

# Ammonia Emissions from Agricultural Operations: Fertilizer

By Robert Mikkelsen

Nitrogen fertilizer is an essential component on most farms. Although urea-based fertilizers are the most common global N source, they are susceptible to loss as ammonia ( $\text{NH}_3$ ) gas when left on the soil surface. Ammonia losses from fertilizer can represent a significant economic loss for farmers and can have a negative effect on air quality, ecosystem productivity, and human health. The major factors controlling  $\text{NH}_3$  losses from fertilizers are reviewed in this article.

Getting the most value from all nutrient inputs is necessary to maximize efficiency. Selecting the right source of nutrient in a particular cropping situation requires a consideration of economic, environmental, and social objectives. One of the objectives is to keep all nutrient losses to a minimum. Some N fertilizers can be subject to volatile losses to the atmosphere. Regulatory agencies are increasing their awareness of the role of N gases in the atmosphere and their potentially undesirable consequences.

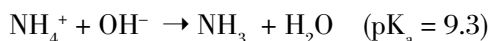
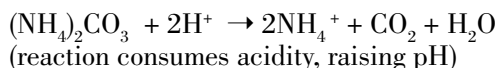
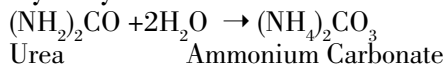
A previous article (*Better Crops* No. 1, 2009) discussed the loss of  $\text{NH}_3$  from animal production facilities. While livestock operations are the largest contributor to  $\text{NH}_3$  emissions in North America, losses from N fertilizer also contribute significantly to total emissions. Where significant  $\text{NH}_3$  loss occurs following fertilization, it is possible that the crops may be under-fertilized due to this unintentional N loss.

A variety of soil chemical properties interact with environmental conditions at the site of the fertilizer application to determine the extent of  $\text{NH}_3$  loss (Figure 1). This article reviews some of the major factors that contribute to  $\text{NH}_3$  loss from N fertilizer.

**Nitrogen Source** All fertilizers containing ammonium ( $\text{NH}_4^+$ ) are theoretically subject to volatile loss. However, properties of each specific fertilizer and its reactions after contacting the soil can result in large differences in N loss. The potential for  $\text{NH}_3$  volatilization is largely governed by the alkalinity (pH) of the zone surrounding the fertilizer particle or droplet. Many  $\text{NH}_4^+$ -containing fertilizers such as ammonium nitrate or ammonium sulfate initially form a slightly acidic solution when they dissolve in the soil (pH between 4.5 and 5.5). In most circumstances, these N forms do not have significant  $\text{NH}_3$  loss.

When urea is applied to soil, it reacts chemically with water (hydrolysis) and the urease enzyme to produce ammonium carbonate – an unstable compound that can quickly decompose to release  $\text{NH}_3$  gas. Ammonium carbonate is commonly used for smelling salts because it readily releases  $\text{NH}_3$ . Whether applied alone or in a solution, urea undergoes these reactions when applied to soil:

## Hydrolysis Reactions of Urea



Abbreviations and notes: N = nitrogen; CEC = cation exchange capacity.

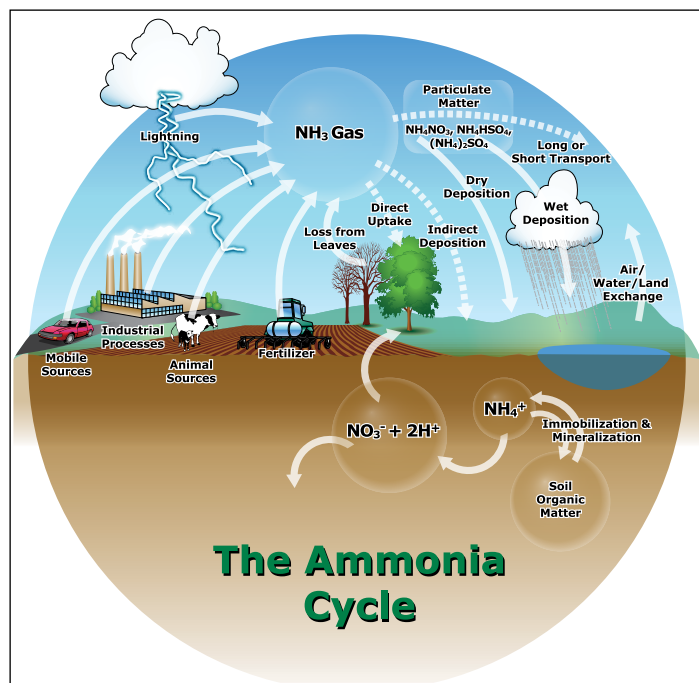


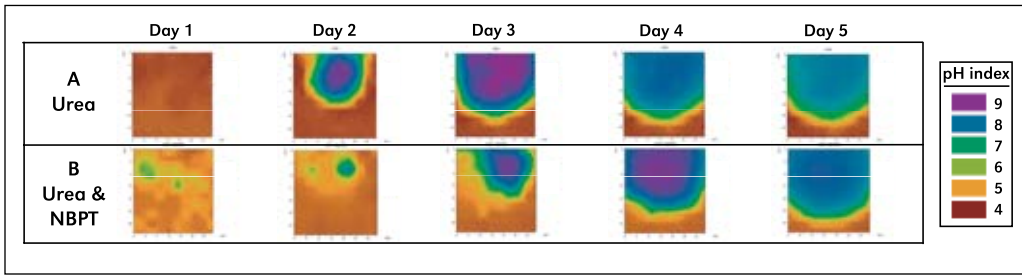
Figure 1. Ammonia emission, transport, and deposition from major sources.

Field factors favoring  $\text{NH}_3$  volatilization losses from surface-applied urea:

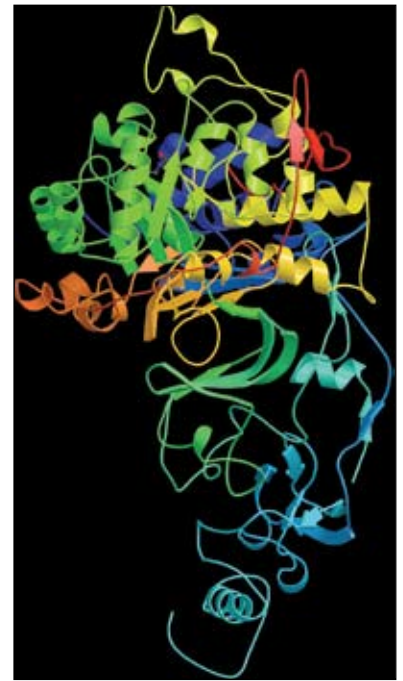
- No rain or irrigation after application (or light mist)
- Crop residue on the soil surface
- High temperatures
- High soil pH
- Low clay and organic matter (low CEC)
- Initially moist soil followed by drying

When broadcast on the soil surface, both liquid or dry urea or urea-containing sources can be susceptible to  $\text{NH}_3$  loss. There are some reports where liquid urea sources are more susceptible to  $\text{NH}_3$  loss than dry fertilizers and other reports that indicate opposite results. These apparent contradictions are likely due to the specific field conditions influencing the movement of urea into the soil, where it becomes protected from volatilization loss.

**Placement** Fertilizers are most commonly broadcast on the soil surface, applied as a surface band, or applied as a subsurface band. Leaving urea-containing fertilizer on the soil surface without incorporation (by tillage or rainfall/irrigation) increases the risk of  $\text{NH}_3$  volatilization in the days following application. Since urea moves freely with water until it



**Figure 2.** The effect of (A) urea alone or (B) urea with NBPT urease inhibitor on soil pH over 4 days following application. The soil pH increased from 4.6 to over 9 surrounding the granule within 1 day following fertilization with untreated urea. Each image is approximately 1 in. (27 mm) square of soil. Data from Stephan Blossfeld and Agrotain International.



**Figure 3.** Chemical model of the urease enzyme responsible for hydrolysis.

Source: Protein Data Bank (PDB 1E9Z) Supramolecular Assembly and Acid Resistance of *Helicobacter Pylori* Urease. Ha, N.-C., Oh, S.-T., Sung, J.Y., Cha, K.-A., Hyung Lee, M., and Oh, B.-H. 2001. *Nat. Struct. Biol.* 8: 480.

Estimates of  $\text{NH}_3$  volatilization from urea fertilizer vary widely due to the many conditions where this popular fertilizer is used. Published reports of volatile N loss from surface-applied urea range from near zero to close to 100% in extreme conditions. When urea or urea-containing N sources remain on the soil surface for a prolonged period of time, typical losses between 10 and 40% may be expected. In your environment,  $\text{NH}_3$  losses may be greater or less than this. Always use appropriate fertilizer management practices such as right source, rate, timing, and placement to keep  $\text{NH}_3$  losses to a minimum.

hydrolyzes to  $\text{NH}_4^+$ , apply urea immediately prior to rainfall or irrigation if possible to allow it to move with water beneath the soil surface.

Broadcasting urea onto the canopy of crops (such as a pasture or a forest) may result in significant  $\text{NH}_3$  losses. Surface banding the added N in concentrated zones can reduce  $\text{NH}_3$  losses compared with spraying the urea N across the field in this situation. In forested soils,  $\text{NH}_3$  loss following urea application can be greater from bare soil than from soil with a complete forest floor due to the pH buffering capacity of the humus layer.

Ammonia loss is a concern in no-till crop production where N is commonly applied to the soil surface. No-till practices may result in a layer of crop residue that can increase the risk of  $\text{NH}_3$  losses, compared with bare soil. Volatile losses can be significant in these circumstances since i) urease activity is generally high in crop residues, ii) crop residues form a barrier which can prevent urea from reaching the mineral soil, and iii) a vegetative mulch may keep the soil more moist – all of which can increase  $\text{NH}_3$  loss.

When subsurface application is not feasible, application of urea in a surface band is superior to broadcast application for minimizing  $\text{NH}_3$  loss. This occurs as the capacity of the soil to hydrolyze urea is exceeded within this localized band, giving additional time for downward movement of urea into the soil where it is protected from  $\text{NH}_3$  loss. Therefore, the most effective way to conserve urea is to get urea into the soil and not on top of the soil for a prolonged period.

**Soil pH** The conversion of  $\text{NH}_4^+$  to  $\text{NH}_3$  gas is governed by pH. A variety of reactions occur following N fertilization that will influence the microsite pH. During urea hydrolysis, the pH surrounding the granule initially rises ( $> \text{pH } 8$ ) as ammonium bicarbonate is formed (**Figure 2**). It is during this

period of urea hydrolysis and increased pH that  $\text{NH}_3$  loss is most likely. Many environmental factors can influence the rate of urea hydrolysis, such as the urea concentration, urease enzyme activity, temperature, moisture, and the presence of crop residues. During the warm growing season, it is common for most of applied urea to be hydrolyzed within a week.

Ammonia loss occurs even from acid soils since urea hydrolysis causes the pH to rise at the site of the fertilizer placement and transform  $\text{NH}_3$  to a gas. The example in **Figure 2** shows the soil pH rising from 4.6 to over 9 following urea application. A greater pH buffering capacity of soil is generally related to less volatile  $\text{NH}_3$  loss, and soils that are high in clay and organic matter tend to have greater pH buffering.

The bacterial process of nitrification subsequently oxidizes  $\text{NH}_4^+$  to  $\text{NO}_3^-$ , releasing acidity in the process and dropping the soil pH below the initial soil pH before urea was added. As  $\text{NH}_4^+$  is oxidized to  $\text{NO}_3^-$ , the risk of volatile loss decreases. However, once in the  $\text{NO}_3^-$  form, other pathways of N loss become more likely (such as denitrification or leaching).



**Moisture** is the major mechanism for moving surface-applied urea into the soil.



An extensive set of field studies was conducted in the Central Valley of California to estimate large-scale  $\text{NH}_3$  losses from applied fertilizer. Total  $\text{NH}_3$  losses ranged from 0.9 lb to 6.2 lb N/A (averaging 3.2% of applied N) from a variety of cropping situations using  $\text{NH}_4$ -based fertilizers. The researchers suggested a state-wide average  $\text{NH}_3$  emission factor for all N fertilizer applications to be 2.4% of added N fertilizer.

**Soil Moisture** When urea or  $\text{NH}_4^+$ -based fertilizers are added to dry soil, the dissolution is slow and biological and chemical reactions do not rapidly occur. Urea hydrolysis also becomes very slow and approaches zero when the soil is quite dry. Higher  $\text{NH}_3$  losses are expected when the relative humidity of the air is greater than the critical humidity of urea. However, moisture is the major mechanism for moving surface-applied urea into the soil and essential in making the nutrients available for plant uptake from the soil solution.

**Soil Properties** Soil cation exchange sites are a major mechanism for removing  $\text{NH}_4^+$  from the soil solution. Soils with a greater CEC generally have the ability to retain more  $\text{NH}_4^+$  and reduce volatile losses. Since sandy soils generally have lower CEC and buffer capacity, the magnitude of soil pH changes and  $\text{NH}_3$  losses can be significant.

**Windspeed** Losses of  $\text{NH}_3$  from surface-applied urea generally increase in windy conditions. Since windy conditions and drying soils are often related, both of these factors tend to aggravate the potential for volatile  $\text{NH}_3$  loss.

**Temperature** Ammonia losses generally increase with rising temperatures due to effects on both chemical and biochemical reactions. Higher temperatures speed the hydrolysis of urea, resulting in a higher soil pH and greater  $\text{NH}_3$  concentrations. Higher temperatures also shift the equilibrium to favor  $\text{NH}_3$  gas over the  $\text{NH}_4^+$  form. Therefore,  $\text{NH}_3$  loss may be slightly higher during the warmer part of the year, and daily spikes may occur during hot times of the day. However, since soil drying also favors  $\text{NH}_3$  loss, this factor often interacts with temperature and windspeed.

**Urea Hydrolysis** Urease enzymes are produced by almost all plants, animals, and microorganisms. Its absence is almost never a limiting factor for converting urea into  $\text{NH}_4^+$  (**Figure 3**).

**Flooded Soils** Volatile losses of  $\text{NH}_3$  from irrigation and flood water may be large. A high concentration of  $\text{NH}_3$ , high water pH, warm temperature, and elevated wind speed all contribute to the likelihood of loss. When broadcast into floodwater, urea is more susceptible to volatilization than a fertilizer such as ammonium sulfate since the pH is likely to rise as urea is hydrolyzed to ammonium carbonate. Photosynthesis by plants and algae in water will also increase the pH of the water when  $\text{CO}_2$  is depleted during the daytime, causing pH to rise as high as 9. During nighttime,  $\text{CO}_2$  is released during respiration and the water pH decreases again. Placement of urea below the soil surface largely eliminates  $\text{NH}_3$  volatile loss.

When anhydrous or aqua  $\text{NH}_3$  is added to irrigation water, significant volatile losses can occur as water is applied to the field through sprinklers or irrigation furrows. Less  $\text{NH}_3$  loss occurs when using UAN (a 1:1 mixture of urea and ammonium nitrate) since only half of the fertilizer is present as urea.



Photo courtesy of Agrium Advanced Technology

**Coatings** on controlled release fertilizer can effectively reduce the amount of soluble urea exposed to the soil environment and minimize  $\text{NH}_3$  loss.

**Fertilizer Modifications** Fertilizer must sometimes be applied when conditions are not optimal. Several approaches have been used to reduce  $\text{NH}_3$  losses from fertilizer in these circumstances, including urease inhibitors, fertilizer coatings, acidification, or the addition of calcium salts.

A number of compounds have been screened to identify an effective way to block or delay urea hydrolysis. The product most commonly used, especially in North America, is N-(n-Butyl)-thiophosphoric triamide (NBPT) sold under the commercial name of Agrotain. This product is combined with urea to inhibit the urease enzyme for a period of several days to two weeks depending on the application rate (**Figure 2**). NBPT is especially beneficial for gaining time for rainfall or irrigation to move surface-applied urea into the soil where it is not susceptible to volatile loss.

A variety of materials have been successfully used as coatings for controlled-release fertilizers to limit the solubility of urea. Coatings can effectively reduce the amount of soluble urea exposed to the soil environment at any one time and significantly reduce N losses in many circumstances.

Urea can be reacted with a variety of strong acids to maintain a low pH in the vicinity of the fertilizer granule or solution. Commercial products of urea-sulfuric acid and urea-phosphoric acid are available for specialized purposes.

The addition of soluble calcium salts (such as  $\text{CaCl}_2$ ) to urea has been shown to reduce  $\text{NH}_3$  loss from both acid and calcareous soils by depressing pH as well as reacting with the carbonate molecules formed during urea hydrolysis. Urea fertilizer containing boron and copper compounds to partially inhibit urease activity and a coating of acidic monoammonium phosphate is also commercially available to help minimize  $\text{NH}_3$  loss.

Ammonia volatilization from applied N fertilizers represents an economic loss of a valuable resource and a potential concern for air quality. With careful management and awareness of the conditions conducive for loss, N fertilizer can be properly managed to minimize the potential for volatile loss. **DC**

*Dr. Mikkelsen is IPNI Western North America Regional Director, based at Merced, California; e-mail: rmikkelsen@ipni.net.*