ORIGINAL ARTICLE



Nitrous oxide emissions with enhanced efficiency and conventional urea fertilizers in winter wheat

Haibo An · Jen Owens D · Brian Beres · Yuejin Li · Xiying Hao

Received: 14 January 2020/Accepted: 9 January 2021/Published online: 13 February 2021 © Crown 2021

Abstract Optimizing nitrogen fertilizer management can reduce nitrous oxide (N2O) emissions. This study tested if split applying enhanced efficiency fertilizers (EEFs) resulted in lower N₂O emissions than applying equivalent rates of urea at planting. In semiarid southern Alberta, field trials were conducted during three years (planting to harvest) in rainfed winter wheat crops. Annual fertilizer rates ranged from 146 to 176 kg N ha⁻¹. Fertilizer types were urea, and three EEFs (polymer-coated urea, urea with urease and nitrification inhibitors, and urea with a nitrification inhibitor). Each fertilizer type was applied three ways: 100% banded at planting, split applied 30% banded at planting and 70% broadcast in late fall, and split applied 30% banded at planting and 70% broadcast at Feekes growth stage 4 (GS4, post-tiller formation, wheat entering the greening up phase in the early spring). Nitrous oxide was measured using static chambers between sub-weekly and monthly from

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10705-021-10118-9.

H. An · Y. Li

College of Grassland, Resources and Environment, Inner Mongolia Agriculture University, Inner Mongolia, China

H. An · J. Owens (⊠) · B. Beres · X. Hao
Agriculture and Agri-Food Canada Lethbridge Research and Development Centre, Lethbridge,
AB, Canada
e-mail: Jennifer.Owens@Canada.ca

planting to harvest. Over three years, cumulative N₂O emissions ranged from 0.16 to 1.32 kg N ha⁻¹. This was equivalent to emissions factors between 0.009 and 0.688%. Cumulative N₂O emissions and emissions factors did not differ between fertilizer types, but they were lower when fertilizer was split applied at GS4 compared to in late fall ($P \le 0.10$). Our study suggests that EEFs do not reduce N₂O emissions from rainfed winter wheat crops, but a well-timed split application with a majority of fertilizer applied after winter can minimize N₂O emissions.

Keywords Nitrogen fertilizer · Nitrification inhibitor · Polymer-coated urea · Urease inhibitor

Introduction

Optimizing nitrogen (N) fertilization by aiming to match N supply from fertilizer with N crop demand can reduce excess available soil N, and when this is achieved, soil N₂O production may also be minimized. There are a few strategies that may help accomplish this. The first is substituting urea with enhanced efficiency fertilizers (EEFs). Enhanced efficiency fertilizers can prolong N as ammonium (NH₄⁺), which can help reduce nitrate (NO₃⁻) accumulation in soil thereby preventing N transformations to gaseous N forms like N₂O (Akiyama et al. 2010; Trenkel 2010). Types of EEFs include slow-release fertilizers that physically encapsulate urea allowing fertilizer to gradually diffuse into the soil, and fertilizers containing chemical urease inhibitors (UI) and nitrification inhibitors (NI) which slow the conversion of urea to NH_4^+ , and NH_4^+ to NO_3^- , respectively. A second strategy that may help optimize N fertilization is split applying fertilizer at different times throughout a crop cycle rather than applying once at planting. This strategy attempts to time fertilizer application with accelerated plant N demand. This can improve crop N use efficiency thereby minimizing available N accumulation in soil. Since neither split application nor EEFs directly inhibits N₂O production, they are not universal prescriptions for mitigating fertilizer-induced N₂O emissions.

Developing a fertilizer strategy will consider crop characteristics. For winter wheat, only 30% of it's total N is required before the tillering stage (Mahler et al. 1994). Split fertilizer application whereby a majority of N is applied in spring (April) prior to Zaddocks growth stage 24 has been shown to maximize yield and N use efficiency (Mahler et al. 1994). However, fertilizer split-applied at planting in the fall and early spring risks partly missing the window of accelerated crop N uptake after the tillering stage. This risk could be minimized by applying fertilizer in late fall, which would eliminate the need to properly time fertilizer application in the spring, but risks enhancing N₂O emissions during late winter thaw events. A solution may be to split apply EEFs. Delaying N availability with EEFs may compensate for an ill-timed fertilizer application in cases where the timing of fertilization is not synchronized with crop N demand.

How coupling EEFs and split application affects fertilizer-induced N_2O emissions in semiarid climates is difficult to predict, especially for winter crops. Natural variation in precipitation in these climates makes it challenging to anticipate which soil conditions will coincide with high N availability from fertilizer. The timing and amount of rainfall following N fertilizer application affects urea hydrolysis (Black et al. 1985, 1987) and N₂O production (Austin et al. 2004). Therefore, applying N fertilizer to dry soil does not necessarily lead to increases in N₂O emissions (Barton et al. 2008), and relatively low cumulative N₂O emissions and emissions factors are expected from fertilized soils in dry climates (Hergoualc'h et al. 2019). The objectives of this study were to test whether different combinations of EEFs and split application reduced N₂O emissions and emissions factors compared with urea applied 100% at planting in a rainfed, semiarid winter wheat crop. We hypothesized that applying all fertilizer in the fall will increase N₂O emission but a split application of EEFs at planting and in the spring will minimize N₂O emissions and emissions factors.

Materials and methods

Site description and management

This study was conducted in Lethbridge, Alberta, Canada. The mean annual precipitation is 370.2 mm, mean annual air temperature is $5.5 \,^{\circ}$ C (1988–2017), and the elevation is 910 m.

Three trials took place from 2014 to 2017, each trial starting in September and ending in July of the following year. The trials were conducted on different fields each year: "Year 1" (2014-2015) at 49° 34' 03.6" N, 112° 44' 02.0" W; "Year 2" (2015–2016) at 49° 40' 49.7" N, 112° 27' 24.3" W; and "Year 3" (2016–2017) at 49° 40' 48.5" N, 112° 45' 39.5" W. All sites were located within 20 km of each other (Supplementary Figure S1). The soil is an Orthic Dark Brown Chernozem (Typic Haploborall). Soil had a heavy clay texture in Year 1 and a clay soil texture in Years 2 and 3 (Soil Classification Working Group 1998). Soil chemical and physical properties for each soil are shown in Table 1. Methods used to determine the initial soil properties are detailed in the Supplementary Data.

Crop details

A rotation of canola and barley was cultivated for at least four years prior to the start of the trials, and fertilized with 39 kg ha⁻¹ of 34-17-0 urea-ammonium-phosphate. Winter wheat (*Triticum aestivum*, AC Flourish, a Canada Western Red Winter milling quality variety) was seeded in the fall into standing canola (*Brassica* spp.) using a SeedHawk seeder (Vaderstad Industries Inc., Langbank, Saskatchewan, Canada).

Table 1 Means (± standard error of the mean) of soil properties across the study years, determined before first fertilizer application

Variable	Year 1 (2014–2015)	Year 2 (2015–2016)	Year 3 (2016–2017)
Soil			
рН	8.29 (0.07)	6.71 (0.12)	7.08 (0.35)
Electrical conductivity (dS m ⁻¹)	0.24 (0.07)	0.16 (0.02)	0.13 (0.02)
Water-extractable organic carbon (mg C kg ⁻¹)	64.10 (2.71)	49.41 (5.79)	54.60 (1.63)
Nitrate (mg N kg ⁻¹)	3.35 (0.45)	13.59 (1.66)	2.91 (0.18)
Ammonium (mg N kg ⁻¹)	2.30 (0.38)	3.48 (1.31)	2.91 (0.59)
Total carbon (g kg^{-1})	17.04 (0.36)	14.60 (0.47)	12.72 (0.58)
Total nitrogen (g kg ⁻¹)	1.81 (0.03)	1.50 (0.03)	1.44 (0.05)
C/N ratio	9.45 (0.35)	9.73 (0.21)	8.86 (0.14)
Bulk density (g cm^{-3})	1.17 (0.01)	1.10 (0.01)	1.02 (0.01)
Clay (g kg ⁻¹)	596 (7)	289 (4)	340 (14)
Sand (g kg ⁻¹)	121 (4)	404 (2)	376 (15)
Silt (g kg ⁻¹)	283 (6)	306 (5)	284 (10)
Climate			
Temperature			
Overall	6.1	6.5	5.1
Autumn	10.8	9.9	8.6
Winter	- 1.0	0.2	- 3.7
Spring and summer	13.7	13.8	13.5
WFPS (%)			
Overall	48.2	37.4	38.7
Autumn	37.3	31.0	34.5
Winter	56.3	39.3	40.4
Spring and summer	40.9	36.6	38.4
Precipitation (mm)			
Overall	235.5	270.5	261.5
Autumn	20.5	7.6	50.8
Winter	94.5	83.3	68.8
Spring and summer	120.5	179.6	141.9

Mean air temperature, soil water-filled pore space (WFPS) at 50 mm, and total precipitation for each year, presented over the course of the entire sampling time and by season (autumn = September–October inclusive, winter = November–March inclusive, and spring and summer = April–July inclusive) temperature and precipitation from the Lethbridge weather station

Determining fertilizer rates

Soil N supply was estimated each year before the first fertilizer application using plant root simulator (PRS) probes (Western Ag Innovations, Saskatoon, SK, Canada). These synthetic ion exchange resins strips were buried in the soil and mimic the properties of root exchange to determine soil nutrient availability. These data were used to forecast N fertilizer requirements with the PRSTM Nutrient Forecaster model (Hangs et al. 2002).

Enhanced efficiency fertilizers may improve N use efficiency, but they are more expensive than conventional fertilizers. Cereal crop N use is generally < 50% of fertilizer applied (Raun and Johnson 1999). Applying higher rates of N as fertilizer may maximize yield but may not provide the greatest profit per area. Therefore, the fertilizers were applied at 80% of the target rate, targeting a 5380 kg ha⁻¹ (80 bu ac⁻¹) crop.

Experimental design

Treatments (three applications, four fertilizer types) were arranged in a complete block design with three blocks. Each block also contained one non-fertilized treatment (control) for a total of 39 plots. Plots were 3.7 m wide \times 15.2 m long, with 1 m buffers. Each block measured 60.1 m \times 15.2 m.

Each fertilizer type was applied with each of the following timings and placements: (1) 100% of N banded in the fall at planting (hereafter referred to as "planting"); (2) 30% banded in the fall at planting and 70% broadcast in late fall (hereafter referred to as "late fall"); and (3) 30% banded in the fall at planting and 70% broadcast at Feekes growth stage 4 (GS4, post-tiller formation, wheat entering the greening up phase in the early spring, hereafter referred to as "GS4") (Large 1954). Fertilizer applied at seeding was side-banded and at other times was surface broadcast unincorporated in-crop.

The four fertilizer types were: (1) urea (46% N w/w); (2) polymer-coated urea (hereafter referred to as "PCU"; ESN® Environmentally Smart Nitrogen, Nutrien, Saskatoon, SK, Canada; 44% N w/w); (3) SuperU (hereafter referred to as "NI + UI"; Koch Agronomic Services, Wichita, KS, USA; 46% N w/w) which is urea with the nitrification inhibitor dicyandiamide (DCD) and urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT); and (4) urea impregnated with Instinct (hereafter referred to as "NI"), the nitrification inhibitor nitrapyrin (Dow AgroSciences, Indianapolis, IN, USA; 46% N w/w).

The total fertilizer application rates and dates of fertilizer application for each year are presented in Table 2.

Ancillary environmental variables

Daily total precipitation (mm), mean volumetric soil moisture (%, measured at 50 mm soil depth), and mean air temperature (°C) were monitored for the duration of the experiment at a nearby weather station (within 15 km of each site, 49.68° N, 112.75° W, 991 m elevation).

Soil bulk density from each field was determined by taking at least three randomly situated intact soil cores (height = 150 mm, inner diameter = 65 mm) and oven drying at 105 °C for 72 h. Soil water-filled pore space (WFPS, %) at 50 mm soil depth was calculated using the volumetric water content measured from the weather station and the average soil bulk density (Linn and Doran 1984).

N_2O sampling and analysis

Soil-to-atmosphere N₂O fluxes were measured using vented static chambers (300 mm inner diameter, 100 mm height, one chamber per plot) with a PVC base collar installed to a depth of 50 mm (Chang et al. 1998). Samples were collected between 8:00 am and 12:00 pm local time. Wheat inside the collars was clipped regularly. Gas samples (11.3 mL) were extracted from the chamber headspace using a syringe at 0, 15, 30, and 60 min after securing the chamber lid to the collar. Gas samples were immediately transferred to an evacuated vial (5.8 mL, Exetainer®, Labco Ltd., Lampeter, United Kingdom) and analyzed using a Varian 3800 gas chromatograph equipped with an electron capture detector (Varian Inc., Walnut Creek, CA, USA). The injector and column temperatures were kept at 55 °C. The carrier was P10 gas (10% methane, balance argon). The channel was maintained at a static pressure of 150 kPa.

 Table 2
 The dates of fertilizer application at planting, late fall, and Feekes growth stage 4 (GS4), and rates of N application for each year

Year	Date	Date				u ⁻¹)
	Planting	Late fall	GS4	100%	30%	70%
Year 1	September 17, 2014	November 19, 2014	April 13, 2015	175	52.5	122.5
Year 2	September 24, 2015	November 17, 2015	April 12, 2016	146	43.8	102.2
Year 3	September 16, 2016	November 15, 2016	April 7, 2017	176	52.8	123.2

Nitrous oxide fluxes (g N $ha^{-1} day^{-1}$) were calculated using the slope of either a quadratic or linear regression of the N₂O concentration over time (1 h), the ideal gas law (assuming standard atmospheric pressure adjusted for elevation of each site), air temperature (daily average), chamber area (0.0707 m^2) , and chamber volume (~ 7 L, adjusted individually for each chamber using the internal radius of the chamber area and heights of the chamber walls above the surface which were measured at the start of the trial) (Venterea et al. 2012). All regressions were strong (e.g. $R^2 > 0.80$) indicating no serious quality control issues. Quadratic regression was selected except when the R^2 of the linear regression was higher. The minimum detectable fluxes (Parkin et al. 2012) were \pm 1.9 µg N m⁻² h⁻¹ for fluxes calculated using linear regression and \pm 6.5 µg N m⁻² h^{-1} for fluxes calculated using quadratic regression. All fluxes were determined to be above the minimum detectable flux.

Nitrous oxide fluxes were measured approximately twice a week after planting for two months, weekly for a month after the late fall fertilizer application, and weekly for two months after the GS4 fertilizer application. Throughout the winter, the N_2O fluxes were measured once or twice a month.

Winter N₂O measurements were made following the same protocol as measurements at other times of the year. When snow was present in the chambers, the volume of the chamber occupied by snow was calculated. This was done using the radius of the internal chamber area and the height of the snow pack. This snow-filled volume was adjusted using a snow water equivalent value that was estimated using a jar to take snow samples and assuming the density of water is 1 g cm⁻³ (Sturm et al. 2010). The volume of the chamber occupied by snow, as represented by the snow water equivalent, was subtracted from the volume of the chamber without snow, and this adjusted headspace volume was used in the winter N₂O flux calculations.

Nitrous oxide fluxes were measured a total of 31, 30, and 29 times in Years 1, 2, and 3, respectively. Final N_2O measurements were made on July 29, 2015, in Year 1, on July 21, 2016, in Year 2, and on July 19, 2017, in Year 3.

Winter wheat was harvested on July 30, 2015, in Year 1, July 29, 2016, in Year 2, and July 27, 2017, in Year 3. For the purposes of this study, the "winter wheat crop cycle" starts at planting and ends with the last N_2O measurement, and was therefore 315 days for Year 1, 301 days for Year 2, and 306 days for Year 3.

Cumulative N_2O emissions (kg N ha⁻¹) over the winter wheat crop cycle were calculated by linearly interpolating between sampling dates and summing the values.

Emissions factors

The N₂O emissions factors (N₂O-N emitted as a % of N applied as fertilizer) were calculated by subtracting the control treatment cumulative N₂O emissions from each fertilized soil cumulative N₂O emissions, dividing by the total N applied as fertilizer and multiplying by 100 (Gregorich et al. 2005).

Soil ammonium and nitrate concentrations

Soil samples were collected a total of 9, 13, and 11 times in Years 1, 2, and 3, respectively, using a hand auger. For the first month after planting, weekly soil samples (0-150 mm) were collected. Thereafter, monthly soil samples were collected, except during the winter in Years 1 and 3 when the soil was frozen. Fresh soils were extracted for NO_3^- and NH_4^+ by 2 mol L^{-1} KCl (Keeney and Nelson 1982) at a 1:5 (weight:volume) ratio of soil to solution, mixed for 30 min., and analyzed using a modified Indophenol Blue technique (Sims et al. 1995) with a MultiSkan Go Microplate Spectrophotometer at 650 nm (Thermo Scientific, Waltham, MA, USA). Gravimetric soil moisture was determined for each soil sample by oven-drying ~ 10 g field moist soil at 105 °C for 72 h. The gravimetric water content was used to present soil NH_4^+ and NO_3^- as mg N kg⁻¹ dry weight of soil.

Data presentation and statistical analysis

Data were assessed for normality using the Shapiro– Wilk test and for homogeneity of variance using Levene's test (RStudio, version 3.4.4). None of the datasets were transformed.

Linear associations between daily N₂O fluxes, WFPS, air temperature, soil NH₄⁺, and soil NO₃⁻ were evaluated for each combination of Year, fertilizer type, and fertilizer application using Pearson's correlation coefficient (r) at $P \leq 0.05$ using the *corr.test* base function in R Statistics. Because daily N_2O fluxes were measured more frequently than soil NH_4^+ and NO_3^- concentrations, linear interpolation was used to estimate NH_4^+ and NO_3^- concentrations for association with daily N_2O fluxes. Linear multiple regression models with daily N_2O fluxes as the dependent variable, and WFPS, soil temperature, soil NH_4^+ , and soil NO_3^- as potential independent predictors were evaluated for each combination of Year, fertilizer type, and fertilizer application using the *lm* base function in R Statistics. Models for all combinations of one, two, three, or four of these predictors were evaluated and final models were selected based on the adjusted R^2 and Akaike Information Criterion (Kutner et al. 2004).

A mixed-model ANOVA was conducted to determine if there were differences in cumulative N_2O emissions and emissions factors between different fertilizer types, application, and Years. Block was treated as a random effect. Only cumulative N_2O emissions from fertilized soils were statistically compared. Multiple comparisons of means were conducted using Tukey's HSD test using the *agricolae* package in R Statistics when main effects or their interactions were significant at a 0.05 probability level. Differences that may be biologically or chemically important were explored when the probability level was between 0.05 and 0.10.

Results

Soil environmental conditions, and ammonium and nitrate concentrations

There were some differences in soil conditions between years. Soil pH and clay content were relatively higher in Year 1 compared to the other years (Table 1). The overall average WFPS was highest in Year 1 (48.2%) and similar in Years 2 and 3 (37.4 and 38.7%) (Table 1). Water-filled pore space increased following precipitation except during the winter, where WFPS increased during thaw events (Figs. 1, 2, 3b, c).

Considering all data, NH_4^+ ranged from 0.05 to 81.70 mg N kg⁻¹ (Figs. 1, 2, 3d, g, j) and NO_3^- ranged from 0.11 to 58.52 mg N kg⁻¹ (Figs. 1, 2, 3e, h, k).

In Year 1 and Year 2 for all applications, and Year 3 for 100% applied at planting, NH_4^+ and NO_3^- increased after fertilization at planting. There were no clear patterns in NH_4^+ and NO_3^- when fertilizer was applied in late fall or at GS4.

Winter NH_4^+ and NO_3^- were only measured during Year 2. During Year 2, from the start of December to the end of February, NH_4^+ ranged from 1.83 to 51.43 mg N kg⁻¹ and NO_3^- ranged from 0.75 to 18.53 mg N kg⁻¹ from fertilized treatments. In the winter, NH_4^+ concentrations tended to be higher in treatments where all fertilizer was applied in the fall (Fig. 2d, g).

Over all years, growing season (March 1 onwards) NH_4^+ ranged from 0.06 to 39.71 mg N kg⁻¹ and NO_3^- ranged from 0.02 to 57.63 mg N kg⁻¹ from fertilized soils. In Year 2, NO_3^- increased in all treatments including the control following precipitation-induced increases in WFPS (Fig. 2e, h, k).

Nitrous oxide fluxes

In Year 1, small spikes in N₂O fluxes followed fertilizer application, most notably when fertilizer was applied 100% at planting (Fig. 1f). Urea applied 100% at planting showed the highest average N₂O fluxes within the month after application (5.12 g N ha⁻¹ day⁻¹). In treatments where all fertilizer was applied 100% at planting or split applied in late fall, N₂O fluxes of similar magnitudes were measured in the fall and winter (Fig. 1f, i). All fertilizer types and applications showed relatively low N₂O fluxes during the spring and summer, even when fertilizer was applied at GS4; from March 1 onward, N₂O fluxes were ≤ 3.55 g N ha⁻¹ day⁻¹ from all fertilized soils.

In Year 2, N₂O fluxes tended to be relatively low after fertilizer application at planting, during the late fall fertilizer application, and during the winter. From until March 1, fluxes planting were ≤ 5.44 g N ha⁻¹ day⁻¹ from all fertilizer types and applications except Urea applied at GS4 (Fig. 2f, i, l). Nitrous oxide fluxes showed greater variability from all fertilizer types and applications during the spring and summer when temperatures were warm and there was available soil NO_3^- ; from March 1, 2016, onward, mean fluxes were $2.94 \text{ g N} \text{ ha}^{-1} \text{ day}^{-1}$, ranging from 0.11 to 11.81 g N ha⁻¹ day⁻¹. Nitrous oxide fluxes from Urea applied at GS4 were notably higher throughout the trial (mean of **Fig. 1** a Air temperature, **b** precipitation

(rain + snow), c waterfilled pore space at 50 mm, and mean (\pm the standard error of the mean) soil ammonium, soil nitrate and nitrous oxide fluxes for fertilizer applied 100% at planting (d-f), 30% applied at planting and 70% applied in late fall (g-i), and 30% applied at planting and 70% applied at Feekes growth stage 4 (j-l) for Year 1 (2014-2015). The black arrows represent the timing of fertilizer application



Deringer

Fig. 2 a Air temperature, **b** precipitation (rain + snow), c waterfilled pore space at 50 mm, and mean (\pm the standard error of the mean) soil ammonium, soil nitrate and nitrous oxide fluxes for fluxes applied 100% at planting fertilizer (d-f), 30% applied at planting and 70% applied in late fall (gi), and 30% applied at planting and 70% applied at Feekes growth stage 4 (j-I) for Year 2 (2015-2016). The black arrows represent the timing of fertilizer application



Deringer

Fig. 3 a Air temperature, **b** precipitation (rain + snow), c waterfilled pore space at 50 mm, and mean (\pm the standard error of the mean) soil ammonium, soil nitrate and nitrous oxide fluxes for fluxes applied 100% at planting fertilizer (d-f), 30% applied at planting and 70% applied in late fall (gi), and 30% applied at planting and 70% applied at Feekes growth stage 4 (j-I) for Year 3 (2016–2017). The black arrows represent the timing of fertilizer application



Deringer

7.46 g N ha⁻¹ day⁻¹, ranging from 2.01 to 17.51 g N ha⁻¹ day⁻¹) compared to all other fertilizer types and applications.

In Year 3, N₂O fluxes did not increase after fertilizer application. Nitrous oxide fluxes were ≤ 2.49 g N ha⁻¹ day⁻¹ from all fertilizer types and applications before the winter (until November 30, 2016). Mean daily N₂O fluxes in the winter, spring, and summer (between December 1, 2016, and July 19, 2017) reached a maximum of 7.03 g N ha⁻¹ day⁻¹. During this time period, average WFPS was low (39.3%) with some instances of precipitation-induced increases (maximum = 60.9%), and NO₃⁻ concentrations were low, averaging $3.71 \text{ mg N kg}^{-1}$ from all fertilized soils.

Segmented by application, N_2O fluxes were positively correlated with NO_3^- and NH_4^+ when fertilizer was split applied in late fall and GS4. When fertilizer was split applied in GS4, N_2O fluxes were also negatively correlated with WFPS (Table 3). When grouped by fertilizer type, N_2O fluxes were positively correlated with NO_3^- in Urea and NI + UI, and negatively correlated with NO_3^- in PCU. Nitrous oxide fluxes from NI and NI + UI were negatively correlated with WFPS, and N_2O fluxes from NI + UI were positively correlated with air temperature. There were no consistent trends in correlation results when data was grouped by both fertilizer type and application regime (Table 3).

When grouped by Year, fertilizer type, or applications, the multiple regression models produced generally low R^2 values ranging from 0 to 0.14 (Table 3). None of the environmental or soil variables were able to significantly predict N₂O fluxes when 100% of the fertilizer was applied at planting (Table 3).

Cumulative nitrous oxide emissions and emissions factors

Cumulative N₂O emissions from the controls (no N applied) were equivalent to 0.08 kg N ha⁻¹ (\pm 0.03 standard error of the mean) in Year 1, 0.32 kg N ha⁻¹ (\pm 0.03) in Year 2, and 0.50 kg N ha⁻¹ (\pm 0.10) in Year 3. When considering all fertilizer types and applications, cumulative N₂O emissions from the fertilized treatments were significantly lower ($P \leq 0.05$) in Year 1 (mean = 0.32 kg N ha⁻¹, ranging from 0.16 to 0.59 kg N ha⁻¹) than in Year 2 (mean = 0.63 kg N ha⁻¹, ranging from 0.32 to

1.32 kg N ha⁻¹) or Year 3 (mean = 0.67 kg N ha⁻¹, ranging from 0.52 to 0.97 kg N ha⁻¹). In Years 1, 2, and 3, an average equivalent of 0.133%, 0.215%, and 0.093% of the N applied as fertilizer was emitted as N₂O-N, respectively, and the emissions factors were significantly ($P \le 0.05$) lower in Year 3 than in Year 2.

Differences in fertilizer type did not cause differences in cumulative N₂O emissions and emissions factors, but effects related to application were detected (Table 4). Fertilizer applied in late fall resulted in significantly higher cumulative N₂O emissions and emissions factors compared to fertilizer applied at GS4 ($P \le 0.10$). However, neither split-application regime resulted in cumulative N₂O emissions or emissions factors that differed from when 100% of the fertilizer was applied at planting.

There were significant interactions between Year and fertilizer type, and fertilizer type and application, for cumulative N₂O emissions (Table 4). Cumulative N₂O emissions were higher from NI and UI + NI during Year 2 compared to NI and NI + UI during Year 1 ($P \le 0.05$, Supplementary Table S1). The significant interaction effects for cumulative N₂O emissions detected between fertilizer type and application were from higher N₂O emissions from NI applied in late fall compared to NI applied at GS4 and Urea applied at planting (all $P \le 0.10$).

Discussion

Fertilizer-induced N₂O emissions were minimized by split application in spring but were not lowered by enhanced efficiency fertilizers

Coupling split fertilizer application and EEFs did not result in lower cumulative N₂O emissions or emissions factors compared to applying 100% of the urea at planting. Enhanced efficiency fertilizers did not lessen cumulative N₂O emissions or emissions factors compared to urea. Others have noted that EEFs, especially PCU and NI, can reduce N₂O emissions compared to conventional fertilizers but they are more effective when soils are wet (Akiyama et al. 2010; Feng et al. 2016). Likely due to relatively dry soil conditions, we found no evidence that delays in N availability from EEFs compensated for ill-timed split fertilizer application thereby reducing N₂O emissions. The only

Year	Fertilizer type	Application ^a	Correlation				Multiple re	gression ^b				
			N ₂ O fluxes	versus								
			$\mathrm{NO_3}^-$ r	$\mathrm{NH_4^+}$	Temp.	WFPS	b0 Intercept	b1 NO ₃ ⁻	$b2 { m NH_4^+}$	b3 Temp	b4 WFPS	\mathbb{R}^2
Y1			0.19^{***}	0.06	- 0.04	0.21^{***}	- 0.191	0.028	I	I	0.019	0.07***
Y2			0.05	- 0.06	0.17^{***}	-0.04	2.163	I	I	0.055	I	0.03^{***}
Y3			-0.15*	- 0.04	0.11^{**}	-0.08	2.322	-0.068	I	0.015	I	0.03^{**}
	Urea		0.14^{**}	0.05	0	-0.09	1.857	0.037	I	I	I	0.02^{**}
	PCU		-0.13^{**}	0.02	0.10	-0.02	1.907	-0.029	I	0.019	I	0.03^{**}
	IN		-0.03	0.10	0.05	-0.12^{*}	2.761	I	I	I	-0.020	0.01^{*}
	NI + UI		0.30^{***}	0.12*	0.12*	-0.23^{***}	3.007	0.073	I	I	-0.043	0.14^{***}
		Planting	-0.06	- 0.07	0.06	-0.06	1.787	I	-0.009	I	I	0
		Late fall	0.18^{***}	0.11^{**}	0.08	-0.07	1.311	0.033	0.033	0.026	I	0.06^{***}
		GS4	0.14^{**}	0.28^{***}	0.04	-0.17^{**}	2.288	0.028	0.104	I	-0.026	0.10^{***}
	Urea	Planting	0.04	-0.14	0.06	0.07	1.436	I	-0.016	I	I	0.02
	Urea	Late fall	- 0.12	- 0.06	0.09	0.05	1.762	I	-0.014	I	I	0
	Urea	GS4	0.37^{**}	0.31^{**}	-0.01	-0.25^{**}	3.963	0.132	0.141	I	-0.061	0.23^{***}
	PCU	Planting	- 0.13	- 0.03	0.06	-0.02	2.631	-0.034	I	I	I	0.02
	PCU	Late fall	$- 0.21^{*}$	-0.19*	0.13	0.07	1.662	-0.036	I	0.026	I	0.07
	PCU	GS4	- 0.08	0.03	0.12	-0.11	1.409	Ι	I	0.020	I	0.01
	IN	Planting	0.03	- 0.11	0.14	-0.21^{*}	3.301	I	I	I	-0.036	0.04*
	IN	Late fall	0.02	0.15	-0.05	0.01	2.347	I	0.028	I	I	0.02
	NI	GS4	-0.15	0.16	0.09	-0.21^{*}	2.756	-0.021	I	I	-0.029	0.08
	NI + UI	Planting	-0.05	- 0.12	- 0.09	-0.06	1.374	I	-0.009	I	I	0.01
	NI + UI	Late fall	0.60^{***}	0.20*	0.15	-0.28^{**}	2.401	0.126	0.073	0.047	-0.044	0.48^{***}
	NI + UI	GS4	- 0.06	0.36^{**}	0.15	-0.28^{**}	2.959	I	0.086	I	-0.042	0.16^{***}

Nutr Cycl Agroecosyst (2021) 119:307-322

 $^{*}P < 0.05$

 $^{*}P < 0.01$

^aPlanting, 100% of fertilizer applied at planting; Late fall, 30% of fertilizer applied at planting and 70% applied in late fall; GS4, 30% of fertilizer applied at planting and 70% applied at Feeks growth stage 4

^bMultiple regression model parameters are in the form: N_2O fluxes = $b0 + b1NO_3^- + b2NH_4^+ + b3Temp + b4WFPS$

Year	Fertilizer	Application regi	me	Cumulative N ₂ O	(kg N ha ⁻¹)	Emissions factors (%)
All	All	100% at planting		0.53 (0.05) ab		0.139 (0.032) ab
All	All	30% at planting	and 70% at late fall	0.65 (0.07) b	0.65 (0.07) b	
All	All	30% at planting	and 70% at GS4	0.49 (0.05) a		0.122 (0.025) a
All	Urea	All		0.51 (0.05)	0.51 (0.05)	
All	PCU	All		0.54 (0.06)		0.143 (0.035)
All	NI	All		0.59 (0.07)		0.184 (0.039)
All	NI + UI	All		0.59 (0.09)		0.186 (0.057)
Year 1	All	All		0.32 (0.03) a		0.133 (0.018) ab
Year 2	All	All		0.63 (0.07) b		0.215 (0.050) b
Year 3	All	All		0.67 (0.03) b		0.093 (0.018) a
Source of variation df		df	SS	MS	F-statistic	P values
Cumulativ	ve N_2O					
Applicatio	on (A)	2	0.431	0.215	2.779	0.069
Fertilizer	(F)	3	0.130	0.043	0.559	0.644
Year (Y)		2	2.696	1.348	17.397	< 0.001
$Y \times F$		6	1.160	0.193	2.494	0.030
$\mathbf{Y} \times \mathbf{A}$		4	0.207	0.052	0.669	0.615
$\mathbf{F} \times \mathbf{A}$		6	1.433	0.239	3.083	0.009
$Y\timesF\times$	А	12	1.056	0.088	1.136	0.345
Residuals		71	5.501	0.077		
Emissions	s factors					
Application (A)		2	0.165	0.083	2.448	0.094
Fertilizer	(F)	3	0.075	0.025	0.740	0.531
Year (Y)		2	0.326	0.163	4.830	0.011
$Y \times F$		6	0.510	0.085	2.519	0.288
$\mathbf{Y} \times \mathbf{A}$		4	0.079	0.020	0.584	0.674
$\mathbf{F} \times \mathbf{A}$		6	0.571	0.095	2.822	0.105
$Y \times F \times$	А	12	0.479	0.040	1.184	0.309
Residuals		71	2.394	0.034		

Table 4 Average (\pm standard error of the mean) of the cumulative N₂O emissions and emissions factors by each year, fertilizer type, and application

ANOVA degrees of freedom (df), sum of squares (SS), mean sum of squares (MS), F-statistic and P values are presented at the bottom of the table for main effects and interactions

Differences between groups for main effects are delineated with letters. Groups that do not share a letter are significantly different at $P \le 0.10$

significant decreases in N_2O emissions and emissions factors occurred when fertilizer was split applied at GS4 compared to split applied in late fall, but there were no significant differences in cumulative N_2O emissions between single- and split-applications. The differences in the timing of split applied fertilizers can be attributed to differences in crop activity. In late fall, winter wheat growth slows. Rather than being used by the crop, fertilizer N applied in late fall was likely lost as N_2O from denitrification over the winter (Malhi and Nyborg 1983), which can make substantial contributions to total N_2O emissions (Wagner-Riddle et al. 2008). Nitrogen applied at GS4, which coincides with the greening up phase, was likely used by wheat for growth as this stage corresponds to increased plant N demand (Fowler et al. 1989; Alcoz et al. 1993; Rozas et al. 2004). Consistent with our results, others have similarly reported lower cumulative N_2O emissions from wheat fertilized in the spring compared to the fall (Ellen and Spiertz 1980; Sowers et al. 1994; Burton et al. 2008).

Environmental controls of N_2O fluxes

Nitrous oxide fluxes are known to exponentially increase when soil moisture increases beyond a threshold in the presence of warm temperatures and available N (Dobbie et al. 1999). Enhanced efficiency fertilizers or split fertilizer application can help reduce residual soil N after fertilization by matching N supply with plant N demand, and as a consequence, reduce soil N availability for N₂O production. However, in a semiarid climate, soil moisture is a limiting factor for N₂O production. Because of this, the timing of split application as it pertained to season and environmental conditions, rather than the fertilizer type, affected N₂O emissions.

An assessment of the environmental controls on N2O fluxes failed to reveal strong relationships between N2O fluxes and the measured variables; r values for the correlations and R² values for the regression models were low. This was most notable when fertilizer was applied 100% at planting, and with the NI fertilizer treatment (Table 3). When all fertilizer was applied at planting, especially in soil that is generally dry but not so dry as to inhibit urea hydrolysis, substantial amounts of urea-N could have been lost as ammonia (NH₃) (Ferguson and Kissel 1986). Similar reports have been made regarding NI, which can enhance NH₃ losses following fertilizer application by extending the amount of time N remains in soil as NH_4^+ (Soares et al. 2012; Recio et al. 2018). These potential losses of N through unmeasured pathways may be hampering our ability to characterize the controls of N2O fluxes in these treatments.

Urea and NI + UI, and the split application regimes, showed positive relationships between N₂O fluxes, and NO₃⁻ and NH₄⁺. This can be attributed to enhanced variation in N₂O fluxes and soil N concentrations after fertilizer application, and in the spring and summer when crops were active, and warm temperatures and intermediate-level WFPS could support mineralization and nitrification (Addiscott 1983; Stark 1996). Different relationships were observed with PCU, which was negatively related to NO_3^- but positively related to temperature. Temperature is a strong predictor of urea release from PCU (Golden et al. 2011). The negative relationship between N₂O fluxes and NO₃⁻ in the PCU treatment suggests the delay in N release caused subsequent N transformations in soil and NO₃⁻ availability to misalign with conditions that were permissible for N₂O production.

The negative relationships often observed between N_2O fluxes and WFPS are likely an artifact of the relationships between WFPS and temperature inherent of a semiarid climate; when soil was wetter and more favorable for high N_2O production, temperatures were low which limited microbial activity (Holtan-Hartwig et al. 2002).

The WFPS values measured during our study ranged from 25 to 67% over all three years. This is lower than considered optimal for denitrificationinduced N₂O fluxes (Linn and Doran 1984; Abbasi and Adams 2000; Müller and Sherlock 2004). However, denitrification and nitrifier-denitrification can make significant contributions to total N₂O production in soils fertilized with urea under aerobic conditions (Venterea et al. 2015). Others have reported that nitrification can be the primary pathway for N₂O production in semiarid soils (Aguilera et al. 2013). However, relatively lower N₂O emissions are expected from aerobic biological pathways (Zhu et al. 2013). Low soil moisture explains why any increases in N₂O fluxes immediately after fertilizer application were not disproportionately high compared to other times (Van der Weerden et al. 2016; Awale and Chatterjee 2017) as fertilizer-induced N_2O fluxes can be muted by dry soil conditions (Barton et al. 2008).

It should be noted that our soil sampling schedule likely impacted our interpretation of the N_2O fluxes and soil N variability. More frequent measurements of N_2O fluxes and soil N concentrations occurred after planting than at other times. It is likely that we missed some variations in these factors after the late fall or GS4 application, or during the winter when our measurements were less frequent.

Cumulative emissions and emissions factors were low for fertilized soil

The North American Great Plains are characterized by unpredictable precipitation and high evapotranspiration, and this leads to low soil moisture and therefore low N_2O emissions (Padbury et al. 2002; Rochette et al. 2008). Our cumulative N_2O emissions from fertilized soils (0.16 to 1.32 kg N ha⁻¹) were within range of those reported from studies conducted nearby. From the Parkland Region of Alberta, Canada, N_2O emissions from dryland wheat fertilized with urea were up to 2.02 kg N ha⁻¹ (Lemke et al. 1999). Nitrous oxide emissions from wheat rotations in Bozeman, Montana, USA, ranged from 0.10 to 0.65 kg N_2O -N ha⁻¹ year⁻¹ (Dusenbury et al. 2008).

Our emissions factors ranged from 0.009 and 0.688% of the N applied, which is within the range of the disaggregated IPCC emissions factors of between 0.0 and 1.1% for dry climates (Hergoualc'h et al. 2019). A majority of our emissions factors were < 0.20%, which is consistent with an estimate of 0.16% created using the IPCC Tier II methodology for Brown and Dark Brown soils on the Canadian Prairies (Rochette et al. 2008). Most of the highest emissions factors measured during our study occurred in Year 2 and when aggregated by application, the highest values occurred with the late fall split application. The impacts of split fertilizer application have not been previously considered as a part of a regional emissions factor for the Canadian Prairies, but our results suggest that for dryland, over winter crops, such an evaluation may have some merit.

Emissions factors were highest in Year 2 and lowest in Year 3, which was inconsistent with the yearly variation in cumulative N₂O emissions. This discrepancy suggests fertilizer N was not used as efficiently in Year 2 compared to Year 3, however, we did not measure yield factors so this was not addressed in this study. While the fertilizer application rates were similar between years, the phenological requirements for N (and therefore plant N uptake) will vary based on wheat health, which will be affected by factors like temperature and precipitation (Fowler et al. 1989). Our fertilizer rates were not excessive for the system as crop N requirements were estimated by the PRS probes prior to fertilizer application (Hangs et al. 2002) and we only applied at 80% of the recommended rates. It is likely that a combination of plant dynamics and climate variability affected yearly emissions factors.

Implications for fertilizer best management practices in dryland winter wheat crops

Ideally, best management practices for fertilizer will minimize N_2O emissions. We found that EEFs did not mitigate N_2O emissions compared to Urea. The semiarid climate conditions in our study area are typical of the Northern Great Plains where wheat crops are commonly cultivated. Enhanced efficiency fertilizer use in this location may be a more suitable fertilizer option for irrigated fields where water inputs can be regulated, or for spring crops, where soil is likely to be wetter and more permissible to high N_2O fluxes.

For mitigating N₂O emissions using split application, the timing of the application is important. Split applying all fertilizer before the winter can amplify cumulative N₂O emissions and emissions factors. However, split application requires additional labor and fuel costs and there is additional risk that climate or soil conditions could prevent driving on the fields at a time ideal for the second application. When selecting a fertilization strategy, most producers would evaluate the gains in yield and factors like protein (not measured in this study) along with the logistics of split application, but considerations of N₂O emissions are more difficult for them to estimate. Our study showed that applying 100% of the fertilizer at planting did not result in significantly different N₂O emissions or emissions factors compared to split application at GS4. However, if split application leads to greater yield and protein, a split application at GS4 may be a worthwhile risk and provide an added benefit of slightly reduced average N₂O emissions in dryland winter crops.

Conclusions

For dryland winter wheat crops, split application with a majority of fertilizer being applied in the spring at the greening up stage of the crop cycle showed the greatest potential to minimize N_2O emissions. As fertilizer management decisions are not made solely on N_2O emissions, future research should also incorporate N concentrations in crop yields as this would provide a more complete evaluation of the fate of N fertilizer. If wheat grain N concentrations are greater when fertilizer is split applied at planting and GS4, and N_2O emissions are minimized, then the enhanced risk associated with split application may be outweighed by the combined agronomic returns and environmental benefits.

Acknowledgements We gratefully acknowledge the scholarship provided to the lead author by China Scholarship Council Ministry of Education, P. R. China, and Lethbridge Research and Development Centre. Thank you to Key Laboratory of Grassland Resources, Ministry of Education P.R. of China. Funding for this research was provided by Agriculture and Agri-Food Canada, Ducks Unlimited Canada, Alberta Wheat Commission, Winter Cereals Manitoba Inc., Saskatchewan Winter Cereals Development Commission, Dow AgroServices, Koch Agronomic Services, and Western Ag Innovations. Thank you to Courtney Soden, Kui Liu, James Elwood, and Elisha Jones for their technical assistance.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References

- Abbasi MK, Adams WA (2000) Gaseous N emission during simultaneous nitrification-denitrification associated with mineral N fertilization to a grassland soil under field conditions. Soil Biol Biochem 32:1251–1259
- Addiscott T (1983) Kinetics and temperature relationships of mineralization and nitrification in Rothamsted soils with differing histories. J Soil Sci 34:343–353
- Aguilera E, Lassaletta L, Sanz-Cobena A, Garnier J, Vallejo A (2013) The potential of organic fertilizers and water management to reduce N₂O emissions in Mediterranean climate cropping systems. A review. Agric Ecosyst Environ 164:32–52
- Akiyama H, Yan X, Yagi K (2010) Evaluation of effectiveness of enhanced-efficiency fertilizers as mitigation options for N₂O and NO emissions from agricultural soils: metaanalysis. Glob Change Biol 16:1837–1846
- Alcoz MM, Hons FM, Haby VA (1993) Nitrogen fertilization timing effect on wheat production, nitrogen uptake efficiency, and residual soil nitrogen. Agron J 85:1198–1203

- Austin AT, Yahdjian L, Stark JM, Belnap J, Porporato A, Norton U, Ravetta DA, Schaeffer SM (2004) Water pulses and biogeochemical cycles in arid and semiarid ecosystems. Oecologia 141:221–235
- Awale R, Chatterjee A (2017) Enhanced efficiency nitrogen products influence ammonia volatilization and nitrous oxide emission from two contrasting soils. Agron J 109:47–57
- Barton L, Kiese R, Gatter D, Butterbach-bahl K, Buck R, Hinz C, Murphy DV (2008) Nitrous oxide emissions from a cropped soil in a semi-arid climate. Glob Change Biol 14:177–192
- Black A, Sherlock R, Cameron K, Smith N, Goh K (1985) Comparison of three field methods for measuring ammonia volatilization from urea granules broadcast on to pasture. J Soil Sci 36:271–280
- Black A, Sherlock R, Smith N (1987) Effect of timing of simulated rainfall on ammonia volatilization from urea, applied to soil of varying moisture content. J Soil Sci 38:679–687
- Burton D, Li X, Grant C (2008) Influence of fertilizer nitrogen source and management practice on N₂O emissions from two black chernozemic soils. Can J Soil Sci 88:219–227
- Chang C, Janzen H, Cho C (1998) Nitrous oxide emission from long-term manured soils. Soil Sci Soc Am J 62:677–682
- Dobbie K, McTaggart I, Smith K (1999) Nitrous oxide emissions from intensive agricultural systems: variations between crops and seasons, key driving variables, and mean emission factors. J Geophys Res Atmos 104:26891–26899
- Dusenbury M, Engel R, Miller P, Lemke R, Wallander R (2008) Nitrous oxide emissions from a northern great plains soil as influenced by nitrogen management and cropping systems. J Environ Qual 37:542–550
- Ellen J, Spiertz J (1980) Effects of rate and timing of nitrogen dressings on grain yield formation of winter wheat (*T. aestivum* L.). Fertil Res 1:177–190
- Feng J, Li F, Deng A, Feng X, Fang F, Zhang W (2016) Integrated assessment of the impact of enhanced-efficiency nitrogen fertilizer on N₂O emission and crop yield. Agric Ecosyst Environ 231:218–228
- Ferguson R, Kissel D (1986) Effects of soil drying on ammonia volatilization from surface-applied urea. Soil Sci Soc Am J 50:485–490
- Fowler D, Brydon J, Baker R (1989) Nitrogen fertilization of notill winter wheat and rye. I. Yield agronomic responses. Agron J 81:66–72
- Golden B, Slaton N, Norman R, Gbur E, Wilson C (2011) Nitrogen release from environmentally smart nitrogen fertilizer as influenced by soil series, temperature, moisture, and incubation method. Commun Soil Sci Plant Anal 42:1809–1824
- Gregorich E, Rochette P, VandenBygaart A, Angers D (2005) Greenhouse gas contributions of agricultural soils and potential mitigation practices in Eastern Canada. Soil Till Res 83:53–72
- Hangs R, Greer K, Sulewski C, Hicks D (2002) Plant root simulatorTM-probes: an effective alternative for routine soil testing. In: Soil and crops workshop proceedings. University of Saskatchewan

- Hergoualc'h K, Akiyama H, Bernoux M, Chirinda N, Del Prado A, Kasimir Å, MacDonald D, Ogle SM, Regina K, van der Weerden T (2019) 2019 Refinement to the 2006 IPCC guidelines for national greenhouse gas inventories: agriculture forestry and other land use, p 11
- Holtan-Hartwig L, Dörsch P, Bakken L (2002) Low temperature control of soil denitrifying communities: kinetics of N₂O production and reduction. Soil Biol Biochem 34:1797–1806
- Keeney DR, Nelson D (1982) Nitrogen—inorganic forms. In: Page AL (ed) Methods of soil analysis. Part 2. Chemical and microbiological properties. American Society of Agronomy, Soil Science Society of America, Madison, pp 643–698
- Kutner M, Nachtsheim C, Neter J (2004) Applied linear regression models, 4th edn. McGraw-Hill, New York
- Large EC (1954) Growth stages in cereals illustration of the Feekes scale. Plant Pathol 3:128–129
- Lemke R, Izaurralde R, Nyborg M, Solberg E (1999) Tillage and N source influence soil-emitted nitrous oxide in the Alberta Parkland region. Can J Soil Sci 79:15–24
- Linn DM, Doran JW (1984) Effect of water-filled pore space on carbon dioxide and nitrous oxide production in tilled and nontilled soils. Soil Sci Soc Am J 48:1267–1272
- Mahler RL, Koehler FE, Lutcher L (1994) Nitrogen source, timing of application, and placement: effects on winter wheat production. Agron J 86:637–642
- Malhi S, Nyborg M (1983) Field study of the fate of fall-applied 15N-labelled fertilizers in three alberta soils 1. Agron J 75:71–74
- Müller C, Sherlock RR (2004) Nitrous oxide emissions from temperate grassland ecosystems in the Northern and Southern Hemispheres. Glob Biogeochem Cycles 18:GB1045-1
- Padbury G, Waltman S, Caprio J, Coen G, McGinn S, Mortensen D, Nielsen G, Sinclair R (2002) Agroecosystems and land resources of the northern Great Plains. Agron J 94:251–261
- Parkin T, Venterea R, Hargreaves S (2012) Calculating the detection limits of chamber-based soil greenhouse gas flux measurements. J Environ Qual 41:705–715
- Raun WR, Johnson GV (1999) Improving nitrogen use efficiency for cereal production. Agron J 91:357–363
- Recio J, Vallejo A, Le-Noe J, Garnier J, García-Marco S, Álvarez JM, Sanz-Cobena A (2018) The effect of nitrification inhibitors on NH₃ and N₂O emissions in highly N fertilized irrigated Mediterranean cropping systems. Sci Total Environ 636:427–436
- Rochette P, Worth DE, Lemke RL, McConkey BG, Pennock DJ, Wagner-Riddle C, Desjardins R (2008) Estimation of N₂O emissions from agricultural soils in Canada. I. Development of a country-specific methodology. Can J Soil Sci 88:641–654

- Rozas HRS, Echeverría HE, Barbieri PA (2004) Nitrogen balance as affected by application time and nitrogen fertilizer rate in irrigated no-tillage maize. Agron J 96:1622–1631
- Sims G, Ellsworth T, Mulvaney R (1995) Microscale determination of inorganic nitrogen in water and soil extracts. Commun Soil Sci Plant Anal 26:303–316
- Soares JR, Cantarella H, de Campos Menegale ML (2012) Ammonia volatilization losses from surface-applied urea with urease and nitrification inhibitors. Soil Biol Biochem 52:82–89
- Soil Classification Working Group (1998) The Canadian system of soil classification. NRC Research Press, Ottawa
- Sowers KE, Miller BC, Pan WL (1994) Optimizing yield and grain protein in soft white winter wheat with split nitrogen applications. Agron J 86:1020–1025
- Stark JM (1996) Modeling the temperature response of nitrification. Biogeochemistry 35:433–445
- Sturm M, Taras B, Liston GE, Derksen C, Jonas T, Lea J (2010) Estimating snow water equivalent using snow depth data and climate classes. J Hydrometeorol 11:1380–1394
- Trenkel ME (2010) Slow-and controlled-release and stabilized fertilizers: an option for enhancing nutrient use efficiency in agriculture. IFA, International Fertilizer Industry Association, Paris
- Van der Weerden TJ, Luo J, Di HJ, Podolyan A, Phillips RL, Saggar S, de Klein CAM, Cox N, Ettema P, Rys G (2016) Nitrous oxide emissions from urea fertiliser and effluent with and without inhibitors applied to pasture. Agric Ecosyst Environ 219:58–70
- Venterea R, Parkin T, Cardebas L, Petersen S, Petersen A (2012) Data analysis considerations. In: De Klein C, Harvey M (eds) Nitrous oxide chamber methodology guidelines. Global research alliance on agricultural greenhouse gases. Ministry for Primary Industries, Wellington, pp 95–121
- Venterea RT, Clough TJ, Coulter JA, Breuillin-Sessoms F, Wang P, Sadowsky MJ (2015) Ammonium sorption and ammonia inhibition of nitrite-oxidizing bacteria explain contrasting soil N₂O production. Sci Rep 5:12153
- Wagner-Riddle C, Hu Q, Van Bochove E, Jayasundara S (2008) Linking nitrous oxide flux during spring thaw to nitrate denitrification in the soil profile. Soil Sci Soc Am J 72:908–916
- Zhu X, Burger M, Doane TA, Horwath WR (2013) Ammonia oxidation pathways and nitrifier denitrification are significant sources of N₂O and NO under low oxygen availability. Proc Natl Acad Sci 110:6328–6333

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.