Nitrogen Fertilizers and Management

Section 3

Formulations

Management / Use Efficiency

Nitrogen Fertilizers

1. Ammonium-forming fertilizers:

- Anhydrous ammonia
- Urea

2. Ammonium fertilizers :

- Ammonium sulfate
- Ammonium/phosphorus combinations (MAP, DAP, 10-34-0)

3. Nitrate fertilizers :

- Potassium nitrate
- Calcium nitrate (CN-9)

4. Combination fertilizers:

- Ammonium nitrate
- Urea-ammonium nitrate (UAN) solutions
- Calcium ammonium nitrate (CAN-17)

5. Organic materials:

- Manure and other animal byproducts
- Compost

More about each type of fertilizer covered in this module:
. Those that form Ammonium (NH_4^+) on reaction with soil moisture or by urease conversion
. Ammonium-containing materials
. Nitrate-containing materials
. Materials that have a combination of N forms (ammonium and nitrate)
. Organic materials that release mineral N over time, through soil microbial activity

Ammonium-forming Fertilizers

- **Anhydrous ammonia**

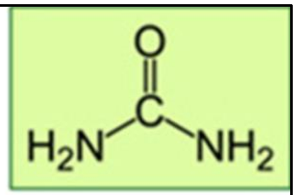
Anhydrous ammonia application to soil *or water*:

$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$

Soil applied
    In moist soil instantly converted
Water run
    Converted to NH_4^+

Anhydrous ammonia is the cheapest N source, but using it efficiently is not easy. When it contacts irrigation water or moist soil, it forms ammonium and hydroxyl ions, raising the pH around the site of application.

Ammonium-forming Fertilizers



- **Urea**

- Highly soluble, uncharged, moves freely with water
  - Not as easily as negatively charged NO_3^-

- Enzymatic hydrolysis produces NH_4^+

$$\text{Urea} + 2\,H^+ \xrightarrow{\text{urease}} 2NH_4^+ + HCO_3^-$$

Ammonium Bicarbonate pH $\uparrow$

Urea is an organic molecule with two N groups attached to a carbon atom. It requires the action of the soil enzyme urease to break it down, forming NH4+ and bicarbonate. Bicarbonate increases soil pH. Initial urea hydrolysis is to increase pH. In total after the NH4 is converted to NO3 the over all reaction is to decrease pH

Ammonium-forming Fertilizers:

Urea hydrolysis occurs rapidly:

$$\text{Urea} + 2\,H^+ \xrightarrow{\text{urease}} 2NH_4^+ + HCO_3^-$$

In a few days conversion complete

Rate of hydrolysis …

- Increases as temperature increases
- Decreases as concentration increases

(Broadbent et al., Proc. SSSA 22:303-307, 1958)

Figure: The rate at which urea is broken down by urease depends on both the concentration of urea applied, and the soil temperature. However, except for in very cold soils uncommon to California, urea incorporated into soil is normally converted to ammonium-N within a few days of application.

Ammonium Fertilizers

- **Ammonium sulfate [$(NH_4)_2SO_4$]**
- **Ammonium/phosphorus combinations**
  - Monoammonium phosphate (MAP)
  - Diammonium phosphate (DAP)
  - Ammonium polyphosphate (10-34-0)
- Ammonium fertilizers:
  - Are *temporarily* resistant to leaching
    Until converted to nitrate

Note: Though these forms are temporarily resistant to leaching, this timeframe is likely as short as a matter of days during the summer.

However, they will attach to the soil particles near the surface in the 1st irrigation. Upon conversion they will move with the water front in the 2nd irrigation.

Nitrate Fertilizers

- Potassium nitrate
- Calcium nitrate (CN-9)

Nitrate is negatively charged and moves with the water front

Combination Fertilizers

- **Ammonium nitrate (NH_4NO_3)**
- **Calcium ammonium nitrate** (CAN-17)
  - 32% of N as ammonium, 68% as nitrate
- **Urea ammonium nitrate (UAN) solutions**
  - 50% of N as urea, 25% ammonium, 25% nitrate
  - different concentrations (UAN-28, UAN-32, etc.)

Combination fertilizers are heavily used by horticultural crops in California.
They act mainly as nitrate fertilizers within days of application.
The fate of ammonium is the same as ammonium forming fertilizers based on the % ammonium.

Combination fertilizers can provide a rapidly availability of nitrate and a continued supply as the ammonium is converted to nitrate.

Organic Materials

- **Manure and other animal byproducts**
- **Cover crop, Compost and green waste**

- Contain both:
  - Mineral N (immediately available) NH_4 and NO_3
  - Organic N (slowly available after microbial conversion)

Mineralization rate is dependent on C:N ratio, temperature and moisture content



Organic materials differ from mineral fertilizers mostly by the rate at which the N content mineralizes, becoming plant-available. A wide range of organic materials are applied to fields in California, and the differing characteristics (most notably N content, and C:N ratio) impact N availability.

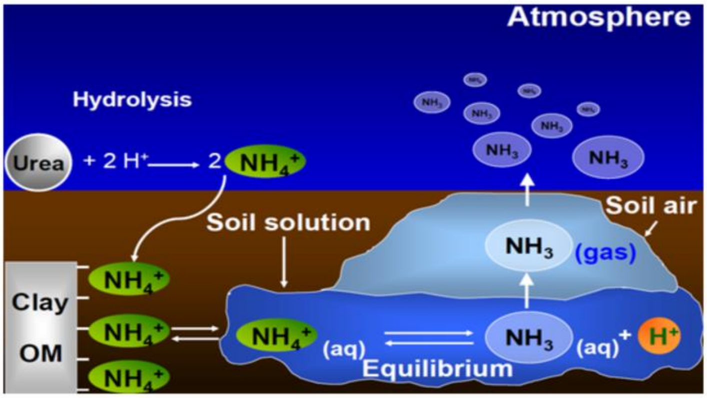
Nitrogen Transformations:

Volatilization and Denitrification

Management considerations to improve
Nitrogen Use Efficiency

Volatilization

- **The loss of gaseous NH_3 to the atmosphere**



When is volatilization most significant?

- Soil injection of anhydrous ammonia, poorly sealed
- Anhydrous ammonia injection into irrigation water
- Loss from urea after hydrolysis, before nitrification
- Loss from urea after surface application w/o irrigation or rainfall

Note: In the liquid phase of the soil (the soil solution), or in irrigation water, there is an equilibrium between NH4+ (which is not volatile) and NH3 (which is);
the NH3 can diffuse out of the solution and be released to the atmosphere.
Anhydrous ammonia and urea are most prone to volatilization.

Higher pH soils have higher rates

Volatilization: Corn/Ammonia Example

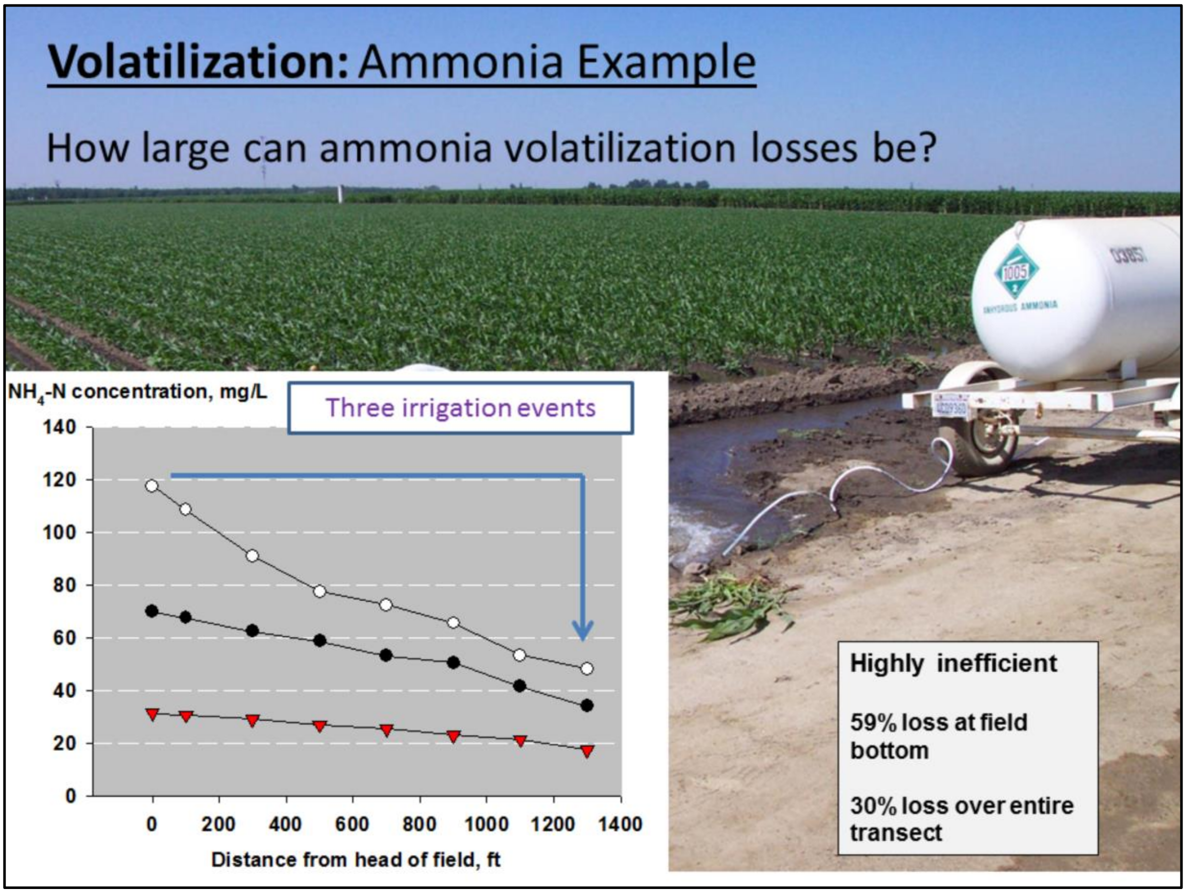
Anhydrous ammonia application impacts solution pH

Site	pH irrig water	pH irrig water + AA
1	7.3	9.9
4	7.8	10.0
5	7.4	10.0
6	7.1	9.0
9	7.3	10.1
12	7.3	9.2
13	7.8	10.2

pH 9 = loss 30%

(Anhydrous ammonia injection into irrigation water Tulare Co. 2008 – C. Frate and J. Deng)

Table: In this example from Tulare County, ammonia was run into furrow irrigated silage corn. In all cases the rise in water pH was substantial, well into the range where large volatilization losses would be expected.



To quantify ammonia volatilization from water-run anhydrous ammonia, UC Davis agronomist Dr. Stu Pettygrove and farm advisors conducted trials in furrow-irrigated fields. Anhydrous ammonia was injected at the head ditch and then sampled down the length of the furrow.

Figure: Ammonium-N concentration decreased significantly down the furrow at all fertigation events. This graph shows results from 3 irrigation events in a sandy loam field. Ammonium concentrations declined by more than 50% down the length of the furrow; when evaluated on a whole-field basis, ammonia volatilization averaged about **30% of applied N**. Beyond this significant N loss, the uniformity of N application was very poor.

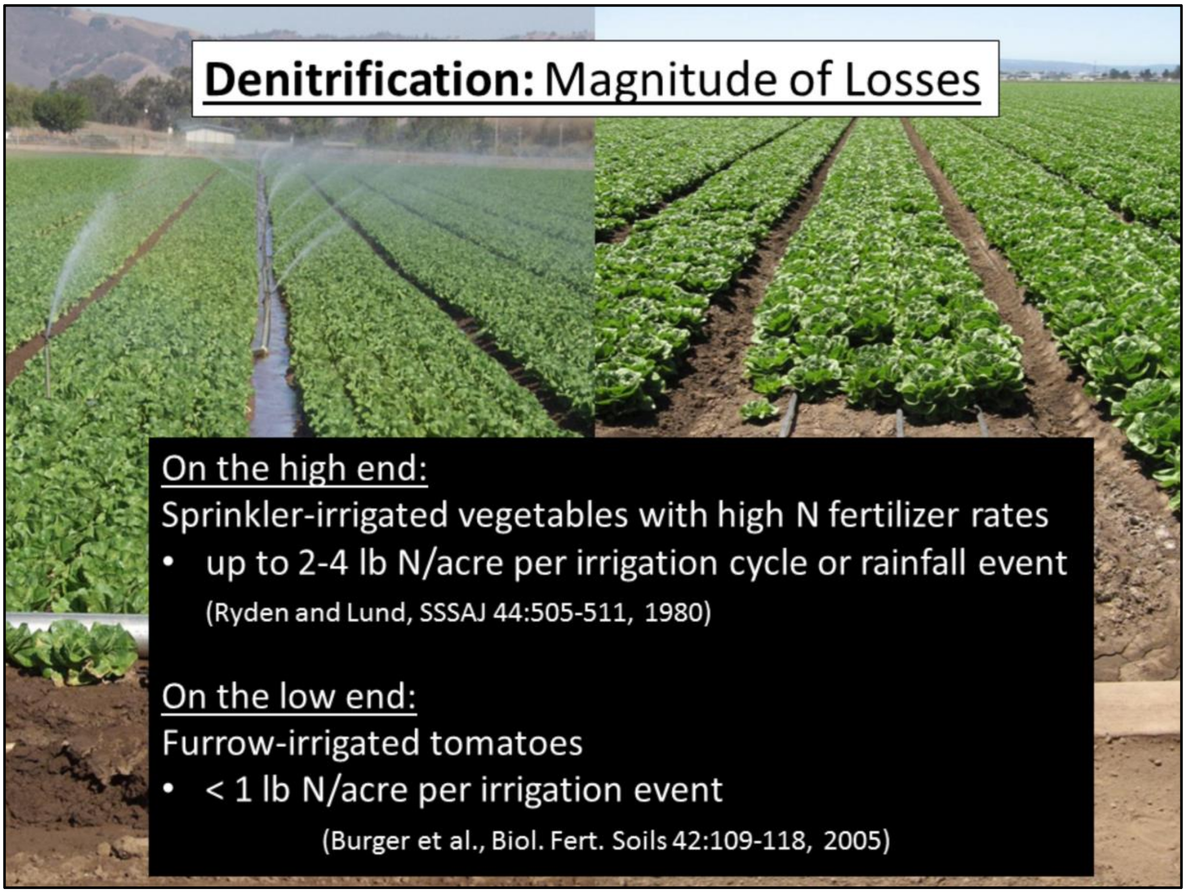
Volatilization: Urea

30% loss in 14 days without rainfall or irrigation

Factors that increase volatilization :

- Surface application without incorporation or irrigation
- High temperature
- High wind speed
- Low soil buffering capacity

When urea is surface-applied and not incorporated, volatilization losses can be high, particularly in the presence of the listed factors. For example, landing on moist soil or drawing dew can cause urea prills to hydrolize. This raises their surrounding pH, increasing volatilization in the manner described. Urea volatilization can be agronomically significant.



On the high end: This 1970s study indicated that denitrification accounted for a significant fraction of applied N. In some fields, these losses added up to more than 100 lbs N/acre annually. However, that cropping system was ideal for denitrification, with high N application rates and frequent, saturating irrigation events.

Note: The upper limit of this study is unlikely under most field conditions because 1) the switch to drip irrigation means less field saturation and 2) most fields receive much less N than the 600 lbs/acre applied annually in some of these monitored fields.

In the past five years, intensive effort has been made to quantify nitrous oxide emissions in irrigated fields. Based on that work, and the assumption that N_2O represents 10% of total N emissions from denitrification, denitrification appears to account for < 30 lb N/acre per season for most irrigated crops in California. Exceptions to this rule would be sprinkler-irrigated vegetables and furrow-irrigated forage crops that receive heavy applications of animal manure.

Denitrification:

Rates Vary with Cropping / Irrigation System

		Seasonal lbs of N fertilizer per acre	Seasonal lbs of N lost to atmosphere per acre
Almond		210	
	Drip		8
	Microsprinkler		3
Vineyard			
	Drip	5	1
Tomato		267	
	Furrow		18
	Drip		8
Corn Silage			
	Furrow	325	31

N loss estimated from N_2O loss

Figure: For multiple crops and irrigation types (furrow and drip), nitrous oxide losses from volatilization tend to fall between ¼ lb and 6 lb per acre per year. While this is a small proportion of a grower's total N budget, it translates into high potential for these crops to collectively contribute to greenhouse gas emissions.

Higher N applied = higher losses
Furrow irrigation = higher losses
Micro sprinklers = lower losses than drip

Microsprinklers spread the water and fertilizer over a larger area.
Drip had more anaerobic microsites

Vineyard: Garland, G. M.; Suddick, E. C.; Burger, M.; Horwath, W. R.; Six, J. Direct N2O emissions following transition from conventional till to no-till in a cover cropped Mediterranean vineyard (*Vitis vinifera). Agric., Ecosyst. Environ.*

Almond: lsina, M.M., A.C. Borges, A.C and D.R. Smart, D.R. 2012. Spatiotemporal variation of event related N2O and CH4 emissions during fertigation in a California almond orchard. Ecosphere

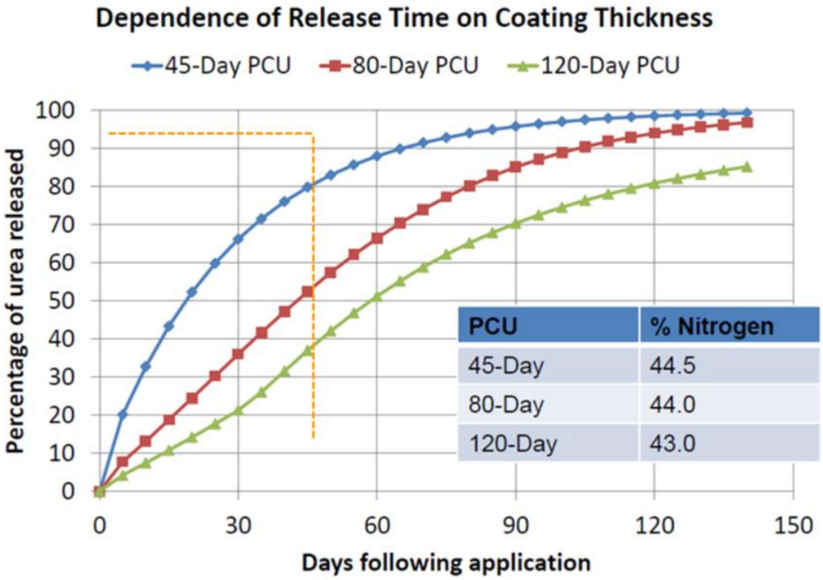
As water-filled pores increased from 60 to 70%, an abrupt shift from mostly nitrification to mostly denitrification occurred. This experiment measured ^{15}N tracers in the greenhouse gas nitrous oxide (N_2O) emitted by both processes.
Source: Image from Elements of the Nature and Properties of Soils, 3/e by N. Brady and R. Well. [Bar graph from Bateman and Baggs (2005)]

Data shown are N2O losses, not including N_2 ; N_2O typically represents only 10-20% of total denitrification.

Manipulating N Transformations for Improved N Efficiency

Controlled Release Fertilizers

Release rating is based on time to release 80% of N at a standard temperature:



PCU	% Nitrogen
45-Day	44.5
80-Day	44.0
120-Day	43.0

Figure: Here, the release times of three polymer-coated urea fertilizers are compared. The fertilizers have coatings of different thicknesses, shown in the table as the slightly lower N content of the 120-day material compared to those with more rapid release; the thicker the coating, the slower the release rate. These release ratings are only relative, however, as soil temperature also plays a role.

Note: Care is particularly important when dealing with materials with shorter release times because they have thinner coatings.

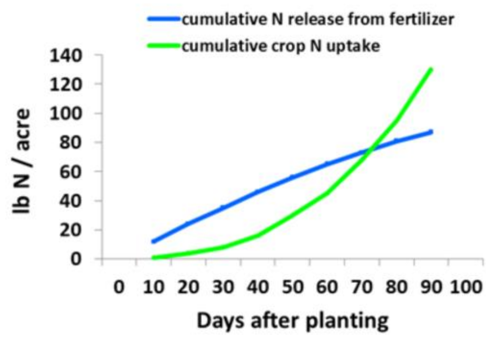
Controlled Release Fertilizers:

Benefits:

- May reduce leaching potential compared to preplant or single sidedress systems
  - weather, soil, and crop factors determine whether this benefit is realized

Drawbacks:

- Higher cost per unit of N
- Match between N release and crop N uptake is often imperfect
  - more appropriate in some cropping scenarios than in others



These products are most effective where fertilization is done by heavy preplant or early season applications, with potential for significant leaching from rain or poorly managed irrigation. Their use was limited by their higher cost per unit N. Recently that price disparity has decreased, and products with thinner coating and faster release time have come on the market.

Figure: Here a problem with controlled release products is illustrated. N release is reasonably linear, but crop N uptake is curvilinear. Efficient use depends on choosing a product with the appropriate release characteristic, applied at the right time.

Summary

- Selecting the appropriate N source for the crop / irrigation management situation can lead to the greatest nitrogen use efficiency.

- Reducing nitrogen losses of:
  - Volatilization
  - Leaching
  - Runoff
  - Denitrification