

Nitrous oxide emissions in Midwest US maize production vary widely with band-injected N fertilizer rates, timing and nitrapyrin presence

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Abstract

Nitrification inhibitors have the potential to reduce N₂O emissions from maize fields, but optimal results may depend on deployment of integrated N fertilizer management systems that increase yields achieved per unit of N₂O lost. A new micro-encapsulated formulation of nitrapyrin for liquid N fertilizers became available to US farmers in 2010. Our research objectives were to (i) assess the impacts of urea–ammonium nitrate (UAN) management practices (timing, rate and nitrification inhibitor) and environmental variables on growing-season N₂O fluxes and (ii) identify UAN treatment combinations that both reduce N₂O emissions and optimize maize productivity. Field experiments near West Lafayette, Indiana in 2010 and 2011 examined three N rates (0, 90 and 180 kg N ha⁻¹), two timings (pre-emergence and side-dress) and presence or absence of nitrapyrin. Mean cumulative N₂O–N emissions (Q_{10} corrected) were 0.81, 1.83 and 3.52 kg N₂O–N ha⁻¹ for the rates of 0, 90 and 180 kg N ha⁻¹, respectively; 1.80 and 2.31 kg N₂O–N ha⁻¹ for pre-emergence and side-dress timings, respectively; and 1.77 versus 2.34 kg N₂O–N ha⁻¹ for with and without nitrapyrin, respectively. Yield-scaled N₂O–N emissions increased with N rates as anticipated (averaging 167, 204 and 328 g N₂O–N Mg grain⁻¹ for the 0, 90 and 180 kg N ha⁻¹ rates), but were 22% greater with the side-dress timing than the pre-emergence timing (when averaged across N rates and inhibitor treatments) because of environmental conditions following later applications. Overall yield-scaled N₂O–N emissions were 22% lower with nitrapyrin than without the inhibitor, but these did not interact with N rate or timing.

Keywords: nitrogen, nitrous oxides, nitrapyrin, maize production systems, yield-scaled nitrous oxide emissions, urea–ammonium nitrate

Abbreviations

N	Nitrogen
N ₂ O	Nitrous oxide
NO ₃	Nitrate
NH ₄	Ammonium

EF	Emission factor
UAN	Urea–ammonium nitrate
WFPS	Water filled pore space
GHG	Greenhouse gas
AOV	Analysis of variance

1. Introduction

Agriculture has been identified as the major contributor of anthropogenic nitrous oxide (N₂O) emissions worldwide



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(Smith *et al* 2007). The Midwest region (Iowa, Illinois, Indiana, Michigan, Minnesota, Ohio and Wisconsin) is the main producer of maize and soybeans in the US, but is also a region with high N₂O emissions (Larsen *et al* 2007) because of extensive N fertilizer use in grain production. Several management-related factors affect N₂O–N emissions following application of common N fertilizers (such as rate, timing, placement and source). However, it is not completely understood how each of these factors contributes, especially in combination, to the N₂O–N emitted. In the Midwest, emissions range between 0.2 and 6.3% (or more) of the fertilizer N applied (Flynn and Smith 2010, Linquist *et al* 2012). These reported ranges differ considerably from the current IPCC default for N₂O emissions factor (EF) of 1.0% of annual N fertilizer application (2007 IPCC guidelines, available online). This disparity has prompted the search for N management systems that lead to lower N₂O losses.

The N rate applied relative to crop N demand has an important impact on N₂O released from agricultural soils, particularly when N rates exceed certain agronomic thresholds (Snyder *et al* 2009). The threshold level cannot be generalized because of variations across cropping systems and environments, but an approximation can be derived from calculating the surplus between the N applied and the crop's total plant N uptake during the growing season (Van Groenigen *et al* 2010).

Synchrony between N supply and N demand is also important in the temporal scale. Ideally, N application closer to a crop's most active N uptake period should reduce potentially negative environmental factors. Side-dress applications could lead to greater recovery efficiencies of N and reduce the risks of losing N through leaching, nitrification/denitrification, and other processes. Nevertheless, delaying N fertilizer applications does not always lower N₂O emissions (Zebarth *et al* 2008).

Whether the fertilizer N form affects the N₂O–N released to the atmosphere is a subject of much discussion (Snyder *et al* 2009). Interactions between the fertilizer source, tillage, and soil temperature and moisture conditions complicate attempts to reach general conclusions regarding N source effects (Harrison and Webb 2001, Bouwman *et al* 2002, Venterea *et al* 2005).

Another management practice with potential for abatement of N₂O emissions is the use of nitrification inhibitors in conjunction with N fertilizer. These chemicals have been commercialized since the early 1960s, and nitrapyrin was the first such product (Prasad and Power 1995). Nitrapyrin (known commercially as N-ServeTM) impacts on crop yield, soil mineral N and N losses to the environment have received considerable study in anhydrous ammonia fertilizer systems (e.g. review by Wolt 2004), but there are far fewer studies with this chemistry in liquid N fertilizer systems. A more recent study comprising diverse N fertilizer forms (Halvorson *et al* 2010) found a 29% reduction in N₂O–N released from urea–ammonium nitrate (UAN) when this liquid fertilizer was supplemented with both urease and nitrification inhibitors. In another experiment, Halvorson and Del Grosso (2012) reported a 50% reduction for growing-season N₂O

emissions comparing UAN with and without both urease and nitrification inhibitors.

Few studies have compared the simultaneous impact of multiple management factors on N₂O emissions. One study compared alternative N sources and crop rotations (Hernandez-Ramirez *et al* 2009). Other studies focused on the dual factors of N rate and N source, or N rate and timing of application (reviewed by Snyder *et al* 2009, Stehfest and Bouwman 2006). However, the authors are not aware of any study that combined N rate, N application timing and nitrification inhibitor treatment factors to determine their individual or interacting factor consequences on N₂O emissions from maize fields.

Besides management practices, there are several soil factors that modulate and control the primary processes of nitrification and denitrification that are involved in N₂O gas release. The soil moisture content, expressed as water filled pore space (WFPS), is one of the major influences on denitrification and, therefore, on N₂O emissions (Linn and Doran 1984). Temperature is another main controlling factor in N₂O emissions; as temperatures increase N₂O emission rates also increase, but typically at a non-linear (exponential) rate. This relationship is often expressed in terms of the Q_{10} value (Smith *et al* 2003). Additional soil factors related to N₂O emissions include redox potential (Turner and Patrick 1965, Kralova *et al* 1992), carbon availability, total organic carbon and water-soluble carbon (Drury *et al* 1991), and soil pH (Van den Heuvel *et al* 2011).

Commonly, N₂O emission measurements from agricultural systems are presented on a cumulative or flux basis, and are analyzed without regard for the crop productivity level attained in the cropping system being analyzed. This approach can identify superior management practices that reduce GHG emitted, but societal food security needs are compromised if crop productivity declines appreciably. The recent derivation of 'yield-scaled N₂O', i.e. the amount of N₂O released per unit of production, e.g. grain yield (Flynn and Smith 2010, Van Groenigen *et al* 2010, Linquist *et al* 2012, Grassini and Cassman 2012, van Kessel *et al* 2012) has permitted more holistic assessment of crop management practices.

The aims of this study were to: (i) assess the impact of UAN management practices (timing, rate and nitrification inhibitor) and environmental variables on N₂O fluxes during the maize growing season, and (ii) identify UAN treatment combinations that both reduce N₂O emissions and increase maize productivity.

2. Materials and methods

2.1. Site and treatment description

This study was conducted for two growing seasons (2010 and 2011) on dark prairie soil at the Purdue University Agronomy Center for Research and Education (40°28'07"N, 87°00'25"W) near West Lafayette, Indiana. The soil series are Chalmers, a fine-silty, mixed, superactive, mesic Typic Endoaquolls. The mean annual air temperature is 10.5 °C and the mean annual precipitation is 970 mm (30-year

period from 1981 to 2010). The rotation employed each year was maize (*Zea mays* L.) following soybeans (*Glycine max* (L.) Merr.), planted on conventionally tilled soils.

The experiment comprised 12 treatments arranged in a randomized complete block design, with three treatment factors and four replications. The plots were 27 m long by 4.5 m (six rows) wide. Specific soil properties for the 2010 site included: pH: 6.2, organic matter content: 3.3%, P: 25 mg kg⁻¹ and K: 183 mg kg⁻¹, while the same soil properties (0–20 cm) for the 2011 site were pH: 6.3, organic matter content: 4.2%, P: 27 mg kg⁻¹ and K: 139 mg kg⁻¹. Treatment factors evaluated included N rate: 0, 90 and 180 kg N applied ha⁻¹; two timings of application: pre-emergence or side-dressed (applied at V6 maize growth stage, approximately 30 d after planting); and the presence or absence of nitrapyrin (InstinctTM, Dow Agrosiences LLC, Indianapolis, IN). The N source (UAN, 28% N solution) was applied with a DMI 2800 Nutriplacer applicator (Case-IH) equipped for coulter-band injection to a soil depth of 8–10 cm, approximately 38 cm from the maize rows. Zero N plots received water instead of UAN so that traffic and coulter disturbance patterns were uniform in all plots. Nitrapyrin, stored in a companion tank to the primary UAN tank, was pressure-injected into the UAN fertilizer flow at a rate equivalent to 0.56 kg nitrapyrin active ingredient ha⁻¹ in plots requiring this nitrification inhibitor. Maize hybrid Mycogen 2T-789 (114 RM) was planted on 21 April 2010 and 5 May 2011. The average final population achieved was 81 900 pl ha⁻¹ in 2010 and 86 000 pl ha⁻¹ in 2011, and all plots received 22 kg N ha⁻¹ of starter fertilizer (10–34–0) at planting (same timing as pre-emergence). Therefore, total N applied was 22, 112 or 202 kg N ha⁻¹, but these treatments will be referred to as N rates of 0, 90 or 180 kg of N ha⁻¹ throughout the manuscript to reflect the differential treatment applications. In 2010, N₂O fluxes, N₂O emissions and maize yield from zero N plots without nitrapyrin (i.e. control plots) were assumed to be similar for pre-emergence and side-dress applications, and therefore only one control plot was used to represent both timings. This assumption was later validated with the consistent 2011 data between the duplicate control plots for both timings of application (pre-emergence and side-dress).

2.2. Data collection and analysis

Field measurements of GHG (N₂O, CO₂ and CH₄) emissions from the soil surface in all 48 plots were made after planting and treatment applications at approximately 10-d intervals in 2010 and at 7-d intervals in 2011. Sampling continued until mid-August (approximately three weeks after silk emergence) when N₂O emissions were very low and stable. Since whole-plant maize N uptake at physiological maturity crops exceeded fertilizer N applied in both years (Burzaco 2012), these in-season measurements likely characterized the majority of N₂O–N fluxes associated with UAN applications. Vented aluminum chambers (Mosier *et al* 2006) were placed over anchors in each plot following maize planting and UAN application using protocols reported by Omonode *et al*

(2010). The anchors were installed approximately 10 cm deep into the soil perpendicular to the maize rows. The chambers were 0.12 m high by 0.70 m long by 0.35 m wide, with an internal vent tube to equilibrate pressure and temperature. Four gas samples were collected at 10-min intervals between 0 and 30 min. To collect the samples, 25 ml of air were extracted from the headspace inside the chamber, 5 ml discarded and the remainder injected into previously evacuated vials (12 ml Exetainer, Labco, High Wycombe, UK) to a pressure of 0.032 kPa. All samples were collected between 10 am and 2 pm (Eastern Standard Time), and analyzed shortly after collection using a gas chromatographer (CP 3800; Varian, Sunnyvale, CA). The detectors used in the gas chromatographer included electron capture detector for N₂O, flame ionization detector for methane, and thermal conductivity detector for carbon dioxide. Vials containing a known concentration of gases (1170 μl CO₂ l⁻¹, 9.24 μl CH₄ l⁻¹ and 1.43 μl N₂O l⁻¹) were run every 16 samples for calibration purposes.

Every time field GHG emissions were sampled, soil water content and temperature were measured in the vicinity of each anchor. To assess soil water content, a 0.12 m deep probe (TDR 300 Serial 346; Field Scout Spectrum Technologies, Plainfield, IL) was used. This instrument was calibrated by extracting undisturbed soil cores from the experimental site. The cores were oven-dried in order to calculate the soil bulk density, porosity, air-filled porosity and WFPS, after USDA (2011). Also, thermometers (WatchDog B-series, Field Scout Spectrum Technologies, Plainfield, IL) were installed in every plot, at a depth of 10 cm, to record soil temperatures throughout the growing season. Other soil parameters characterized from the experimental sites included soil fertility to a depth of 0.2 m and soil mineral N (NO₃ and NH₄) concentrations to a depth of 0.3 m. Soil mineral N samples were collected at each GHG sampling date in 2010, and for every other sampling date in 2011. The regression coefficient, obtained by plotting gas concentrations as a function of elapsed time, was used to calculate N₂O production rates, after Hernandez-Ramirez *et al* (2009).

Grain yield was measured after maturity. In 2010, grain-yield data were obtained by harvesting the center two rows of every plot (4 reps) with a plot combine. In 2011, severe weather conditions in mid-August caused substantial lodging and stalk breakage, and plot grain yields were estimated by hand harvesting 10 m in center two rows of all plots.

2.3. Statistical analysis

Homogeneous variances between years for flux and emissions enabled combined analyses of 2010 and 2011 data. Fluxes of N₂O were analyzed on a per-year basis and pooled for Spearman-rank correlation determination between N₂O fluxes and environmental variables. For the latter, N₂O fluxes were ln-transformed (based on the Transreg procedure) because the original data were non-normally distributed. To determine the impact of the treatments on the N₂O fluxes, the ln-transformed fluxes of N₂O were analyzed using PROC MIXED, with a

repeated-measurements statement in the model options, since the data for GHG emissions were collected from the same sampling position inside each plot each season.

Assessment of cumulative N₂O–N released during the growing season began with correction of actual daily fluxes for differences between sampling-time versus mean daily soil temperatures at the 5-cm depth. These temperature differences were employed in the estimation of a Q_{10} factor, as described by Borken *et al* (2003), Parkin and Kaspar (2003, 2006) and Hernandez-Ramirez *et al* (2009). The cumulative N₂O–N emissions were estimated by linear interpolation between sampling dates (Vehlfhof and Oenema 1995). Cumulative emissions were analyzed using the PROC MIXED procedure. Analyses were performed on both ln-transformed data and non-transformed data, but since neither the significance of the factors nor the mean separation of the treatments differed between transformed and non-transformed data, all cumulative fluxes were analyzed without transformation. Emission factors were calculated by subtracting the cumulative N₂O–N emissions for the control plots (0 N) from the cumulative N₂O–N emissions from the fertilized plot, and dividing by the N rate applied. As previously mentioned, all plots (including the ones with 0 N) received 22 kg of N ha⁻¹ as a starter fertilizer; however, for calculation purposes we will treat 0 N as control. Finally, Q_{10} -cumulative-N₂O–N emissions were divided by the corresponding grain yield to obtain yield-scaled N₂O (Flynn and Smith 2010, Van Groenigen *et al* 2010, Linquist *et al* 2012). Although log-transformed yield-scaled N₂O was used to run ANOVA, the back-transformed means are reported. Mean separations were done using LSD in most cases, and Scheffe’s test when the family wise error needed control (i.e. for multiple pairwise comparisons).

3. Results

3.1. Treatment effects on N₂O fluxes

The analysis of variance performed on the daily ln-transformed N₂O–N fluxes are presented in table 1. The N rate effect was highly significant (p -value <0.0001) in both individual and combined years, and every increment in N rates significantly increased daily flux. Raising the N fertilizer rate from 90 to 180 kg N ha⁻¹ brought about almost a two-fold increase in the N₂O–N fluxes, and this change was consistent across years, even though the absolute values for fluxes between years differed significantly (table 1). Increasing the N fertilizer rate from 0 to 90 kg N ha⁻¹ had a similar effect, though the flux rate increased by 54% in 2010 and by 127% in 2011.

Nitrapyrin presence significantly reduced ln N₂O–N fluxes by an average 1.7 g N₂O–N ha⁻¹ d⁻¹ (across N rates and application timings) when both years were analyzed together (table 1). Timing effects (averaged across N rates and nitrapyrin levels) varied by year. In 2010, a non-significant increase in daily fluxes of about 1 g N₂O–N ha⁻¹ d⁻¹ was observed following side-dress application. However, in 2011 side-dress application resulted in a significant reduction

Table 1. Mean separations for the year and treatment effects on daily N₂O–N fluxes. The analysis was performed on ln N₂O–N, and the data presented here are the back-transformed results. Different letters indicate statistically significant differences (LSD 5%). ANOVA summary is pertinent for the treatment effects on ln N₂O–N daily fluxes for years 2010, 2011 and both years pooled together. (Notes: *, **, *** significant at 0.05, 0.01 and 0.001 probability levels, respectively.)

		N ₂ O–N (g ha ⁻¹ d ⁻¹)		
Year		2010	2011	Both
		6.3 b	10.7 a	
N (kg ha ⁻¹)	0	2.8 c	5.5 c	4.7 c
	90	4.3 b	12.5 b	8.2 b
	180	8.0 a	23.5 a	14.2 a
Timing	Pre	4.2 a	13.1 a	9.0 a
	Side	5.2 a	10.8 b	7.6 a
Inhibitor	Without	5.3 a	12.7 a	9.2 a
	With	4.1 b	11.1 a	7.5 b
ANOVA				
		p -value		
		2010	2011	Both
Year		na	na	***
Nitrogen		***	***	***
Timing		ns	**	ns
Inhibitor		*	ns	*
Year × nitrogen		na	na	**
Nitrogen × timing		ns	***	ns
Nitrogen × inhibitor		**	ns	ns
N × timing × inhibitor		ns	ns	ns

of 2.3 g N₂O–N ha⁻¹ d⁻¹ relative to pre-emergence N application.

Greater N₂O flux rates were observed for 2011 than for 2010 in both 90 and 180 kg N ha⁻¹ applied rates, but this trend was not observed in the control plots (table 2). The N rate interacted significantly with application timing in 2011, since the flux rates for 180 kg N ha⁻¹ applied pre-emergence were significantly greater than the flux rates with the same rate of side-dress N. In 2010, the N rate interaction with nitrapyrin was significant because the reduction of N₂O–N emissions with the nitrification inhibitor was only significant for 90 kg N ha⁻¹ (table 2).

3.2. Cumulative emissions of N₂O–N

The cumulative emissions of N₂O–N for the two growing seasons (2010 and 2011) were significantly affected by N rate and inhibitor treatments (table 3). However, only the simple effects of the individual treatment factors were significant, and no interactions were significant (AOV not shown). Although cumulative N₂O–N emissions were 0.7 kg N₂O–N ha⁻¹ in 2011 compared to 2010, treatment effects were consistent across growing seasons. As expected, N fertilizer rate had a major influence on the cumulative N₂O–N released (table 3) as the cumulative N₂O–N released more than doubled when the N rate increased from 0 to 90 kg of N ha⁻¹, and almost doubled again following 180 kg N ha⁻¹ compared

Table 2. Mean separations for the significant individual and combined year and treatment interaction effects on daily N₂O–N. The analysis was performed on ln N₂O–N, and the data presented here are the back-transformed results. Different letters indicate statistically significant differences (LSD 5%). Without inhibitor (wo/I), and with inhibitor (w/I).

Combined years (2010–2011)		2010		2011	
Year × N	N ₂ O–N (g ha ⁻¹ d ⁻¹)	N × I	N ₂ O–N (g ha ⁻¹ d ⁻¹)	N × Timing	N ₂ O–N (g ha ⁻¹ d ⁻¹)
2010—0	4.6 d	0—wo/I	2.9 b	0—pre-emergence	5.1 d
2010—90	5.9 cd	0—w/I	2.7 b	0—sidedress	5.9 d
2010—180	9.3 bc	90—wo/I	6.4 a	90—pre-emergence	13.4 bc
2011—0	4.9 d	90—w/I	2.8 b	90—sidedress	11.6 c
2011—90	11.3 b	180—wo/I	7.6 a	180—pre-emergence	31.2 a
2011—180	21.3 a	180—w/I	8.4 a	180—sidedress	17.7 b

Table 3. Mean separation for the main-factor effects on N₂O–N cumulative emissions for the 2010 and 2011 growing seasons (118 and 97 d, respectively). Different letters indicate statistically significant differences at Scheffe-5%.

Factor (<i>p</i> -value)	Cumulative N ₂ O–N (kg ha ⁻¹)
Year (0.0012)	
2010	1.55 b
2011	2.56 a
N rate (<0.0001)	
0	0.81 c
90	1.83 b
180	3.52 a
Timing (0.0502)	
Pre-emergence	1.80 a
Side-dress	2.31 a
Inhibitor (0.0298)	
Without	2.34 a
With	1.77 b

to 90 kg N ha⁻¹. Emissions observed from side-dress applications were 0.6 kg of N₂O–N ha⁻¹ greater than those with pre-emergence applications (table 3); this difference was significant at alpha = 0.10 (*p*-value 0.0502). Lastly, presence of nitrapyrin reduced cumulative N₂O–N by 0.6 kg ha⁻¹.

3.3. Yield-scaled N₂O–N

Grain yields were only affected by N rates, and by the N rate × year interaction (table 4). Grain yields averaged 5.12, 8.82 and 11.22 Mg ha⁻¹ for rates of 0, 90 and 180 kg N ha⁻¹, respectively. The interaction between year and N rate occurred because the high N rate (180 kg N ha⁻¹) yielded ~2 Mg ha⁻¹ more in 2010 than in 2011.

The effects of N rate, year by N interaction, and inhibitor on log-yield-scaled N₂O–N emissions were all significant (table 4). The high N rate (180 kg N ha⁻¹) had 161 g N₂O–N Mg grain⁻¹ greater yield-scaled emissions than the zero N rate, but the medium (90 kg N ha⁻¹) and zero N rates did not differ significantly. Overall, the side-dress timing of application had higher yield-scaled emissions than the pre-emergence timing (210 and 257 g N₂O–N Mg grain⁻¹ for side-dress and pre-emergence, respectively), significant

Table 4. Treatment mean separations for grain yield (GY), and yield-scaled N₂O–N. Means presented in this table are obtained from the back-transformed data for yield-scaled means. Pre-emergence (Pre), and side-dress (Side). Different letters indicate statistically significant differences within columns (Scheffe-5%). *p*-values for each variable are included at the bottom of the table. (Notes: *, **, *** significant at 0.05, 0.01 and 0.001 probability levels, respectively.)

Timing	N (kg ha ⁻¹)	Inhibitor	GY (Mg ha ⁻¹)	Yield-scaled N ₂ O (g Mg ⁻¹)
Pre	0	No	5.41 d	174 cd
Pre	0	Yes	5.09 d	157 cd
Pre	90	No	8.32 c	211 bcd
Pre	90	Yes	8.58 c	135 d
Pre	180	No	11.11 ab	312 ab
Pre	180	Yes	10.70 abc	268 bcd
Side	0	No	5.02 d	178 cd
Side	0	Yes	4.97 d	159 cd
Side	90	No	8.93 bc	285 bc
Side	90	Yes	9.51 abc	187 bcd
Side	180	No	11.69 a	418 a
Side	180	Yes	11.35 ab	314 ab

ANOVA	
	<i>p</i> -value
Year	ns
Nitrogen	***
Year × nitrogen	***
Timing	ns
Inhibitor	*
Nitrogen × timing	ns
Nitrogen × inhibitor	ns
N × Timing × inhibitor	ns

at alpha = 0.10 (*p*-value 0.0531). Lastly, the nitrification inhibitor significantly reduced yield-scaled emissions (263 and 203 g N₂O–N Mg grain⁻¹ for without and with the inhibitor, respectively).

3.4. Weather conditions

Weather conditions, especially precipitation during the growing season (May–October), varied widely between years and with respect to normal values (table 5). Total precipitation in June of 2010 was double the precipitation for June in the 30-year period data set. The year 2011 was characterized by unusually high precipitation in April and May and by heat and drought stresses during the period bracketing silking (July).

Table 5. Weather characterization for the experimental site for years 2010, 2011 and normal data from the 30 year series 1981–2010. Precipitation (pp) in millimeters (mm) and mean temperature (temp.) in degrees centigrade (°C).

Month	2010		2011		1981–2010	
	pp (mm)	Temp. (°C)	pp (mm)	Temp. (°C)	pp (mm)	Temp. (°C)
April	52.7	14.3	168.5	10.7	90.9	10.5
May	119.1	17.7	183.4	16.4	120.9	16.4
June	209.0	24.1	94.5	22.2	103.9	21.6
July	107.4	24.1	64.5	25.4	106.7	23.0
August	67.1	23.5	76.2	22.0	91.7	22.0
September	53.8	19.1	72.6	17.0	71.6	18.3
October	22.4	13.0	26.1	12.1	77.5	11.7

Later on, around R3 stage, strong winds and hail severely impacted the crop, causing some lodging and stalk breakage. Total precipitation per month varied considerably in both years, but the frequency of extreme precipitation events also varied. In 2010, cumulative daily precipitations above 60 mm occurred only once during the growing season while other precipitation events never exceeded 30 mm (figure 1(G)). However, in 2011 there were 5 d with precipitation above 30 mm, 2 d above 40 mm and 1 d higher than 70 mm (figure 2(G)).

3.5. Environmental effects on N₂O fluxes

Environmental variables were significantly correlated with the N₂O–N fluxes observed (without applying the Q_{10} correction), although the impact and significance of some variables on the overall emissions changed between years (table 6). In 2010, soil NO₃ and NH₄ concentrations, WFPS, soil temperature and accumulated precipitation up to 48 h prior to sampling had the highest correlation coefficients (all highly significant) with mean N₂O–N daily fluxes.

Even though the soil NO₃ and NH₄ coefficients were significant for 2011, the impact of mineral N fractions on N₂O–N fluxes appeared less relevant in 2011. Of the other soil variables assessed, WFPS was the most relevant parameter affecting N₂O–N fluxes in 2011 while soil temperature was not significant (table 6). The precipitation accumulated up to 120 h prior to gas sampling was most highly correlated with N₂O–N fluxes. When the data from both years were pooled together, the most relevant non-treatment factors were soil NO₃, WFPS, and cumulative precipitation 48 h prior to sampling. The N₂O–N fluxes for all the treatments, together with the observed values of soil temperature, WFPS, and precipitation are summarized in figure 1 (year 2010) and figure 2 (year 2011).

4. Discussion

The cumulative N₂O–N emissions were 28% higher with side-dress timing of applications (table 3; significant at $p = 0.0502$). This can be related to the peaks observed in N₂O–N fluxes soon after side-dress N applications (figures 1 and 2, for 2010 and 2011, respectively). The N₂O–N flux peaks in 2010 after side-dress applications (figures 1(E) and (F)) could be attributed to WFPS values greater than the 0.6 threshold (Sehy *et al* 2003) coupled with higher temperatures (almost 10 °C

higher for 1 June 2010 versus 20 May 2010) along with higher availability of mineral N close to the soil surface so soon after side-dress fertilization (Malhi and McGill 1982, Smith *et al* 1998, Choudhary *et al* 2002, Dobbie and Smith 2003, Ma *et al* 2010). The high WFPS and soil temperatures observed during three samplings after side-dress applications of N during 2011 were also conducive to very notable peaks in N₂O–N fluxes. When fluxes were analyzed with the repeated measurement statement, side-dress applications had greater mean fluxes in 2010 (at alpha = 0.10), but lower mean fluxes in 2011, when compared to pre-emergence timings (table 1). However, when the cumulative N₂O–N emissions were calculated by linear interpolation between sampling dates, the peaks in N₂O fluxes had a significant impact on the cumulative N₂O–N emissions, and greater overall N₂O–N emissions were observed for side-dress timing.

Prior studies of fall versus spring N fertilizer applications have observed reductions in the cumulative N₂O–N emitted with delayed N applications (Hao *et al* 2001, Hultgreen and Leduc 2003). Results from the few studies that evaluated the impact of spring-applied N on N₂O emissions are inconsistent. Ma *et al* (2010) in Ontario, Canada compared pre-emergence applications of urea to side-dress applications of UAN but were not able to arrive at a firm conclusion regarding timing effects; however, their study's short monitoring period (28 d), and changes in both N source and placement may have been contributing factors. Zebarth *et al* (2008) compared a single rate (150 kg N ha⁻¹) of ammonium nitrate either broadcast-applied at pre-emergence or side-dressed at V6 growth stage in New Brunswick, Canada, and found no significant effect of application timing on N₂O emissions.

The effect of nitrapyrin on N₂O emissions in the present study was an overall 26% reduction, averaged across the 90 and 180 kg N ha⁻¹ rates and the two application timings, for the two years combined. These results are consistent with the effects of nitrapyrin on N₂O–N emissions reported by other authors. Using information from a meta-analysis performed by Akiyama *et al* (2010), the effect of nitrapyrin was calculated as achieving an average 39% reduction in N₂O emissions. Another recent Indiana study (Omonode and Vyn 2013) observed an average 35% reduction in N₂O emissions when nitrapyrin was used with sidedress N application at a single rate of 200 kg N ha⁻¹. A Colorado study (Halvorson *et al* 2010) found a 35% reduction in N₂O emissions when

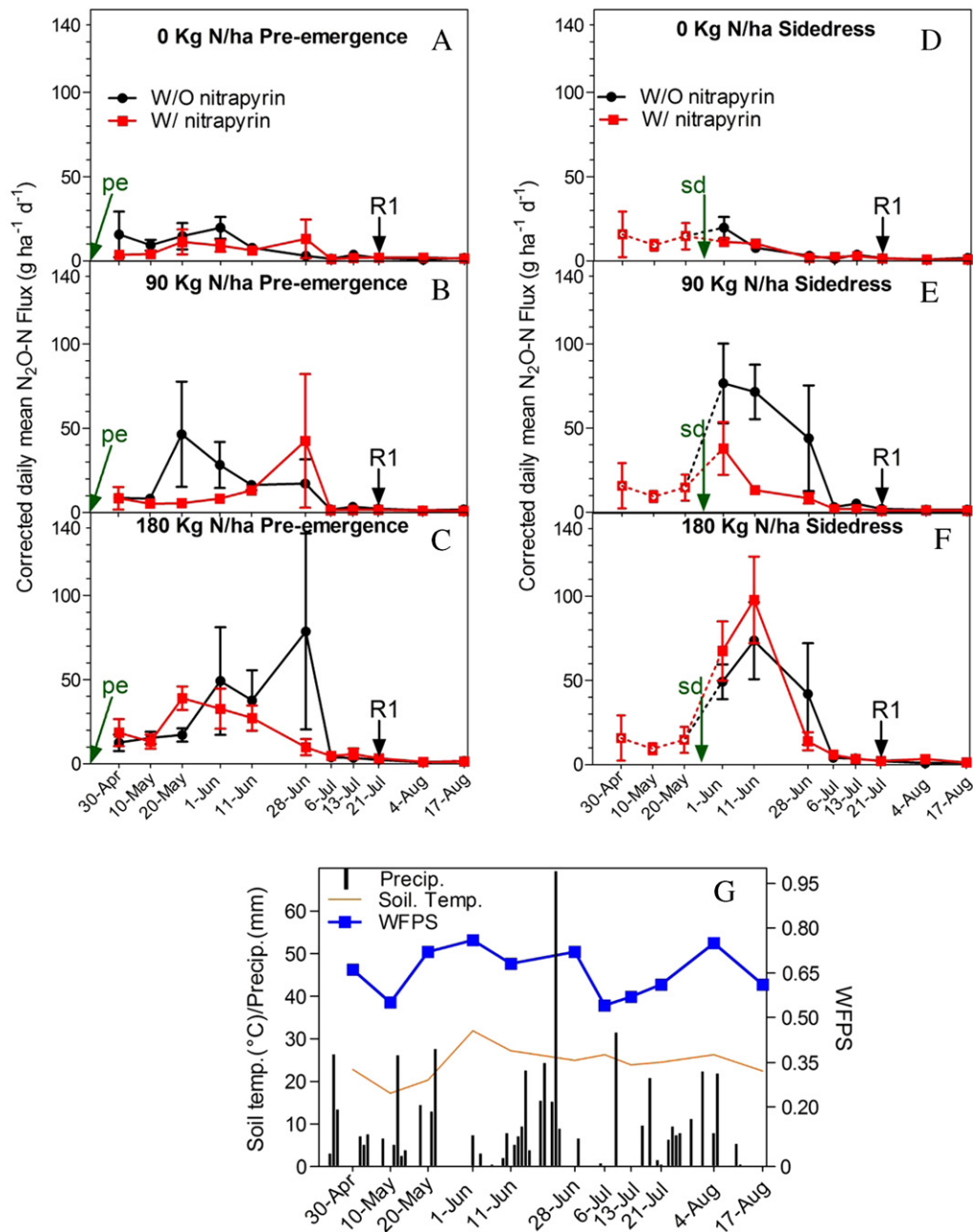


Figure 1. Q_{10} corrected daily mean N_2O-N emissions in grams per hectare per day ($g\ ha^{-1}\ d^{-1}$) for 2010 in pre-emergence N treatments (panels (A)–(C)) and side-dress N treatments (panels (D)–(F)); N rates of 0 (panels A and D); 90 (panels (B) and (E)); and 180 (panels (C) and (F)) $kg\ N\ ha^{-1}$. Broken lines in panels ((D)–(F)) represent N_2O-N fluxes from zero N plots without nitrapyrin. Soil temperature, water filled pore space (WFPS, dimensionless) and precipitation (panels (G)). None of the treatments (N rate, N timing, inhibitor) affected the WFPS or ST, hence panel (G) presents the means from the 12 treatment-plots times 4 replications. Occurrence of pre-emergence (pe) and side-dress N application (sd) and mean silking stage (R1) are marked with an arrow.

soil surface, band-applied UAN was used in conjunction with both a urease and nitrification inhibitor.

The effects of N rate on daily mean N_2O-N fluxes, as well as on cumulative N_2O-N emissions, were the most significant and consistent treatment response factors across years. The overall losses of N_2O-N represented 1.01% of N applied at $90\ kg\ N\ ha^{-1}$ and 1.22% of N applied at $180\ kg\ N\ ha^{-1}$. These emission factors were obtained by subtracting the cumulative N_2O-N emissions for the control plots from the cumulative N_2O-N emissions from the fertilized plot, and dividing by

the N rate. For rates of $90\ kg\ N\ ha^{-1}$, emissions ranged from 0.82% to 1.20% of fertilizer N lost as N_2O for pre-emergence and side-dress applications, respectively. For N rates of $180\ kg\ N\ ha^{-1}$, the N_2O-N emissions represented 1.13% and 1.30% of fertilizer N for pre-emergence or side-dress timing of application, respectively. These data suggest that reducing the N rate achieved a greater reduction in N_2O-N emissions with pre-emergence timing. When N was side-dress applied (at V6 growth stage), the N_2O-N reductions obtained when lowering the N rate were less evident (Burzaco 2012).

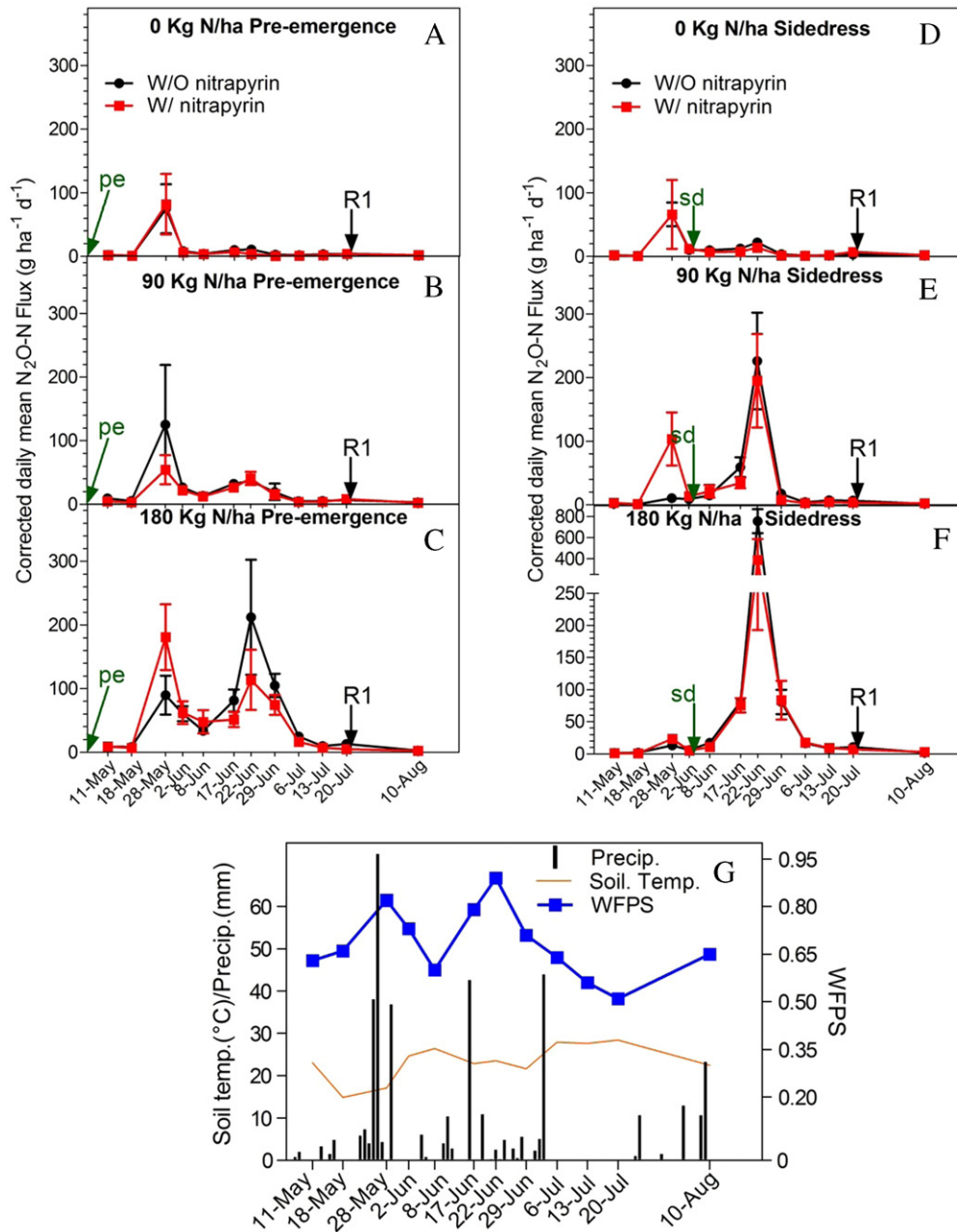


Figure 2. Q_{10} corrected daily mean N_2O-N emissions in grams per hectare per day ($g\ ha^{-1}\ d^{-1}$) for 2011 in pre-emergence N treatments (panels (A)–(C)) and side-dress N treatments (panels (D)–(F)); N rates of 0 (panels (A) and (D)); 90 (panels (B) and (E)); and 180 (panels (C) and (F)) $kg\ N\ ha^{-1}$. Soil temperature and water filled pore space (WFPS, dimensionless), and precipitation (panels (G)). None of the treatments (N rate, N timing, inhibitor) affected the WFPS or ST, hence panel (G) presents the means from the 12 treatment-plots times 4 replications. Occurrence of pre-emergence (pe), side-dress N application (sd) and mean silking stage (R1) are marked with an arrow.

The variation coupled with the range of values documented for emissions factors for the current research, emphasize the need to reconsider if a 1% value for N_2O-N emissions, as suggested by IPCC (2007 IPCC guidelines, available online), is universally applicable, or if different standards should be considered according to the characteristics of a given production region. Alternatively, an indicator that considers crop productivity (e.g. yield-scaled N_2O) as well as emissions could provide another approach.

Application of N rates that are close to the ‘Maximum Return to N’ (MRTN), a concept developed by Sawyer *et al*

(2006) for maize N management, was applied by Millar *et al* (2010) to develop a protocol for the reduction of N_2O emissions based primarily on N management. For the rates explored in the present experiments, the reduction in N rate was always at the expense of the harvested grain yield, so a strategy that promotes large reductions in N rate to control N_2O emissions would only be a partial solution, unless the current N applied widely exceeds the optimum for the crop. In the latter scenario, significant reductions in N application are possible while maintaining yield and reducing N_2O emissions (Li *et al* 2010, Liu *et al* 2011). There is still a need for research

Table 6. Spearman correlation coefficients for N₂O fluxes for 2010, 2011 and combined growing seasons. (Notes: water filled pore space (WFPS) and *, **, *** significant at 0.05, 0.01 and 0.001 probability levels, respectively.)

Year	Soil attribute				Preceding accumulated precipitation				
	NO ₃	NH ₄	Temperature	WFPS	24 h	48 h	72 h	96 h	120 h
2010 ^a	0.75***	0.46***	0.22***	0.29***	0.03	0.245***	-0.19***	-0.21***	-0.15***
2011 ^b	0.14***	0.11**	-0.04	0.46***	0.29***	0.27***	0.23***	0.31***	0.34***
2010 and 2011 ^c	0.35***	0.21***	0.05	0.39***	0.21***	0.27***	0.11***	0.17***	0.16***

^a n: 468.

^b n: 576.

^c n: 1044.

that involves comparisons of multiple N rates (more than 4), with smaller increments (approximately 20–30 kg of N ha⁻¹ increments), each with and without a nitrification inhibitor, to evaluate if a given level of N fertilization plus a nitrification inhibitor could result in similar maize yields as a higher N rate without the inhibitor. Also, it is important to assess if this yield difference added to the savings in N fertilizer are enough to offset the inhibitor cost.

A holistic approach that seeks to intensify grain production per unit of N₂O loss by reducing N₂O–N released from maize fields, without limiting grain yield (Rabbinge 1993), could be achieved through: (i) adopting management practices that reduce N₂O emissions *per se*, (ii) maintaining or increasing maize yield, or (iii) adopting a combination of both approaches, and assessing this through estimates such as yield-scaled N₂O–N emissions (Flynn and Smith 2010, Van Groenigen et al 2010, Linquist et al 2012). Mean yield-scaled N₂O–N emissions in the present research ranged between 135 and 418 g N₂O–N Mg yield⁻¹, though most of the means were less than 300 g N₂O–N Mg yield⁻¹ (table 4). Although no references report results on this parameter directly for the Midwestern USA, estimation of yield-scaled N₂O–N emissions from six site-years of positive corn yield response in Michigan (to the same N rates chosen for this study, but with pre-plant incorporated urea) can be approximated from figures showing corresponding cumulative N₂O–N emissions in Hoben et al (2011). The crudely estimated ranges in yield-scaled N₂O–N emissions from the Hoben et al (2011) data also show wide location/year and N rate variation from <100 to approximately 400 g N₂O–N Mg yield⁻¹. Using data from irrigated maize in Colorado (USA) (Halvorson et al 2010), a mean value of 137 g N₂O–N Mg yield⁻¹ was calculated for treatments that received UAN. Both mean yields (11.81 versus 8.39 Mg grain ha⁻¹), and fertilizer-induced emission factors were quite different for Halvorson et al (2010) and the current study (0.16 versus about 1.1%). Another maize production study by Gagnon et al (2011) reported yield-scaled N₂O emissions averaging 186 g N₂O–N Mg yield⁻¹ for UAN fertilizer applied at 3 N rates (100, 150 and 200 kg N ha⁻¹).

Results from the current research showed that yield-scaled N₂O–N emissions were significantly higher with side-dress timing of applications at alpha = 0.10 (*p*-value = 0.0531). Even though this difference is at a higher alpha than the 0.05, 0.01 and 0.001 otherwise utilized in this research, it is worth discussing because the *p*-value is

relatively small, especially in the context of highly variable N₂O–N emissions. Higher cumulative N₂O–N emissions with side-dress timing of application were accompanied by maize yields also approximately 0.4 Mg ha⁻¹ more than after pre-emergence applications. However, the effect of timing of N application on grain yield was not great enough to offset the higher values for N₂O–N emissions; hence yield-scaled N₂O emissions from side-dress treatments were also significantly greater (at alpha = 0.10). Over the two years, emissions averaged 257 g for side-dress compared to 210 g of N₂O–N Mg⁻¹ of grain following pre-emergence UAN applications (Burzaco 2012).

When two management-factor combinations were tested, the use of the nitrification inhibitor with the side-dress rate of 90 kg N ha⁻¹ was associated with somewhat greater (but non-significant) grain yields, a significant reduction in cumulative N₂O–N, and a non-significant reduction in the yield-scaled N₂O–N. At higher N rates (180 kg of N ha⁻¹), neither the grain yield nor the cumulative N₂O–N emissions were significantly affected by the use of nitrapyrin. As a result, the yield-scaled N₂O did not vary greatly, especially for pre-emergence applications. For side-dress applications, about 100 g lower N₂O–N released per Mg grain yield occurred when the nitrification inhibitor was applied (Burzaco 2012).

Soil NO₃ concentration was the soil variable most highly correlated with the fluxes of N₂O–N in 2010, whereas this was not observed in 2011 (table 6). Arguably, sampling for soil mineral N every other time gas samples were collected in 2011 (because of reduced funding levels) could explain why this variable was not as highly correlated to N₂O–N fluxes in 2011 as in 2010 (*ρ*: 0.14 versus 0.75). Also, composite soil samples for NO₃ and NH₄ concentrations were collected from plots, yet this might not be the best approach to use to relate N₂O fluxes to soil mineral N status, especially when N fertilizer has recently been banded and injected (Ginting and Eghball 2005).

A highly significant effect of soil temperature was observed in 2010 only (*ρ*: 0.22). In experiments done at the same Purdue University research farm, Hernandez-Ramirez et al (2009) reported that soil temperature was the covariate most correlated with N₂O fluxes (*ρ*: 0.34). The treatments applied in the current research (e.g. N rate, N timing and nitrification inhibitor) did not have any direct or indirect effects on soil temperature. However, the treatments employed by Hernandez-Ramirez et al (2009) (continuous maize and

maize–soybeans rotations versus prairie grass) affected soil temperature, and so it is understandable that the correlation between soil temperature and N_2O –N fluxes was higher in that research. In another earlier N_2O –N emissions study for maize production systems on the same soils and location, Omonode *et al* (2010) found significant effects of long-term tillage systems on soil temperatures. Lastly, data from the present research showed that cumulative precipitation from the 48 h period prior to sampling had highest correlations with N_2O fluxes, while Hernandez-Ramirez *et al* (2009) reported higher correlations with cumulative precipitations up to 120 h prior to sampling. The predictive value of a given period of precipitation on N_2O emissions will probably vary by year, and will be very specific to precipitation timing and intensity relative to N applications, plus the initial soil moisture content at precipitation onset.

5. Conclusions

The main driver of the response variables (N_2O fluxes, cumulative N_2O emissions, maize yield and yield-scaled N_2O) was the N fertilizer rate; both N application timing and nitrification inhibitor were secondary factors. Nevertheless, delaying the timing of application to V6 (side-dress) was associated with greater cumulative N_2O –N emissions across both years and especially higher N_2O –N daily fluxes in 2010. The effect of the inhibitor in reducing N_2O –N emissions, both daily and cumulative, was significant when both years were combined. Side-dress applications of 180 kg N ha^{-1} at V6 with an inhibitor seems to be an alternative that reduces N_2O emissions and maximizes yield, but this management practice combination involved greater mean yield-scaled N_2O –N than after 90 kg N ha^{-1} applied pre-emergence without an inhibitor. However, these differences in yield-scaled N_2O –N were not statistically significant, and grain yield increased about 3 Mg ha^{-1} in response to UAN rates of 180 kg N ha^{-1} versus 90 kg N ha^{-1} . Subsequent Midwest USA research should address nitrification inhibitor effects on both grain yield and N_2O emissions at smaller N rate increments.

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