Journal of Agricultural Science; Vol. 10, No. 6; 2018
ISSN 1916-9752 E-ISSN 1916-9760
Published by Canadian Center of Science and Education

Pronitridine Nitrification Inhibitor With Urea Ammonium Nitrate for Corn

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Received: March 5, 2018 Accepted: April 3, 2018 Online Published: May 15, 2018

doi:10.5539/jas.v10n6p16 URL: https://doi.org/10.5539/jas.v10n6p16

Abstract

Nitrification inhibitors have been used to enhance the efficiency of nitrogen fertilizers. This research evaluated the effectiveness of nontreated urea ammonium nitrate (UAN) at 0, 67, 135, 202, and 270 kg N ha^{-1} as well as UAN treated with nitrification inhibitors (pronitridine at 9.4 and 18.8 L ha^{-1} or nitrapyrin at 0.5 kg a.i. ha^{-1}) to enhance N uptake and increase yield of corn (*Zea mays* L.). The study took place from 2012-2014 in upstate Missouri on a claypan soil. During the experiments, environmental conditions (high, medium, and low yielding years) affected corn response to pronitridine and nitrapyrin. In general, UAN plus pronitridine at 9.4 L ha^{-1} had similar effects on corn compared pronitridine at a higher (18.7 L ha^{-1}) rate. During a high-yielding year (2014), in order to produce yields equivalent to 67 kg N ha^{-1} plus pronitridine at 9.4 L ha^{-1} or nitrapyrin, UAN needed to be increased 14 to 19%. Similarly, the amount of nontreated UAN needed to be increased 8 to 11% for yields to be equivalent to UAN at 135 kg N ha^{-1} plus pronitridine at 9.4 L ha^{-1} or nitrapyrin. Grain N removal and agronomic efficiency was highest with pronitridine at 9.4 L ha^{-1} and nitrapyrin combined with 67 and 135 kg N ha^{-1}, respectively. This research indicates that pronitridine was as effective as nitrapyrin when added to a pre-emergence application of UAN placed between the rows in a dribble band.

Keywords: corn, enhanced efficiency fertilizer, nitrification inhibitor, nitrogen, nitapyrin, pronitridine, urea ammonium nitrate

1. Introduction

Nitrogen is a critical input for high-yielding corn production. In 2010, nitrogen applied to corn in the United States totaled over 5 million Mg (USDA-ERS, 2015). More than 40% of U.S. N consumption is nitrogen solution (USDA-ERS, 2015), of which a majority is urea ammonium nitrate (UAN). Urea ammonium nitrate, which is made by dissolving ammonium nitrate and urea in water, contains 50% N as amide, 25% as nitrate and 25% as ammonium. Liquid UAN can be applied in the spring, but it is commonly used for sidedress applications. Nitrogen fertilizer is susceptible to loss, which depends on environmental and field conditions. When soils are saturated for an extended period and conditions are warm, denitrification may be a major loss mechanism especially on poorly drained soils. In such conditions, nitrification inhibitors may benefit farmers. Others have reviewed the development and effects of nitrification inhibitors on reducing N loss and crop production (Stelly, 1980; Prasad & Power, 1995; Wolt, 2004; Cook et al., 2015).

Nitrification inhibitors have been utilized not only to reduce gaseous and leaching loss of N fertilizer by delaying nitrification of N fertilizers in the soil (Bremner & Blackmer, 1979; Aulakh et al., 1984; Bronson et al., 1992; Delgado & Mosier, 1996; Weiske et al., 2001; O'Callaghan et al., 2010; Khalil, 2011; Omode & Vyn, 2013; Aita et al., 2014; Fisk et al., 2015; Frame, 2017), but also to increase crop yields (Randall et al., 2003; Ruser & Schulz, 2015; Ren et al., 2017). The most consistent results in the north central U.S. with nitrapyrin (2-chloro-6-(trichloromethyl) pyridine) and dicyandiamide (DCD) were reported on coarse-textured soils with reduced rates of N (Malzer et al., 1989). Extensive research has evaluated how nitrapyrin affects *Nitrosomonas* in soils as a bactericide with anhydrous ammonia (Hughes & Welch, 1970; Bremner et al., 1981; Bronson et al., 1992). Nitrapyrin is effective for six to eight weeks in warm soil and can persist longer in cold soils (Trenkel, 2010). Nitrapyrin was marketed in the early 1970's (Prasad & Power, 1995), and it was recently reformulated as a water-based microencapsulated product (Instinct, Dow AgroSciences, Indianapolis, IN) for use with liquid fertilizer solutions to delay ammonium conversion to nitrate and subsequently reduce the potential for gaseous and leaching loss of N (Burzaco et al., 2013; Omonode & Vyn, 2013; Kyveryga & Blackmer, 2014). The probability of a yield response to nitrapyrin was greatest when spring precipitation was high (Kyveryga & Blackmer, 2014). Wolt's (2004) review found that nitrapyrin increased grain yields 7% and that it reduced leaching loss 16% and greenhouse gas emissions 51%. Dicyandiamide was introduced into the U.S. in the 1980's for use with UAN solutions. *Nitrosomanas* bacteria are suppressed as a bacteriostatic effect with DCD and may stabilize ammonium for 4 to 10 weeks (Mason, 1987; McCarty & Bremner, 1989; O'Callaghan et al., 2010; Trenkel, 2010; Khalil, 2011).

The Midwestern U.S. has approximately four million ha of claypan soils (Buckley et al., 2010). Waterlogged soil conditions are favorable for denitrification and gaseous N loss (Zurweller et al., 2015; Ren et al., 2017). Claypan soils have a clay layer that is usually less than 50 cm below the soil surface that causes poor internal drainage (Buckley et al., 2010; Nelson & Smoot, 2012). These soils are prone to gaseous loss of N fertilizer due to saturated conditions (Nash et al., 2012, 2015; Zurweller et al., 2015). Loss of N to the atmosphere may approach 30% (Wilkison et al, 2000). Numerous studies have investigated nitrification inhibitors in soils at high risk of leaching potential, and once N is leached out of the root zone plant N uptake is reduced (Mason, 1987; McCarty & Bremner, 1989; Francis et al., 1993; Martin et al., 1994). A new nitrification inhibitor, pronitridine (CAS RN 1373256-33-7, Centuro™, Koch Agronomic Services, Witchita, KS), was recently developed to enhance the efficiency of N applications in corn (Vetsch & Schwab, 2014; Gabrielson & Epling, 2016). Pronitridine contains a nitrification inhibitor (DCD) plus 30% N fertilizer (Nitamin Nfusion, Koch Agronomic Services, Witchita, KS) which is a reaction product of ammonia, DCD, formaldehyde, and urea. It was formulated to inhibit nitrification and reduce leaching of the nitrification inhibitor in agriculture crop production systems (Gabrielson & Epling, 2016). In wet spring conditions in Minnesota, nitapyrin and pronitridine increased corn grain yields 0.8 to 1.1 Mg ha^{-1} (Vetsch & Schwab, 2014). No known research has evaluated corn response to pronitridine with UAN on poorly drained soils. The objective of this research was to evaluate the effectiveness of UAN treated with pronitridine or nitrapyrin nitrification inhibitors to enhance N uptake and increase corn yield.

2. Methods

2.1 Location

Field experiments were conducted at the University of Missouri Greenley Research Center near Novelty, MO (40.02324 N, 92.18162 W) from 2012 to 2014. The soil was a Putnam silt loam (fine, smectitic, mesic, Vertic Albaqualfs). The study was arranged in a randomized complete block design with five replications in plots 3 by 15 m. This research was arranged as two-factor experiment with five N rates (0, 67, 135, 202, and 270 kg N ha^{-1}) and nitrification inhibitors (nontreated, pronitridine (Centuro™, Koch Agronomic Services, Witchita, KS) at 9.4 L ha^{-1}, pronitridine at 18.8 L ha^{-1}, and nitrapyrin (Instinct®, Dow AgroSciences, Indianapolis, IN) at 0.5 kg a.i. ha^{-1}). UAN rates were adjusted to offset pronitridine's N contribution so the total amount of N applied was the same. Fertilizer was applied pre-emergence by dribble banding between rows with a CO_2-propelled hand sprayer. Nitrapyrin may affect nitrification up to 10 cm from the band (Omonode & Vyn, 2013). Selected management practices are reported in Table 1.

2.2 Soil Sampling and Field Measurements

Before applying fertilizer, composite soil samples were taken from the plot area from each replication using a Uhland probe from four depths (0-15 cm, 16-30 cm, and 31-46 cm). Soil properties, presented by year in Table 2, were analyzed using standard soil testing analytical procedures for Missouri (Nathan et al., 2006). The 0-15 cm sample was analyzed for pH (0.01 *M* $CaCl_2$), organic matter content, cation exchange capacity (CEC), available P (Bray 1-P), and extractable (1 *M* NH_4AOc) K, Ca, and Mg. Soil samples from all depths were analyzed for nitrate and exchangeable ammonium concentrations. Precipitation was collected on site (Table 3) throughout the growing season using an automated weather station (Campbell Scientific, Inc., Logan, UT).

Chlorophyll meter readings for 10 ear leaves $plot^{-1}$ were collected to determine N deficiency (Zhang et al., 2008) using a Minolta SPAD-502 (Konica Minolta Optics, Inc.) at VT (Abendroth et al., 2011). Ear leaves (10 $plot^{-1}$) were collected at R1, dried, and analyzed for total N concentration by combustion using a total C:N analyzer (LECO, TruSPEC CN Analyzer, St. Joseph, MI). In 2012 and 2013, ear leaf N concentration and SPAD meter readings were determined prior to the onset of drought conditions (USDM, 2015).

Plant populations were determined prior to harvest. Grain yield, moisture, and test weight were determined using a Wintersteiger Delta (Salt Lake City, UT) equipped with a HarvestMaster GrainGage (SBDS800, Juniper Systems Inc., Logan, UT). Grain yields were adjusted to 150 g kg^{-1} prior to subjecting data to ANOVA. Grain samples were collected and analyzed for N concentration by combustion using a total C:N analyzer (LECO, TruSPEC CN Analyzer, St. Joseph, MI). In 2013 and 2014, grain samples were also analyzed for protein, oil, and starch concentration with a Foss Infratec 1241 Grain Analyzer (Eden Prairie, MN). Agronomic efficiency was calculated as $(Y-Y_0)/F$ where Y = grain yield of the harvested portion of corn with nutrient applied, Y_0 = grain yield of corn with no nutrient applied, and F = amount of nutrient applied in order to determine the short-term impact of N on productivity (Dobermann, 2007; Fixen et al., 2014).

Table 1. Selected management practices and application information in 2012, 2013, and 2014

Field information	2012	2013	2014
Previous crop	Soybean	Soybean	Soybean
Tillage	No-till	No-till	No-till
Planting date	2 April	2 May	9 April
Hybrid	DKC 62-97VT3	DKC 62-97VT3	DKC 62-97VT3
Seeding rate (seeds ha^{-1})	79,000	81,500	81,500
Fertilizer application dates			
Pre-emergence	6 Apr.	7 May	10 Apr.
Maintenance	12 Apr.	28 Nov. 2012	11 Apr.
(N-P_2O_5-K_2O in kg ha^{-1})	(18-90-135)	(18-90-135)	(22-90-157-22 S-2.2 Zn)
Crop protection chemicals			
Fungicide	NA†	NA	10 July, Azoxystrobin‡ (0.12 kg a.i. ha^{-1}) + propiconazole (0.10 kg a.i. ha^{-1})
Insecticide	NA	22 May, Lambda-cyhalothrin (20 g a.i./ha)	NA
Herbicide			
Fall	15 Nov. 2011, Simazine (1.23 kg a.i. ha^{-1}) + glyphosate (0.53 kg a.i. ha^{-1}) + COC (2.34 L ha^{-1})	17 Nov. 2012, Simazine (1.23 kg a.i. ha^{-1}) + glyphosate (0.53 kg a.i. ha^{-1}) + COC (2.34 L ha^{-1})	NA
POST	11 May, Acetochlor (0.94 kg a.i. ha^{-1}) + flumetsulam (0.03 kg a.i. ha^{-1}) + clopyralid (0.1 kg a.i. ha^{-1}) + glyphosate (1.38 kg a.i. ha^{-1})	14 May, Acetochlor (2.28 kg a.i. ha^{-1}) + atrazine (2.25 kg a.i. ha^{-1})	6 May, Acetochlor (2.65 kg a.i. ha^{-1}) + atrazine (1.88 kg a.i. ha^{-1}) + glyphosate (1.06 kg a.i. ha^{-1}) + DAS (0.02 kg L^{-1})
Late POST	5 June, Glyphosate (1.55 kg a.i. ha^{-1}) + mesotrione (0.09 kg a.i. ha^{-1}) + DAS (0.02 kg L^{-1}) + COC (2.34 L ha^{-1})	22 May, Glyphosate (1.55 kg a.i. ha^{-1}) + mesotrione (0.09 kg a.i. ha^{-1}) + NIS (0.25% v/v) + UAN (2.34 L ha^{-1})	11 June, Glyphosate (1.06 kg a.i. ha^{-1}) + topramezone (0.02 kg a.i. ha^{-1}) + atrazine (0.25 kg a.i. ha^{-1}) + DAS (0.02 kg L^{-1})
Harvest date	24 Aug.	26 Sep.	6 Oct.

Note. †Abbreviations: COC, crop oil concentrate; DAS, Diammonium sulfate; NA, None applied; NIS, nonionic surfactant; POST, postemergence; UAN, urea ammonium nitrate.

‡Acetochlor (2-chloro-2'-methyl-6'ethyl-N-ethoxymethylacetanilide); atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine); azoxystrobin, methyl (E)-2-{2-[6-(2-cyanophenoxy) pyrimidin-4-yloxy]phenyl}-3-methoxyacrylate; clopyralid, 3,6-dichloro-2-pyridinecarboxylic acid, monoethanolamine salt; diammonium sulfate ($(NH_4)_2SO_4$); flumetsulam, N-(2,6-difluorophenyl)-5-methyl[1,2,4]triazolo-[1,5-a]pyrimidine-2-sulfonamide; glyphosate (N-(phosphonomethyl)glycine); lambda-cyhalothrin, [1a(*S**),3a(Z)]-(±)-cyano-(3-phenoxyphenyl)methyl-3-(2-chloro-3,3,3-trifl uoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate; mesotrione (2-[4-(Methylsulfonyl)-2-nitrobenzoyl]cyclohexane-1,3-dione); propiconazole, 1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]Methyl]-1H-1,2,4-triazole; and simazine, 2-chloro-4,6-bis(ethylamino)-s-triazine; topramezone, [3-(4,5-dihydro-3-isoxazolyl)- 2-methyl-4-(methylsulfonyl)phenyl] (5-hydroxy-1-methyl-1H-pyrazol-4-yl) methanone

2.3 Statistical Analysis

Data from all years showed a rate response to UAN rates, but the response was affected by the amount and timing of rainfall each year (Table 3). Enhanced-efficiency N products such as nitrification inhibitors typically perform at rates of N where loss can be detected in plant measurements and ultimately yield (Frye et al., 1989; Malzer et al., 1989). Therefore, data were sorted by N rate and subjected to individual ANOVA using PROC

GLM (SAS, 2014). Nitrification inhibitor means were separated using Fisher's Protected LSD (P = 0.1) to determine differences among nitrification inhibitor treatments at specific N rates. In the absence of a significant interaction, data were combined over years. Quadratic regression analysis (Cerrato & Blackmer, 1990) was performed using best-fit analysis determined with SigmaPlot (Vers. 8.02, SPSS Inc., Chicago, IL), and significance was determined using SAS (2014). A linear regression analysis evaluated the relationship between grain N and protein concentration, and significance was determined using SAS (2014).

Table 2. Soil test information from 0 to 15 cm in 2012, 2013, and 2014. Soil nitrate (NO_3-N) and ammonium (NH_4-N) concentration at three depths on 6 April 2012, 1 May 2013, and 9 April 2014

Soil test information	Soil depth	2012	2013	2014
pH (0.01 M $CaCl_2$)	0-15 cm	5.9±0.2†	6.1±0.1	6.0±0.2
Bray 1-P (kg ha^{-1})	0-15 cm	29.9±21.1	72.6±13.1	40.0±5.2
K (kg ha^{-1})	0-15 cm	228±31	430±38	228±53
Ca (kg ha^{-1})	0-15 cm	4834±307	4753±438	4026±726
Mg (kg ha^{-1})	0-15 cm	585±94	573±56	453±99
CEC (cmol$_c$ kg^{-1})‡	0-15 cm	14.9±1.3	14.8±1.2	12.4±1.8
OM (g kg^{-1})	0-15 cm	33.0±2.9	31.8±1.5	26.2±1.9
NO_3-N (mg kg^{-1})	0-15 cm	9.5±1.5	16.1±2.8	15.3±5.7
	16-30 cm	4.9±0.4	7.7±1.1	9.2±2.1
	31-46 cm	5.0±0.5	8.0±1.3	7.6±1.7
NH_4-N (mg kg^{-1})	0-15 cm	3.9±0.3	4.5±1.1	3.1±0.5
	16-30 cm	3.7±0.7	5.0±1.4	5.2±0.8
	31-46 cm	4.5±0.7	7.9±1.8	6.2±0.9

Note. † Standard deviation.

‡ Abbreviations: CEC, cation exchange capacity; OM, organic matter.

3. Results and Discussion

3.1 Precipitation

The first year of this research was classified as an extreme drought (2012), and the second a severe drought (2013) (USDM, 2015). Precipitation was nearly 200 mm below average, primarily during grain fill in July (Table 3), which reduced overall yields (< 3.1 Mg ha^{-1}) in 2012 (Figure 1). In 2013, temperatures during pollination were favorable (data not presented) for high yield potential, but only 48 mm of rain fell in July and none in August (Table 3), which resulted in small seed size (visual observation). In 2014, precipitation (Table 3) and air temperature (data not presented) through the summer months were favorable for high yields. Although claypan soils are highly productive, they can be susceptible to extreme weather conditions that limit yield (Nelson & Smoot, 2012; Buckley et al., 2010). The maximum corn yields in the absence of a nitrification inhibitor were determined to be at 166 kg N ha^{-1} in 2012, 248 kg N ha^{-1} in 2013, and 237 kg N ha^{-1} in 2014 (Figure 1), which was affected by precipitation during the growing season (Table 3).

Table 3. Monthly precipitation average (10-year) and precipitation during the growing season at Novelty in 2012, 2013, and 2014

Month	10-year average†	2012	2013	2014
	------------ mm ------------			
Apr.	104	119	194	106
May	134	63	261	26
June	133	57	92	225
July	109	19	48	51
Aug.	110	76	0	164
Sep.	90	90	79	175
Total	680	483	674	747

Note. † Averaged from 2000 to 2011.

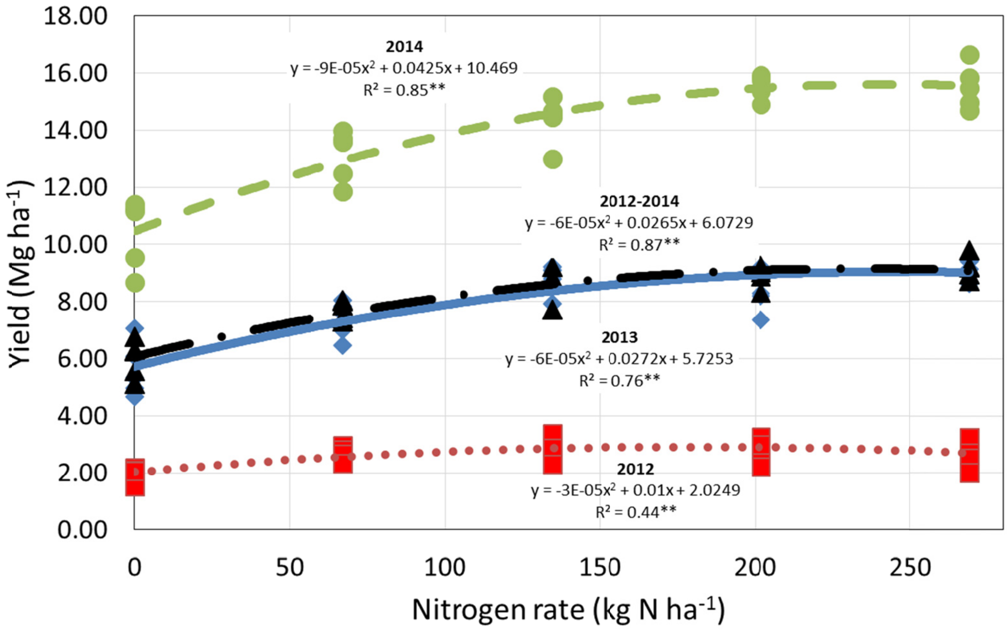

Figure 1. Corn yield response to N rates in the absence of a nitrification inhibitor in 2012 (dotted line), 2013 (solid line), 2014 (dashed line) and the average (dash-dot line) from 2012-2014 at Novelty, Missouri. Individual points represent plot data from each replication represented in each year

3.2 UAN at 67 kg N ha^{-1}

When N was applied at 67 kg N ha^{-1}, no difference in SPAD (*P* = 0.29), ear leaf N concentration (*P* = 0.29), plant population (*P* = 0.62), grain moisture (*P* = 0.74), test weight (*P* = 0.82), yield (*P* = 0.40), grain N concentration (*P* = 0.76), agronomic efficiency (*P* = 0.76), protein (*P* = 0.93), oil (*P* = 0.87), or starch (*P* = 0.92) concentration was observed among the nitrification inhibitors (Table 4). Corn grain yield with UAN at 67 kg N ha^{-1} plus nitrapyrin was 7.98 Mg ha^{-1} and with pronitridine at 9.4 L ha^{-1} was 7.89 Mg ha^{-1}. In order to obtain the same yield with nontreated urea (Figure 1), rates would have to be increased to 78 kg N ha^{-1} (14%) to be equivalent to pronitridine at 9.4 L ha^{-1} and to 83 kg N ha^{-1} (19%) to be equivalent to nitrapyrin. Increased grain yields with nitrification inhibitors were typically observed at the lower end of a rate response, which was similar to other research (Frye et al., 1989; Malzer et al., 1989). Grain N concentration was higher in 2012 than in 2013 or 2014. The greatest grain N concentration was observed in the nontreated control, which probably was due to 2012's extreme drought conditions (USDM, 2015). However, grain N concentration was greatest with pronitridine at 9.4 L ha^{-1} in 2013 and pronitridine at 18.7 L ha^{-1} in 2014 under higher yielding environments. No difference between treatments was observed in 2014. No effects have been reported of DCD or nitrapyrin on corn seed germination (Pal et al., 2016), which was consistent for all of the N rates evaluated (Tables 4-6). This was expected because nitrogen was dribble banded between the corn rows.

3.3 UAN at 135 kg N ha^{-1}

When the N amount was 135 kg N ha^{-1}, there was no difference in SPAD values (*P* = 0.66), plant population (*P* = 0.27), grain moisture (*P* = 0.93), test weight (*P* = 0.50), grain N concentration (*P* = 0.92), grain N removal (*P* = 0.82), agronomic efficiency (*P* = 0.82), protein (*P* = 0.33), oil (*P* = 0.40), or starch (*P* = 0.36) concentration among treatments (Table 5). Ear leaf N concentration was ranked nontreated control (26.55 g kg^{-1}) = nitrapyrin (26.03 g kg^{-1}) ≥ pronitridine at 18.8 L ha^{-1} (25.50 g kg^{-1}) = pronitridine at 9.4 L ha^{-1} (24.76 g kg^{-1}). This indicated no advantage of a nitrification inhibitor at VT when ear leaf N concentration was determined. In the extreme drought conditions of 2012, grain yields for nitrification inhibitors were similar (USDM, 2015). Spring conditions were favorable for gaseous N loss (N_2O and NH_3) following fertilizer applications, as reported by Nash et al. (2015) in a separate experiment on site. Claypan soils that have been waterlogged for one week had greater N_2O emissions than soils with no waterlogging (Zurweller et al., 2015). Excessive precipitation or temperature following application may have affected leaching or decomposition of DCD or nitrapyrin (Bronson et al., 1989; McCarty & Bremner, 1989); however, the pronitridine formulation may have reduced the leaching potential compared to DCD (Gabrielson & Epling, 2016). Grain yields were greatest in the nontreated control (8.71 Mg ha^{-1}) and were similar to pronitridine at 18.8 L ha^{-1} and nitrapyrin in 2013 during a moderately yielding year when N was probably not limiting due to summer drought conditions. In the high-yield environment of 2014, nitrapyrin and pronitridine at 9.4 L ha^{-1} increased yields 0.44 to 0.5 Mg ha^{-1} compared to the nontreated control at 135 kg N ha^{-1}, which indicated the benefit of a nitrification inhibitor in such production environments when N rates were reduced. This was similar to other research when a reduced rate of UAN was applied with nitrapyrin (Habibullah et al., 2017). In 2014, nontreated UAN amounts (Table 5) needed to be increased to 147 kg N ha^{-1} (8%) and 151 kg N ha^{-1} (11%) in order to obtain yields similar to pronitridine at 9.4 L ha^{-1} and nitrapyrin, respectively (Figure 1). The increase in the yield may be due reduced gaseous N loss in the presence of the nitrification inhibitors (Bronson et al., 1992; Zaman et al., 2009; Chen et al., 2010; Halvorson et al., 2010; Carneiro et al., 2010; Khalil, 2011; Di & Cameron, 2012; Burzaco et al., 2013; Omonode & Vyn 2013). This could be because spring conditions generally were wet (Table 3), gaseous N losses in claypan soils as high as 30% have been reported (Wilkison et al., 2000), and summer conditions were favorable for high yields. Similar effects between nitrapyrin and pronitridine were expected as Martin et al., (1994) reported finding similar effects of nitrapyrin and DCD on total inorganic soil N.

Table 4. Corn response to nitrification inhibitors with urea ammonium nitrate when N amount was 67 kg N ha^{-1}. Data were combined over years in the absence of a significant interaction

Nitrification inhibitor	SPAD	Ear leaf N	Population	Moisture	Test weight	Yield	Grain N			Grain N removal	Agronomic efficiency†	Protein‡	Oil‡	Starch‡
							2012	2013	2014					
		g kg^{-1}	No. ha^{-1}	g kg^{-1}	kg hL^{-1}	Mg ha^{-1}	-------- g kg^{-1} --------			kg ha^{-1}	kg kg app.$^{-1}$	g kg^{-1}	g kg^{-1}	g kg^{-1}
Non-treated	49.4	23.9	72,620	177	71.6	7.73	12.87	10.01	10.57	82	36.0	73.0	34.1	742
Pronitridine at 9.4 L ha^{-1}	49.7	24.5	69,650	180	71.6	7.89	12.44	11.18	10.43	86	41.6	74.1	34.2	742
Pronitridine at 18.7 L ha^{-1}	47.9	23.4	71,380	181	71.5	7.71	12.11	9.80	11.31	84	38.9	73.3	34.8	741
Nitrapyrin	49.0	24.0	70,150	175	71.8	7.98	12.66	9.51	10.94	85	40.3	73.4	34.6	741
LSD (P = 0.1)	NS	NS	NS	NS	NS	NS	--------- 0.91 ---------			NS	NS	NS	NS	NS
P > F	0.29	0.29	0.62	0.74	0.82	0.40	0.04			0.76	0.76	0.93	0.87	0.93

Note. † Calculated as: kg grain produced kg N^{-1} applied (Fixen et al., 2014).

‡ Protein, oil, and starch concentrations were determined in 2013 and 2014.

Table 5. Corn response to nitrification inhibitors with urea ammonium nitrate when N amount was 135 kg N ha^{-1}. Data were combined over years in the absence of a significant interaction

Nitrification inhibitor	SPAD	Ear leaf N	Population	Moisture	Test weight	Yield			Grain N	Grain N removal	Agronomic efficiency†	Protein‡	Oil‡	Starch‡
						2012	2013	2014						
		g kg^{-1}	No. ha^{-1}	g kg^{-1}	kg hL^{-1}	------ Mg ha^{-1} ------			g kg^{-1}	kg ha^{-1}	kg kg app.$^{-1}$	g kg^{-1}	g kg^{-1}	g kg^{-1}
Non-treated	52.2	26.55	72,870	175	72.1	2.83	8.71	14.32	11.78	98	29.8	79.7	35.1	737
Pronitridine at 9.4 L ha^{-1}	51.5	24.76	70,890	174	72.6	3.03	7.94	14.76	11.94	100	31.0	77.9	33.3	741
Pronitridine at 18.7 L ha^{-1}	51.7	25.50	69,650	174	72.4	2.92	8.34	14.44	11.77	99	30.0	79.5	34.4	739
Nitrapyrin	52.1	26.03	71,140	172	72.5	2.93	8.32	14.82	11.85	101	31.5	80.9	34.9	737
LSD (P = 0.1)	NS	1.01	NS	NS	NS	--------- 0.44 --------			NS	NS	NS	NS	NS	NS
P > F	0.66	0.03	0.27	0.93	0.50	0.06			0.92	0.82	0.82	0.33	0.40	0.36

Note. † Calculated as: kg grain produced kg N^{-1} applied (Fixen et al., 2014).

‡ Protein, oil, and starch concentrations were determined in 2013 and 2014.

3.4 UAN at 202 kg N ha^{-1}

Urea ammonium nitrate at 202 kg N ha^{-1} had corn ear leaf SPAD meter readings at R1 that showed UAN treated with nitrapyrin had greener ear leaves than pronitridine at 9.4 L ha^{-1}, but values were similar to pronitridine at 18.7 L ha^{-1} and the nontreated control (Table 5). However, ear leaf N concentration was greatest (27.2 g kg^{-1}) with pronitridine at 9.4 L ha^{-1}. Nitrification inhibitor treatments had similar plant populations at harvest (P =

0.99), grain moisture (*P* = 0.88), test weight (*P* = 0.74), grain N concentration (*P* = 0.60), grain N removal (*P* = 0.46), agronomic efficiency (*P* = 0.45), protein (*P* = 0.95), oil, (*P* = 0.79), and starch (*P* = 0.79) concentration. Grain yield for the nitrification inhibitors was ranked pronitridine at 9.4 L ha^{-1} (9.02 Mg ha^{-1}) = pronitridine at 18.7 L ha^{-1} (9.01 Mg ha^{-1}) = non-treated (8.94 Mg ha^{-1}) ≥ nitrapyrin (8.63 Mg ha^{-1}). Differences between pronitridine and nitrapyrin might be due to differences in the longevity of these products in the soil or the ability to affect ammonia volatilization (Fox & Bandel, 1989; Aita et al., 2014; Frame, 2017). Yield data indicate that adequate N was supplied to the crop for high yields at 202 kg N ha^{-1} or greater, and no advantage was observed when adding a nitrification inhibitor when compared to the nontreated control.

Table 6. Corn response to nitrification inhibitors with urea ammonium nitrate when N amount was 202 kg N ha^{-1}. Data were combined over years in the absence of a significant interaction

Nitrification inhibitor	SPAD	Ear leaf N	Population	Moisture	Test weight	Yield	Grain N	Grain N removal	Agronomic efficiency†	Protein‡	Oil‡	Starch‡
		g kg^{-1}	No. ha^{-1}	g kg^{-1}	kg hL^{-1}	Mg ha^{-1}	g kg^{-1}	kg ha^{-1}	kg kg app.$^{-1}$	g kg^{-1}	g kg^{-1}	g kg^{-1}
Nontreated	54.1	26.6	71,140	178	72.5	8.94	12.32	109	25.3	85.9	34.2	736
Pronitridine at 9.4 L ha^{-1}	52.6	27.3	71,140	175	72.6	9.02	12.70	112	26.6	85.6	34.8	733
Pronitridine at 18.7 L ha^{-1}	54.2	26.5	71,380	175	72.6	9.01	12.49	111	26.3	85.2	33.7	736
Nitrapyrin	55.5	26.2	70,890	177	72.6	8.63	12.54	107	24.4	86.2	34.4	735
LSD (*P* = 0.1)	1.8	NS	NS	NS	NS	0.33	NS	NS	NS	NS	NS	NS
P > F	0.07	0.49	0.99	0.88	0.74	0.09	0.60	0.46	0.45	0.95	0.79	0.79

Note. † Calculated as: kg grain produced kg N^{-1} applied (Fixen et al., 2014).

‡ Protein, oil, and starch concentrations were determined in 2013 and 2014.

3.5 UAN at 270 kg N ha^{-1}

Slight differences among nitrification inhibitors were observed for test weight and starch concentration with pronitridine at 9.4 L ha^{-1}, nitrapyrin, and the nontreated control having similar test weights and starch concentrations when N was applied at 270 kg N ha^{-1} (data not presented). All of the corn response parameters that were evaluated were similar among nitrification inhibitors with UAN at 270 kg N ha^{-1} (data not presented). This amount of N was excessive to detect differences among nitrification inhibitors, in keeping with other nitrification inhibitor research throughout the U.S. (Fox & Bandel, 1989; Frye et al., 1989; Malzer et al., 1989). In well-drained soils of the mid-Atlantic, a nitrification inhibitor did not increase N fertilizer efficiency or yield (Fox & Bandel, 1989). However, nitrapyrin has increased yields 22 to 33% in waterlogged conditions (Ren et al., 2017). DCD has been reported to leach in some instances (McCarty & Bremner, 1989) while temperature and amount could affect nitrification (Di & Cameron, 2004). This could affect the efficacy of this nitrification inhibitor, but the leaching capabilities and effects of environmental conditions on the fate of pronitridine have not been reported. In claypan soils, we would expect limited deep leaching, could be affected by the prevalence and intensity of rainfall (Blevins et al, 1996). Differences in decomposition rate of DCD and nitrapyrin based on soil type (Bronson et al., 1989) could affect the crop response observed, but comparisons with pronitridine have not been reported. In a recent meta-analysis of enhanced efficiency fertilizers for corn management systems, nitrapyrin or NBPT plus DCD combined with UAN showed no significant effect (*P* = 0.84) on corn yield data (Cook et al., 2015). However, nitrapyrin and DCD have reduced N_2O emissions 20 to 90% (Chen et al., 2010; Di & Cameron, 2012; Halvorson et al., 2010; Carneiro et al., 2010; Khalil, 2011; Burzaco et al., 2013; Omonode & Vyn, 2013), which can enhance the efficiency of a UAN application.

3.6 Protein and Grain N Concentration

Since N treatments included a range of amounts, this provided an opportunity to evaluate relationship between grain N concentration, which was determined chemically, and protein, which was determined with NIR for all treatments in 2013 and 2014. This linear relationship (grain N concentration = 0.1409 × protein concentration) indicated that NIR could provide a good estimate (R^2 = 0.75) of grain N concentration with a more cost-effective, safer, and quicker determination (Figure 2). A standard factor of 6.25 has been used to calculate protein concentration based on N content in the grain, which can be affected by other N compounds (FAO, 2003). Grain protein N content has ranged from 13 to 19%, which has a conversion factor of 0.13 to 0.19 (FAO, 2003) where our conversion factor (0.1409) for corn produced over several N rates was within this range. Therefore, calculating N uptake based on protein amount could be a useful tool for evaluating the efficiency of N treatments, especially when protein concentration is determined during harvest (Long et al., 2008). As more data are collected, an improved relationship may be determined over various corn production systems and environments.

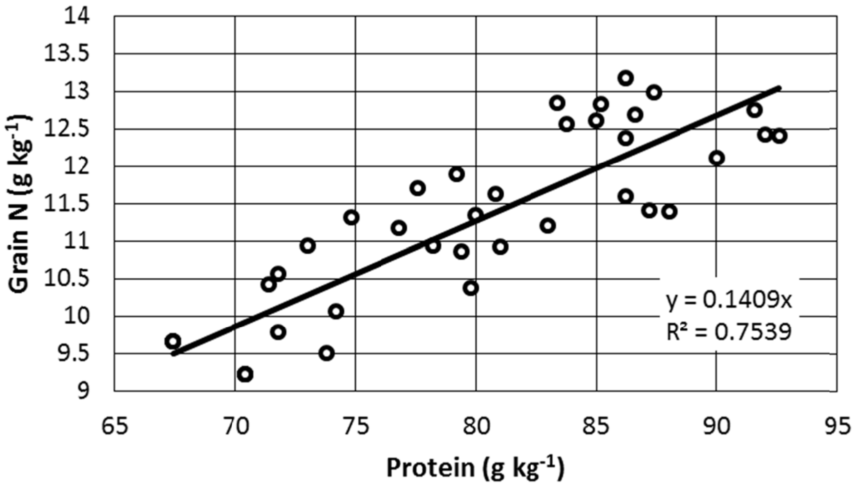

Figure 2. Relationship between corn grain protein concentration and grain N concentration at Novelty, Missouri. Individual points represent average protein and grain N concentrations for each N amount in the presence or absence of a nitrification inhibitor in 2013 and 2014

4. Conclusions

In conclusion, corn response to pronitridine and nitrapyrin depended on the N rate and environmental conditions during the experiments, which affected overall grain yields. In general, urea ammonium nitrate plus pronitridine at 9.4 L ha^{-1} affected corn similarly to a higher (18.7 L ha^{-1}) rate. The amount of additional UAN required to produce yields equivalent to 67 kg N ha^{-1} plus pronitridine at 9.4 L ha^{-1} or nitrapyrin needed to be increased 14 to 19%. Similarly, the amount of nontreated UAN needed to be increased 8 to 11% in a high yielding year (2014) for yields to be equivalent to UAN at 135 kg N ha^{-1} plus pronitridine at 9.4 L ha^{-1} or nitrapyrin. Grain N removal and agronomic efficiency was greatest with pronitridine at 9.4 L ha^{-1} and nitrapyrin applied with 67 and 135 kg N ha^{-1}, respectively, but it was not significantly greater than the other treatments. This research indicates that pronitridine was as effective as nitrapyrin when added to a dribble band of UAN.

Acknowledgements

The author would like to thank Chris Dudenhoeffer and Lynn Bradley for their technical support and Koch Agronomic Services, LLC for their financial support of this research.

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