

Nitrogen Fertilizer Additives

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Introduction

Nitrogen is by far the most extensively applied fertilizer for agronomic crop production in Arkansas. Urea [$\text{CO}(\text{NH}_2)_2$] and urea-ammonium nitrate fertilizers are the most commonly used nitrogen fertilizers in Arkansas because of their low price and high nitrogen analysis relative to most other nitrogen fertilizers. Urea-nitrogen is subject to volatilization loss as ammonia (NH_3) gas if not properly incorporated shortly after application. Once incorporated into the soil, urea and other ammonium-forming (NH_4^+) nitrogen fertilizers will eventually be converted to nitrate (NO_3^-), which is prone to leaching and/or denitrification. For more information on the nitrogen cycle, refer to Extension fact sheet FSA2148, *The Nitrogen and Phosphorus Cycle in Soils*. This fact sheet will review the University of Arkansas System Division of Agriculture's current knowledge base on nitrification and urease (or ammonia volatilization) inhibition as it concerns when nitrogen fertilizer additives should be used and their effectiveness.

What Are Nitrogen Fertilizer Additives?

Nitrogen fertilizer additives are substances added to a water-soluble or readily available fertilizer that extend the time a particular form of nitrogen remains in the soil. Nitrogen fertilizer additives are added to nitrogen fertilizer by the manufacturer when the nitrogen fertilizer is made or by the applicator shortly before the fertilizer is applied to the field. In most cases, these products temporarily inhibit or

delay, but do not permanently prevent, a specific process of the nitrogen cycle.

The emphasis on responsible and efficient nutrient management is now greater than ever. The development of conservation programs that offer partial payment for farmers to implement efficient nutrient management practices and the rising cost of fertilizers make products that stabilize fertilizer nutrients a lucrative market. Reducing soil and fertilizer nitrogen movement from agricultural fields into the surrounding landscape has both environmental and agronomic benefits and has led to the marketing of a number of products that claim to 'stabilize' nitrogen. Many of these products are unproven in laboratory and field research conducted by unbiased and knowledgeable researchers. Oftentimes, these products are aggressively marketed with well-designed advertisements, informational brochures and web sites but lack specific information regarding their mechanisms or modes of action that explain how they 'stabilize' nitrogen (or other nutrients). Although some products provide a mode of action with wording that includes scientific terms, the wording is usually vague and lacks scientific support.

The use of legitimate nitrogen fertilizer additives does not guarantee that maximum crop yield can be produced with lower nitrogen rates. While the use of lower nitrogen rates to produce maximum yield is a possible outcome, the expected benefits of additives occur when conditions exist for significant loss of the nitrogen in conventional fertilizers via ammonia

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volatilization and/or leaching, runoff and denitrification of nitrate. Unfortunately, the frequency and magnitude of nitrogen losses cannot always be predicted since they are often the result of weather-related events.

Nitrification Inhibition

Nitrification is the two-step microbial process that converts ammonium (NH_4^+) into nitrite (NO_2^-) and eventually into nitrate (NO_3^-). The first step of the process is performed by specific ammonia-oxidizing bacteria (*Nitrosomonas* spp. being the most common one) and the second step by nitrite-oxidizing bacteria (*Nitrobacter* spp.). Ammonium and nitrate are both plant-available nitrogen forms, but ammonium is the more stable nitrogen form in the soil. Ammonium is a cation and can be retained by the soil's cation exchange properties, making it far less mobile than nitrate, an anion. Nitrate is susceptible to loss by runoff, leaching in permeable soils (sands and sandy loams) and denitrification [reduction to nitrous oxide (N_2O) and dinitrogen (N_2) gasses] in poorly drained soils when anaerobic soil conditions persist. Applying ammonium or an ammonium-forming nitrogen fertilizer is desirable since ammonium is less susceptible to denitrification and leaching losses. Eventually, however, the nitrification process converts ammonium supplied from fertilizer or mineralized from organic matter, manures or biosolids into nitrate.

The requirements for nitrification are ammonium, a population of nitrifying organisms, oxygen and a suitable environment (e.g., pH, temperature and moisture). The nitrification process is affected by soil chemical and physical properties associated with different soils. In general, nitrification increases as soil temperature, moisture and pH increase. Near optimal soil conditions for nitrification include a temperature range of 77-95°F, soil moisture near field capacity and pH near 8.0. The nitrification process is very slow or negligible at soil temperatures

<40°F, and soil bacteria become inactive when the soil becomes very dry. The nitrification process ceases under anaerobic (saturated) soil conditions, such as when the permanent flood is established on a rice field.

Laboratory incubation experiments using Memphis (6.4 pH) and Calhoun (7.5 pH) silt loams show the effect that three constant temperatures had on the nitrification rate of urea fertilizer when soil moisture was near optimal (20 percent moisture, -85 kPa; Figure 1). In both soils,

soil microbial activity was negligible at the lowest temperature, and all of the nitrogen added as urea remained as ammonium for 28 days. For the Memphis soil, nearly all of the added urea-nitrogen had been converted from ammonium to nitrate by 14 days at 77°F and 28 days at 59°F. Nitrification was slightly more rapid in the Calhoun soil with most of the added urea-nitrogen converted from ammonium to nitrate by 14 days at 77°F and 21 days at 59°F. Average soil temperatures in Arkansas are warm enough for nitrification from

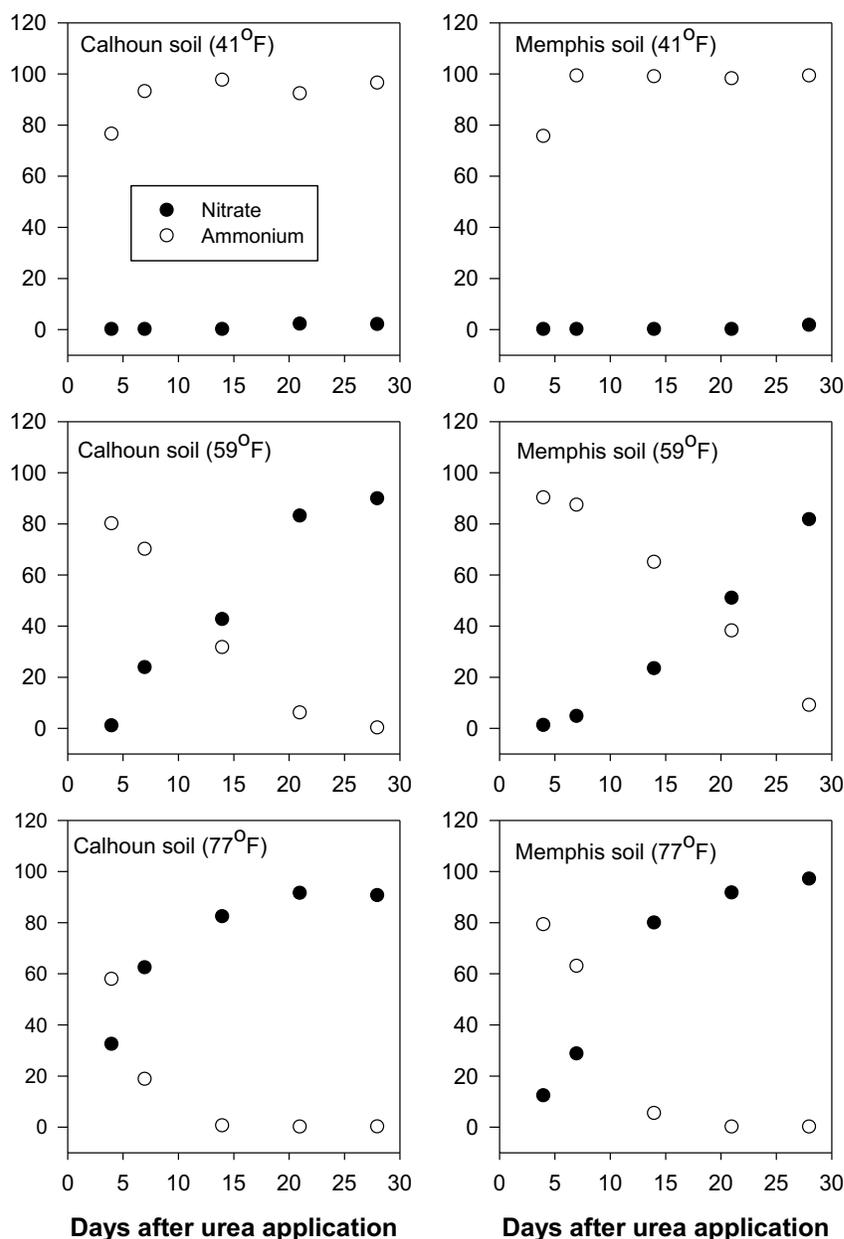


Figure 1. The effect of three temperatures (laboratory incubation) and time on the proportions of soil nitrate and ammonium (nitrification) for 28 days following urea fertilizer application on Calhoun (pH 7.5) and Memphis (pH 6.4) silt loam soils.

March through November of most years (Table 1).

Nitrification inhibitors are chemicals that temporarily delay or slow nitrification by affecting the activity of the *Nitrosomonas* spp. bacteria. Nitrification inhibitors have been used mostly in the Midwest for fall application of anhydrous ammonia. Generally, nitrification inhibitors have not been used extensively in the mid-South and southern United States because they have not been highly effective. By 'highly effective' we simply mean that the length of time these products delay/slow nitrification has not offered a significant nitrogen management advantage across a wide array of soils. Preliminary results from recent laboratory experiments have shown that dicyandiamide (DCD) and nitrapyrin (Corteva Agriscience, Indianapolis, Indiana) have effectively delayed nitrification on some soils, but had little or no effect on the nitrification rate of other soils (Table 2). For example, the DCD in Super U (Koch Fertilizer, LLC, Wichita, Kansas)

had little or no effect on the amount of ammonium remaining after 10 days for the Calhoun soil but delayed nitrification in the DeWitt and Henry soils. Additional research is needed to identify the soil characteristics that would allow us to accurately predict whether a nitrification inhibitor would be of significant benefit in slowing the conversion of ammonium to nitrate and thus reducing nitrate-nitrogen losses.

Nitrogen management strategies for corn, cotton, grain sorghum, rice and wheat in the mid-South usually involve split applications with the majority of the nitrogen fertilizer side-dressed near the onset of rapid crop growth. These nitrogen management strategies minimize the potential benefits of a legitimate nitrification inhibitor. However, there is still interest and a place for nitrification inhibitors in our nitrogen management systems, especially on sandy-textured soils and for nitrogen that is applied preplant. The ability to apply a greater proportion of nitrogen fertilizer preplant or weeks in

advance of planting would be advantageous for many growers. University researchers will continue to evaluate potential nitrification inhibitors under laboratory and field conditions and incorporate legitimate nitrification inhibitors into nitrogen management recommendations when appropriate. The legitimacy of a product's claim as a nitrification inhibitor can be quickly and efficiently examined in the laboratory before it is field tested.

Several products (active ingredients) are currently recognized as legitimate and documented nitrification inhibitors; however, our discussion here will concern dicyandiamide (DCD) and nitrapyrin, the two nitrification inhibitors being marketed in Arkansas and surrounding states. The active ingredients in these products have proven to be effective at inhibiting nitrification in industry and university research, which has been peer reviewed and published in refereed journals. The process (e.g., mode of action) by which a chemical inhibits

Table 1. Average monthly soil temperatures (4-inch depth of bare soil) during 2009 and 2010 for three sites in eastern Arkansas.

Site	Month												
	Year	Jan	Feb	Mar	April	May	June	July	Aug	Sept	Oct	Nov	Dec
Rohwer (Gallion sl)	2009	40.8	43.2	49.5	56.1	64.7	73.8	75.8	75.8	71.8	56.6	49.4	42.0
	2010	37.8	37.5	42.5	61.7	72.2	83.6	82.3	md†	md	md	52.1	42.0
Marianna (Calloway sl)	2009	42.0	46.6	53.1	51.7	72.0	83.5	83.6	84.9	79.5	63.3	57.1	43.9
	2010	40.8	40.1	51.5	66.2	76.1	87.7	88.8	90.8	82.2	70.4	56.1	42.9
Keiser (Sharkey cl)	2009	38.3	44.1	50.1	58.4	69.7	78.3	81.6	81.0	75.9	60.6	53.8	41.3
	2010	38.3	36.2	49.1	63.2	72.5	85.5	87.7	90.7	80.1	67.5	52.5	40.1

† Missing data.

Table 2. The net percentage of urea or Super U fertilizer remaining as ammonium after 10 and 20 days in three silt loam soils incubated at 77°F and 25% gravimetric soil moisture (Golden et al., 2009).

N fertilizer	Month	Soil†		
	Time (days)	Calhoun series	DeWitt series	Henry series
		% of added fertilizer present as ammonium		
Urea	10	<1	36	11
	20	0	4	<1
Super U	10	8	77	54
	20	0	65	49

† Soil properties: 1.0% total C, 0.10% total N, and soil pH values of 6.2 (DeWitt), 7.3 (Henry) and 7.6 Calhoun.

nitrification can differ. For example, the inhibitor nitrapyrin is a bactericide and has been registered with the EPA as a pesticide since 1974. Dicyandiamide, on the other hand, is not a bactericide and is not required to be registered with the EPA. The mode of action of DCD is by inhibition of *ammonium monoxygenase*, an enzyme required by ammonia-oxidizing bacteria to metabolize ammonium into nitrite.

Nitrapyrin (also called Optinyte™) is the active ingredient in N-Serve and Instinct formulations. Instinct formulations contain an encapsulated form of nitrapyrin used with UAN, urea or liquid manure, whereas N-Serve is used exclusively with anhydrous ammonia. Encapsulation allows Instinct formulations to be impregnated onto the surface of granular (ammonium) fertilizers or to be spray applied to the field without immediate volatile loss of the active ingredient. Dicyandiamide is the active ingredient in Agrotain Plus, Super U (Koch Fertilizer, LLC, Wichita, Kansas), and the product sold as Guardian (Conklin Company, Inc., Shakopee, Minnesota) and is applied directly onto or incorporated into the fertilizer granule or solution. A number of other products that have shown to be effective nitrification inhibitors have been registered previously or are available in other countries. The publication entitled *Nitrification Inhibitors for Corn Production* (<http://www.extension.iastate.edu/publications/NCH55.pdf>) provides a list of product trade and chemical names and gives an excellent review on the use of nitrification inhibitors.

Ammonia Volatilization Inhibition

Ammonia (NH₃) volatilization is a soil surface loss mechanism that may occur when an ammonium or ammonium-forming fertilizer is surface applied and not incorporated immediately. All ammonium fertilizers can to some degree be lost via ammonia volatilization, but since the first

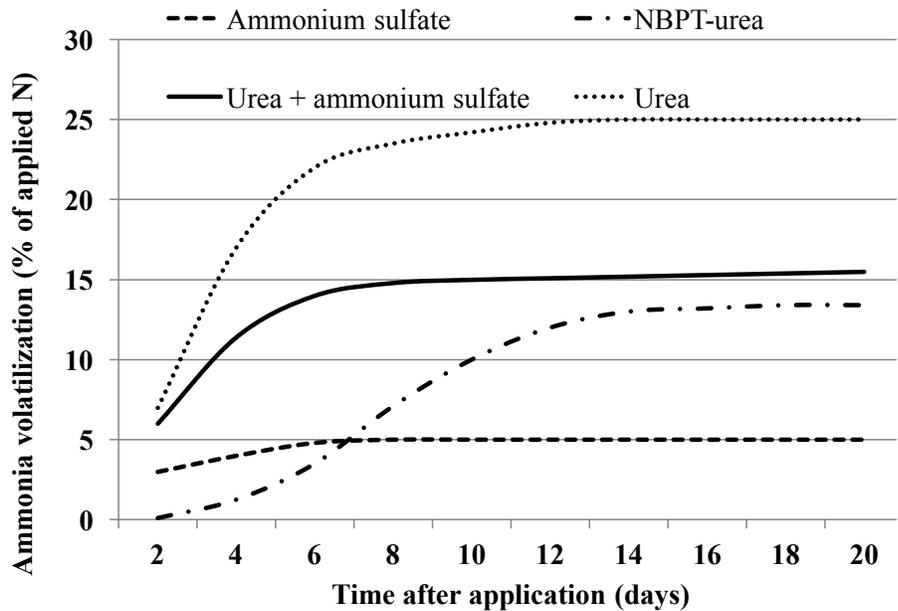


Figure 2. Ammonia volatilization losses of urea, NBPT-treated urea, ammonium sulfate and a urea/ammonium sulfate blend on a Calloway silt loam. Flood was applied on day 10. (Norman et al., 2009)

reaction in the hydrolysis of urea is alkaline forming, urea-containing fertilizers are more prone to loss by this mechanism than ammonium sulfate [(NH₄)₂SO₄] which is an acid-forming nitrogen fertilizer. Urea nitrogen when applied to a soil is hydrolyzed by the urease enzyme (urea amidohydrolase) and converted first to ammonium carbonate [(NH₄)₂CO₃] and then to ammonia gas. Urease is everywhere in the environment and can be found in soils, manures, on plants and plant residues. The urease enzyme is believed to be released to the environment from living and disintegrating microbial cells.

Losses of urea as ammonia gas increase as wind speed, soil moisture, humidity (>70 percent), soil pH and temperature increase. Under warm (spring and summer) conditions, urea needs to be incorporated with tillage, rainfall (>0.5 inch rainfall) or irrigation within 2 days following application to significantly reduce gaseous ammonia loss. Ammonia volatilization loss of surface-applied urea to a dry silt loam soil can reach 20 percent to 30 percent in 5 days when the temperature exceeds 75-80°F (Figure 2). The speed of the urea-urease reaction decreases

as temperature declines, and thus there should be less ammonia volatilization loss of urea when applied in the winter to wheat compared to in the spring or summer to corn, cotton, grain sorghum or rice. Ammonia volatilization loss of urea is much more rapid and extensive when urea is applied at high rates or to a muddy silt loam soil compared to a dry silt loam soil (Figure 3). Also, the ammonia loss potential tends to be lower in clayey soils because of their higher cation exchange capacity compared to silt or sandy loam soils (Figure 4).

One approach to reduce potential ammonia volatilization loss of urea when immediate incorporation is not possible is to amend urea or urea-ammonium-nitrate with a chemical that inhibits or slows urease activity, or conversion of urea to ammonia gas. A urease inhibitor allows the urea prill time to dissolve and move into the soil before hydrolysis to ammonia occurs or allows time to be incorporated either mechanically or by water (e.g., irrigation or rain). Enabling the urea to hydrolyze to ammonia after it has been dissolved or moved into the soil allows the ammonia produced from the urea to acquire a hydrogen (H+) atom from the soil and

become ammonium (NH₄⁺), which is a salt that is retained by the soil's cation exchange properties. Only a few chemical compounds have been shown to effectively

inhibit urease activity. While all the compounds listed in Table 3 can minimize ammonia volatilization of urea, the compound N-(n-butyl) thiophosphoric

triamide (NBPT) is the only one that has seen widespread implementation on a commercial scale and has substantial published literature to support its efficacy. The patent on NBPT has expired (circa 2002), allowing a number of companies to develop and market their own products that include NBPT. The urease inhibitor NBPT is the active ingredient in several products that have proven to reduce ammonia loss of urea in unbiased research. BASF released the product Limus which contains both NBPT and NPPT (N-(n-propyl) thiophosphoric triamide). The Limus product has been shown to effectively reduce ammonia volatilization from urea, but to our knowledge NPPT has not been tested as a stand-alone product.

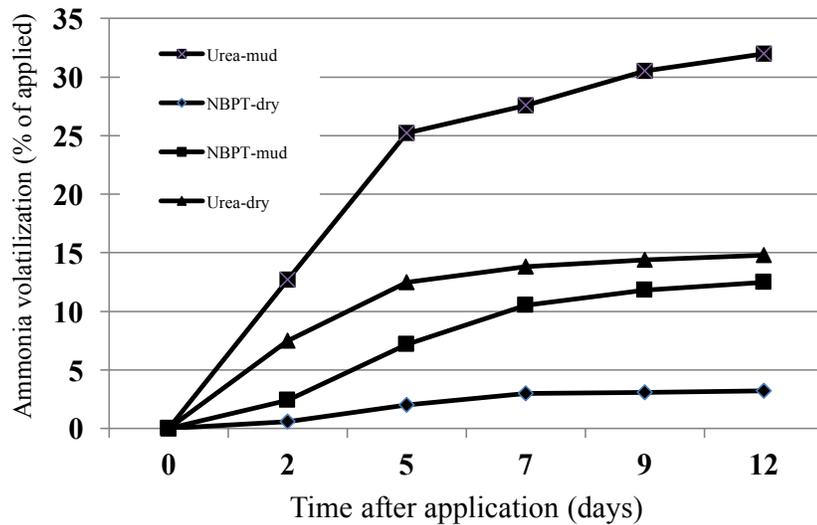


Figure 3. Ammonia volatilization losses when urea and NBPT-treated urea were applied to a dry or muddy soil 5 days prior to flooding. (Norman et al., 2006)

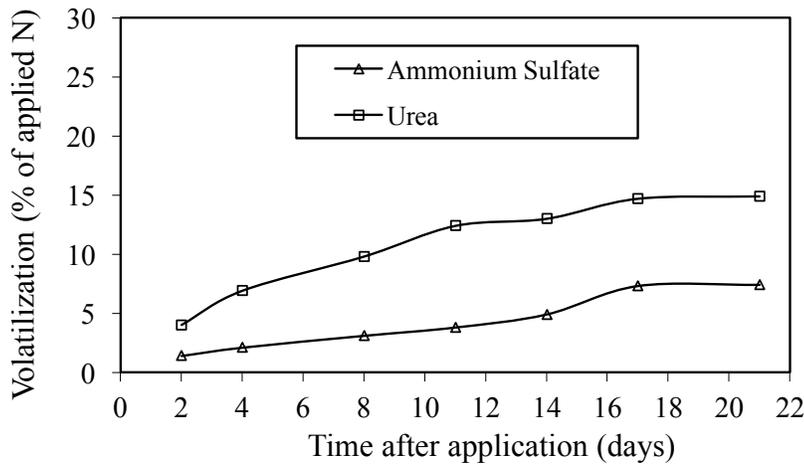


Figure 4. Ammonia volatilization loss of urea and ammonium sulfate when applied to a Perry clay. (Griggs et al. 2007).

Table 3. Documented Urease Inhibitors

Abbreviation	Name of Active Ingredient
NBPT	N-(n-butyl) thiophosphoric triamide
NPPT	N-(n-propyl) thiophosphoric triamide
PPD	phenylphosphorodiamidate
TPT	thiophosphoryl triamide
ATS	ammonium thiosulfate
TU	thiourea
MU	methyl urea

Table 4. Rice grain yield when urea, NBPT-treated urea, ammonium sulfate (AS) and a urea/AS blend (1:1 urea/AS blend on a N weight basis) were applied 1, 5, and 10 days before flooding. (Norman et al., 2009)

N Source	N rate	Application Time (days before flooding)		
		1	5	10
	pounds N/A	bushels per acre		
Urea	120	187	160	154
Urea + NBPT		188	182	175
AS		181	178	171
Urea/AS blend		179	166	161
LSD (0.05)		8.6		

A good number of trials have been conducted in Arkansas that have consistently shown the effectiveness of NBPT in reducing ammonia volatilization losses from surface-applied urea when conditions for ammonia volatilization were present. Table 4 shows rice grain yield as affected by flooding 1, 5 and 10 days after urea or NBPT-treated urea were applied to the dry surface of a Calloway silt loam. Results from this study underscore the importance of timely soil incorporation of the urea fertilizer and utility of NBPT when timely incorporation is not possible. When flooding was conducted the day after N fertilizer application, rice fertilized with urea produced a

grain yield similar to NBPT-treated urea. However, rice grain yield significantly decreased when the flood was delayed until 5 days after application when urea was the N source, but not when NBPT-treated urea was the N source. Rice grain yield for all of the N fertilizer sources significantly decreased when the flood was further delayed until 10 days compared to 1 day, but more so for urea compared to NBPT-treated urea. Research in Arkansas shows that under warm/summer conditions, ammonia loss from surface-applied urea occurs most rapidly the first 5 days after application to a silt loam (Figure 2) and the first 10 days when applied to a clay soil (Figure 4). The use of NBPT can help minimize urea loss via ammonia volatilization when applied to a muddy soil; however, every effort should be made to apply urea to a dry soil even when NBPT is used.

A number of NBPT-containing products are now available for adding to urea and UAN fertilizers. These products may contain different amounts of the active

ingredient NBPT. The concentration of each individual ingredient is typically given on the product label. However, some NBPT-containing products have elected to not show the specific concentration of NBPT on the label, which makes it difficult to compare the cost and potential effectiveness among products applied at equal NBPT rates. A limited amount of research has shown that the duration and magnitude of urease inhibition is dependent on NBPT rate, which makes knowledge of a product's NBPT concentration critical. Application of the proper NBPT rate to urea or urea-ammonium-nitrate fertilizer is important and assumes that the ability of NBPT to inhibit ammonia volatilization is not affected by the other ingredients that may be included in the actual product or other products (other inhibitors and drying agents) that may also be added to the fertilizer. Manufacturers of NBPT-containing products are encouraged to list the concentration of each individual ingredient including NBPT on the label. The most common recommended NBPT

application rate ranges from 1.3 to 1.8 pounds NBPT per ton of urea which is equivalent to the addition of 0.065 to 0.09 percent NBPT by weight. Note that the NBPT application rate for urea-ammonium-nitrate fertilizer is different than that for granular urea.

Farmers have adopted the use of NBPT as a management tool for surface-applied urea, particularly in rice fields where establishing a flood in 2 days or less is difficult, or in upland crops where urea may remain on the soil surface for extended periods of time following application (e.g., not incorporated by tillage or irrigation). The high adoption rate of products containing NBPT has stimulated the marketing of numerous products with claims of similar benefits (i.e., reducing ammonia volatilization). Before the University of Arkansas System Division of Agriculture recommends a product that claims to have inhibitory effects on the enzyme urease or simply "ammonia volatilization loss of urea" the products must be subjected to a laboratory test, which measures ammonia

Table 5. List of tested and recommended NBPT-containing urease inhibitors (based on product labels available in March, 2019) and suggested application rates for urea and urea-ammonium-nitrate (UAN).

Product Name	Manufacturer	Weight Per Gallon lb/gallon	NBPT Concentration %	Recommended Volume†	
				Urea	UAN
				qt/ton fertilizer	
Agrotain Advanced	Koch Fertilizer, LLC	8.87	30	2.0	1.0
Agrotain Ultra	Koch Fertilizer, LLC	8.84	26.7	3.0	1.5
ANVOL‡	Koch Fertilizer, LLC	9.26	16	1.5	0.75
Arborite AG-NT	Weyerhaeuser NR Co.‡	9.15	24.0	3.0	1.5
ContaiN	AgXplore	8.5	unknown§	4.0	2.0
Factor	Rosen's, Inc.	9.09	24.5	3.25	1.625
Limus	BASF	9.06	16.88#	3.0	1.5
N-Fixx PF	Helena Chemical	8.50	unknown§	3.0-4.0	1.5-2.0
Nitrain	Loveland Products	8.93	26.7	3.0	1.5-2.8
Nitrain Express	Loveland Products	8.99	24.8	3.0	1.5
N-Veil	Invictis Crop Care, LLC	8.92	26.7	3.0-4.0	2.0-3.0
PinnitMax	Corteva Agriscience	9.26	50	1.5	0.75

† One ton of fertilizer approximates 181 gallons of 32% UAN and 187 gallons of 28% UAN.

‡ Arborite AG-NT (Nitrolock Technology) distributed by Gavilon Fertilizer

§ Unknown, the product label does not specify the concentration of NBPT in the product.

Limus contains 16.88% NBPT and 5.63% NPPT, which is a proprietary urease inhibitor owned by BASF.

¶ ANVOL contains 16% NBPT and 27% duromide which has also been shown to reduce ammonia volatilization loss.

volatilization from urea amended with the commercial product of question compared to the volatilization losses of urea and NBPT-treated urea. At the time of the writing of this fact sheet, only the NBPT-containing products listed in Table 5 have been tested and shown to effectively inhibit ammonia volatilization from urea when applied at 0.08 to 0.09 percent NBPT.

An alternative to NBPT-treated urea for minimizing ammonia volatilization losses is the use of ammonium sulfate. Ammonium sulfate is much less prone to ammonia volatilization loss compared to urea due to its slightly acidic properties (Figures 2 and 4). Fertilization with ammonium sulfate can result in grain yields similar to NBPT-treated urea when conditions are conducive for ammonia volatilization loss (Table 4). Also, when sulfur is required in addition to nitrogen, supplying a portion of the fertilizer-N as ammonium sulfate is logical. Shortcomings of ammonium sulfate are that it typically costs considerably more than urea, on a N weight basis, and the lower N analysis of ammonium sulfate compared to urea may increase application expenses. Ammonium sulfate is typically not used solely as the pre-flood N source for rice, but is often blended with urea to offset some of the costs and still possibly gain some of the beneficial effects of the ammonium sulfate, such as plant-available sulfur. Although

blending ammonium sulfate with urea can lower total ammonia volatilization loss (Figure 2), the decrease in ammonia loss from the blend may not be enough to result in significantly greater grain yields compared to urea nor grain yields similar to ammonium sulfate or NBPT-treated urea (Table 4).

Summary

- Nitrification inhibitors delay the conversion of ammonium to nitrate by temporarily inhibiting the activity of *Nitrosomonas* bacteria and have the potential to reduce nitrate leaching and denitrification losses. However, the longevity and effectiveness of nitrification inhibitors in the mid-South are limited due to the warmer climate (compared with the Midwest).
- Research of nitrification inhibitors will continue in the hope of understanding the soils, crops and situations where and when they can be of benefit in the mid-South. The use of best management practices, such as split applications and specific application timings of nitrogen fertilizer, should be used until we better understand when a nitrification inhibitor is a viable option.
- Urease inhibitors work on the enzyme urease, which is responsible for the conversion of urea to ammonium.

During this process, nitrogen can be lost by volatilization of ammonia gas if the urea is not properly incorporated soon after application. Ammonium sulfate is less prone to ammonia volatilization loss compared to urea and is an alternative to NBPT-treated urea.

- The only documented urease inhibitors being marketed at the time this information was prepared contain NBPT, the active ingredient in the products listed in Table 5. The most common recommended NBPT application rates range from 1.3 to 1.8 pounds NBPT per ton of urea which is equivalent to the addition of 0.065 to 0.09 percent NBPT by weight. Caution should be exercised when using products that do not list specific NBPT concentrations on the label.
- NBPT-treated urea should be used if >2 days are required for incorporation on a silt loam soil and when >7 days on a clay soil.
- Any other purported N stabilization products that claim inhibition of ammonia volatilization of urea cannot be recommended for use because we have tested them and they do not inhibit this process, we have not tested them or we are currently testing them.

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