SF1581 (Revised)

Nitrogen Extenders and Additives

FOR FIELD CROPS

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Nitrogen (N) management for crop production continues to be difficult due to transformations of N fertilizers when applied to soil and the uncertainties of weather (Cabrera et al., 2008).

Nitrogen fertilizer in the form of urea is subject to ammonia volatilization through the activity of the urease enzyme found ubiquitously in soil (Kissel et al., 2008). Nitrate fertilizer is subject to leaching (Randall et al., 2008) or denitrification (Coyne, 2008), depending on the water content of the soil and water movement through the soil. Ammonium forms of N can be fixed (Kissel et al., 2008) or transformed to nitrate through the activities of specific soil bacteria (Norton, 2008). Because of these and other processes, N use efficiency is low.

Nitrogen often is applied to crops in the north-central region of the U.S. before planting. During the first four to six weeks after planting, corn requires only about 5 percent of the N applied. The following two to four weeks of growth require a large proportion of the total seasonal N requirement because the rate of N uptake dramatically increases past the V6 growth stage (Bender et al., 2013).

In winter wheat, low levels of plant-available N are required for overwintering. However, once wheat breaks dormancy, a large proportion of N uptake occurs during the next few weeks. In spring wheat, a small of amount of N is required to establish the crop during the first two to four weeks after seeding; however, most of the remaining N is required during the next 30 days.

To address some of the delayed N requirement issues of winter wheat, much of the crop is top-dressed in the spring. In corn, some growers use side-dress applications; however, spring preplant application is most common, with fall application preferred by growers in some Northern and Midwestern states. In spring wheat in the northern Plains, some post-N applications are made.

Due to the variability in rainfall during growing seasons, postemergence N applications to spring wheat as a primary source of the major plant N requirement are discouraged (Franzen, 2009), especially in northern areas with compressed growing seasons, except under irrigation.

To increase N use efficiency, by increased yields or decreased N rates, a number of products have been developed to delay the N transformation process so that the period of time in which the N source remains available for uptake is close to the time of maximum N uptake. These products can be classified into the following groups: nitrification inhibitors, urease inhibitors and slow-release N products.

Nitrification Inhibitors

Nitrification is the process of oxidizing ammonium (NH_4^+) to nitrate (NO_3^-). The process usually proceeds in two steps:

Step 1:
(*Nitrosomonas* sp aerobic bacteria):
$NH_4^+ + 1\frac{1}{2} O_2 \rightarrow NO_2^- + H_2O + 2H^+$

Step 2:
(*Nitrobacter* sp aerobic bacteria):
$NO_2^- + \frac{1}{2} O_2 \rightarrow NO_3^-1$

The nitrification process proceeds at temperatures above 32 F, with rate maximized near 75 F. Nitrification is an aerobic process and will not proceed in saturated soils, but it is maximized under moist, aerated soil conditions. Nitrification also is maximized between soil pH 6.5 and 8.

Specific nitrification inhibitors are required because inhibition of the second nitrification step should not occur. Otherwise, nitrite which is toxic to plants, could accumulate. Nitrification control is generally through inhibition of a specific enzyme pathway in bacteria involved in step one of nitrification.

Nitrapyrin

Nitrapyrin (2-chloro-6-[trichloromethyl] pyridine, Figure 1) has been studied and commercially used since the late 1960s. Work by

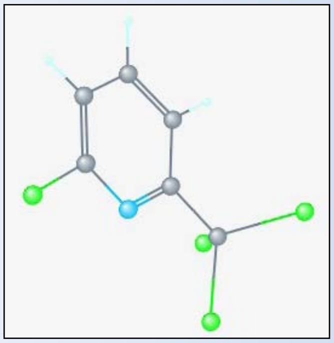

Figure 1. Nitrapyrin (2-chloro-6-[trichloromethyl] pyridine). Gray spheres = carbon; light blue = hydrogen; green = chlorine; cyan = nitrogen.
(Image from PubChem, https://pubchem.ncbi.nlm.nih.gov/compound/nitrapyrin#section=3D-Conformer)

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Janssen (1969), which was summarized by Hergert and Wiese (1980), showed that nitrapyrin was active as a nitrification inhibitor and the degree of nitrification was influenced by the nitrapyrin rate as a ratio of nitrapyrin to anhydrous ammonia. Greater N recovery with nitrapyrin-treated anhydrous ammonia than anhydrous ammonia alone was measured in April (190 days after application), June (230 days) and July (280 days) when anhydrous ammonia was applied from late October to early November.

N-Serve® (Dow AgroSciences LLC, Indianapolis, Ind.) is formulated mostly for use with anhydrous ammonia and is labeled for immediate incorporation or injection and not as a surface-applied product due to rapid nitrapyrin volatilization.

Illinois studies in the mid-1970s showed that when injected into anhydrous ammonia or applied with urea, the rate of nitrification decreased (Figures 2 and 3) (Touchton et al., 1978a, 1978b; Touchton et al., 1979a); however, low rainfall during the years of the experiments did not consistently increase corn N uptake or corn yield in Illinois (Touchton et al., 1979b). A lack of yield response from the use of N-Serve also was reported in Iowa by Blackmer and Sanchez (1988); however, Stehouwer and Johnson (1990) reported higher corn yield from fall-applied N containing nitrapyrin, which was related to higher N availability later in the season.

Greater corn yield with N-Serve included in fall-applied N also was reported by Randall et al. (2003) and Randall and Vetsch (2005) in Minnesota; however, spring-applied N was highest yielding with greatest N-use efficiency.

Yield increases during the seven Minnesota study years were 15 bushels per acre more for fall anhydrous ammonia + N-Serve versus fall anhydrous ammonia alone, and 27 bushels per acre more for spring anhydrous ammonia, compared with fall anhydrous ammonia (Randall et al., 2008).

A Wisconsin study (Hendrickson et al.,1978) found that on May 6, 1976, following an Oct. 6, 1975, application of anhydrous ammonia, 53 percent of the recoverable N was ammonium-N with N-Serve (0.5 pound/acre nitrapyrin active ingredient [a.i.]), compared with 11 percent ammonium-N without N-Serve. N-Serve also increased the ammonium-N concentration in Minnesota research (Malzer, 1977) through June 8 of the following spring. In North Dakota (Moraghan and Albus, 1979), greater ammonium-N following fall anhydrous ammonia application was present through July 5 of the following spring.

Grain yield increases with the use of N-Serve have been inconsistent due to the variability of rainfall necessary to lead to nitrate leaching in sandier soils or denitrification in high-clay soils. Based on numerous studies, the mode of action of nitrapyrin is well-defined and its activity against Nitrosomas bacteria is supported by its Enrivonmental Protection Agency-issued U.S. federal label.

Malzer et al. (1979) recorded a corn yield increase with the optimum N rate in fall anhydrous ammonia application with N-Serve, but a split application of N resulted in similar yield with N-Serve as without it. Hergert et al. (1978) showed that the benefit of N-Serve use under irrigated sands increased as evapotranspiration increased.

N-Serve use in anhydrous ammonia has several issues that complicate general use. It has a corrosive formulation, and when added directly into ammonia nurse tanks, it loosens rust inside the tanks that may clog application flow screens. It is also corrosive to aluminum float gauges inside nurse tanks, and gaskets deteriorate much faster than normal.

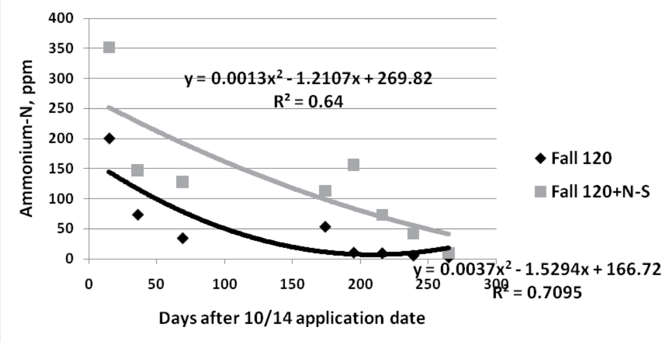

Figure 2. Ammonium-N concentration in soil after 120 pounds/acre of N as anhydrous ammonia was applied Oct. 14, 1975, with and without 1 pound/acre of active ingredient (two times labeled rate) N-Serve®/nitrapyrin (N-S). Differences between treatments were significant at all sampling dates through day 239.
(Touchton et al., 1978)

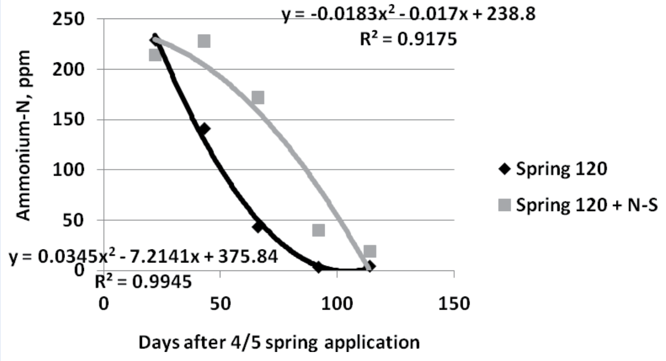

Figure 3. Ammonium-N concentration in soil after 120 pounds/acre of N as anhydrous ammonia was applied April 5, 1976, with and without 1 pound/acre of active ingredient (two times labeled rate) N-Serve®/nitrapyrin (N-S). Differences between treatments were significant at all sampling dates through day 114.
(Touchton et al., 1978)

Anhydrous ammonia retail suppliers and farmers who inject N-Serve directly into ammonia nurse tanks must install stainless steel float gauges and special gaskets to keep tanks better maintained and operational, and increase user safety. N-Serve use with anhydrous ammonia also can be metered into the ammonia flow stream on applicators. This is initially a more expensive application strategy to employ, but it avoids the problems associated with nurse tank injection.

Instinct® (Dow AgroSciences LLC, Indianapolis, Ind.) is a microencapsulated nitrapyrin formulation that can be applied with fertilizer left on the soil surface for up to a 10-day delay of ammonium fertilizer nitrification, according to recent labels.

Research has been conducted at a number of universities on effectiveness of Instinct. University of Nebraska studies in 2008 and 2009 (Ferguson et al.) showed no yield benefits to the use of nitrapyrin (GF-2017, Instinct); however, the plots were hampered by heavy rainfall in June (2008) and spatial variability (2009). In Wisconsin, two years of work with Instinct resulted in corn yield increases in 2008 but not in 2009 (Laboski, unpublished data).

In Illinois, yield did not increase due to the use of Instinct with urea ammonium nitrate (UAN) during six site-years (Fernandez, 2010). Iowa (Barker et al., 2014) and Minnesota (Randall, unpublished data) research also showed no yield increase with Instinct, compared with N fertilizer alone. Also, research in Iowa (Sassman, 2014) found no yield increase and a slight yield decrease with UAN+Instinct injected or broadcast/incorporated in the spring. Even though some of the study years in these research projects were wet, Instinct had a poor record of performance.

The lack of field performance with Instinct could be related to the formulation of the microencapsulation. N-Serve used in anhydrous ammonia performs well due to the complete availability of the nitrapyrin a.i. to affect nitrification at the time of application, as well as the a.i. concentration in the ammonia injection band. Instinct releases more slowly, and the concentration at any one time may be less than that with N-Serve, especially with broadcast application.

Support for this explanation comes from unpublished laboratory experiments by Goos at North Dakota State University (Figure 4). Urea was added uniformly to soil at 200 parts per million (ppm) of N. After four weeks of incubation, about 120 ppm remained as ammonium-N when the soil was treated uniformly with nitrapyrin as N-Serve.

At 1 ppm of nitrapyrin as Instinct, no ammonium was found. Achieving an equivalent concentration of ammonium remaining (68 percent) as with 1 ppm nitrapyrin (a.i. from N-Serve) required 5 ppm (five times the labeled rate). When Dicyandiamide (DCD) was applied at 5 ppm, which equates to about 2 percent of the total N applied as DCD-N (within the range of acceptable DCD rates for use as a nitrification inhibitor), only about 22 percent of the ammonium remained after the four-week incubation.

An incubation study with Instinct (Sassman and Sawyer, 2013, unpublished data) applied with liquid swine manure or UAN solution showed a decrease in ammonium disappearance with both labelled rates, but greater ammonium was present with the high Instinct rate (Figure 5). Interestingly, nitrification was evident immediately, even with Instinct.

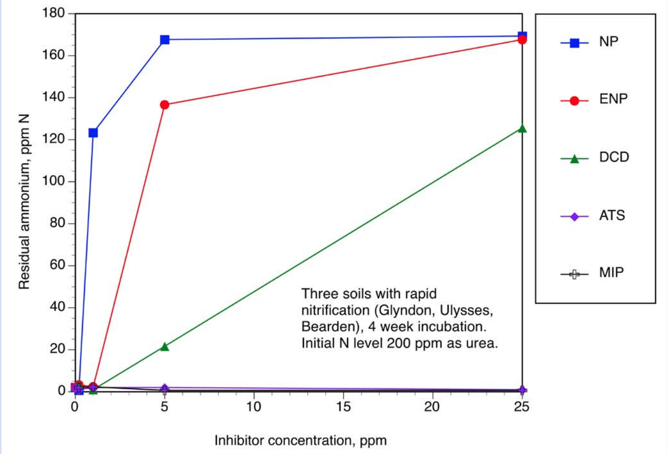

Figure 4. Performance of nitrification inhibitors NP (N-Serve for anhydrous ammonia), ENP (Instinct), DCD (dicyandiamide). Also, nonperformance of ATS (ammonium thiosulfate) and Nutrisphere (MIP). (Goos and Guertal, 2014, unpublished)

In the original Dow AgroSciences patent for Instinct, U.S. Patent number US20090227458 (Dow AgroSciences, 2009), in an efficacy experiment, 0.5 ppm nitrapyrin encapsulated formation with varying sizes and shell thicknesses was added to 25 grams (g) of Drummer soil in a beaker, covered with 25 g of additional soil and mixed. The results indicated that the encapsulated treatments, regardless of shell thickness, were as or more effective than nitrapyrin in the N-Serve 24 treatment. After two weeks, all treatments resulted in more residual ammonium-N, compared with the check without inhibitor.

Nitrapyrin released from Instinct microencapsulation was measured by Menelas (2014) in three soils: Ade (pH 6.8, sandy loam, organic matter [OM] 1.5 percent), Avonburg (pH 6.7, silty clay loam, OM 3.4 percent) and Chalmers (pH 5.7, silty clay loam, OM 4.2 percent). The percent inhibition, defined as [(NH_4 w/inhibitor – NH_4 w/o inhibitor) / (NH_4 w/ inhibitor)] X 100%, is presented in Table 1. These results indicate that a wide range of microencapsulation release rates occurred among soils, which may be important in the efficacy of nitrification inhibition from Instinct.

The half-life of ammonium in soil was measured by Omonode and Vyn (2013) in two Indiana silt loam soils with Instinct in UAN. In the nondrought year of 2011, the half-life of ammonium without inhibitor was 7.5 days at one site and 8.5 days in the other. Use of Instinct increased the half-life of ammonium to 12 days at one site and 14.4 days at the other.

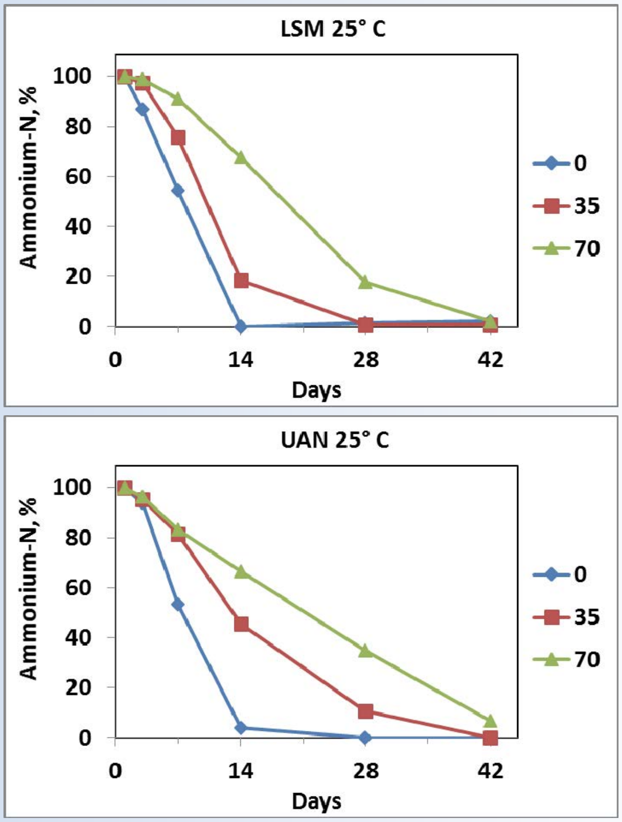

Figure 5. Performance of Instinct (percent of applied ammonium-N remaining) with liquid swine manure (LSM) and UAN solution when applied at the two suggested label rates (35 and 70 fluid ounces/acre equivalent rates) and incubated at 25 C for 42 days. (Sassman and Sawyer, 2013, unpublished)

Table 1. Percent inhibition† of nitrification by Instinct formulation from Menelas (2014) in three Indiana soils.

	Incubation period/Temperature (F)				
Soil	14 days/ 54 F	28 days/ 63 F	42 days/ 72 F	56 days/ 72 F	63 days/ 72 F
Ade	4.0	6.5	5.1	8.4	14.2
Avonburg	4.4	5.0	55.3	87.2	90.9
Chalmers	1.1	3.7	22.6	34.3	41.7

†Percent inhibition of nitrification defined as [(ammonium concentration with inhibitor – ammonium concentration without inhibitor) / (ammonium concentration with inhibitor)] X 100%.

In addition, nitrous oxide released from the soil was reduced 44 percent with the use of the inhibitor. Nitrous oxide emissions also were reduced with Instinct in another Indiana experiment (Burzaco et al., 2013) by 22 percent in a Chalmers soil, which was similar toone of the soils investigated in Menelas, 2014 (Table 1).

Considerable inconsistencies regarding the effectiveness of Instinct were found in laboratory and field trials. The soils in each experiment are known, the rate of a.i. used is known, the conditions of the experiments are known, but the microencapsulation thickness of the material used in the experiments is not known except for the data within the patent release. The Instinct label has no information regarding microencapsulation thickness, so the user must decide whether the release rate after soil application will lead to effectiveness of use.

The overall situation that will determine economic benefit from use of Instinct or N-Serve for a specific application is the presence of conditions for N loss. If rainfall and soil moisture patterns are favorable for loss and nitrapyrin is present in sufficient quantity for slowing nitrification, then yield may be increased through the use of the products. When conditions for loss are not present or more than adequate N is applied, no economic benefit will result. However, reduced nitrous oxide emission may result in environmental benefits.

The use of nitrapyrin to reduce N losses needs to be considered at the scale of a sensitive region, such as a watershed, over a prolonged period of use, as well as within the context of overall goals for abatement of N losses from the agroecosystem to the environment. (Wolt, 2004).

Dicyandiamide

Research on dicyandiamide (DCD or cyanoguanidine) has shown that it can be used as a nitrification inhibitor, although results generally indicate that its effective activity is shorter in time than nitrapyrin (Bronson et al., 1989). Products that contain DCD in the U.S. include Super-U (IMC Phosphate Co., licensed exclusively to Agrotain International LLC) and Guardian fertilizer additive (Conklin Co. Inc.).

DCD contains about 67 percent N and was examined as a slow-release N source early in the last century (Reeves and Touchton, 1986). It was found to decrease crop yield when rates exceeded about 36 pounds per acre (Cowie, 1918). The Guardian label recommends a 2 percent addition to fertilizer. The content of DCD in Super-U is not stated. Growers likely would not overapply either product to the point of crop phytotoxicity if label recommendations were followed.

A review of North Central states' research on DCD was published by Malzer et al. (1989). The review concluded that DCD was similar to nitrapyrin in its nitrification inhibition. Yield differences between fertilizer treated with DCD and fertilizer alone were inconsistent and limited to those soils and conditions where nitrate was lost through leaching or denitrification. The greatest value of any nitrification inhibitor would be in soils where nitrate loss through leaching or denitrification is more likely. A summary by Malzer et al. (1989) is reproduced in Table 2.

In contrast to the relatively low frequency of corn responses in the Midwest, potato responses were more consistently positive (Table 3).

Table 2. Summary of corn grain yield responses to DCD and nitrapyrin at N rates equal to or less than optimum for fine-textured Midwest soils. (from Malzer et al., 1989)

	DCD			Nitrapyrin		
	No. of Comparisons			No. of Comparisons		
	Total	With Significant Advantage	Average Response %	Total	With Significant Advantage	Average Response %
Timing						
Fall	4	1	+1.6	2	0	-0.2
Spring	15	3	+3.4	7	1	-0.4
Side-dress	3	1	+1.4	3	2	+8.1
N Source						
Ammonium sulfate	2	0	-1.0	0	0	–
Anhydrous ammonia	6	1	+3.6	6	1	-1.8
Urea	4	4	+2.2	6	2	+1.1

Table 3. Relative effect of dicyandiamide (DCD) used with three nitrogen sources on potato yield, % Grade A US1A tubers, and apparent N recovery in tubers at Hancock, Wis., 1984-1986. (from Malzer et al., 1989)

		Number of Positive Significant Responses			Average Relative Response to DCD (%)		
N Source	Number of Comparisons	Yield	% Grade A	Tuber N recovery	Yield	% Grade A	Tuber N recovery
Ammonium nitrate	9	3	1	4	+2.0	-3.6	+6.5
Urea-ammonium sulfate	6	3	0	4	+5.1	-10.8	+23.7
Urea-ammonium Nitrate solution	9	2	2	6	+4.0	-5.1	+27.6

The ammonium-N remaining in the soil following ammonia application with nitrapyrin and DCD treatments was explored at four Illinois locations by Sawyer (1985). Within 30 days of a fall application, no differences were found between the control and the DCD and nitrapyrin treatments in the percentage of remaining ammonium-N. In the spring, the DCD and nitrapyrin treatments provided a greater percentage of remaining ammonium-N, compared with the control at three of four locations. The differences are presented in Figure 6 for the Urbana and Dekalb locations.

Spring application of DCD and nitrapyrin were even more effective at some sites (Figure 7). A study in Iowa (Barker et al., 2014) found no effect of SuperU on soil inorganic-N, nitrous oxide emission shortly after application, or corn yield when broadcast incorporated or not incorporated. Inconsistent results with DCD also may be due to some products containing low use rates of DCD.

The use of nitrification inhibitors with liquid manure applications has generated considerable interest. In response to reports of poor corn growth due to injected liquid manure in Illinois, placement studies with and without nitrapyrin were conducted on similar soils.

The results of one study showed that the use of nitrapyrin increased corn plant and grain N concentrations but did not translate into a yield increase (Sawyer et al., 1991). In another study, the use of nitrapyrin was useful in lowering soil nitrite levels in the liquid manure band, which was one reason why poor corn growth was observed in the banded liquid manure fields (Sawyer et al., 1990).

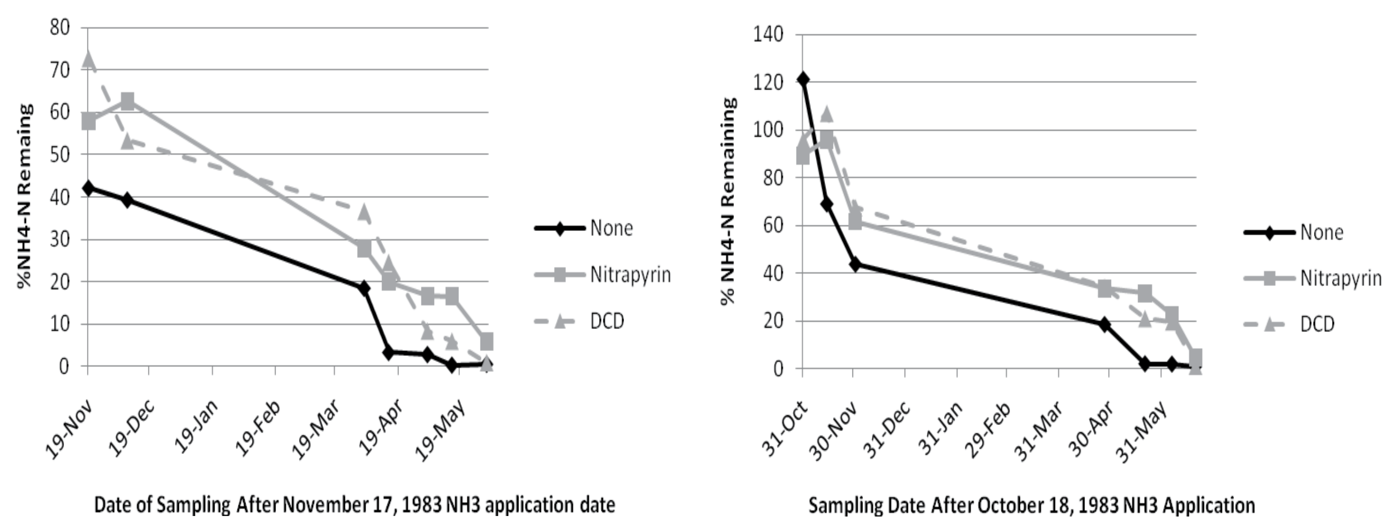

Figure 6. Percent NH_4-N remaining after fall NH_3 application at Urbana (left) and Dekalb (right). (from Sawyer, 1985)

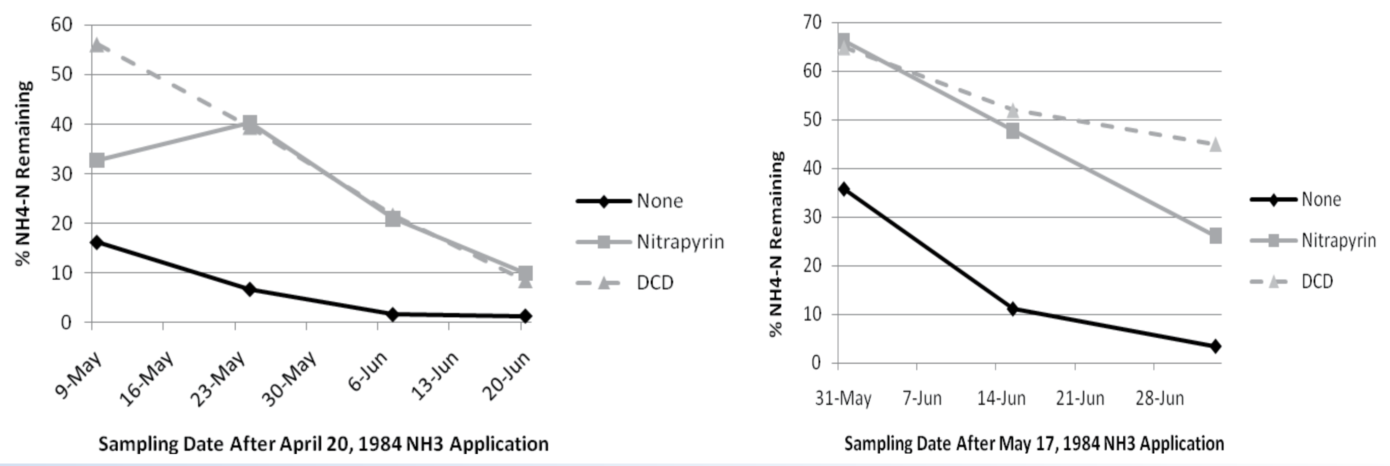

Figure 7. Percent NH_4-N remaining after spring NH_3 application alone, with nitrapyrin and DCD at Monmouth (left) and Brownstown (right). (from Sawyer, 1985)

Urease Inhibitors

Urea is a common fertilizer used by farmers in the north-central states. The chemical formula for urea is $CO(NH_2)_2$. A 3-D image of urea is displayed in Figure 8.

When applied to the soil, the enzyme urease splits the urea into its component parts of ammonia (NH_3) and carbon dioxide (CO_2) through the following reaction (called hydrolysis), with a net increase in pH:

$$CO(NH_2)_2 + H_2O \rightarrow NH_3 \uparrow + CO_2 \uparrow$$

The urease enzyme is a three-dimensional molecule made up of amino acid chains with a Ni ion as a part of the structure. The urease enzyme has a unique configuration that matches the triangular shape and size of the urea molecule (Figure 9).

Urease is utilized in plants and microorganisms, particularly bacteria, to manage the movement of ammonia through the plant and release the ammonia where it is required. When the plant or microorganism decays, the urease enzyme is very resistant to decay and continues to function after whatever organism that produced it is dead and largely decayed.

When urease comes into contact with a urea molecule, the urea is drawn to the active site and transformed into free ammonia and CO_2. If the ammonia released is at or near the surface, NH_3 volatility to the air is likely.

Soils with greater residue at the soil surface have much greater concentrations of urease than those with little residue at the surface. Soils with pH greater than 7 have much greater ammonia volatilization rates than those in acid soils, with the main reason being a higher percentage of NH_4 as NH_3 as pH increases. Therefore, ammonia volatilization potential is greater with these conditions: surface-applied urea, high surface residue, high soil pH, low cation-capacity soils, moist to drying soils, high temperatures and no rainfall after application.

The compound that most consistently has decreased urea volatilization when mixed with urea or urea-ammonium nitrate solutions is NBPT (N-(n-butyl) thiophosphoric acid triamide) (Figure 7). NBPT originally was marketed as Agrotain (Agrotain International LLC), with the commonly used product today branded Agrotain Ultra (Koch Agronomic Services, Wichita, Kan.). The NBPT active ingredient also has been made available to other distributors and manufacturers, so NBPT products today have many brand names.

The mechanism for NBPT is to lock onto the urease enzyme-binding sites, preventing the enzyme from reacting to the urea (Manunza et al., 1999). Agrotain has at least two possible uses in crop production: One is to protect against seed injury for growers, especially in the northern Plains, who apply urea with small-grain seed at planting.

The use of Agrotain has increased the rate of urea that can be applied safely with small-grain seed in some studies (Table 4), although the practice is rarely recommended due to the uncertainty of the length of time required for germination in cooler soils. The other use is to delay ammonia volatilization from surface applied, or near-surface applied urea, for about 10 days (Table 5).

A more recently introduced product is Limus (BASF Corp., Research Triangle Park, N.C.,). Limus contains NBPT and NPPT (N-(n-propyl) thiophosphoric acid triamide) (Figure 10). The same mode of action is utilized by NPPT to inhibit urease as that of NBPT.

Recent research from North Dakota has shown that Limus is at least as effective as an inhibitor as Agrotain Ultra and technical grade NBPT alone (Figure 11).

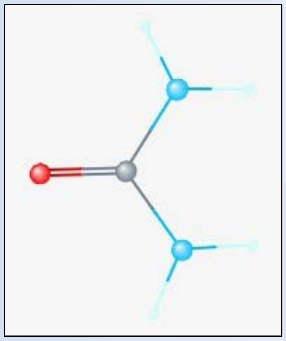

Figure 8. Urea 3-D image Gray is C, red is O, cyan are N, and light blue are H (from Pubchem)

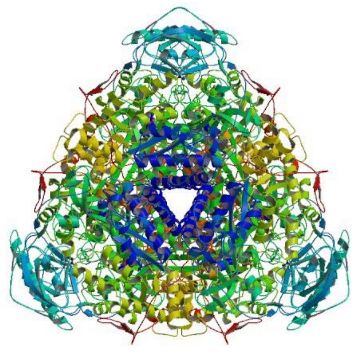

Figure 9. Urease enzyme, oriented to show active site. (from Pubchem)

Table 4. Effect of seed-placed urea with and without Agrotain on stand density and grain yield of barley on a fine sandy loam soil, 1994-96. (from Grant, 2004)

	Stand, Plants/foot		Yield, bu/acre	
Nrate, lb/acre	**No Agrotain**	**Agrotain**	**No Agrotain**	**Agrotain**
0	7.6	7.6	50	50
18	7.9	8.2	55	52
36	7.3	7.7	53	62
54	6.0	7.1	59	57
72	5.7	7.1	63	61
89	4.7	7.1	57	65

Table 5. Cumulative ammonia volatilization losses for urea, ammonium sulfate and urea + NBPT from a Dewitt silt loam soil during a 15-day laboratory incubation at 25 C. (Norman data, University of Arkansas, Fayetteville, from Franzen et al., 2011)

	Days After N Source Application			
	3	**7**	**11**	**15**
N sources	**Cumulative NH3 Loss, % of N Applied**			
Urea	14.5	35.9	51.8	56.9
Ammonium sulfate	0.1	0.2	0.5	0.6
Urea + NBPT[†]	0.006	2.7	12.9	18.3
Urea + Nutrisphere 0.25%	17.6	42.2	57.8	62.7
LSD(0.05)[‡]	12.2			
LSD(0.05)[§]	9.6			

[†] NBPT= N–(n-butyl) thiophosphoric triamide

[‡] LSD to compare means among N sources within the same sampling time.

[§] LSD to compare means among sampling times with the same N source.

Agrotain decreased the rate of ammonia volatilization from urea applied to the surface as dry urea or urea-ammonium nitrate solutions (Brouder, 1996, Table 6; Varsa et al., 1999, Table 7), resulting in yield increases when the fertilizer was treated with NBPT. Ammonia volatilization losses from urea at Brandon, Manitoba, decreased from 40 milligrams (mg) to 2 mg and from 88 to 12 mg with Agrotain in two separate studies for a seven-day period after application (Grant, 2004).

In a Kansas study (Weber and Mengel, 2009), urea was applied in three site-years to the soil surface after corn emergence using a number of nitrogen-extending additives, including Agrotain. The Agrotain treatment was superior to urea alone by 25 bushels per acre in one of the three site-years. The two locations that received significant rainfall immediately following applications did not receive a yield benefit from the Agrotain treatment.

In sorghum, urea + Agrotain and urea + SuperU were 11 and 12 bushels per acre, respectively, greater in yield than with urea broadcast alone (Weber et al., 2009a). At two drier locations, no yield differences occurred between urea + Agrotain and urea alone.

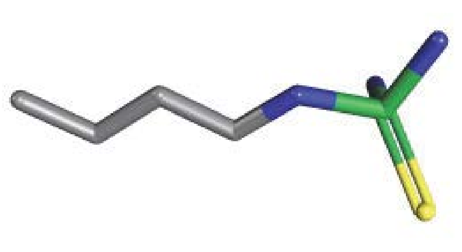

Figure 10. NBPT (N-(n-butyl) thiophosphoric acid triamide) structure. NPPT (n-propyl) also has the basic active-site inhibiting triangular structure, but the tail of the molecule has one more C group than NBPT. (from Pubchem)

A 14-year study in southern Illinois (Ebelhar et al., 2010) showed a 3-bushel corn yield advantage of urea + Agrotain, compared with urea broadcast in conventional till surface and incorporated during 12

Table 6. Mean corn yield from Purdue Agronomy Farm, SEPAC, Pinney, Purdue and Kosciusko locations, with urea and UAN alone and treated with NBPT. (from Brouder, 1996, citing work by Phillips, Mengel and Walker, 1989, unpublished work, Purdue University)

Fertilizer Treatment	Yield, bu/acre
Control (20 lb. N/acre in starter only)	99
Urea broadcast, surface	130
Urea + NBPT broadcast, surface	143
UAN broadcast, surface	135
UAN + NBPT broadcast, surface	140
UAN dribbled, surface	139
UAN spoke injected	142
UAN coulter injected	147
UAN knife injected	145

Table 7. No-till corn yield as affected by N fertilizer sources, Agrotain and placement in Illinois. (from Varsa et al., 1999)

	Belleville		Dixon Springs	
Treatment	Yield, bu/acre			
Control (0N)	34	53	62	73
Urea	106	120	98	100
Urea + Agrotain	134	143	112	112
UAN, surface	123	137	103	107
UAN + Agrotain, surface	128	145	107	114
UAN, dribble	139	137	108	112
UAN + Agrotain, dribble	143	152	110	120
UAN injected	172	176	123	121
Anhydrous ammonia	158	166	122	130

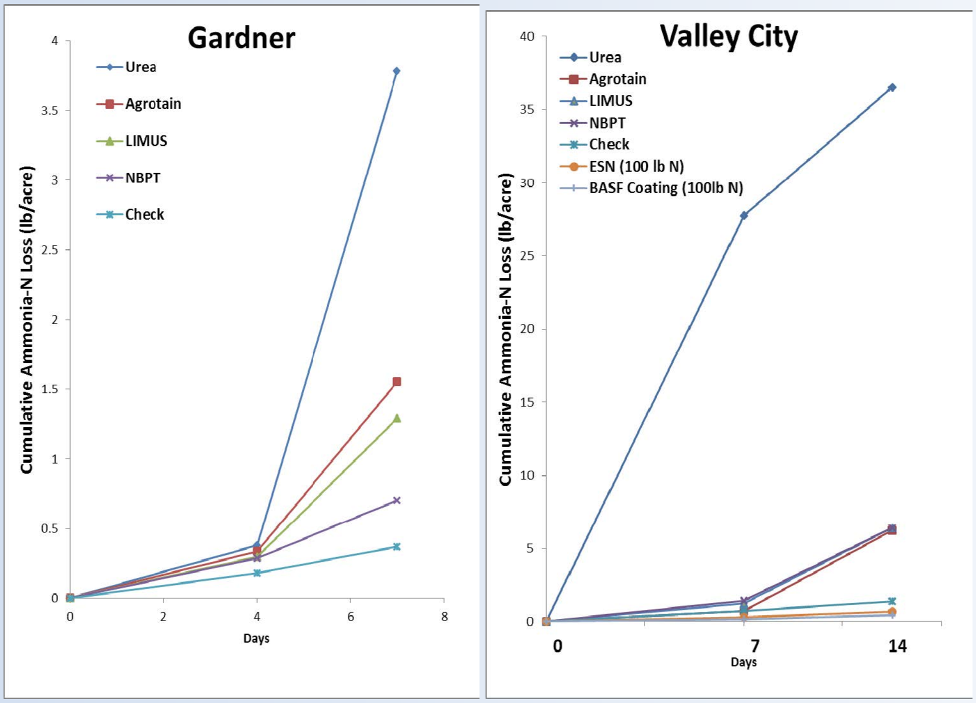

Figure 11. Comparison of cumulative ammonia loss during an eight-day period near Gardner, N.D., on a conventionally tilled, low-residue, neutral-pH soil, compared with 14 days near Valley City, N.D., on a high-residue, long-term, no-till field with slightly acid surface pH. Urea N rate applied was 100 pounds N per acre. (Franzen 2014, unpublished data)

years of treatments. In no-till, urea + Agrotain held an 11 bushel/acre advantage over urea surface applied during four years of treatments.

In Kentucky, 50 pounds of N/acre was applied preplant to all corn plots (Schwab and Murdock, 2009). Side-dress applications of urea and UAN with several additives or formulations were applied to the soil surface at the six-leaf stage. Higher yields were achieved with urea + Agrotain and SuperU than with urea alone. Higher yields were achieved with UAN + Agrotain and UAN + Agrotain Plus (combination of NBPT and DCD formulated for use with UAN) (Table 8) than with UAN alone.

Also notable: The ammonium nitrate treatment was the highest yielding treatment, indicating that some N loss was realized in the Agrotain treatments. The study also demonstrates that grower practices that limit N loss, particularly placement of urea or UAN below the soil surface may be required for maximum yield, even though urease inhibitors are effective in limiting but not eliminating ammonia volatilization.

Table 8. Yield for side-dressed no-till corn in Hardin County, Ky.
(from Schwab and Murdock, 2009)

Treatment	Yield, Bushels per Acre
Check (50 lb. N/acre preplant N only)	117d*
Urea	158c
Urea + Agrotain	201b
SuperU	201b
UAN	150c
UAN + Agrotain	179bc
UAN + Agrotain Plus	175bc
Ammonium nitrate	239a

*Numbers followed by the same letter are not significantly different (5%)

Nitrification and Urease Inhibitors

Ammonium thiosulfate (ATS) and several additional commercial thiosulfates have nitrification- (Goos, 1985; Janzen and Bettany, 1986) and soil urease-inhibiting properties (Goos, 1985). Although ATS has measureable nitrification inhibition properties in some experiments, in others it has very little (Figure 4).

Thiosulfate readily breaks down rapidly when soils are warm. In a laboratory study at 15 C, ATS essentially was mineralized in about a week. Under cooler temperatures, however, significant thiosulfate remained after two weeks in two of three soils, with mineralization complete in all soils by week three.

When thiosulfate was placed in a band with aqua ammonia in the fall in North Dakota (Oct. 3, 1996), thiosulfate resulted in similar spring (May 12, 1997) ammonium and nitrate levels as aqua ammonia treated with nitrapyrin (Goos and Johnson, 1999). Spring wheat yields of aqua ammonia treated with thiosulfate and nitrapyrin were similar, and both were greater than aqua ammonia alone.

In the process of identification of thiosulfates as nitrification and soil urease inhibitors, researchers noted that the compounds would not be expected to perform as well as some other alternative nitrification and urease inhibitors due to the shorter decomposition period for ATS, compared with nitrapyrin (Goos, 1985).

When ATS is put into solution with purified urease, no inhibition occurs. However, ATS reacts with Mn-oxides and forms Mn^{2+} and tetrathionate (S_4O_6, $^{2-}$). Tetrathionate and Mn^{2+} inhibit urease activity. The result of the oxidation reaction is some inhibition of urease with ATS, especially when the UAN is banded. The use of ATS sometimes has been implicated in the increase of nitrites in some experiments.

The second step of nitrification (nitrite to nitrate) is usually instantaneous due to the presence of Mn-oxides (Bartlett et al., 2008). The reactions of ATS with Mn-oxides may be the reason for its nitrification inhibition and the increase of nitrite. Adding ATS to UAN has been shown to reduce ammonia volatilization from surface-applied UAN under greenhouse (Goos, 2013, Figure 12) and field (Grant et al., 1996, Figure 13) conditions.

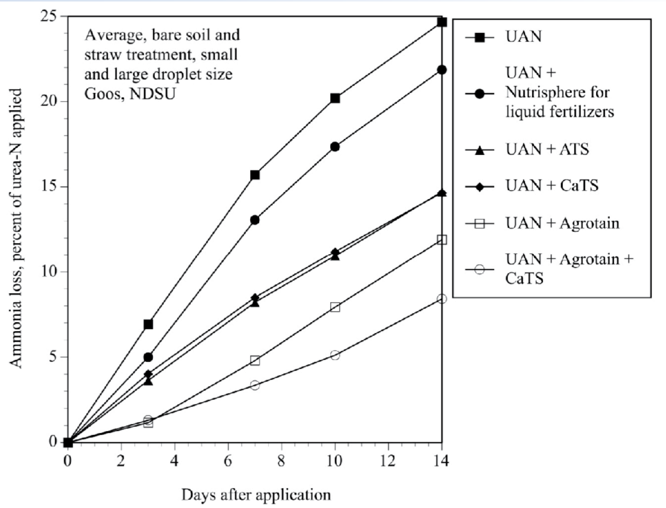

Figure 12. Effect of treatment of UAN with ATS and other amendments on ammonia volatilization through time under greenhouse conditions. (Goos, 2013)

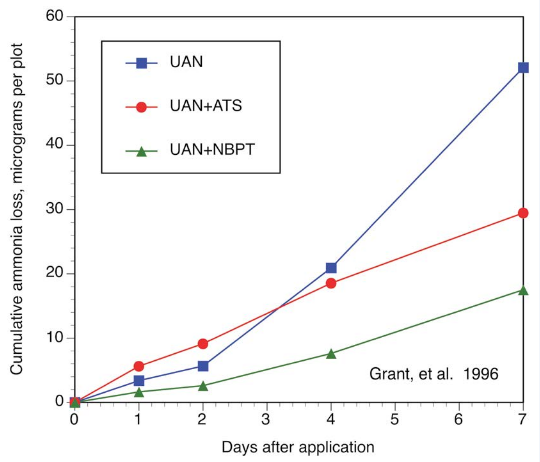

Figure 13. Ammonia volatilization from UAN and UAN with ATS and NBPT through time under field conditions. (Grant et al., 1996)

Goos and Johnson (1992) compared the nitrification rates of banded UAN amended with emulsified nitrapyrin (N-Serve 24E), DCD, ATS and ATS+DCD at three field sites. The results are summarized in Figure 14. The nitrapyrin was most effective at slowing nitrification and ATS was least effective.

One study was unable to duplicate urease inhibition results, but it used different methods than originally presented at rates of ATS from 3.3 to 33 times the rates of Goos, 1985 (McCarty et al., 1990). Thiosulfate activity is regulated by its concentration (effective at S rates of 25 mg kg^{-1}, Goos and Johnson, 2001).

Janzen and Bettany (1986) expressed cautions on high rates of banded ATS (in excess of 100 parts per million, or ppm) due to nitrite accumulation from ATS inhibition of not only the ammonium to nitrite process but the nitrite to nitrate process. The rate used by Goos (1985) was about 43 ppm if expressed as a band with a radius of 2 inches, which did not accumulate nitrite at the use rate in the Janzen/Bettany (1986) study.

The use of thiosulfate was re-examined in Kansas research. Application in the spring of a 5 and 10 percent calcium thiosulfate by volume solution with UAN had similar yield as urea broadcast in no-till (Tucker and Mengel, 2007).

Other Products

The only products with active ingredients that have demonstrated consistent activity as nitrification or urease inhibitors were presented in previous sections. Products containing maleic and itaconic acid blends have not performed as nitrification (Figure 4) or urease inhibitors (Table 5, and their claimed mode of action is not chemically possible (Franzen, 2013; Chien et al., 2014).

Products containing calcium heteropolysaccharide, such as N-Zone (AgXplore, Parma, Mo.), claim to reduce loss of N by processes such as leaching. In an incubation study, this product was not shown to slow nitrification when applied to urea granules (Figure 15). NZONE Max addition to urea did not result in a corn yield benefit in a 2015 North Dakota field experiment (Chatterjee, 2015, unpublished report). Although some labels for these products claim to keep N in the ammonium form longer, careful laboratory experiments show that they do not perform as nitrification inhibitors.

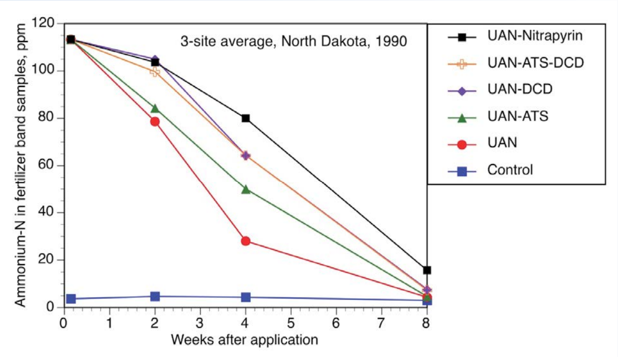

Figure 14. Mean of three field sites, incubation of soil with beginning concentration of 120 ppm ammonium-N as UAN through time. Soil treatments were UAN (urea-ammonium nitrate fertilizer), ATS is ammonium thiosulfate, DCD is dicyandiamide, nitrapyrin is the formulation for anhydrous ammonia. (Goos and Johnson, 1992)

Poly-coated Urea

Poly-coated urea is used to physically maintain urea as a urea molecule and therefore extend N availability during a longer period of time. ESN (Environmentally Smart Nitrogen, Agrium Inc., Calgary, Alberta, Canada) is the most widely distributed and applied poly-coated urea available to crop producers in the north-central region. It does not perform as a nitrification or urease inhibitor, but ample evidence suggests that its use extends the availability of N into the growing season and protects N from loss until urea is released into the soil.

In ESN studies in North Dakota (ESN placed into the soil), fall-applied ESN had more than half of the urea within the pellets remaining throughout the winter, and about one-third were remaining in late May to early June (Table 9). The rate of urea release from the coating depends on temperature and soil moisture. While urea remains inside the poly coating, it is not affected by the urease enzyme, but neither is it available for crop uptake. Dry weather delays release, while moist soil conditions increases the rate of release.

In Michigan during three years (Table 10), few corn yield differences were observed when examining multiple blending ratios of ESN and urea. Preplant application favored a 75 ESN: 25 urea blend when June

Table 9. Urea in ESN remaining after field burial, Casselton, N.D., fall 2013. Ransom, unpublished data, North Dakota State University.

	Date of Burial	
	10/11	10/25
Date of Sampling	% urea remaining	
10/25/2013	89 a[†]	na
11/08/2013	84 a	96 a
04/29/2014	55 bc	65 b
05/13/2014	50 c	59 bc
05/27/2014	37 d	45 cd
06/10/2014	na	38 d

[†] Values followed by the same letter are not significantly different from each other at P<0.05 level of probability.

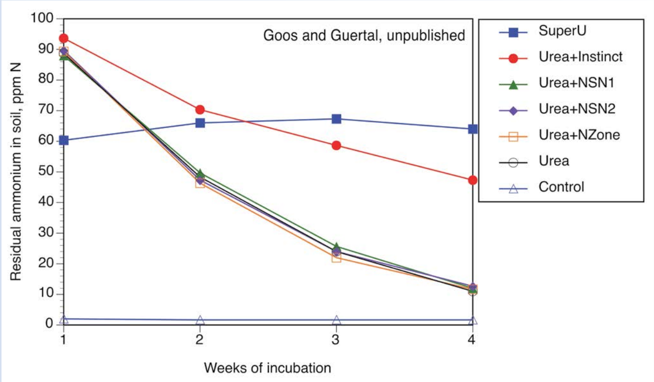

Figure 15. Ammonium-N remaining in the soil after application of Urea and amendments through time. NSN1 and NSN2 are formulations of Nutrisphere-N. Super U contains DCD.

or July rainfall was well above average for the region (2010 and 2013). Nitrogen at-planting application favored a 50 ESN:50 urea blend in years with a normal planting date for the region, but this ratio shifted toward a 25 ESN: 75 urea blend when spring planting was delayed beyond normal ranges. While side-dress applications of ESN did not synchronize well with peak corn N demand in this study, adding ESN extended the activity of N when dry weather conditions were encountered soon after side-dress application (2011).

In North Dakota, preplant N as Instinct-treated urea or ESN did not increase yield or protein content of spring wheat, compared with urea alone (Table 11). In Kansas (Table 12), a 50 ESN:50 urea blend spring applied for corn resulted in greater yield than winter-applied urea or ESN, and spring-applied UAN and spring-applied UAN with Nutrisphere. The 50:50 blend was similar in yield to spring-applied urea, spring-applied 100 percent ESN, spring-applied UAN using coulter injection, spring-applied Agrotain treated urea and spring-applied SuperU.

Table 10. Impact of N application timing and ESN:urea blend ratio on corn grain yield. Preplant incorporated N applications were conducted two to four weeks prior to planting, while side-dress N applications were surface banded at V4-6. Grain yields averaged across 75 and 150 lb. N/acre application rates. (Steinke and Chomas, 2014)

		Blend Ratio (ESN:Urea)				
	Application	100:0	75:25	50:50	25:75	0:100
Year	Timing	Corn grain yield, bushels/acre				
2011	Preplant	146	155	143	139	133
	At-planting	156	150	155	176	172
	Side-dress	160	159	153	156	142
	LSD (0.05)			19		
2012	Preplant	123	135	125	119	127
	At-planting	125	123	126	112	125
	Side-dress	118	125	110	117	125
	LSD (0.05)			18		
2013	Preplant	188	189	179	176	179
	At-planting	177	174	184	181	171
	Side-dress	141	159	175	178	187
	LSD (0.05)			18		

Table 11. Spring wheat protein and yield at three sites in the Red River Valley of North Dakota and Minnesota as affected by source of N (ESN and urea) and Instinct, 200 lb. N/acre applied, spring, 2015. (Ransom, unpublished data, North Dakota State University)

Treatment	Protein, %	Yield, bushels/acre
Check	13.2	50.9
ESN	14.3	70.4
Urea	13.9	71.6
75% ESN:25% Urea	14.4	69.7
50% ESN:50% Urea	14.5	70.8
Urea+ Instinct	14.4	70.1
LSD (0.05)	0.7	7.3

A three-year study in Nebraska (2009-2011) on a coarse-textured soil with irrigation showed ESN applied shortly after corn planting consistently performed better in corn N response, use efficiency and grain yield than UAN applied at the same time or a UAN split application (Maharjan et al, 2016).

A three-year study (2003-2007) at two locations in Iowa (Moore et al., 2008) showed a corn yield advantage for ESN, compared with urea, in only one of nine site-years. The soil ammonium-N concentrations usually were higher with ESN (V6 and V15 sampling), but postharvest soil nitrate-N and ammonium-N concentrations also were higher from ESN, which could lead to increased post-season nitrate loss.

An additional Iowa two-year study (2013-2014) at two locations with ESN and other N additives (Barker and Sawyer, unpublished) found no agronomic or N use efficiency benefit from ESN or other additives, compared with urea, when broadcast with or without incorporation.

In Ohio, a spring season was cooler than normal and ESN treatment did not perform as well as some other treatments (Table 13). The Ohio work supports the use of ESN in a blend in case the environment is unfavorable for urea release through the polymer coating of ESN.

Table 12. Corn grain yield as affected by 80 lb. N/acre applied as N source, timing, method of application and additive. (Manhattan, Kan. Weber and Mengel 2009)

Treatment	Yield, bushels/acre
Control	104
Winter urea	138
Winter ESN	154
Spring urea	165
Spring Urea + Agrotain	169
Spring Urea as SuperU	173
Spring ESN	167
Spring 50% ESN:50% Urea	174
Spring UAN broadcast	148
Spring UAN + Nutrisphere	149
Spring Coulter UAN	162
LSD (0.05)	19

Table 13. Soft red winter wheat yield response to N source and timing from 80 lb. N/acre, Custer, Ohio. (Lentz 2012)

	N Timing			
	2009		2010	
	Feekes GS 3-4	Feekes GS 6	Feekes GS 3-4	Feekes GS 6
N Source	bushels/acre			
Ammonium Sulfate	89.4	92.6	77.8^{a}	77.5^{a}
Urea	84.8	91.1	77.1^{a}	78.6^{a}
75% Urea: 25% ESN	86.0	85.6	74.0^{ab}	73.6^{ab}
50% Urea: 50% ESN	87.8	81.9	75.4^{a}	70.2^{bc}
25% Urea: 75% ESN	83.9	79.7	70.0^{bc}	66.7^{c}
ESN	80.6	82.1	68.3^{c}	60.1^{d}
LSD (0.05)	NS	5.2		
Zero Spring N check	64.5	45.3		

2010 yields followed by the same letter are not significantly from each other at $P < 0.05$.

Summary

Nitrapyrin and DCD are well-documented nitrification inhibitors, and NBPT and NPPT are well-documented urease inhibitors. Agronomic and environmental benefits may not be realized in every year because rainfall patterns and rainfall intensity dictate whether N will be leached, volatilized or denitrified.

Ammonium thiosulfate has measureable nitrification and urease inhibitors but is not nearly as effective as the well-documented chemistries. Polymer-coated ureas have the greatest benefit in sandy or water-logged soils, or any conditions with a high probability for N loss.

Using N extenders and additives has two potential economic benefits: increase yield or decrease the optimum fertilizer N required. Before deciding whether to use an alternative N product or amendment, producers must consider the major N loss mechanism in a particular soil and field.

These products add additional cost to a farming operation, so producers need to give careful thought to selecting the product appropriate for a specific field. In addition, when considering products not explained in this publication, look for independent field trials, preferably conducted by land-grant university researchers, to verify effectiveness and mode of action.

Using N extenders and additives has two potential economic benefits:

increase yield or decrease the optimum fertilizer N required.

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