

SOILS AND FERTILIZERS
MODULE 6A
NITROGEN FERTILIZER – MANUFACTURE, MATERIALS, AND USES

PART 1: AMMONIA, AMMONIA DERIVATIVES, AND SPECIALTY FERTILIZERS

1. Introduction

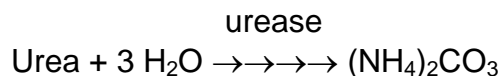
- a. Florida uses large quantities of nitrogen fertilizer, particularly ammonium nitrate. In 1996-97, 238,126 tons of nitrogen was consumed in the state. Florida ranked 15th among U.S. states in N use. The top five N-consuming states were Illinois, Iowa, Texas, Nebraska, and Kansas, all over 700,000 tons per year.
- b. In developing countries, urea use is high (stable in handling, high N concentration, easy to transport).
- c. All solid source and slow-release forms of N will probably eventually be urea or urea-based materials.
- d. Ammonium sulfate is primarily an industrial by-product of the Bessemer process of making steel; valuable source of N; contains sulfur as well; mediates high soil pH as is found in places in Florida; the ammonium portion of the molecule is what acidifies the soil.
- e. Anhydrous ammonia is not used in Florida because of the sandy soil (will lose a lot through volatilization); this form of N is used in the Midwest on wheat and corn; some crops such as vegetables and citrus are sensitive to it; it is the cheapest source of N.
- f. Florida also uses several “specialty” N materials like calcium nitrate (a source of soluble Ca), potassium nitrate, and controlled-release N.

2. Nitrogen production

- a. Electrical discharges (like lightning) will fix atmospheric nitrogen.
 - i. $N_2 + O_2 \rightarrow 2NO$
 - ii. $2NO + O_2 \rightarrow 2NO_2$
 - iii. $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$
 - iv. Nitric acid (HNO_3) is washed out of the air with precipitation.
 - v. Maybe get 10 lbs of N per acre per year added with rainfall.
- b. Chilean sodium nitrate and potassium-sodium nitrate (only mined sources of N)
 - i. $NaNO_3$ (16-0-0), $NaNO_3-KNO_3$ (15-0-14).
 - ii. 100% water soluble nitrate nitrogen.
 - iii. Commercial production began in about 1840; Vast regions in the deserts of northern Chile; Material is mined, purified, then exported.
 - iv. Contains sodium (Na), which is not a plant nutrient and can cause problems in some soils of the non-humid areas.
- c. Main synthetic processes for N production (Requires fixation of atmospheric N; air is 79% N).
 - i. The result of atmospheric N fixation, anhydrous ammonia (NH_3), is the basic building block for almost all synthetic N fertilizers.

- ii. Haber-Bosch process: React hydrogen and nitrogen gases in the presence of a catalyst at high temperature and pressure
 - (1) Production of hydrogen gas: CH_4 (methane) + $\text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$
 - (2) Production of ammonia: $3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3$
 - iii. The conversion is only 28% effective, but is the best available to get N in a useful form.
 - iv. Nitrogen gas is easily available from the atmosphere, but obtaining the hydrogen is difficult. Most comes from methane, which comes from natural gas generated at oil well sites. Thus, the primary constituents of anhydrous ammonia are **natural gas, steam, and air**. The purification of the natural gas is the source of most of the cost of production.
3. Properties of ammonia (NH_3)
- a. Anhydrous ammonia is the cheapest source of N.
 - b. It is 82% N, and is the most concentrated form of N.
 - c. Plants cannot use NH_3 ; it must be converted to the ammonium ion (NH_4^+) or nitrate ion (NO_3^-) for uptake by roots; in the Midwest there is a delay in its conversion in cool weather, thus it is applied in the fall for the next spring crop; can also mix in N-Serve which prevents the conversion of NH_4^+ to NO_3^- .
 - d. Very stable in the anhydrous state, but extremely caustic when it contains a very small amount of water; must use all stainless steel fittings; if a line breaks and a person is sprayed, they will be burned.
 - e. NH_3 is a gas at atmospheric pressure, but shipped as a liquid at 200 psi; it is toxic at high atmospheric concentration (fatal at 0.5-1.0% in the air); it is toxic to soil organisms and plants when injected, therefore it is also a soil fumigant.
 - f. NH_3 must be injected into the soil 6-12" and trapped by soil water to avoid loss by volatilization; if used in Florida, need to inject at least 9" deep, before planting crop to avoid toxicity; best to apply after a rain for best absorption; soil will be sterilized around the injection point, but soil organisms will return in a number of days.
4. Ammonia derivatives
- a. Nitric acid (HNO_3)
 - i. Highly corrosive liquid sometimes used as a component in solution fertilizers.
 - ii. Combined with ammonium to manufacture ammonium nitrate.
 - b. Ammonium nitrate (NH_4NO_3)
 - i. White, crystalline solid, 33.5% N content, highly water soluble (can be used to make liquid fertilizers).
 - ii. Although not explosive in its pure form, about 75% of the ammonium nitrate produced is used to manufacture dynamite, explosives, and solid rocket propellants (NH_4NO_3 plus 6% fuel oil by weight can substitute for dynamite).
 - iii. Fertilizer material is usually prilled, then coated white (MgCl_2) or beige (clay) to prevent absorption of water from the atmosphere.
 - iv. Water solubility, 118 g/100 ml H_2O at 0 C, 843 g/100 ml H_2O at 100 C; Salt index, 2.99.
 - v. Can surface-apply on non-calcareous soils.

- vi. Very hygroscopic; cannot store in the open for a long period of time; when mixed with urea, a critical relative humidity is reached such that H₂O forms almost immediately; if NH₄NO₃ is mixed with KCl, a conditioner is needed or a gummy mess will occur.
 - vii. Contains both plant-available sources of N in a 50-50 ratio; high solubility means that nitrate will leach quickly, with ammonium not too far behind (a **mobile** source of N).
- c. Ammonium sulfate (NH₄)₂SO₄
- i. Mostly produced as a by-product of the Bessemer process of steel making. It is an important source of N and S.
 - ii. Crystalline solid, 21% N, white, except for by-product sources that are usually gray in color.
 - iii. Solubility is low (70.6 g/100 ml H₂O at 0 C, 103 g/100 ml at 100 C), therefore seldom used to make N solutions.
 - iv. Neutralizing equivalent is 5.35 lbs CaCO₃ (highest acidity potential of N sources, thus good for use on high pH soils in Florida).
 - v. Salt index, 3.25 (will cause salt burn at high rates).
 - vi. Very stable product, does not absorb water readily, thus makes good blends with other materials.
 - vii. Contains two essential elements for plants, N and S.
- d. Urea CO(NH₂)₂
- i. White, crystalline solid containing 45% N, usually marketed in prilled form.
 - ii. Salt index, 1.62 (low).
 - iii. Good physical properties; Does not absorb water readily.
 - iv. Very soluble in water (even more than NH₄NO₃); can dissolve in excess of 1000 g/100 ml H₂O at 100 C; urea is very often used to make solution fertilizers.
 - v. Molecule is non-ionic when dissolved, thus in pure form it can leach very fast.
 - vi. The enzyme urease, which occurs universally and is abundant in soil, is required for the conversion of urea to ammonium for plant availability:



- vii. Urea should not be surface-applied without moving it into the soil (tillage or irrigation) because large losses of N can occur due to volatilization.
- viii. Urea is termed a soluble synthetic organic N source, but is not a slow-release fertilizer.
- ix. If manufactured at too high a temperature, biuret may form, which is toxic to plants; if used as a foliar spray, urea should contain less than 0.25% biuret.
- x. Urea is used as a starter material for the manufacture of slow-release N fertilizers.
- xi. Urea became the world's leading N fertilizer in the mid-1970s.

5. Specialty nitrogen fertilizers
 - a. Calcium nitrate $\text{Ca}(\text{NO}_3)_2$ (15.5% N)
 - i. Specialized; used more in Florida than anywhere else, especially on vegetables.
 - ii. Produced in Norway (Hydro Agri “Viking Ship”).
 - iii. Highly soluble; mixes readily; a mobile form of N and Ca.
 - iv. Very hygroscopic; absorbs water readily; will not sit in a dry state for very long.
 - v. Calcium nitrate will increase soil pH.
 - vi. Good solubility in cool weather leads to fast-acting N as NO_3 for winter vegetable production; can be used as a foliar spray.
 - b. Potassium nitrate KNO_3 (13% N)
 - i. Salt index, 4.65 (high).
 - ii. Potassium nitrate will make the soil slightly more alkaline.
 - iii. Desirable characteristics: N present as NO_3 , contains 44% K_2O , negligible chlorine content, not very hygroscopic.
 - c. Ammonium phosphates
 - i. Monoammonium phosphate (MAP) $\text{NH}_4(\text{H}_2\text{PO}_4)$ 11-48-0
 - (1) High acidity around a MAP granule (pH 3.47), therefore good for use in high pH soil.
 - ii. Diammonium phosphate (DAP) $(\text{NH}_4)_2(\text{HPO}_4)$ 18-46-0
 - (1) High alkalinity around a DAP granule (pH 7.98), therefore good for use in low pH soil (do not use in high pH soil because P becomes unavailable due to insolubilization with Ca, and the ammonia volatilizes).

PART 2: SLOW-RELEASE, ORGANIC, AND SOLUTION NITROGEN

1. Slow-Release and Controlled-Release Nitrogen
 - a. Background
 - i. Numerous studies nationwide on crop recovery of applied N have found that only about 50 to 60% of N fertilizer added to the soil is taken up by crop plants during a growing season. The incomplete recovery is mostly due to the rapid dissolution of N fertilizers, which releases N at a higher rate than can be taken up by the plant over a short period of time.
 - ii. One approach to increase N fertilizer efficiency is to control the rate of N release to the soil solution, which can be done one of two ways: 1) develop N fertilizer compounds with limited water solubility, or 2) modify water-soluble compounds to delay the release of their N.
 - iii. Another approach is to combine N fertilizers with chemicals that control unwanted N transformations in the soil, i.e. develop fertilizers amended with inhibitors of biochemical activity in the soil, such as nitrification or the conversion of urea to ammonium.
 - iv. Advantages of using slow-release N fertilizers: 1) reduction of N loss via leaching and surface runoff; 2) reduction of chemical and biological

- immobilization reactions in soil that decrease the supply of available N; 3) reduction of N loss via ammonia volatilization, or denitrification following nitrification.
- v. If slow-release fertilizers work under Florida conditions (high temperatures, high rainfall), then they should work just about anywhere.
- b. Mode of release
- i. Coated materials: Water-soluble materials containing ammonium (NH_4) and/or nitrate (NO_3) where dissolution is controlled by a physical barrier, e.g. by a coating.
 - ii. Solubility control: these are materials of limited water solubility, which, during their chemical and/or microbial decomposition, release plant-available N, e.g. the ureaforms and oxamide.
- c. Coated materials
- i. General information: Coatings applied to soluble materials usually are of three types:
 - (1) impermeable coatings with tiny holes through which solubilized materials diffuse.
 - (2) impermeable coatings that must be broken by abrasive, chemical, or biological action before N can be released.
 - (3) semipermeable coatings through which water diffuses until the inner osmotic pressure ruptures the coating or stretches it to increase its permeability.
 - ii. Sulfur-coated urea (SCU) 32-37% N
 - (1) First produced as an experimental material by TVA in the 1950s; first produced commercially in 1972.
 - (2) Produced by spraying molten sulfur (S) on a falling curtain of preheated urea particles in a rotating drum; a sealant is then applied to close pores in the S coating, followed by a conditioner to improve handling properties.
 - (3) Dissolution rate is controlled by varying the average thickness of the S coating; microbial population will also control release rate in soil.
 - (4) Can have problems with cracking of sulfur coating with abrasion.
 - (5) Sulfur coating slows down the release of the N from urea; soil microbes are required to a degree to break down the S coating; release can also occur through cracks.
 - (6) Factors that modify dissolution rates of SCU particles:
 - (a) N release rate increases with increase in soil temperature (biodegradation factor).
 - (b) the coating ruptures sooner in dry soil relative to wet soil.
 - (c) particles lying on soil surface tend to rupture sooner than particles within the soil.
 - (d) plant roots accelerate the dissolution rate of SCU.
 - (e) dissolution appears to be little affected by the soil pH in the range of 5 to 8.
 - (f) biological oxidation of the S in the coating residue is slow but eventually lowers soil pH because of sulfuric acid formation.

- (7) If SCU is applied during cool weather, can get a mottled appearance on plant leaves (yellow spots).
- (8) SCU gets an unfair break when analyzed to determine its classification for the fertilizer tag; samples are ground up (standard method for all materials) to determine water solubility; thus, the material dissolves, and the material must be labeled as a water-soluble N source, although it is slow-release.
- iii. Polymer-coated fertilizer (Example: Osmocote or Sierra)
 - (1) Osmocote: a complete mixed fertilizer (For example, 18-6-12).
 - (2) Coating: several layers of different composition; main component is a copolymer derived from soybeans.
 - (3) Nutrient release mechanism: Water vapor moves through the microscopic pores in the coating, causing the internal osmotic pressure to stretch the semipermeable and flexible coating, thereby enlarging the pores sufficiently to permit solution to pass through the coating.
 - (4) Release of nutrients is dependent on the presence of water (needs to be buried in the soil?).
 - (5) Use of the material is generally restricted to specialized operations due to its cost.
- iv. Plastic (resin) coated urea (Examples: Meister, Nutricote, Escote)
 - (1) Mixed soluble nutrients coated with polyoleum plastic (PVC).
 - (2) Works by varying the size of the pores through which N diffuses (for example, designed to last 70, 100, 150, 200, or 270 days).
 - (3) Non-existent burn potential.
 - (4) Plastic coating does not degrade very fast.
 - (5) Expensive.
- d. Uncoated organic materials (Urea is the main building block for all of these materials.)
 - i. Urea-aldehyde condensation products (Ureaforms)
 - (1) Trade names: Blue Chip, Powder Blue, Nitraform, Ureaform, Methylene urea (all about 40% N).
 - (2) A typical ureaform product may contain 30% of its N in forms that are soluble in cold water; the quality of the remaining N is determined by its solubility in boiling water (this should dissolve an additional 40% of the N for the material to have acceptable agronomic response).
 - (3) The chemical bonds of the ureaform material must be broken by microbial action to make the N available; factors that influence microbial activity in the soil will thus influence the N availability.
 - (4) Soil temperature is a major factor even in Florida; below 65 F generally see a substantial decrease in microbial activity, so at low temperature ureaform may not release N fast enough for a crop.
 - (5) Ureaforms are used mostly with turfgrasses, landscaping, ornamental horticulture, some citrus, and greenhouses.
 - ii. Isobutylidene diurea (IBDU) 31% N
 - (1) Manufactured in Japan and Germany; Expensive.

- (2) Relatively water-insoluble (0.2 g dissolves in 1 liter of water); dissolution is relatively insensitive to temperature, thus can be used in cool weather; release is not microbial dependent, but depends only on the dissolution rate of the particles.
- (3) One of the best slow-release N sources, especially in cool weather.
- (4) Because of the cost, IBDU is used primarily in specialty areas such as landscaping, golf courses, and nurseries; use in citrus groves is increasing.

*** If comparing responses of crops to slow-release N sources, IBDU is best, SCU is intermediate, and UF is worst; might use a combination of IBDU and SCU in the winter in a turfgrass situation.

*** Release rates in summer: SCU and IBDU, about 60 days; UF, about 90 days; it may take about 30 days for the less-soluble material to become available, thus may need to apply a soluble form of N along with the slow-release N; the activity of the soluble N will subside as the activity of the slow-release N kicks in.

iii. Oxamide $\text{NH}_2(\text{CO})_2\text{NH}_2$ 31.8% N

- (1) One of the best slow-release N products; All aspects of oxamide as slow-release N are excellent.
- (2) Water solubility is 0.4 g per liter of water (slightly higher than IBDU); release of N is not sensitive to temperature, thus it may be used in cool or warm weather.
- (3) The main problem limiting its use is the high cost of production, about \$2 per lb of N.
- (4) Oxamide may have an effect as a plant growth regulator as well as an N source because it appears to inhibit the formation of ethylene in plants.

e. Processed waste products

- i. The release of N from organic material is dependent on biological reactions (related to activity of soil flora and fauna).
- ii. Carbon to nitrogen ratio (C:N) of the material in question determines the release rate of N; if it is above 30:1, then can expect slow release.

f. Inhibitors

i. Nitrification inhibitors

- (1) Prevention of the conversion of NH_4 to NO_3 in the soil; keep fertilizer products in the NH_4 form longer, thus less likely to leach.
- (2) N-SERVE (nitrapyrin), produced by DowElanco; inhibits the action of Nitrosomonas bacteria, which convert NH_4 to NO_2 in the soil.
- (3) DCD (dicyandiamide), contains 66% N, has been tested as both a nitrification inhibitor and a slow-release N source; used in Europe.
- (4) In general, nitrification inhibitors do not work well in Florida; N-Serve has too high a vapor pressure relative to Florida soil temperatures to remain long enough in the soil; DCD also does not work well at high soil temperature.

ii. Urease inhibitors - Retard the hydrolysis of urea in the soil

2. Use of slow-release nitrogen fertilizers
 - a. The cost of slow-release materials is greater than for conventional materials, thus must consider the potential savings in other areas that would more than make up the cost difference, e.g. **lower overall N rate**, or **lower application cost** due to the less frequent applications that would be necessary with slow-release N.
 - b. Environmental concerns may also favor the use of slow-release materials.
 - c. The type of crop to be grown will determine if slow-release forms would be advantageous or detrimental; e.g. slow-release would not be appropriate for radishes, but might be great for sugarcane, citrus, or turfgrass.

3. Nitrogen Solution Fertilizers (Three types: high pressure, low pressure, and no pressure.)
 - a. High pressure solution - Anhydrous ammonia (NH_3), 82% N
 - i. Shipped and stored at 180-200 psi.
 - ii. Must be injected into the soil.
 - b. Low pressure solutions
 - i. Nitranous solutions
 - (1) Combination of anhydrous ammonia and ammonium nitrate, or anhydrous ammonia and urea; stored in fiberglass tanks; contain about 40% N.
 - (2) Have a high vapor pressure (30 psi), therefore need to incorporate in the soil to avoid loss to the air.
 - (3) Main advantage is a low salt-out temperature, which is below 32 F (salt-out temp is the temp at which solid crystals reform in the solution).
 - (4) Not used much in Florida, but are used more in cooler climates.
 - ii. Aqua ammonia ($\text{NH}_3 + \text{H}_2\text{O}$) 21% N
 - (1) Water solutions of ammonia; form a lot of heat when mixed, thus must be cooled before using to bring down the vapor pressure such that NH_3 loss is minimized.
 - (2) Applied to moist soil, then incorporated, but not as deep as with anhydrous ammonia; do not apply to the soil surface without incorporation.
 - (3) Does not kill as much of the soil microbial population as anhydrous ammonia.
 - c. Non-pressure solutions
 - i. Urea-ammonium nitrate solution (Uran) 28, 30, or 32% N.
 - (1) Most common non-pressure N solution, especially in Florida.
 - (2) The 32% N solution contains 33-35% urea and 45-47% ammonium nitrate; salt-out temperature is 32 F.
 - (3) Can be surface-applied with no loss of N through immediate volatilization (no vapor pressure).
 - (4) Can also be applied foliar if diluted enough to prevent leaf burn.
 - ii. Ammonium nitrate solution (Feran) 21% N
 - (1) Ammonium nitrate dissolved in water; salt-out temperature is 47 F.
 - d. Advantages of using nitrogen solutions
 - (1) Ease of handling, transportation, and application.
 - (2) Application uniformity is very good; each drop has exactly the same properties as any other.

- (3) Can be combined with pesticide application or applied with irrigation water (fertigation).
 - (4) Easily blended to form NPKS mixed liquid fertilizers.
 - (5) Solutions do not leach any more than solid fertilizers; leaching has to do with excess rain or irrigation; if water carrier evaporates following solution fertilizer application, then have solid fertilizer again (i.e. liquid and solid fertilizers will behave in a similar manner in the soil); citrus groves and golf courses use a lot of solution fertilizer.
- e. Disadvantages of using nitrogen solutions
- (1) Takes some specialized equipment to handle.
 - (2) May cost more than solid fertilizer, especially due to transportation cost since much of the weight is water.

Nitrogen form	Cost per lb of N (\$)
Ammonia NH ₃	0.15
N solution (21% N)	0.32
Ammonium nitrate NH ₄ NO ₃	0.28
Urea CO(NH ₂) ₂	0.33
Ammonium sulfate (NH ₄) ₂ SO ₄	0.27
Sulfur-coated urea	0.43
Calcium nitrate Ca(NO ₃) ₂	0.59
Sodium-potassium nitrate	0.80
Urea formaldehyde	0.60-0.70
IBDU	1.10
Potassium nitrate KNO ₃	1.40
Methylene urea (Nutralene)	1.11
Osmocote 18-4-12	0.69/lb material
Sierra 16-6-10	0.95/lb material
Escote 19-6-12	0.86/lb material
Nutricote 17-6-8	1.04/lb material
Prokote Plus	0.95/lb material
Meister 17-6-12	0.78/lb material
Oxamide	2.00/lb material

Average plant concentrations of essential elements.

Element	Abbreviation	Number of atoms relative to molybdenum
Molybdenum	Mo	1
Copper	Cu	100
Zinc	Zn	300
Manganese	Mn	1,000
Boron	B	2,000
Iron	Fe	2,000
Chlorine	Cl	3,000
Sulfur	S	30,000
Phosphorus	P	60,000
Magnesium	Mg	80,000
Calcium	Ca	125,000
Potassium	K	250,000
Nitrogen	N	1,000,000
Oxygen	O	30,000,000
Carbon	C	35,000,000
Hydrogen	H	60,000,000