

NITROGEN INHIBITORS: HOW DO THEY WORK TO REDUCE N LOSSES?



Abstract

Applying nitrogen (N) fertilizer at the exact time of need is often operationally unrealistic for wheat growers in Washington. Instead, N is commonly applied early, before its rapid uptake by plants. However, this practice may result in reduced return on investment and increased environmental risks associated with N loss through runoff, leaching, volatilization, and denitrification. Nitrogen inhibitors are products that temporarily retard conversion of fertilizers to the forms that can be lost through these pathways.

This publication describes how N is lost after fertilizer applications, how N inhibitors can reduce such losses, and how to choose the right product for the forms of your fertilizers and application timings.

Introduction

Nitrogen (N) is an essential nutrient for plant yield and quality. Soil can provide plant N through organic matter mineralization, some deposition during rainfall events, and residual inorganic-N in soil. However, crops often need more N to produce the yield and required quality. As such, N fertilizers, mainly inorganic commercial fertilizers, are a major N source in crop production (Table 1).

Optimizing N availability ensures maximum yield and appropriate protein content and other quality factors in grains. However, achieving the right amount of N availability for a crop is difficult because N is subject to loss through various pathways. These including ammonia (NH_3) volatilization, denitrification, nitrate (NO_3^-) leaching, and runoff (Table 2). In addition, N can also be chemically fixed by soil minerals when ammonium (NH_4^+) is trapped in the interlayers of clay minerals. The amount of N loss from soils can range from 30 to 70%, depending on weather, soil type, field management, and N

Table 1. Common fertilizer N sources in Pacific Northwest dryland cropping systems and their chemical composition.

Fertilizer sources	Chemical composition
Urea	$\text{CO}(\text{NH}_2)_2$
Anhydrous ammonia	NH_3
Aqua ammonia	NH_3 solution
Ammonium nitrate	NH_4NO_3
Ammonium sulfate	$(\text{NH}_4)_2\text{SO}_4$
Urea ammonium nitrate (UAN)	$\text{CO}(\text{NH}_2)_2$ & NH_4NO_3 solution

management practices (e.g., rate, form, timing, and method of N application) (Boyer et al. 2002; Raun and Johnson 1999). The wide range in potential N losses results in a great deal of uncertainty of N availability, which in turn, makes it difficult for farmers to make decisions on N applications.

Nitrogen losses can be reduced by synchronizing N availability with the optimal period of plant uptake. This synchronization is challenging, because substantial N loss from crop fields is a result of management in addition to unpredictable weather, especially precipitation, temperature fluxes, and wind. Nitrogen inhibitors are products that temporarily retard conversion of fertilizers to the forms of N that can be lost through volatilization, leaching, and denitrification. Many products have been tested with varying levels of success worldwide on a range of major crops (Franzen 2011). Many research studies have concluded that the use of some N inhibitor products can significantly reduce N loss, although there are mixed results for yield increase (Burzaco et al. 2014; Dell et al. 2014; Kyveryga and Blackmer 2014; Harris et al. 2013; Zaman et al. 2013; Watts et al. 2014).

Table 2. Nitrogen loss mechanism definitions.

Loss mechanism	Definition
Ammonia (NH ₃) volatilization	Loss of N as gaseous NH ₃ from soil to atmosphere
Denitrification	Loss of N as gaseous NO _x and N ₂ form (converted from NO ₃ ⁻ under anaerobic conditions) from soil to atmosphere
Leaching	Loss of N as NO ₃ ⁻ moves deeper than root zone as water moves through the soil profile
Runoff	Loss of N through surface water runoff

The objective of this article is to summarize how N inhibitors affect N cycling, explain the types of N inhibitors and how they work, and describe under what conditions N inhibitors have the most potential to reduce N loss. Although many N inhibitor products are available, the basic active ingredients and functional principles are similar. Understanding how the active ingredients work will help you choose the product that contains the proper ingredient(s) for your fertilizer form and timing.

Nitrogen Losses from Applied Anhydrous Ammonia, Aqua Ammonia, or Other Ammonium-Forming Fertilizers

How Do the Nitrogen Losses Happen?

These fertilizers (Table 1) undergo a series of transformations after being applied into the soils (Figure 2; Table 2), that can lead to many pathways of N loss. N applied in the form of anhydrous or aqua NH₃ is subject to immediate loss through volatilization. N loss through volatilization is very little if the fertilizer is injected deep within the soil, but the volatilization loss may be greater when the fertilizer is injected into dry soils, sandy soils, or heavy and wet soils that do not seal well following the injection.

When these NH₄⁺-forming fertilizers are applied under optimum soil conditions—temperatures between 68 and 95°F and moisture at 70–80% of total pore space (Havlin et al. 2005)—nitrification occurs quickly, converting NH₄⁺ or NH₃ to nitrate (NO₃⁻) (Figure 1; Figure 2). Nitrate is primarily lost from two pathways: (1) leaching out of the root zone with vertical water

flow and (2) through denitrification carried out by anaerobic microorganisms, where NO₃⁻ is converted into gaseous N forms of nitrogen oxides (NO_x, including nitrogen dioxide NO₂; nitrogen oxide NO; and nitrous oxide, N₂O) and dinitrogen (N₂), and then lost to the atmosphere.

Because NO₃⁻ is both water soluble and weakly bound to the positively charged soil particles' surface sites, leaching is the major N loss pathway during heavy rainfall and snowmelt events and seasons. Nitrogen loss through denitrification occurs under water-logged conditions and during freeze and thaw cycles. Substantial amounts of N can be lost through denitrification when standing water occurs throughout late winter and early spring in flats and other low areas. Nitrogen loss through runoff can occur in high rainfall regions in the Pacific Northwest (PNW), especially in hilly fields where annual rainfall exceeds 18 inches.

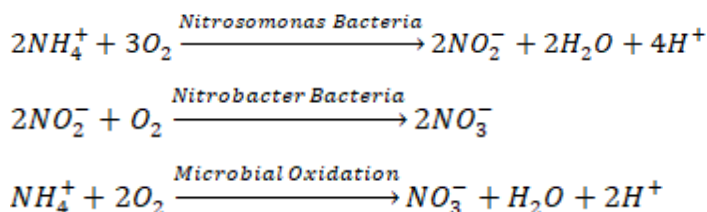


Figure 1. Equations describing two-step transformation from ammonium- to nitrite-form nitrogen (top; step 1); from nitrite- to nitrate-form nitrogen (middle; step 2); and summary of nitrification that transforms nitrogen from ammonium- to nitrate-form (bottom).

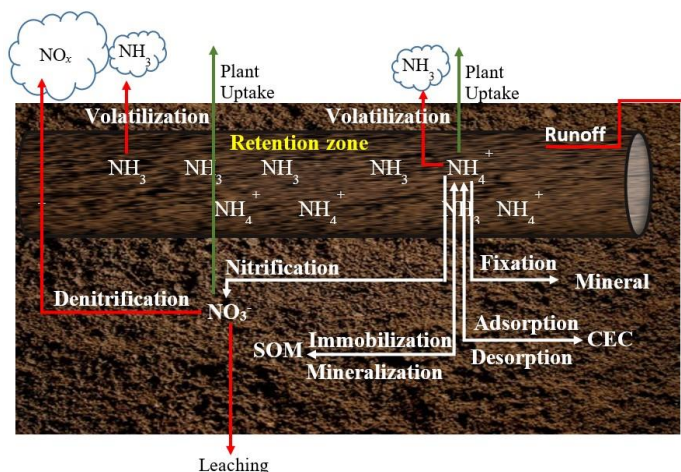


Figure 2. The fate of injected anhydrous or aqua ammonia in the soil (designed by Haiying Tao, WSU).

In low rainfall zones of the PNW, a common practice in wheat production systems is to apply anhydrous or aqua NH₃ in the summer or fall during summer fallow. Under dry soil conditions in summer, the conversion of deep injected NH₄⁺ or NH₃ to NO₃⁻ is limited and can be delayed until the rain season. Then, during late winter and early spring, the NO₃⁻ can be redistributed in the whole root zone by rainfall and snow melt, providing a growing-season-long supply of N for the wheat crop. In intermediate- and high-rainfall zones, Anhydrous or aqua NH₃ is commonly applied in the fall or early winter. Ammonium (NH₄⁺) or NH₃ will not be converted to NO₃⁻ when the air temperatures are typically less than 40°F or soil temperature is less than 50°F,

preventing N loss through leaching or denitrification during winter and early spring. However, unpredictable weather is always a risk factor when using these practices. Warm conditions can occur during these timeframes, and nitrification can convert NH_4^+ to NO_3^- in two to three weeks with adequate moisture. These conditions can result in substantial N loss through leaching and denitrification if warmer-than-normal and wetter-than-normal weather conditions occur between fertilizer application and prior to periods of rapid N uptake by the growing crop.

How Do N Inhibitors Prevent Nitrogen Losses?

Nitrification inhibitors temporarily slow the nitrification process where soil bacteria (*Nitrosomonas*) convert NH_4^+ to nitrite (NO_2^-), inhibiting the first step of nitrification so that the fertilizer stays in its NH_4^+ form (Figure 1, top equation). Keeping fertilizer in the NH_4^+ form can prevent N loss via leaching and denitrification, which are the major N loss pathways in high rainfall areas; however, risk of N loss via volatilization is increased and practices must be used to minimize this loss mechanism (e.g., injection deep into the soil).

Two common active ingredients in nitrification inhibitors include nitrapyrin (2-chloro-6 [trichloromethyl] pyridine) and dicyandiamide (DCD). Previous research has reported that nitrapyrin can effectively inhibit nitrification for two to six weeks under conditions that are favorable for nitrification (Havlin et al. 2005). In contrast, research results are inconsistent about the duration of DCD's effectiveness, ranging from the same as nitrapyrin's effectiveness period to as long as three months (Havlin et al. 2005; Malzer et al. 1989; Sawyer 1985).

Examples of nitrapyrin-containing products include N-Serve, Instinct II, and Instinct HL (Dow AgroSciences) where the application rate of nitrapyrin is acre-based. N-Serve is an oil-soluble product for use with anhydrous NH_3 and urea fertilizers and may be used with aqua NH_3 or liquid urea when combined with a compatibility agent. Care must be taken when mixing and using N-Serve as it is corrosive to aluminum. Instinct II or Instinct HL are water-based, micro-encapsulated products for use with aqua NH_3 , liquid urea, and urea ammonium nitrate (UAN) and can be mixed with liquid fertilizers, insecticides, and herbicides. Instinct II or Instinct HL are no more corrosive to standard liquid fertilizer equipment than liquid fertilizer alone.

Because nitrapyrin can volatilize, products should be injected or incorporated mechanically, by rainfall, or with irrigation soon after application.

Products containing only DCD are generally used with liquid N. DCD is readily soluble and stable in anhydrous NH_3 (Havlin et al. 2005). Examples of DCD-containing products include AgrotainPlus, SuperU, Guardian DF, and Guardian DL.

Nitrification inhibitors are most effective under conditions favorable for rapid nitrification and at high risk for leaching or denitrifications. These conditions are summarized in Table 3.

Table 3. Conditions when nitrification inhibitors are most likely to reduce N loss.

Soil condition	Air temperature	Soil temperature
Coarse texture and low soil organic matter	>40°F	>50°F
Poorly drained soils, chance of heavy rainfall	>40°F	>50°F
pH is optimum for bacteria activities (pH = 6–7)	>40°F	>50°F
During frequent freeze-thaw or dry-wet cycles	Any	Any

N Loss from Applied Urea ($\text{CO}(\text{NH}_2)_2$) or Urea-Based Fertilizers

How Do the Nitrogen Losses Happen?

When urea-based fertilizers, such as granular urea, fluid urea, or fluid urea-ammonium nitrate (UAN), are applied to soil, urea is hydrolyzed by the enzyme urease to form NH_4^+ (Figure 3, top equation). The NH_4^+ then undergoes a series of transformations in the soil (Figure 4) that can lead to the various pathways of N loss as described in Table 2.

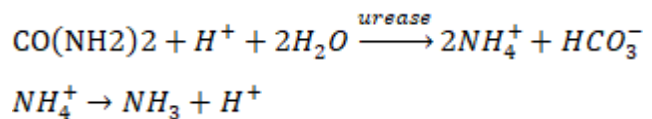


Figure 3. Equations describing hydrolysis that transforms urea to ammonium in soils (top) and the transformation that further converts ammonium to the gaseous form of ammonia (bottom).

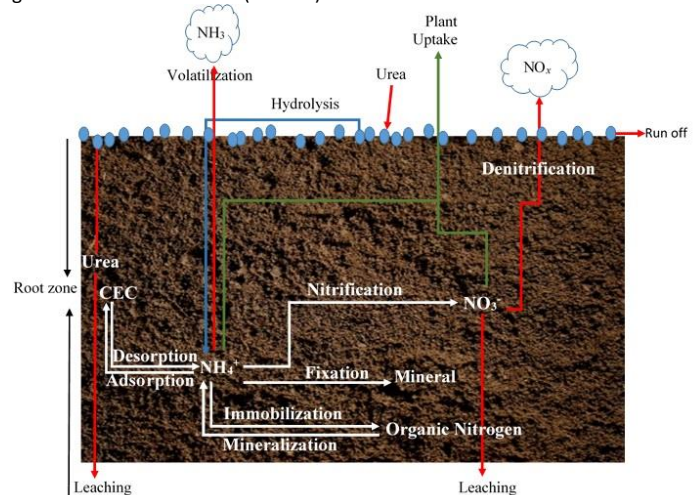


Figure 4. The fate of surface applied urea (designed by Haiying Tao, WSU).

A common practice in intermediate and high rainfall zones in the PNW is to topdress winter cereals with urea in the spring. In general, it takes greater than 0.5 inch of rainfall within 24 to 48 hours after surface application to transport urea to the depth that will minimize volatilization loss (Jones et al. 2013). If urea is left on the soil surface, the potential for volatilization loss is high because the conversion of urea to NH_4^+ proceeds rapidly in warm, moist soil surface in the spring, and much of the NH_4^+ converts to the gaseous NH_3 form if spring air conditions are dry and warm (Figure 3; Figure 4). Windy conditions in the spring also favor volatilization loss. In addition, urea hydrolysis temporarily increases soil pH around the urea molecule, which is a favorable condition for volatilization (Havlin et al. 2005). Additionally, a research conducted in Montana found that if urea is applied onto cold, snow-covered soils the volatilization losses can also be high (Jones et al. 2013).

How Do N Inhibitors Prevent Nitrogen Losses?

Urease inhibitors delay urea hydrolysis, preventing conversion of urea to NH_4^+ and subsequent NH_3 volatilization (Figure 3; Figure 4) (Rogers et al. 2015). The common active ingredient in urease inhibitors is N-(n-butyl) thiophosphoric triamide (NBPT). NBPT inhibits urea hydrolysis by locking onto urease enzyme-binding sites and preventing the urease enzyme from reacting with urea as shown in Figure 4, top equation (Manunza et al. 1999). While regional differences have been reported, research has shown that urease inhibitors can be effective for 10 to 14 days (Havlin et al. 2005).

Agrotain (Koch Agronomic Services) is an example of a NBPT-containing product where NBPT is manufactured and sold by multiple other companies with varying formulations. Another product that has shown to be an effective urease inhibitor is BASF Limus (BASF) which is comprised of both NBPT and NPPT (N-(n-propyl) thiophosphoric triamide). Application rates for different active ingredient concentrations may vary between products, thus, rates should follow product label recommendations.

Generally, urease inhibitors are most effective under conditions of high N volatilization potential. These conditions include when urea-containing fertilizer (dry urea or UAN) is placed on the soil surface, broadcast in heavy surface residue, or applied to soils with a pH greater than 7.0 or low buffer capacity (such as sandy soils) (Grant 2004). Another possible benefit of urease inhibitors is the reduction of seed injury when urea-containing fertilizer is applied at planting (Grant 2004).

Dual-Purpose Products Including Both Nitrification and Urease Inhibitors

Some products function as both nitrification and urease inhibitors and can be chosen when conditions for both volatilization and leaching and denitrification are high.

Examples of dual-purpose inhibitors include Agrotain Plus (formulated for UAN, contains both DCD and NBPT) and SuperU (granular urea coated with both DCD and NBPT) (Koch Agronomic Services). Another compound, ammonium thiosulfate (ATS) is thought to inhibit nitrification maybe because elemental sulfur oxidation slightly acidifies soil, which can reduce bacteria activity in the fertilizer application zone. ATS has also been evaluated as a urease inhibitor because its reduced sulfur compounds are thought to temporarily inhibit urea hydrolysis (Goos 1985). However, ATS's N inhibitor effect is inconclusive because the improved N-use efficiency could also be a result of correcting sulfur deficiency (Goos 1985).

Slow-Release N Fertilizers—Another Option to Control N Losses

Slow-release (or controlled release) N reduces N loss by delaying N release to soil and gradually feeding crops during the growth period. Generally, slow-release N is most beneficial when fertilizer is applied before rapid uptake by plants—i.e., in cold temperatures, on the soil surface, in soil with high leaching potential, or at hillslope locations with high water ponding risk. In general, the warmer the soil temperature, the faster the release rate because most of the slow-release N requires microbial activity—which increases with warmer soil temperatures.

Sulfur- and polymer-coated urea are examples of slow-release N fertilizers. Control of N in sulfur-coated urea depends on coating imperfections—cracks and fractures that allow water to dissolve urea—and coating degradation by microbes. Polymer coatings are porous to allow water to diffuse into the encapsulated urea. With time, the urea solution slowly diffuses from the coating into the soil.

Polymer-coated N products include ESN (Agrium), Polyon (Koch Turf & Ornamental), Nitamin NFusion (Georgia-Pacific), aqua FUSION (Wilbur-Ellis), and XCU (Koch Turf & Ornamental). These products are coated with polymer, sulfur,

and wax. Polymer-coated urea can last up to 52 weeks, depending on coating material, uniformity, and thickness.

Methylene urea (MU) are uncoated slow-release N products that are manufactured by reacting urea with formaldehyde, resulting in a slightly slower N release due to the chemical change in the fertilizer and resulting decrease in the time of degradation by microbial activity. Nutralene (Koch Turf & Ornamental) is an example of an MU.

Is Any Product a Right Choice for You?

Before large-scale adoption, farmers should first test enhanced-efficiency fertilizer products at a smaller scale on their own farms. On-farm product evaluation can be conducted by running side-by-side replicated strip trials for a few years (Kyveryga et al. 2018). By running trials over multiple years, farmers can evaluate at what climate conditions (mainly rainfall and temperature after fertilizer applications) the stabilizing product is superior to fertilizer applications without using the product. The treatment design will depend on your purpose. For example, if you want to know whether an inhibitor product can increase yield, treatments would be current management versus current management plus an inhibitor. If you want to know whether an inhibitor product can lead to reduced N loss, allowing reduced N-application rates, treatments would be current management versus reduced N rate plus an inhibitor.

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