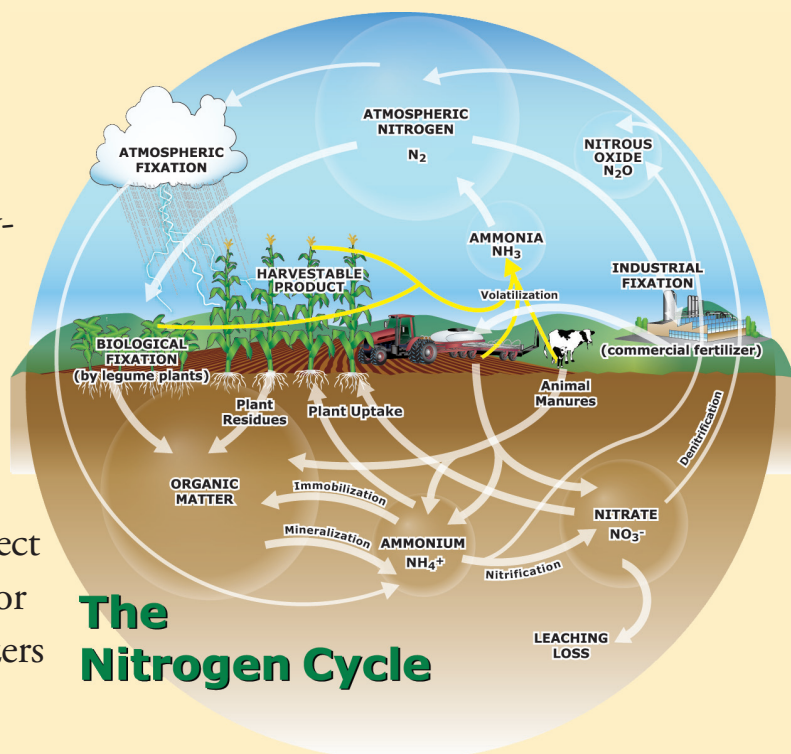


## AMMONIA VOLATILIZATION

Nitrogen (N) fertilizer is essential for growing most crops. Some ammonium and urea-based fertilizers are susceptible to loss as ammonia ( $\text{NH}_3$ ) gas, especially when left on the soil surface. Ammonia losses from fertilizer can represent a significant economic loss and may have a negative effect on air quality and human health. The major factors controlling  $\text{NH}_3$  losses from fertilizers and animal wastes are discussed here.



**The Nitrogen Cycle**

Emissions of  $\text{NH}_3$  into the atmosphere have more than doubled since pre-industrial times due to increases in livestock numbers, fertilizer N use, and combustion of fossil fuels. Volatilization of  $\text{NH}_3$  from fertilizers and animal wastes can be a major pathway of nutrient loss. This is both an economic loss of a valuable resource and a potential concern for air quality (**Figure 1**).

The factors controlling  $\text{NH}_3$  loss from crop production systems are well understood and awareness of these factors can help reduce these losses. Emission of  $\text{NH}_3$  from fertilized soils can range from near zero to up as much as 50% of the applied N. Ammonia losses can be largely eliminated by proper placement or timing of N fertilizing materials. Animal wastes are more difficult to manage than fertilizer materials for reducing  $\text{NH}_3$  loss, but they should also be used as efficiently as possible.

Consider the following factors that influence  $\text{NH}_3$  loss in

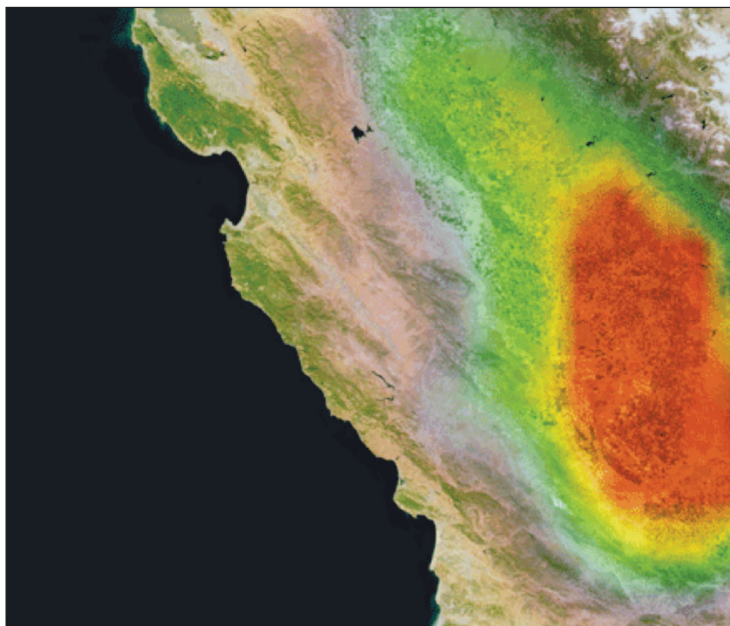
order to improve management decisions that will minimize this loss:

### Nitrogen Source

All fertilizers that contain or produce ammonium ( $\text{NH}_4^+$ ) are subject to volatile loss to some degree. Each of these fertilizer N materials reacts uniquely, resulting in source specific differences in the potential for N loss from the soil (**Figure 2**). The vulnerability for  $\text{NH}_3$  volatilization from fertilizer is largely governed by the alkalinity (pH) of the zone surrounding the granule or droplet as it reacts with the soil.

Some  $\text{NH}_4^+$ -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 acidic N sources do not lose significant amounts of  $\text{NH}_3$ —only up to few percent of

Nitrogen Notes is a series of bulletins written by scientific staff of the International Plant Nutrition Institute (IPNI). This series was supported by a grant from the California Department of Food & Agriculture and through a partnership with the Western Plant Health Association. This series is available as PDF files at [www.ipni.net/publications](http://www.ipni.net/publications).

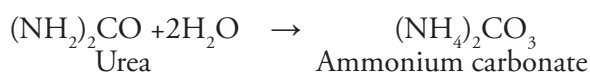


**Figure 1.** Atmospheric  $\text{NH}_3$  over the San Joaquin Valley, California, measured by the IASI satellite in 2008. Red shading is the most concentrated area of  $\text{NH}_3$ . Clarisse, L. et al., 2009. *Nature Geoscience* 2, 479-483.

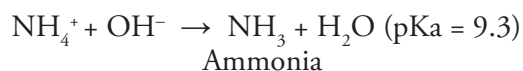
the total N.

Other N fertilizers form alkaline conditions, which are more susceptible to  $\text{NH}_3$  loss. For example when urea is applied to soil, it reacts rapidly with water and urease enzymes in a process called hydrolysis, producing ammonium carbonate—an unstable compound that quickly decomposes to release  $\text{NH}_3$  gas. Whether applied as a solid fertilizer or in a solution, urea undergoes the following reactions when applied to soil:

### Hydrolysis Reactions of Urea

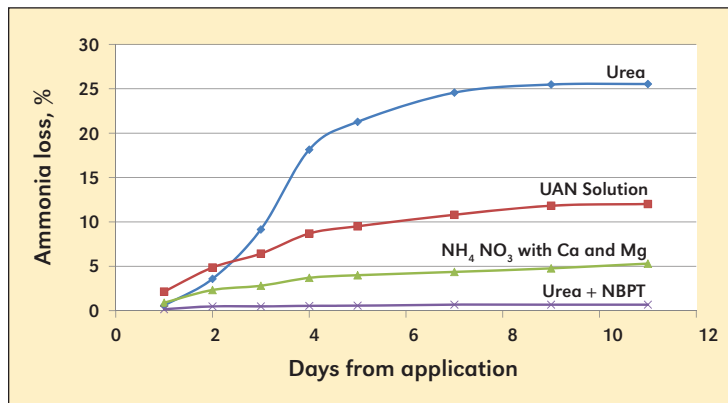


(this reaction consumes acidity, raising pH)



Anhydrous ammonia ( $\text{NH}_3$ ) fertilizer is subject to considerable volatile losses if it is not applied properly. This N fertilizer is directly applied to soil as a pressurized liquid that immediately becomes a vapor after leaving the tank. Ammonia is always placed at least 4 to 8 inches below the soil surface to prevent its loss to the atmosphere. Various types of tractor-drawn knives and shanks are used to place the  $\text{NH}_3$  in the correct location. Ammonia rapidly reacts with soil water to form  $\text{NH}_4^+$ , which is retained on the soil cation exchange sites.

Ammonia is sometimes dissolved in water to produce “aqua ammonia”, a popular liquid N fertilizer in some areas. In some



**Figure 2.** The effect of N fertilizer source and the use of a urease inhibitor on urea on  $\text{NH}_3$  volatilization from surface-applied fertilizer. From Holcomb, J. and D. Horneck, 2011. Oregon State University.

circumstances, considerable  $\text{NH}_3$  can be lost from surface applications or during water-run applications of aqua ammonia.

### Placement

Proper placement of urea and ammonium fertilizers is one of the key management factors for minimizing  $\text{NH}_3$  loss. Leaving urea-containing fertilizer on the soil surface without incorporation (through tillage or rainfall/irrigation) greatly increases the risk of  $\text{NH}_3$  volatilization in the days following application. Since urea moves freely with water until it hydrolyzes, urea is often applied immediately prior to rainfall or irrigation so it can move with water beneath the soil surface.

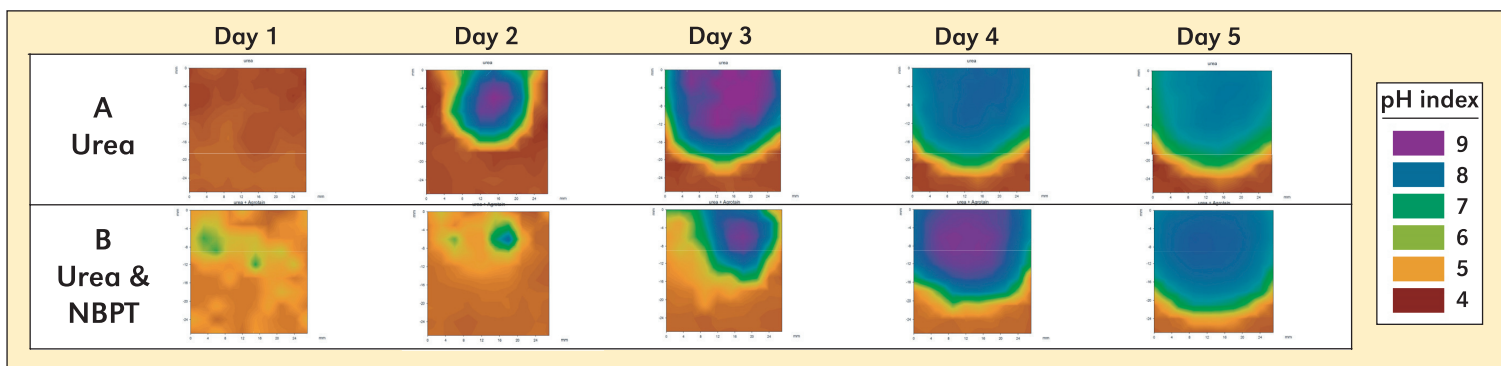
Ammonia loss is a concern in no-till crop production where fertilizer is commonly spread on the surface to avoid disturbing the soil. No-till practices that develop a layer of crop residue can increase the risk of  $\text{NH}_3$  losses from surface-applied urea, compared with bare soil. Volatile losses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

When subsurface application is not feasible, placing 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.

### 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 to influence the pH near the granule or droplet. During urea hydrolysis, the pH surrounding the granule initially rises ( $> \text{pH } 8$ ) as ammonium carbonate is formed. It is during urea hydrolysis and increased pH that  $\text{NH}_3$  loss is most likely to occur. Many environmental factors influence the rate of urea hydrolysis, such as the urea concentration, urease enzyme activity, temperature,

# Nitrogen NOTES



**Figure 3.** The effect of (A) urea alone or (B) urea with NBPT urease inhibitor on soil pH over 5 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 Blossfield and Agrotain International. From Mikkelsen, R.L. 2009. Better Crops with Plant Food, Vol 49(4), 9-11.

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 may occur in acidic soils too, since urea hydrolysis causes the pH to rise immediately surrounding the fertilizer granule. The example in **Figure 3** shows the soil pH rising in this zone from 4.6 to over 9 following urea applications. A soil with greater pH buffering capacity (high clay or organic matter) generally has less volatile  $\text{NH}_3$  loss than a poorly buffered soil (sandy texture).

## Soil Moisture

When urea or  $\text{NH}_4^+$ -based fertilizers are applied to dry soils with low humidity, they tend to dissolve slowly. Such conditions can slow down many biological and chemical reactions, including  $\text{NH}_3$  volatilization. On the other hand, if the soil is moist, warm, and water is evaporating from the surface, there is a higher potential for  $\text{NH}_3$  loss following surface application of fertilizer.

## Soil Properties

Soil cation exchange sites are important for removing  $\text{NH}_4^+$  from the soil solution. Soils with greater cation exchange capacity (CEC) generally have the ability to retain more  $\text{NH}_4^+$  and reduce volatile losses. Since sandy soils typically have lower CEC and buffer capacity, the magnitude of soil pH changes and  $\text{NH}_3$  losses are usually larger in these soils.

## Windspeed

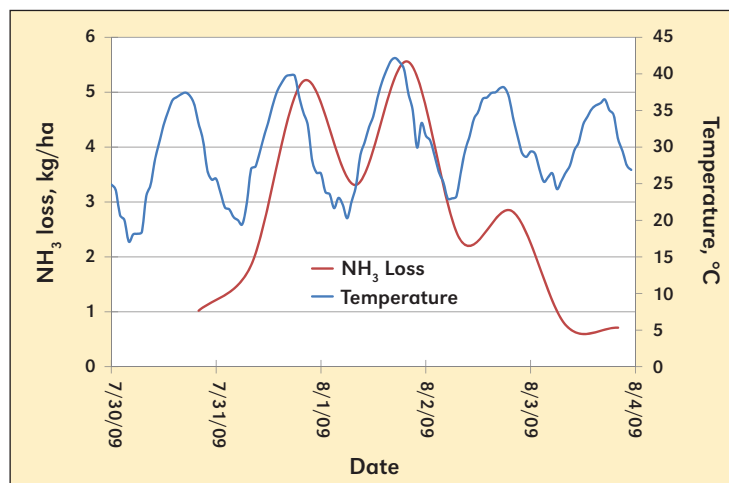
Loss of  $\text{NH}_3$  from surface-applied urea generally increases in windy conditions. Since windy conditions and drying soils are often related, both of these factors tend to increase the potential for volatile  $\text{NH}_3$  loss.

## Temperature

Ammonia losses generally increase with higher temperatures that speed the hydrolysis of urea and shift the chemical equilibrium to favor  $\text{NH}_3$  gas over  $\text{NH}_4^+$ . Therefore  $\text{NH}_3$  loss is often greater during the warmer part of the year, and daily spikes usually occur during warmer times of the day (**Figure 4**).

## Flooded Conditions

Volatile losses of  $\text{NH}_3$  from irrigation and floodwater can 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 (such as with flooded rice), 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. When



**Figure 4.** Ammonia emissions rise and fall each day as the temperatures fluctuate from night to day. From Holcomb, J. and D. Horneck, 2011. Oregon State University.

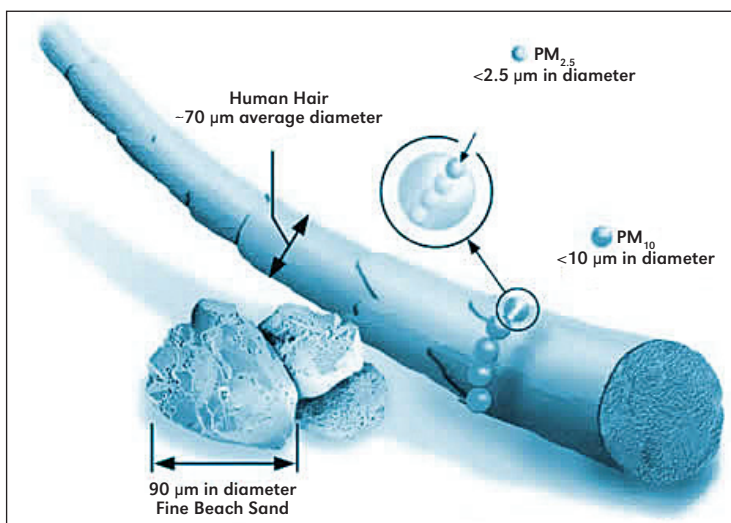
growing flooded rice, photosynthesis by plants and algae growing in water increase the pH of the water as  $\text{CO}_2$  is depleted during the daytime, causing pH to rise as high as 9. During the night,  $\text{CO}_2$  is released during plant respiration (forming carbonic acid) and the water pH decreases again.

## Fertilizer Modifications

Fertilizer must sometimes be applied when conditions are not optimal. Several approaches can be used to minimize  $\text{NH}_3$  losses in these circumstances, including urease inhibitors, fertilizer coatings, and fertilizer acidification (**Figure 2**).

A large number of compounds have been screened to





**Figure 5.** Extremely small particles (PM 2.5) are formed when ammonia reacts with other airborne chemicals. These particles contribute to atmospheric haze and can aggravate health issues for sensitive people. From EPA, Office of Research and Development

identify an effective way to block or delay urea hydrolysis. The most commonly used product 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. NBPT is especially beneficial for gaining time so rainfall or irrigation can 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 at any one time and significantly reduce N losses in many circumstances.

Urea can be reacted with a variety of strong acids to maintain low pH in the vicinity of the fertilizer granule or droplet. Commercial products such as urea-sulfuric acid and urea-phosphoric acid are available for specialized purposes and will reduce  $\text{NH}_3$  loss.

### Ammonia Emissions from Other Agricultural Sources

Agriculture is responsible for over three-fourths of the  $\text{NH}_3$  emissions in the USA, with animal production accounting for the major share. Ammonia becomes a constituent of animal waste when N-rich protein in feed is not completely converted into animal products (such as meat, milk, wool, and eggs). For example, only 25 to 35% of the N fed to dairy cows is used by the animal to produce milk, with the remainder excreted in urine and manure in a variety of compounds. Chemical and microbial processes break down these excreted compounds, resulting in the potential for release of  $\text{NH}_3$  into the air. Nitrogen in poultry manure is mainly in the form of uric acid, which rapidly converts to urea and then to  $\text{NH}_3$ .

Ammonia volatilization begins almost as soon as urea is excreted from animals. The greatest losses from animal pro-

duction typically come from animal buildings and barns, and during land application of manure. On one closely monitored California dairy, 70% of the  $\text{NH}_3$  lost from the farm occurred during field application of wastewater. Losses of  $\text{NH}_3$  during grazing and manure storage can also be large.

High concentrations of  $\text{NH}_3$  in the air have a negative effect on animals in confined buildings, so adequate ventilation of barns and buildings is important. Farm workers should also avoid prolonged exposure to high concentrations of  $\text{NH}_3$ . Ammonia is lighter than air and will rise, making it easily removed from buildings with adequate ventilation.

Ammonia emissions come from automobiles and combustion of fossil fuels. One report estimated that 62 +/- 24 metric tons of  $\text{NH}_3$  are emitted daily in the Southern California South Coast Air basin from transportation sources.

Ammonia is lost from plant leaves when proteins begin to decompose. The magnitude of  $\text{NH}_3$  loss is not well understood, but it has been reported to sometimes exceed 20 kg N/ha for corn and 40 kg N/ha for soybean. Ammonia gas is also taken up by leaves through the stomata, but these processes are not fully understood.

### Ammonia Particle Formation and Deposition

Atmospheric  $\text{NH}_3$  is an environmental concern for two reasons: (1) formation of very fine particles in the air and (2) uncontrolled N deposition back to the soil and vegetation.

When  $\text{NH}_3$  (an alkaline compound) is released into the air, it clings to nearby surfaces and significant amounts can be deposited within a few hundred yards of the source. The remaining  $\text{NH}_3$  can rapidly react with acidic compounds in the air (such as nitric acid or sulfuric acid) to form very small secondary aerosol particles. This fine particulate matter has a diameter of <2.5 microns (referred to as PM 2.5), which is about 30 times smaller than a human hair (Figure 5). Some of these very small particles can persist in the air for several weeks and cause atmospheric haze.

PM 2.5 particles are a health concern because they can be inhaled deeply into the lungs. Short-term exposure to PM 2.5 aerosols can cause eye, nose, throat, and lung irritation, plus coughing and sneezing. There are other sources of PM 2.5, but the contribution of  $\text{NH}_3$  from agriculture can be significant.

Ammonia gas can be transported with the wind, redeposited as far as hundreds of miles from the original source. Ammonium deposited on the soil is generally converted to nitrate, with a release of acidity during nitrification. Widespread  $\text{NH}_3$  fertilization through atmospheric deposition can stimulate plant growth in pristine areas where N was previously limiting. Changes in plant species are noted in undisturbed ecosystems where high  $\text{NH}_3$  deposition occurs.

With careful management, it is possible to maintain  $\text{NH}_3$  losses from fertilizer N at less than a few percent of the total applied. Applying the principles of 4R Nutrient Stewardship (Right Source, Rate, Time, and Place) will minimize the risk of  $\text{NH}_3$  loss. ♦