NITRIFICATION INHIBITOR CLAIMS – ARE THEY REAL?

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Nitrogen management continues to be difficult due to transformations of nitrogen fertilizers that are possible when applied to soil and the uncertainties of weather (Cabrera 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 can be transformed to nitrate through the activities of specific soil bacteria (Norton, 2008). Because of these and other processes, nitrogen use efficiency is low.

Nitrogen is often applied to crops in the North Central region of the US before planting. The first 4 to 6 weeks after planting, corn will only require about 5% of the N applied. The following 2 to 4 weeks of growth require a large proportion of the total season requirement. 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 states. To increase nitrogen use efficiency and thereby increase yields or decrease N rates, a number of products have been developed to delay an N transformation process so that the period of time in which the N source is available for uptake is closer to the time the crop needs the available N. One of the groups of products developed to delay the bacterial process that transforms ammonia or ammonium fertilizers to nitrite/nitrate are the nitrification inhibitors.

Nitrapyrin

N-Serve®, or nitrapyrin (2-chloro-6-[trichloromethyl] pyridine) has been studied and commercially used since the late-1960's. Work by Janssen (1969), summarized by Hergert and Wiese (1980) showed that nitrapyrin was active as a nitrification inhibitor and that the degree of nitrification was influenced by nitrapyrin rate as a ratio of nitrapyrin to anhydrous ammonia. Greater N recovery with nitrapyrin 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.

Illinois studies in the mid-1970's showed that when injected into anhydrous ammonia or applied with urea the rate of nitrification decreased (Figures 1 and 2) (Touchton et al. 1978a, 1978b; Touchton et al., 1979a); however rainfall during the years of the experiments did not result in consistent increase in corn N uptake or corn yield in Illinois (Touchton et al., 1979b). Lack of yield response from the use of nitrapyrin was also reported in Iowa by Blackmer and Sanchez (1988); however Stehouwer and Johnson (1990) reported higher corn yield from fall-applied N with nitrapyrin related to higher N availability later in the season.

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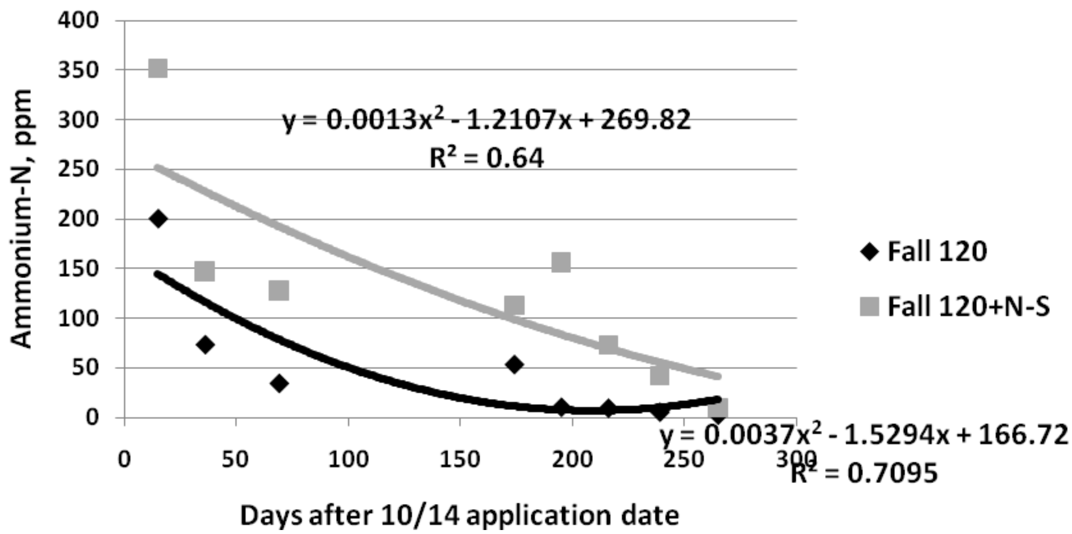

Figure 1. Ammonium-N concentration in soil after 120 lb/acre N as anhydrous ammonia was applied October 14, 1975 with and without 1 lb/acre ai (2X labeled rate) N-Serve® (nitrapyrin). Differences between treatments were significant at all sampling dates through day 239 (Touchton et al., 1978).

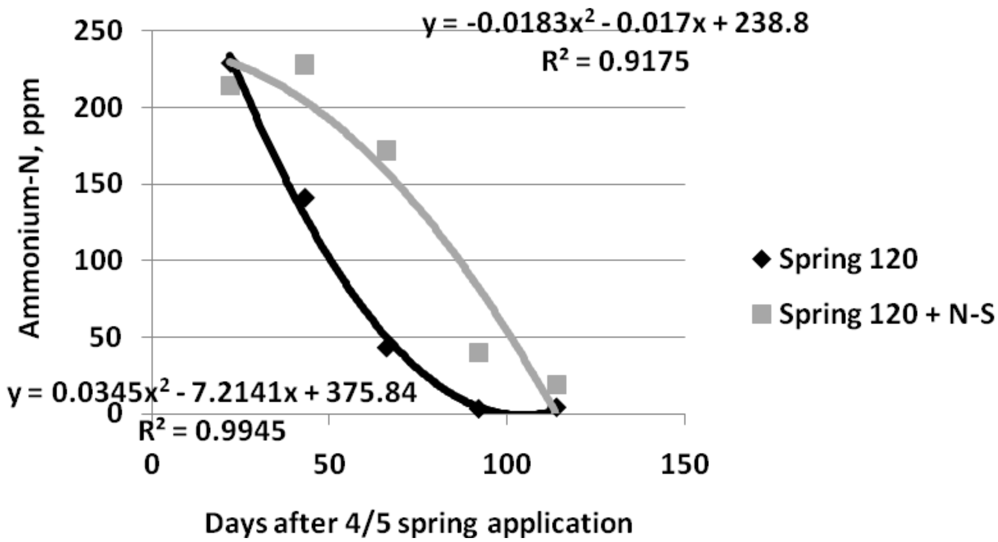

Figure 2. Ammonium-N concentration in soil after 120 lb/acre N as anhydrous ammonia was applied April 5, 1976 with and without 1 lb/acre ai (2X labeled rate) N-Serve® (nitrapyrin). Differences between treatments were significant at days after application all days after application through day 114 (Touchton et al., 1978).

Higher corn yield with nitrapyrin in fall-applied N was also 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. N-Serve® is labeled for immediate incorporation or injection and not as a surface-applied product. Yield increases over the seven Minnesota study years were 15 bushels per acre more for fall anhydrous ammonia + N-Serve over fall anhydrous ammonia alone, and 27 bushels per acre more for spring anhydrous ammonia compared to fall anhydrous ammonia (Randall et al., 2008)

A Wisconsin study (Hendrickson et al.,1978) found that on May 6, 1976 following an October 6, 1975 application of anhydrous ammonia, 53% of the recoverable N was ammonium-N with nitrapyrin (0.5 lb/acre ai) compared with 11% ammonium-N without. Nitrapyrin also increased the ammonium-N in Minnesota (Malzer, 1977) through June 8 of the following spring.

Grain yield increases with the use of a nitrification inhibitor have been inconsistent due to the variability of rainfall necessary to lead to nitrate leaching in sandier soils or denitrification in high clay soils. Malzer et al. (1979) recorded a corn yield increase with the optimum N rate with fall anhydrous ammonia application with nitrapyrin, but a split application of N resulted in similar yield with nitrapyrin as without. Hergert et al. (1978) showed that the benefit of nitrapyrin use under irrigated sands increased as the irrigation water as a percent of evapotranspiration increased. Differences between use of nitrapyrin and without were most pronounced at irrigation water as a percent of evapotranspiration of 86% and higher.

Instinct® is an encapsulated nitrapyrin formulation that can be applied to fertilizer left on the soil surface for up to 10 days for delay of ammonium fertilizer nitrification. It received its label in 2009. Research is ongoing at a number of Universities. University of Nebraska studies in 2008 and 2009 (Ferguson et al., 2008, 2009) 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, 2 years of work with Instinct® resulted in corn yield increases in 2008, but not in 2009 (Laboski, unpublished data). In Illinois, there were no yield increases due to the use of Instinct with UAN over six site-years (Fernandez, 2010). Iowa (Killorn, unpublished data) and Minnesota (Randall, unpublished data) research also showed no yield increase with Instinct compared to N fertilizer alone.

Research on DCD, dicyandiamide, or cyanoguanidine, has shown that it can be used as a nitrification inhibitor, although research has generally shown that its activity may be shorter than nitrapyrin (Bronson et al., 1989). Products that contain DCD in the US include Super-U® (IMC Phosphate Company licensed exclusively to Agrotain International LLC) and Guardian® fertilizer additive (Conklin Company, Inc.). DCD contains about 67% N and was examined as an N source early in the last century (Reeves and Touchton, 1986). It was found to decrease crop yield when rates exceeded about 36 lb/acre (Cowie, 1918). The Guardian label recommends a 2% addition to fertilizer. The content of DCD in Super-U is not stated. It is unlikely that growers would over apply either product to the point of crop phytotoxicity. 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 either 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 1.

Table 1. 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
Sidedress	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

In contrast to the relatively low frequency of corn responses in the Midwest, potato responses were more consistently positive (Malzer et al., 1989).

The rate of ammonium-N remaining in the soil following ammonia application with both nitrapyrin and DCD treatments was explored at four Illinois locations by Sawyer (1985). Within 30 days of a fall application, there were no differences between the control and the DCD and nitrapyrin treatments in % remaining ammonium-N. In the spring, the DCD and nitrapyrin treatments provided greater % remaining ammonium-N compared to the control at 3 of 4 locations. The differences are presented in Figure 3 for the Urbana and Dekalb locations. Spring application of DCD and nitrapyrin was even more effective at some sites (Figure 4).

There is considerable interest in the use of nitrification inhibitors with liquid manure applications. 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).

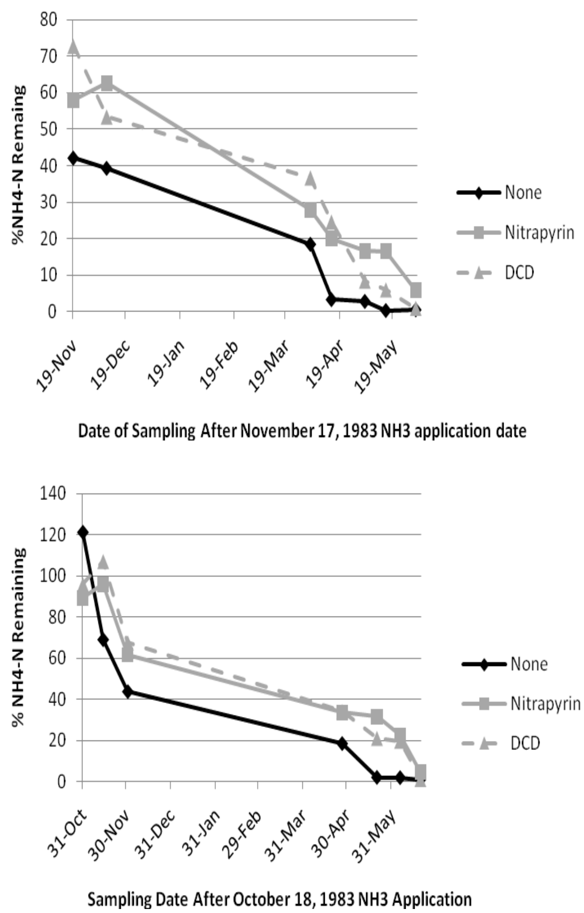

Figure 3. Percent NH_4-N remaining after fall NH_3 application at Urbana (left) and Dekalb (right) (from Sawyer, 1985).

Nitrification and urease inhibitors- the nitrification portion of activity or inactivity

Ammonium thiosulfate (ATS) and several additional commercial thiosulfates have nitrification (Goos, 1985; Janzen and Bettany, 1986) properties. In the process of identification of thiosulfates as nitrification inhibitors, it was 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 to nitrapyrin (Goos, 1985). Thiosulfate activity is regulated by its concentration (effective at S rates of 25 mg kg^{-1} (Goos and Johnson, 2001).

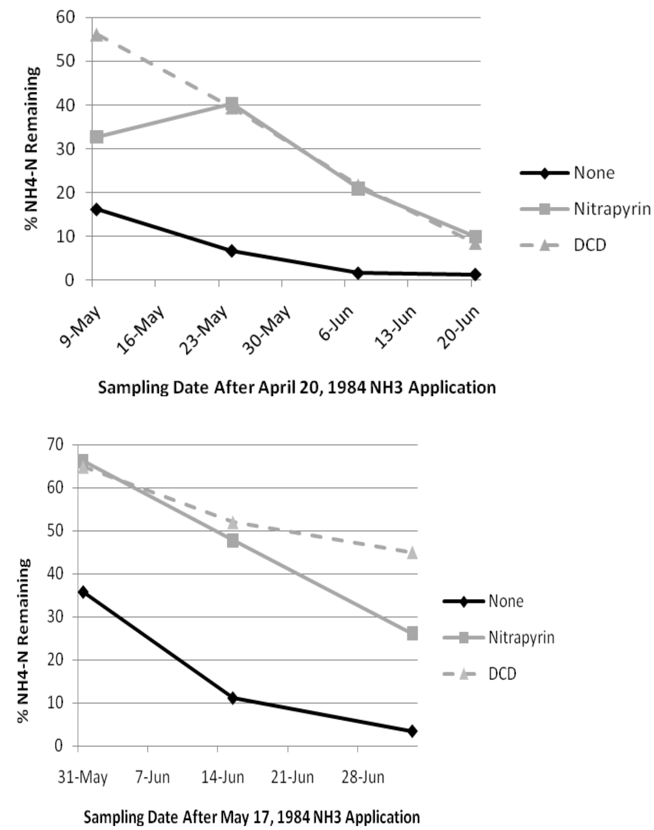

Figure 4. Percent NH_4-N remaining after spring NH_3 application at Monmouth (left) and Brownstown (right) (from Sawyer, 1985).

Thiosulfate readily breaks down rapidly in temperatures of 15^{o}C. In a laboratory study at 15^{o}C, ATS was essentially mineralized in about a week. Under cooler temperatures; however, significant thiosulfate remained after 2 weeks in two of three soils, with mineralization complete in all soils by week 3. When thiosulfate was placed in a band with aqua ammonia in the fall in North Dakota (October 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.

Cautions were expressed by Janzen and Bettany (1986) on high rates of banded ATS (over 100 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 radius 2 inches, which did not accumulate nitrite in the Janzen Bettany (1986) study. Recently, the use of thiosulfate has been reexamined. In Kansas, the application in the spring of a 5 and 10% calcium thiosulfate by volume solution with UAN had similar yield as urea broadcast in no-till (Tucker and Mengel, 2007).

Nutrisphere-N is a product marketed by SFP (Specialty Fertilizer Products) LLC, Leawood, Kansas. The formulation for dry fertilizer is a 30 to 60% maleic itaconic co-polymer calcium salt. The pH of the dry formulation is between 2.5 and 5 according to the label. The rate of use is 0.5 gallon per ton of urea/ammonium sulfate. The formulation for liquid fertilizer is a 40% minimum maleic-itaconic co-polymer. The pH of the liquid product is between 1 and 2 according to the label/MSDS. The rate of mixing with liquid N products is 0.5 gallon Nutrisphere-N per 99.5 gallons of fertilizer solution. A gallon of Nutrisphere-N liquid or dry formulation weighs 9.6 pounds per gallon. Nutrisphere-N is marketed as both a urease inhibitor and a nitrification inhibitor. Marketing literature explains that the activity of Nutrisphere on nitrification is related to its binding to copper ions necessary for the nitrification process in soil bacteria.

The most consistent yield increases and crop uptake of N from the use of Nutrisphere-N has been through work by Gordon (2008). In 2 years of corn at Scandia, KS and 2 years of grain sorghum at Belleville, KS, yield increases to the use of Nutrisphere-N were similar to those achieved with urea-Agrotain and ESN (Tables 2 and 3).

Table 2. Effects of N additive, averaged over source (UAN and urea) and N rate on corn grain yield, earleaf-N and grain-N, Scandia, KS (2-year average) (from Gordon, 2008).

Treatment	Yield, bu/acre	Earleaf N, %	Grain N, %
Check	152	1.72	1.13
Urea/UAN	168	2.57	1.26
ESN	185	2.96	1.33
Nutrisphere-N	183	2.96	1.35
Agrotain	183	2.98	1.36
LSD 5%	6	0.09	0.04

Table 3. Effects of N source and rate on grain sorghum yield, Belleville (2-year average) (from Gordon, 2008).

Treatment	N-rate, lb/acre	Yield, bu/acre
Check	0	71
Urea	40	108
	80	122
	120	128
ESN	40	120
	80	130
	120	132
Urea + Agrotain	40	116
	80	129
	120	133
Urea+ Nutrisphere	40	120
	80	133
	120	132
LSD 5%		5

The consistent results from Gordon (2008) are very curious considering that careful laboratory experiments by Goos (2008; 2012) have shown that Nutrisphere-N has no nitrification ability (Figures 5 and 6).

To test these products for nitrification, another incubation study was conducted (Goos, 2012). Urea treated with Instinct (Nitrapyrin) (Figure 5) and Super U (containing DCD) decreased nitrification, while all other treatments had no effect. In another series of experiments, (Goos, unpublished data) showed that the mode of action claimed for any urease activity by Nutrisphere was flawed.

It is clear from the laboratory experiments that there is no nitrification inhibition by Nutrisphere when used at label rates. Goos observed some small nitrification inhibition when the Nutrisphere for liquid fertilizer is applied in a concentrated band. He attributes this to the strong acidity of the liquid formulation, and not to the Nutrisphere itself (Goos, personal communication, 2010). Acid conditions are known to inhibit nitrification bacteria (Schmidt, 1982).

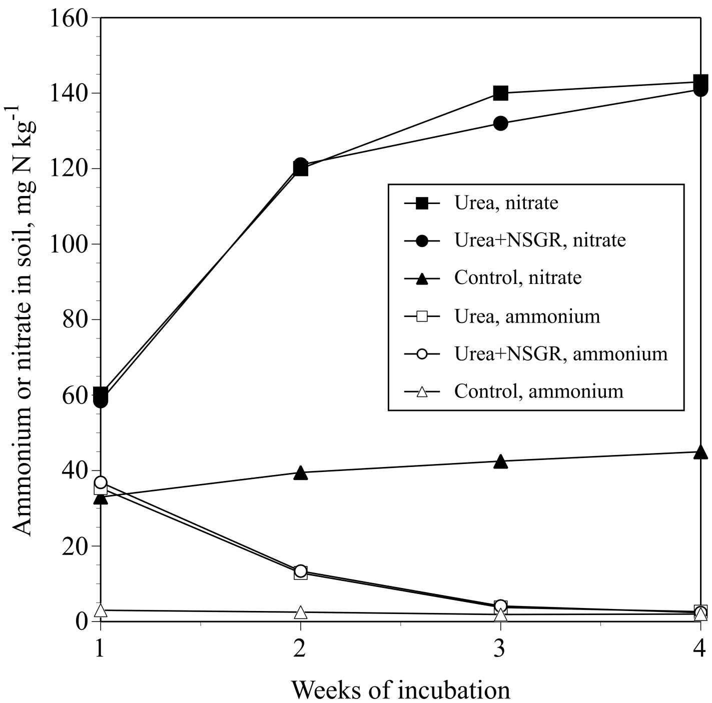

Figure 5. Ammonium and nitrate in a Renshaw soil as influenced by length of incubation and application of urea granules, and urea granules treated with Nutrisphere-N for granular fertilizers (NSGR) (experiment by R.J. Goos; cited in Franzen et al., 2011).

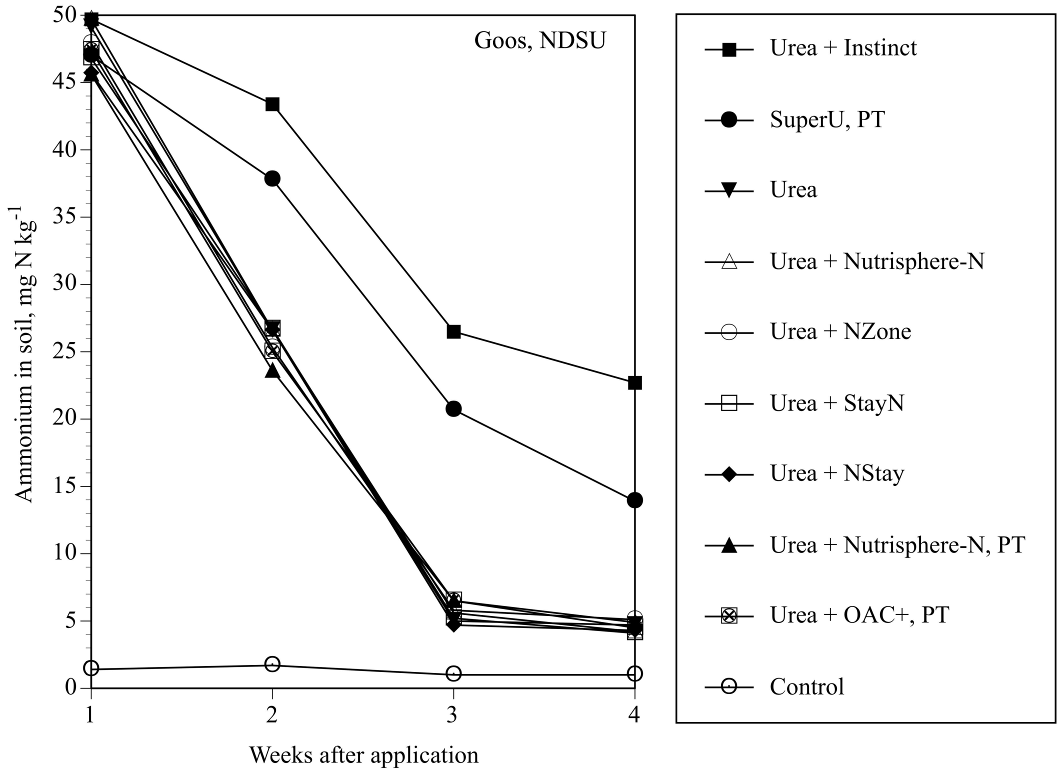

Figure 6. Residual ammonium in a sandy loam soil incubated with urea granules, or urea granules treated with various additives. PT=granules received pretreated, other additives applied to urea by the researcher (from Goos, 2012).

In the field, it is uncommon to consistently find yield or quality responses to the use of Nutrisphere at labeled rate. In North Dakota studies on spring wheat at 8 locations, there were no yield increases or grain N uptake increases with Nutrisphere compared to urea (Franzen et al., 2011). Two additional North Dakota studies on corn showed no yield increase with the use of Nutrisphere (NDSU Carrington Research and Extension Center, unpublished data). In Kansas (Tucker and Mengel, 2008), there were no increases due to Nutrisphere with UAN over UAN surface banded or injected in grain sorghum in 2007. In two years of corn in Kansas, there were no yield increases from the use of Nutrisphere-N UAN compared to surface applied UAN at three total sites (Weber and Mengel, 2009). In 2009, there was no response to Nutrisphere + UAN broadcast on grain sorghum compared to broadcast UAN alone in Kansas at three locations (Weber and Mengel, 2010). There was one sorghum yield increase with surface banded Nutrisphere + UAN compared to UAN surface banded alone and two non-responsive sites. The yield increase with surface band but not broadcast suggests that perhaps the acidity of the Nutrisphere may have delayed nitrification at this site (Schmidt, 1982).

At Waseca, MN in 2009, there was no corn yield difference between urea and urea with Nutrisphere applied in the fall (Randall and Vetsch, 2009). Grain and stover N between urea and urea with Nutrisphere were similar. In Illinois, at two locations in 2008

Nutrisphere-urea was lower in yield than urea, and similar in yield at the two locations with UAN and Nutrisphere-UAN (Ebelhar and Hart, 2009). At Dixon Springs in 2009, Nutrisphere urea, UAN, and ammonium sulfate treatments did not result in higher corn yield than the N sources with Nutrisphere-N (Ebelhar and Hart, 2010), although main effects for Nutrisphere-N on corn yield were significant. In Arkansas and Mississippi, Nutrisphere-N had no effect on rice yields in three field studies compared with urea (Franzen et al., 2011). In South Dakota, Nutrisphere-N did not result in higher corn yield in 2007 (Bly and Woodard, 2007), 2008 (Bly et al., 2008), or 2009 at 2 sites (Bly et al., 2009).

In Idaho, there were no spring wheat yield increases with Nutrisphere over 2 years (Jeffrey Stark, personal communication, 8/23/2010). In barley, however, there were yield increases in 2008 and 2009 with Nutrisphere, but no increase in grain protein over similar rates of urea. Plant N uptake with Nutrisphere was similar to urea without Nutrisphere, suggesting that the yield increase in barley came from some other response other than enhanced N nutrition (Stark, 2008; 2009).

Laboratory studies with Nutrisphere-N show no effect on nitrification or urease activity. Therefore, it is not surprising that the great majority of studies with Nutrisphere show no yield effects. What is surprising is that there are studies that show yield effects, but not from increased N nutrition. The results from Gordon (2008) suggest that under some conditions, Nutrisphere may have some effect on plant growth and development and even N nutrition not related directly to urease inhibition or nitrification. However, the company probably needs to reexamine its label as a nitrification inhibitor and urease inhibitor.

Summary

Certain nitrogen additives provide growers with options for extended activity of nitrogen nutrition for their crops. Their economics depends on rainfall following application, application methods, timing and soil characteristics, especially soil texture. Nitrapyrin has been effective in delaying nitrification. Dicyandiamide (DCD) has also been shown to be effective in delaying nitrification. Thiosulfates have been shown to delay nitrification, but the body of literature to support their use is much smaller than that of nitrapyrin. NBPT (Agrotain) is an effective urease inhibitor. Thiosulfates have shown some urease inhibition characteristics, but again, the body of literature that supports their use is small.

Nutrisphere has been shown to be ineffective as both a nitrification and urease inhibitor. The data that support the use of Nutrisphere is small in comparison to the data that does not support its use. If one accepts that the laboratory studies, conducted in a similar manner to those used to evaluate products like nitrapyrin of DCD containing products, show that Nutrisphere is not a nitrification or a urease inhibitor, than there must be other explanations for small number the field studies that show a yield benefit to the use of the product and in some circumstances even show an accumulation of N. The very acidic nature of the liquid formulation of Nutrisphere suggests that in banded applications, the nitrification delay may be associated with the acidity of the solution more than the Nutrisphere itself. Other new products, including Stay-N, NStay and NZone have failed to support their claims as nitrification inhibitors in careful laboratory experiments.

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