ of $0.76 \text{ kg N ha}^{-1}$ in the current study. Even after adjustment for possible thaw losses using $\Sigma\text{N}_2\text{O}_{\text{thaw}} = \Sigma\text{N}_2\text{O} \times 1.23$, emissions were still less in this study than predicted by the protocol.

Applied Nitrogen and Yield Scaled Nitrous Oxide Emissions

Emissions scaled by the available N applied (EF) were double for urea and SuperU ($0.017 \text{ kg N}_2\text{O-N kg}^{-1} \text{ N}$) than for ESN ($0.007 \text{ kg N}_2\text{O-N kg}^{-1} \text{ N}$). The EFs were greater than those observed for surface placement with irrigated corn in Colorado, which ranged from 0.003 to 0.008, 0.002 to 0.004, and 0.001 to $0.003 \text{ kg N}_2\text{O-N kg}^{-1} \text{ N}$ for urea, ESN, and SuperU, respectively (Halvorson et al., 2010b, 2011). Only a conventionally tilled, continuous corn system had EFs similar to the current study, at 0.009 and $0.008 \text{ kg N}_2\text{O-N kg}^{-1} \text{ N}$ for urea and ESN, but no-till continuous corn and corn–dry bean (*Phaseolus vulgaris* L.) and corn–barley rotations were less ($<0.004 \text{ kg N}_2\text{O-N kg}^{-1} \text{ N}$) (Halvorson et al., 2010a). Our EFs were even much greater than those calculated from Venterea et al. (2011), which we estimated to be 0.002, 0.002, and $0.001 \text{ kg N}_2\text{O-N kg}^{-1} \text{ N}$ for urea, ESN, and SuperU, respectively, for surface placement with unirrigated corn in Minnesota. Similarly, our EFs were higher than those reported for a microplot study with corn in the humid subtropical climate of Nanjing, China, of 0.008, 0.008 and 0.002 for granular urea, a polymer-coated urea, and urea granules infused with the urease inhibitor hydroquinone and DCD, respectively, surface placed at 300 kg N kg^{-1} (Jiang et al., 2010). Whole-season EFs of 0.010 and $0.004 \text{ kg N}_2\text{O-N kg}^{-1} \text{ N}$ were reported by Burton et al. (2008a) for urea and ESN, respectively, banded in the spring in the Red River Valley of Manitoba. For spring wheat grown at the TGAS MAN site with incorporated granular urea, Glenn et al. (2012) reported whole-year EF values of 0.014 to $0.018 \text{ kg N}_2\text{O-N kg}^{-1} \text{ N}$. The Canada IPCC Tier II protocol (Rochette et al., 2008) estimates whole-year EF to be $0.008 \text{ kg N}_2\text{O-N kg}^{-1} \text{ N}$ for the Red River Valley. Clearly, further refinements are needed to Canada's Tier II protocol for the imperfectly drained, clay soils with relatively high organic C content of the Red River Valley. Furthermore, inclusion of an EF modifier for enhanced-efficiency N fertilizers requires more studies with products such as those examined here in the context of placement and timing of application.

Emissions scaled to yield (EI) are useful in assessing which N sources produce the least N_2O per amount of grain output. Thus, EI combines the influence of N additions on emissions but also the benefit of crop response to added N. The range in our EI values was similar for 2009 with rapeseed and 2010 with spring wheat, with a range across the 2 yr of 0.30 to $1.02 \text{ kg N}_2\text{O-N Mg}^{-1}$. Few studies have reported EI. The values in the current study are about one order of magnitude greater than reported for irrigated corn ($0.03\text{--}0.07 \text{ kg N}_2\text{O-N Mg}^{-1}$) in Colorado by Halvorson et al. (2010b) and conventional and no-till corn ($0.05\text{--}0.10 \text{ kg N}_2\text{O-N Mg}^{-1}$) in Minnesota by Venterea et al. (2011). Our EI values were less than reported for more humid climates with winter wheat ($1.0\text{--}2.5 \text{ kg N}_2\text{O-N Mg}^{-1}$) receiving

combinations of urea and farmyard manure in Shaanxi Province, China (Wei et al., 2010) and corn ($1.3\text{--}2.0 \text{ kg N}_2\text{O-N Mg}^{-1}$) receiving urea– NH_4NO_3 , calcium ammonium nitrate, and aqueous NH_3 in Quebec (Gagnon et al., 2011). In our study, EI values were higher for SuperU than the other synthetic N sources among the crop years; however, to recommend an N source solely based on low EI would be erroneous. For example, in 2010, 50% more land area would be required with ESN treatment to approach the same yield of spring wheat as with SuperU. All N sources yielded well compared with the 5-yr area average for rapeseed; however, only urea and SuperU approached the average yield for feed spring wheat in the area. Clearly, further assessment of the beneficial role of managing N_2O emissions using enhanced-efficiency N fertilizers requires more documentation of yield in studies and how representative the yields are for the study region. This would assist life-cycle analysis to implicate N treatments of most benefit to yield return and the environment.

CONCLUSIONS

Nitrous oxide emissions from the N sources broadcast and incorporated into a clay soil of relatively high organic C content was related to early-season N release from the products. Although N release and N_2O emissions were lower for ESN and a solid dairy manure, N availability to rapeseed and spring wheat was insufficient to meet crop demand, resulting in reduced yield and N uptake compared with urea and SuperU. These results highlight the challenge of providing sufficient N with ESN and manure for short-season crops. Blending readily available N sources such as urea with ESN and solid manures requires exploration if early-season crop demand for short-season crops can be met and some benefit still obtained from these sources in reducing emissions. SuperU was ineffective in reducing emissions because the inhibitors seemed unable to prevent N release and nitrification of urea. Further investigations are required to determine if application of SuperU as subsurface bands in clay and high organic C content soils can sustain the function of the urease and nitrification inhibitors to limit N_2O emissions. Scaled estimates of N_2O emissions on an area and yield basis varied for the N sources. More reports of these scaled measures would foster life-cycle analysis to allow evaluation of the benefit of N sources to crop production efficiency and the environment.

ACKNOWLEDGMENTS

We wish to thank the field staff of the Glenlea Research Station as well as Prasanna Adikari, Wole Akinremi, Jr., Mervin Bilous, Robert Ellis, Paulo Fabian, Trevor Fraser, Derek Furutani, Clay Sawka, Brad Sparling, Amanda Stefanson, Tim Stem, Jolene Rutter, Ermias Azaria, and Yoel Tewolde for operation of the field site and assistance in sampling and analysis. This research was funded by the Manitoba Sustainable Agriculture Practices Program, Manitoba Rural Adaptation Council, Canadian Fertilizer Institute, Agrium Inc., Natural Sciences and Engineering Research Council of Canada Discovery Grant Program, and the Canada Research Chairs Program in Applied Soil Ecology. Provision of SuperU and ESN products used in this study by Koch LLC and Agrium Advanced Technologies is greatly appreciated. Discussions with Alan Blaylock, Ray Dowbenko, Greg Schwab, and USDA-ARS scientists of the FAR Project regarding increasing fertilizer N use efficiency and reducing N_2O emissions with enhanced efficiency fertilizers are greatly appreciated.

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