

TECHNICAL NOTE

USDA - Natural Resources Conservation Service
Boise, Idaho

TN NM No. 6 June 2011

THE NITROGEN CYCLE ITS TRANSFORMATION EFFECTS ON WATER, SOIL AND AIR QUALITY RESOURCE CONCERNS IN IDAHO

R. D. Johnson, State Nutrient Management Specialist, NRCS Boise, Idaho

THE NITROGEN CYCLE

We have all seen schematics of the nitrogen cycle (Figure 1). The nitrogen, like all nutrients in the environment, undergoes different processes, both natural and man-made. The objective in discussing the nitrogen cycle is to assist the nutrient management planner or reader in understanding the different processes that Nitrogen undergoes within this natural cycle and the impact it has on Idaho's environment.

This Tech Note is the first of three that will discuss the common nitrogen fertilizer forms, generic fertilizer products, and general classes of chemical and products that are being used to inhibit one or more nitrogen transformation will be discussed as to their effect on the Nitrogen Cycle and potentially reducing Nitrogen Form effect on Idaho's environment. These chemicals are classified into four generic groups; 1) Nitrogen Stabilizer, 2) Nitrification inhibitors, 3) Urease inhibitor, and 4) Slow or Controlled Release Fertilizers. Each group will be discussed as to their effect on the Nitrogen Cycle, nitrogen transformations, forms, and resulting resource concerns.

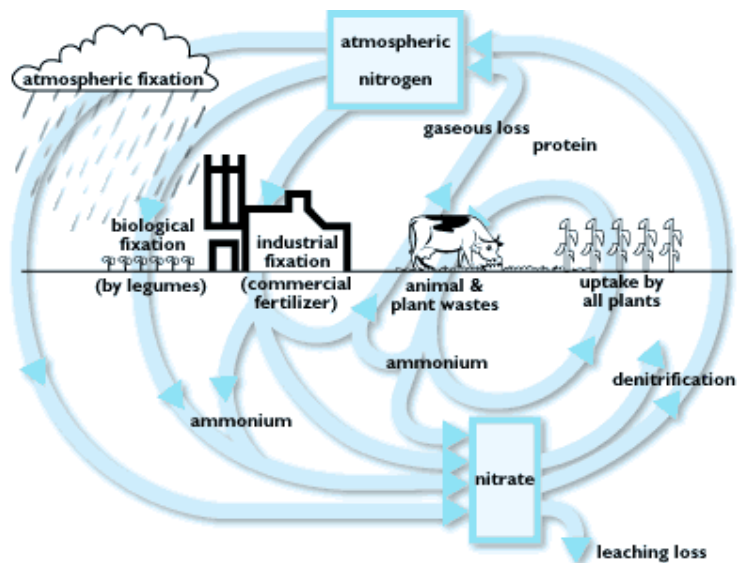


Figure 1. The Nitrogen Cycle (**Nitrogen** - Vision **Ag Home**)

Before discussing the impact of various forms of nitrogen has on Idaho's Environment we need to discuss the new National Nutrient Management Strategy of the 4R's: **Right Source of Nutrients; the Right Time of Application, the Right Rate, and the Right Method of Application.**

Our National Nutrient Management Strategy of the 4R's is a strategy of assisting the producer in managing the application of nitrogen in meeting the Practice Specifications as outlined in the our Nutrient Management Standard, its option jobsheets and program guidelines. This emphasis is designed to address the need for a higher level of nutrient management using the 4R's to meet our National Water Quality objectives. This emphasis is a change in how we look at nitrogen management, a change from looking at increasing nitrogen use efficiency by increase yields or production economics to one that looks at the fact that as nitrogen rates increase there is a corresponding increase in risk to the environment.

The Fertilizer and Chemical Industry will be inventive in providing products and chemicals with varying claims of addressing the environmental resource concerns associated with Nitrogen usage in crop production. Our national and state standard and guidance for supporting the use of these products are based on the recommendation of Land Grant Universities and USDA (ARS). However, national guidance has to be broad to cover the all states; each state has the responsibility to make sure that these products and practices meet regional if not local conditions and farming practices. As new products come on board, our response to their certification in meeting program guidelines will be Land Grant University or ARS research on their ability to be Nitrogen Inhibitors, stabilizers or slow or controlled release formulations. This takes time, so we sometimes have to take the research data from the manufacturer and knowledge of chemical process to make a professional qualification decision.

It is not our intent to indorse or to disqualify a product based on hear say or a company promotional literature. As with our N fertilizer rate recommendations, we based our guidance on research as published or referenced in the UI or adjacent States Land Grant Universities' Research Publications, Fertilizer Guides and Crop Production Guides (FGs). In the development of guidance from literature, there is a significant amount of variability from research locations to locations to fertilizer and chemical product responses, particularly to low rates of applications. This is where it is important to visit with the researcher, just as it important for the planner to visit with the producer as to their past experience with a particular field, soil or climatic conditions during the production of a crop; these are legitimate reasons to question a N rate recommendations obtained from the FGs or the performance of a particular chemical. What is important is to get the producer to look at the nitrogen and water balance in the field in relationship to the growth stage of the crop. The climate, weather and the resulting field conditions dictate when a producer can apply nitrogen or consider using a chemical to extent the availability of N.

The problem is often nitrogen fertilizer prices, application equipment availability and management time end up making the decision when the producer chooses to actually apply nitrogen. Sometimes it a hard sale to get a producer to apply the 4 R's when all they can see is price per acre. So is the use of chemicals the result of trying to address nitrogen loss and the environment? Do our producers have sufficient knowledge to make the observations in trying these chemicals? It is our opportunity to assist and educate, first ourselves and then our producers.

FATE OF FERTILIZER NITROGEN

Nitrogen (N) is one of the primary nutrients essential to crop production and life in general. Nitrogen along with Hydrogen, Carbon, Phosphorus, Oxygen and Sulfur make up the biologically active constituents of life. With the exception of Hydrogen and Oxygen, these primordial nonmetals have the common chemical property of multiple oxidation states, a feature that makes them very active in biological and environmental systems. These six elements make up the core for energy transformation in biological system, however, this also makes them very important environmental constituents. With the exception of Phosphorus, this group of elements can naturally exist as chemically active solids, liquid or gaseous compounds, which make them chemically active in the environment. Of the six elements, nitrogen is the most reactive, having nine oxidation states (-3 to +5) (Table 1.). As we discuss nitrogen's

Oxidation State	Species	Name
-3	NH ₃ , NH ₄ ⁺ , (NH ₂) ₂ CO	Ammonia (gas), Ammonium ion (liquid), Urea (solid or liquid)
0	N ₂	Nitrogen (gas)
+1	N ₂ O	Nitrous Oxide (laughing gas) Green House Gas
+2	NO	Nitric Oxide (gas)
+3	HNO ₂ , NO ₂ ⁻	Nitrous acid (liquid), Nitrite ion (liquid)
+4	NO ₂	Nitrogen Dioxide (gas)
+5	HNO ₃ , NO ₃ ⁻	Nitric Acid (liquid), Nitrate ion (liquid)

key transformations and forms in its cycle, you will see where nitrogen form and their oxidation states play a role in Idaho's environment.

Nitrogen like the other essential plant nutrients is found throughout the environment. It is an essential element for life, however, because of the quantity applied, cultural practices, climatic conditions, crop uptake timing, and fertilizer prices. Nitrogen Form via primary avenues of loss can be used to develop the major resource concern to Idaho's environment (Table 2.). Research shows that only 40 to 70% of the fertilizer nitrogen applied ends up in crop production. UI literature suggests that only about 50% of the applied N is taken up by winter wheat, the primary small grain crop found throughout Idaho, during the year following fertilizer application with about 25% immobilized during residue decomposition or remains in the soil as nitrate, and the remaining 25% is lost from the plant rooting zone by leaching and/or denitrification. Some of the immobilized N will be mineralized (5% per year) and will be available to subsequent crops. Nitrate remaining in the profile at the end of the cropping season will be available to the succeeding crop unless lost over the winter and spring by leaching or denitrification.

Table 2.

Avenues of Loss	Principal Nitrogen Forms	Percent Loss
Immobilization	Organic (-NH ₂), Ammonium (NH ₄ ⁺) and Nitrate (NO ₃ ⁻)	10 – 40%
Erosion	Organic (-NH ₂), Ammonium (NH ₄ ⁺) and Nitrate (NO ₃ ⁻)	0 – 20%
NH ₂ Volatization	Ammonia (NH ₃), Urea (CO=(-NH ₂) ₂)	0 – 30%
Leaching	Nitrate (NO ₃ ⁻) and Urea (CO=(-NH ₂) ₂)	0 – 20%
Denitrification	Nitrate (NO ₃ ⁻) and Nitrite (NO ₂ ⁻)	5 – 35%

Table 3

Fertilizer Chemical Building Blocks

Raw and Inter Materials	Fertilizer	Chemical Formula	Fertilizer Grade	Calcium Carbonate Equivalence per 100 lb of Product	Salt Index per 100 lb of Product
Natural Gas (CH ₄) + Air(N ₂)	Ammonia	NH ₃	82-00-00	-148	47
NH ₃ + H ₂ O	Aqua	NH ₂ OH	20-00-00	-36	11
NH ₃ + CO ₂	Urea	C=O(NH ₂) ₂	46-00-00	-71	75
NH ₃ + O ₂ + H ₂ O	Nitric Acid	HNO ₃	28-00-00	-50	86
NH ₃ + HNO ₃	Ammonium Nitrate	NH ₄ NO ₃	34-00-00	-61	105
Calcium Carbonate + HNO ₃	Calcium Nitrate	Ca(NO ₃) ₂	15-00-00-00S-21Ca	20	53
Urea + NH ₄ NO ₃	Urea Ammonium Nitrate	C=O(NH ₂) ₂ NH ₄ NO ₃	32-00-00	-57	90
Sulfur + O ₂ + H ₂ O	Sulfuric Acid	H ₂ SO ₄	00-00-00-32S	-96	27
NH ₃ + H ₂ SO ₄	Ammonium Sulfate	(NH ₄) ₂ SO ₄	21-00-00-24S	-110	69
	Ammonium thiosulfate	(NH ₄) ₂ S ₂ O ₃	12-00-00-26S	-100	70
Phosphate Rock	MonoCalcium Phosphate	Ca(H ₂ PO ₄) ₂ (CaSO ₄)	00-20-00-12S-20Ca	0	10
Ca ₁₀ F ₂ (PO ₄) ₆ + H ₂ SO ₄			00-45-00-01S-15Ca	0	0
Ca ₁₀ F ₂ (PO ₄) ₆ + H ₃ PO ₄	Phosphoric Acid	H ₃ PO ₄	00-54-00	-110	20
NH ₃ + H ₃ PO ₄	MonoAmmonium Phosphate	NH ₄ H ₂ PO ₄	11-52-00	-75	34
2NH ₃ + H ₃ PO ₄	DiaAmmonium Phosphate	(NH ₄) ₂ HPO ₄	18-46-00	-70	30
NH ₃ + PolyPhos Acid (H ₂ P ₂ O ₇)	Ammonium Polyphosphate	(NH ₄) ₂ H ₃ P ₂ O ₇	10-34-00	-90	20
NH ₃ + H ₂ SO ₄ + H ₃ PO ₄	Ammonium Phosphate Sulfate	NH ₄ H ₂ PO ₄ (NH ₄) ₂ SO ₄	16-20-00-14S	-88	35
Potash Rock or Salt Water	Potassium Chloride	KCl	00-00-60	0	116
Potash + Sulfuric Acid	Potassium Sulfate	K ₂ SO ₄	00-00-52-18S	0	46
Potash + HNO ₃	Potassium Nitrate	KNO ₃	13-00-45	0	74

¹Western Fertilizer Handbook

NITROGEN LEACHING

Leaching is often thought to occur only in coarse-textured soils. Nitrogen leaching is thought to occur only with nitrate-N. The urea molecule once in solution is also subject to leaching due to its neutral charge. Urea remains a potential leachable form until it goes through hydrolysis and conversion to the ammonium form. Both urea and nitrate may be leached from naturally well-drained or tile-drained soils by percolating water. One inch of infiltrating water will move urea in solution and nitrate 1 to 2.5 inches downward in clay loam and sandy soils, respectively. Thus, during periods of excess rainfall or under continuous drip irrigation, leaching may move urea and nitrate out of the effective rooting zone of shallow rooted crops. Another avenue of potential deep nitrogen flow can take place in fine textured soil and field under no-till, where surface applied nitrogen could be moved by preferential flow (crack, worm, insect and root channel flow) deep into the profile.

Crop utilization or uptake of nitrogen will be addressed in Tech Note 7 and is an important factor to consider as we address nitrogen timing and the use of nitrogen inhibiting additives or slow or control release fertilizer products. Cultural practices, cost of fuel, time, large acreages and climate often dictate when nitrogen is applied. This often results in nitrogen being applied several weeks, if not months, ahead of when it is needed by the crop. Because of these and ongoing nitrogen transformation, nitrogen use efficiency is low.

The goal is to work with producers, who often have a price oriented opinion and get concurrence by our investigation to address either water quality or air quality resource concerns from the use of commercial fertilizers or animal waste biosolids. In developing NMP guidance we try to develop uniformity in program, which is difficult because nitrogen management are going to be different from region to region with different technologies used in applying nitrogen and the different field and climatic conditions found across Idaho. For this Tech note four (4) basic forms of nitrogen will be discussed; Ammonia (NH_3), Urea ($\text{NH}_2)_2\text{CO}$), Ammonium (NH_4^+) and Nitrate (NO_3^-). Each of these forms have the ability to contribute to either or both water or air quality resource concerns and each has physical and chemical features that make it unique as potential resource concern constituents. As we discuss these four forms of nitrogen keep in mind that as we look to management practices and products that are listed in either conservation practice or national enhancement jobsheets, the intent is to alter either the physical/chemical features of a nitrogen form or the transformation that the nitrogen form go through under specific environmental conditions.

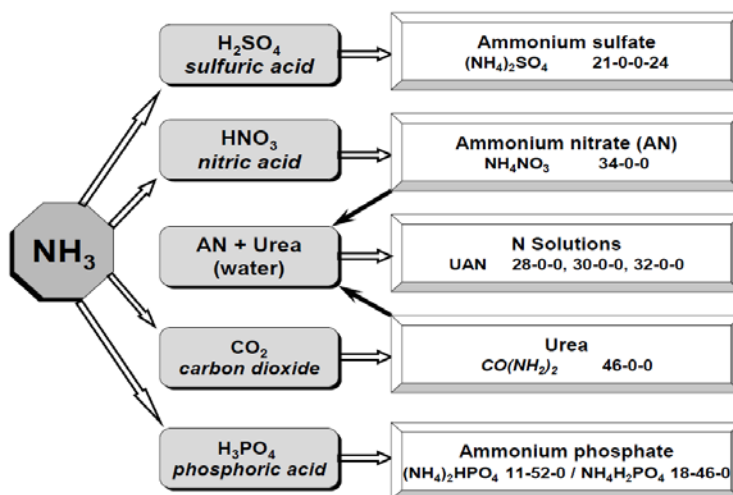
First let's discuss commercial chemical ammoniacal (Ammonia (NH_3), Urea ($\text{NH}_2)_2\text{CO}$), Ammonium (NH_4^+)) fertilizers. Organic fertilizers have their own unique biological and chemical characteristics and transformations, which are too complex to be included in this discussion but will be addressed in Tech Note 9. For practical purposes, the major source of commercial chemical fertilizers all starts with the production of ammonia (NH_3), a process involving the chemical fixation of the atmospheric Nitrogen (Dinitrogen- N_2). In the fixation process inert dinitrogen is chemically reduced to its lowest oxidation state (-3). Following chemical fixation gaseous ammonia is pressurized to form a liquid nitrogen form marketed as Anhydrous Ammonia (82-0-0_{liq/gas}).

Ammonia can be further combined with water, acids, or carbon dioxide to produce the common ammonium fertilizers marketed in Idaho.

Anhydrous ammonia commercially is converted to into a low pressure product by reacting gaseous ammonia with water. The resulting product is Aqua Ammonia (20-0-0_{liq}). Another commercial dry nitrogen product is produced by reacting NH_3 with Carbon Dioxide (CO_2) under heat and pressure to form a compound called carbonyl diamine, which when granulated results in a solid (ammonia) pellet, marketed as Urea (46-0-0_{solid}).

These three ammoniacal products all have the same characteristics, upon exposure to

the atmosphere they will undergo chemical and physical process with the end result of volatilizing off as gaseous ammonia. Ammonia is oxidized with oxygen to form an intermediate gas, Nitric Oxide (NO), which is further oxidized with oxygen to form Nitrogen Dioxide (NO_2). This red color gas is reacted with water to form Nitric Acid (HNO_3). This oxidation process results in production of the nitrate (NO_3^+), the most oxidized form on nitrogen (+5). The nitric acid is reacted with ammonia to produce Ammonium Nitrate (34-0-0_{solid}) or (20-0-0_{liq}). Ammonia is also used in the production of other fertilizer products. These products are the result of reacting ammonia (a base) with Sulfuric, and Phosphoric acids. The resulting ammonium fertilizers; Ammonium Sulfate (21-0-0-24_{solid}), MonoAmmonium Phosphate (11-52-0_{solid}), DiAmmonium Phosphate (18-46-0_{solid}), (10-34-0_{liq}), Ammonium Phosphate



Sulfate (16-20-0-14S_{solid}) along with ammonium nitrate and urea make up the majority of the commercial fertilizers. Ammonium nitrate and urea are combined or chemically mixed to form the fertilizer product Urea Ammonium Nitrate (UAN), (32-0-0_{liq}).

WHAT ARE THE WATER AND AIR RESOURCE CONCERN THAT WE ARE TRYING TO ADDRESS?

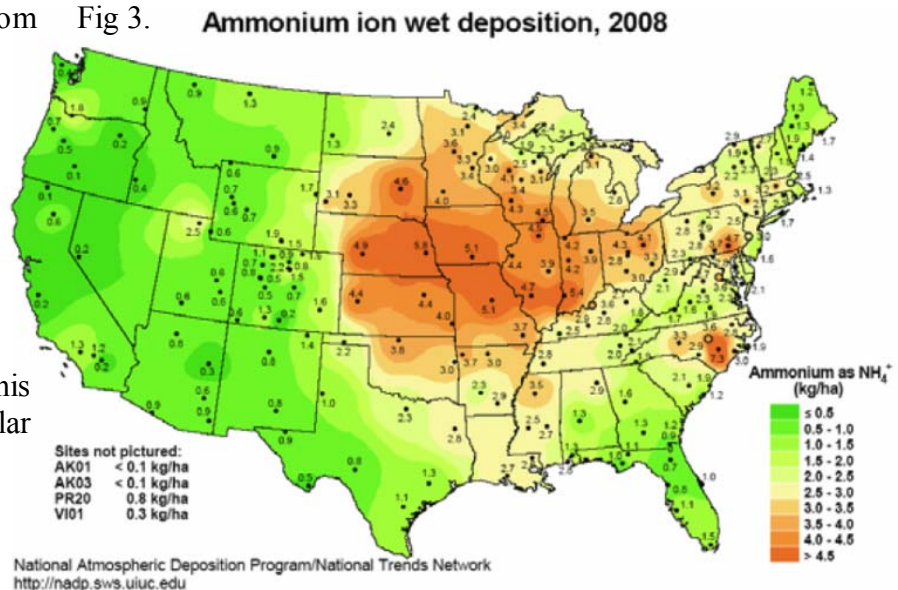
The Ammonia Concern

Studies by the National Research Council (NRC, 2002) identified ammonia emissions as a major air quality concern at regional, national, and global levels. The potential negative impacts of ammonia are many. Deposition of atmospheric ammonia can cause eutrophication of surface waters, where phosphorus concentrations are sufficient to support harmful algal growth. Nutrient enrichment and eutrophication lead to the decline of aquatic species, including those with commercial value. Sensitive crops such as tomatoes, cucumbers, conifers, and fruit cultures can be damaged by over-fertilization caused by ammonia deposition if they are cultivated near major ammonia sources. The deposition of ammonia on soils with a low buffering capacity can result in soil acidification or basic cation depletion.

Volatilized ammonia can travel hundreds of miles from the site of origin. Ammonia emissions from the Midwestern may contribute to eutrophication of the Gulf of Mexico. The Chesapeake Bay is likely receiving ammonia deposition from upwind areas with intensive agricultural operations up wind from the watershed draining into Chesapeake Bay.

In addition to its effects on water, plant, and soil systems, ammonia reacts with other compounds to form particulate matter (PM) with a diameter of 2.5 microns or less, which is referred to as PM_{2.5}. This classification of PM is of particular concern because the small size of the particles allows them to penetrate deep into the lungs.

Several recent community health studies indicate that significant respiratory and cardiovascular problems are associated with exposure to PM_{2.5}. Other problems associated with long-term exposure to fine particles include premature death and increased hospital admissions from respiratory causes. Children, the elderly, and individuals with compromised cardiovascular health or lung diseases, such as emphysema and asthma, are especially vulnerable to such health problems caused by PM_{2.5}. Although studies show that the majority of the ammonia emissions are associated with domestic animal production, U.S. Environmental Protection Agency (EPA) estimates 50 percent to 85 percent, with commercial fertilizers contributing an additional 9 to 10 percent.



Urea and Ammonia Volatilization

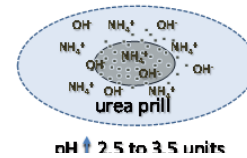
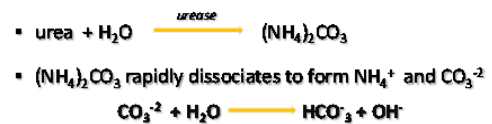
The Best Management Practices (BMPs) suggested for reduction in ammonia loss from applications of ammonia and urea forms of nitrogen are dictated by the moisture, physical conditions of the field, and depth of application of the fertilizer. Ammonia can be applied as a gas, liquid or solid. If applied as a gas following application the gaseous ammonia disperses like a gas. The cooling effect of expansion is sufficient to freeze the injection zone. If moisture is available, ammonia reacts with moisture and upon reaction generates heat and if there is sufficient moisture, the ammonia is converted into a liquid form. The chemical hydration of the ammonia molecule forms ammonium hydroxide (NH_4OH), which gives the nitrogen molecule a positive charge and has the capable of adsorbing to negative charged organic and mineral soil surfaces. This chemical reaction elevates the hydroxyl (OH^-) ions in the solution, which results in elevation of pH above 9 in the inject zone.

Urea, the solid chemical form of ammonia has become a popular topdress-surface applied fertilizer. Research since the late 60's has shown that agronomically urea is an effective topdress material based on economic of production. The fact that urea was subject to ammonia volatilization loss through the activity of the urease enzyme, which is found throughout the environment was discounted because of increasing world supplies and manufacturing economics. The enzymatic biological reaction of urease creates ammonium carbonate (smelling salts), which rapidly dissociates into ammonium and bicarbonate with water causing an elevation of pH. Under this environment the ammonium converts to ammonia and if this occurs at the soil surface results in the loss of ammonia as a gas. Only in recent years has the research shifted from crop production economics to demonstration of the significant of ammonia emissions. The most recent work is a study conducted by researchers at Montana State University showing that even under restricted conditions of cold temperatures that 40% of surface applied urea can be lost through ammonia volatilization. This research concluded that: soil moisture conditions at surface that result in dissolution of urea granules (i.e. prolonged dampness) without rain promote high NH_3 (g) losses, conditions during the late fall or early spring.

Many factors in the environment contribute to volatility. The factors increasing volatility that should be considered when choosing the appropriate rate include:

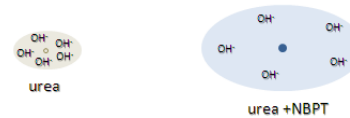
1. Higher soil moisture
2. Drying conditions including low humidity, sun and wind
3. Higher air and soil temperatures
4. Higher pH soils have a higher potential for volatility
5. Lower organic matter and lower CEC soils
6. Higher amounts of crop residue which have higher amounts of urease
7. Length of control needed.

Urea reactions in the soil



NBPT = n-(n-butyl) thiophosphoric triamide

- urease inhibitor
- allows more time for urea to diffuse away from point of application so | soil pH is moderated



... or rainfall events so urea is leached below the soil surface

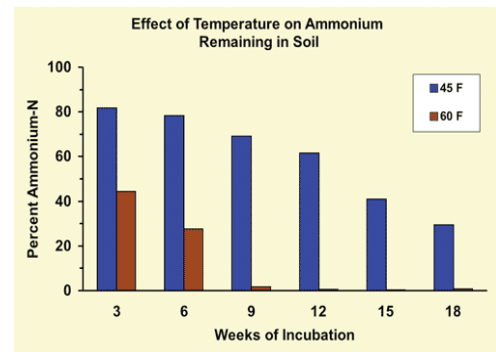
Nitrification

Nitrification is the biological oxidation of ammonia in the formation of two new forms of nitrogen, nitrite and nitrates. The oxidation of ammonia to nitrite is usually the rate limiting step of nitrification. Nitrification is an important step in the nitrogen cycle in soil and in the production of crops in Idaho. The oxidation of ammonia into nitrite is performed by two groups of organisms, ammonia-oxidizing bacteria and ammonia-oxidizing archaea. In soils the most studied ammonia oxidizing bacteria (AOB) belong to the genera *Nitrosomonas* and *Nitrosococcus*. The second step (oxidation of nitrite into nitrate) is done (mainly) by bacteria of the genus *Nitrobacter*. Nitrifying organisms are chemoautotrophs, and use carbon dioxide as their carbon source for growth. Some AOB possess the enzyme, urease, which catalyzes the conversion of the urea molecule to two ammonia molecules and one carbon dioxide molecule. *Nitrosomonas europaea*, as well as populations of soil-dwelling AOB, has been shown to assimilate the carbon dioxide released by the reaction to make biomass, and harvest energy by oxidizing ammonia (the other product of urease) to nitrite. This feature may explain enhanced growth of AOB in the presence of urea in acidic environments. These bacteria known as “nitrifiers” are strict “aerobes,” meaning they must have free dissolved oxygen to perform their work. Nitrification occurs only under aerobic conditions at dissolved oxygen levels of 1.0 ppm or more. At dissolved oxygen (DO) concentrations less than 0.5 ppm, the growth rates are minimal. This may be important in how slowly ammonium converts in cold saturate or near saturated soils, like we have in parts of Northern and Eastern Idaho. Nitrification requires a long retention time, a low food to microorganism ratio, and adequate buffering (alkalinity).

Soil temperature also affects the rate of nitrification. Nitrification reaches a maximum rate at temperatures between 86°F and 95°F. At temperatures of 104°F and higher, nitrification rates fall to near zero. At temperatures below 72°F, nitrification proceeds at a slower rate, but will continue at temperatures of 48°F and less. However, if nitrification is lost, it will not resume until the temperature increases to well over 50°F. Some of the most toxic compounds to nitrifiers include cyanide, thiourea, phenol and heavy metals such as silver, mercury, nickel, chromium, copper and zinc. Nitrifying bacteria can also be inhibited by nitrous acid and free ammonia, both could be present under the conditions that occur in our North and Eastern Idaho Soils.

Together with ammonification, the conversion of organic N (organic matter and decaying proteins), nitrification makes up the mineralization process, which release ammonium-N to the nitrogen pool for crop production and Nitrogen Cycle transformations.

In the nitrification process the oxidation state of nitrogen is elevated to its high oxidation state (+5), in this state the nitrogen molecule with its 3 associated oxygen molecules is transformed from a positive charged molecule to a negative molecule. This transformation makes the nitrate form of nitrogen subject to movement with water or potential leaching. The nitrate molecule is also a chemical well oxygenated molecule, which depending on soil moisture content and biological activity, serving as chemically bound oxygen for soil microbes and is capable of reacting with reduced metals like iron and manganese.



WHY ARE NITRATE-N AND NITRITE-N OF IMPORTANCE?

Nitrogen-containing compounds act as nutrients in streams and rivers. Nitrate reactions [NO_3^-] in fresh water can cause oxygen depletion. Thus, aquatic organisms depending on the supply of oxygen in the stream will die. The major routes of entry of nitrogen into bodies of water are municipal and industrial wastewater, septic tanks, feed lot discharges, animal wastes (including birds and fish) and discharges from car exhausts. Bacteria in water quickly convert nitrites (NO_2^-) to nitrates (NO_3^-).

Nitrates can produce a serious condition in fish called "brown blood disease." Similarly, nitrates react directly with hemoglobin in human blood and other warm-blooded animals to produce methemoglobin. Methemoglobin destroys the ability of red blood cells to transport oxygen. This condition is especially serious in babies under three months of age. It causes a condition known as methemoglobinemia or "blue baby" disease. Water with nitrate-N levels exceeding 10 mg/l (ppm) should not be used for feeding babies. Nitrite-N levels below 90 mg/l and nitrate-N levels below 0.5 mg/l seem to have no effect on warm water fish.

DENITRIFICATION, THE PRODUCTION OF DINITROGEN (NITROUS) OXIDE (N_2O)

Where is the Nitrous Oxide coming from?

Nitrous oxide (N_2O) is produced naturally in soils through denitrification processes. These natural emissions can be increased by a variety of agricultural practices and activities including:

Direct addition of nitrogen to soils:

- Use of synthetic and organic fertilizers
- Production of nitrogen-fixing crops
- Cultivation of high organic content soils
- Application of livestock manure to croplands and pasture

Indirect addition of nitrogen to soils:

- Surface run-off and leaching of applied nitrogen into ground water and surface waters
- Denitrification of the organic nitrogen in livestock manure and urine.

Agricultural activities contribute directly to emissions of greenhouse gases (GHG) through a variety of processes. Nitrous oxide (N_2O) is a major non-carbon-dioxide GHG along with methane (CH_4). Table 4 shows the contribution of the various GHG emissions from Agriculture and the significance of their contribution in Carbon Dioxide Equivalence. The major methane contributors are enteric fermentation in domestic livestock (cow burps), livestock manure management, rice cultivation, agricultural soil management, and field burning of agricultural residues. As depicted in the table domestic livestock generates the major of the methane emissions from agriculture, generating in excess of 30% of the total Carbon Dioxide Equivalence with Agricultural Soil Management generating in excess of 50% of the total Carbon Dioxide Equivalence in the form of nitrous oxide. Carbon dioxide (CO_2) making up in excess of 72% of the GHGs.

Table 4.

Emissions from Agriculture (Tg CO ₂ Eq.)								
Gas/Source	1990	2000	2005	2006	2007	2008	2009	
CH₄	171.2	186.7	190.1	191.7	198.2	197.5	196.8	
Enteric Fermentation	132.1	136.5	136.5	138.8	141.0	140.6	139.8	
Manure Management	31.7	42.4	46.6	46.7	50.7	49.4	49.5	
Rice Cultivation	7.1	7.5	6.8	5.9	6.2	7.2	7.3	
Field Burning of Agricultural Residues	0.3	0.3	0.2	0.2	0.2	0.3	0.2	
N₂O	212.4	224.0	228.7	227.1	227.6	228.8	222.5	
Agricultural Soil Management	197.8	206.8	211.3	208.9	209.4	210.7	204.6	
Manure Management	14.5	17.1	17.3	18.0	18.1	17.9	17.9	
Field Burning of Agricultural Residues	0.1	0.1	0.1	0.1	0.1	0.1	0.1	
Total	383.6	410.6	418.8	418.8	425.8	426.3	419.3	

As an interesting side note, On-farm GHG emissions are significant contributor to the overall global "Greenhouse Effect", however, water vapor has and will be the largest natural contributor to the Greenhouse Effect. Denitrification and the generation of Nitrous Oxide is a natural process in which the nitrate molecule is stripped of oxygen under anoxic or anaerobic conditions. In the process the nitrogen molecule is reduced through a series of intermediate gaseous nitrogen oxide products and may ultimately end up as molecular nitrogen (N₂).

Denitrification can be biological and/or chemical.

The biological process is a respiratory process in which the microbes reduce oxidized forms of nitrogen in response to the oxidation of a carbon source such as organic matter at low oxygen levels (anoxic) in the soil. The process starts with nitrate (NO₃⁻). Once the nitrate is reduced to nitrite (NO₂⁻) then both biological and chemical denitrification takes place with the generation of nitrous (N₂O) and nitric (NO) oxides.

Table 5. Role of Atmospheric Greenhouse Gases (man-made and natural) as a % of Relative Contribution to the "Greenhouse Effect"

Based on concentrations (ppb) adjusted for heat retention characteristics	Percent of Total	Percent of Total -- adjusted for water vapor
Water vapor	-----	95.000%
Carbon Dioxide (CO ₂)	72.369%	3.618%
Methane (CH ₄)	7.100%	0.360%

2009 Agriculture Chapter Greenhouse Gas Emission

Denitrification can take place at anytime that the soil is at or near saturation or when rapid biological activity (high crop residues) are present. The reduction of nitrate under anoxic conditions (when the oxygen levels in the soil drop below 0.5%) involves the same soil organisms that are responsible for nitrification. The condition often takes place during period of high microbial activity when oxygen is in short supply and periods of heavy rainfall or irrigation. In terms of the general nitrogen cycle, denitrification completes the cycle by returning N₂ to the atmosphere. The process is performed primarily by heterotrophic (requires carbon) bacteria (such as *Paracoccus denitrificans* and various pseudomonads).

Research to identify sources of nitrous oxide in soils has indicated that most, if not all, of the N₂O evolved from soils is produced by biological processes and that essentially all of the N₂O evolved through the reduction of nitrate by denitrifying microbes under anaerobic conditions. It is now well established, however, that nitrifying microbes contribute significantly to emissions of N₂O from soils and that most of the N₂O evolves from aerobic soils treated with ammonium or ammonium-yielding fertilizers such as urea is produced during the oxidation of ammonium to nitrate by these microbes. The observation has been verified through studies showing the N₂O emissions can be greatly reduced

through the addition of nitrification inhibitors such as nitrapyrin, which affect the nitrifiers but not the denitrifiers.

NITRIFICATION STABILIZERS, INHIBITORS AND CONTROLLED RELEASE FERTILIZERS, WHERE DO THEY FIT?

By definition:

1. **Nitrogen Stabilizer** – substance added to a fertilizer which extends the time the nitrogen component of the fertilizer remains in the soil in the ammoniacal form. (Official 2001)
2. **Nitrification inhibitor** – substance that inhibits the biological oxidation of ammoniacal nitrogen to nitrate nitrogen (Official 2001)
3. **Urease inhibitor** – substance which inhibits, block or delay the hydrolytic action on the urea molecule by the urease enzyme (Official 1997)
4. **Slow or Controlled Release** - chemical binding with urea or ammonia in a form which delays its availability for plant uptake and use after application, or which extends its availability to the plant. (Official 1985).

Each has the ability of inhibiting nitrification by chemical or physical process. Nitrification inhibitors are used to decrease the possibility that large losses of nitrate will occur between the time a nitrogen fertilizer is applied and the time it is taken up by plants. Urease inhibitors are included in the list but do not have a direct effect on nitrification other than dispersing urea and restricting ammonium production.

TYPES AND USES OF NITRIFICATION INHIBITORS (NIs)

A number of compounds have been shown to inhibit nitrification in laboratory and field studies; however, only Nitrapyrin and Terrazole have U.S. EPA approval for use on cropland in the United States. Additional compounds are used in Japan and other countries and registration is expected for additional compounds in the U.S. N-Serve is currently labeled for corn, sorghum, wheat, cotton, rice, and other crops and is sold in emulsifiable and nonemulsifiable formulations. Dwell was registered as a nitrification inhibitor in 1982, but it is uncertain if the product will be marketed. Both chemicals are effective nitrification inhibitors when 0.5 lb. of active ingredient (a.i.) per acre is used in a band application with anhydrous ammonia or N solution fertilizers. Although only two of the chemicals are currently on the EPA approved list these chemicals will continue to be explored by the chemical industry. The significance of this list demonstrates the sensitive of the nitrification microbes.

WHERE NITRIFICATION INHIBITORS SHOULD BE USED?

Nitrification Inhibitors should be used in areas of high rainfall, finer textured soils, and cold soil temperatures during the winter. However, overall only about 50 and 70% of the trials with spring- and fall applied N has shown yield response from NIs.

There is a good probability of reducing Nitrogen loss from fall applied Nitrogen fertilizers with the application of NIs to ammoniacal fertilizers because of the potential for N loss through ammonia volatilization. The use of NIs will allow producers to apply N fertilizers somewhat earlier than generally considered feasible (50°F is traditionally considered the maximum soil temperature for application of

ammoniacal fertilizers in the fall without a NI). Heavy fall application of Nitrogen is not recommended for low CEC, coarse-textured soils because of the possibility of urea, ammonium and for certain nitrate leaching.

ADDITIONAL CONSIDERATIONS WHEN USING NITRIFICATION INHIBITORS

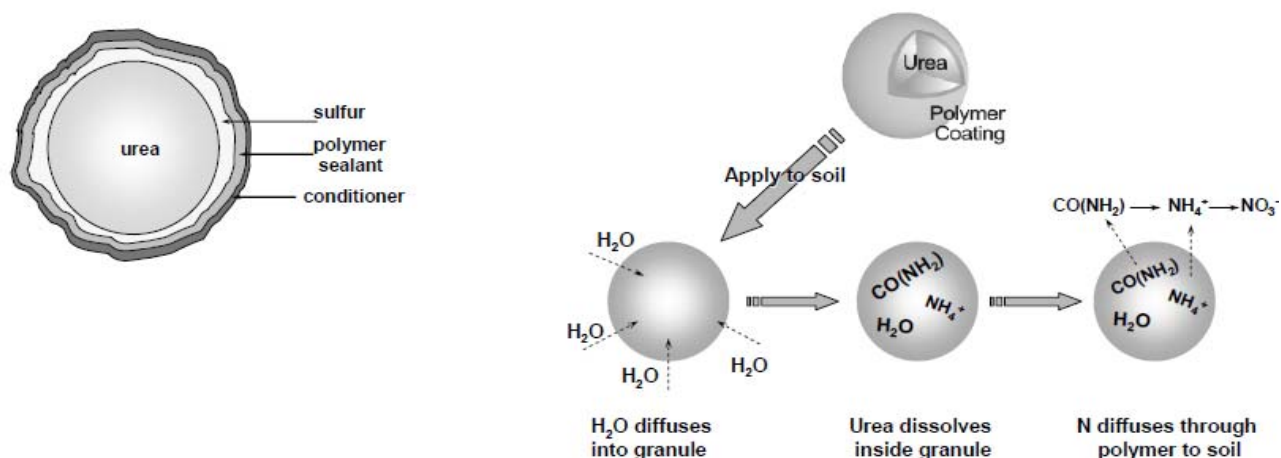
More consistent yield responses have been obtained with no-till grown crops than with conventional tillage systems fertilized in the spring. This finding results from greater infiltration rates, higher water contents, a higher population of denitrifying bacteria in no-till soils and, thus, increased N losses from leaching and/or denitrification.

The commercially available NIs has properties that affect how they can be added to various types of fertilizers. Nitrapyrin and Terrazole can be impregnated on solid fertilizers, or an emulsifiable formulation may be mixed with N solution fertilizers. N-Serve can be added directly to bulk anhydrous ammonia because of its high solubility in liquid ammonia. However, Dwell is not soluble in ammonia, but can be added to anhydrous ammonia with a small electric pump that meters the compound into the ammonia stream between the nitrolator and the manifold system on the applicator.

NITROGEN STABILIZERS AND SLOW OR CONTROLLED RELEASE FERTILIZERS

Slow or Controlled Release Fertilizers are fertilizers containing a plant nutrient in a form which delays its availability for plant uptake and use after application, or which extends its availability to the plant significantly longer than a reference “rapidly available nutrient fertilizer” such as ammonium nitrate or urea, ammonium phosphate or potassium chloride. Such delay of initial availability or extended time of continued availability may occur by a variety of mechanisms. These include controlled water solubility of the material (by semi-permeable coatings, occlusion, or by inherent water insolubility of polymers, natural nitrogenous organics, protein materials, or other chemical forms), by slow hydrolysis of water soluble low molecular weight compounds, or by other unknown means (Official 1985).

Slow or controlled release fertilizers have been around since the early sixties. These products were first developed for the horticultural markets, as a way of delayed feeding for transplant stock and increasing the shelf life of retail plants. In the late sixties with the entry of urea into the commercial fertilizer



market, fertilizer manufacturers started looking for means of coating urea to control the loss of nitrogen through volatilization and leaching.

The first coating agent tried was elemental sulfur, followed by coating that had differing degrees of water soluble. These products were research in production agriculture, but production costs made them unprofitable in commercial field production. With the increased emphasis on environmental concerns, the interest in slow or controlled release fertilizers has been reintroduced to the commercial fertilizer market.

Table 5 lists the majority of the commercial slow or controlled release products and fertilizers we have

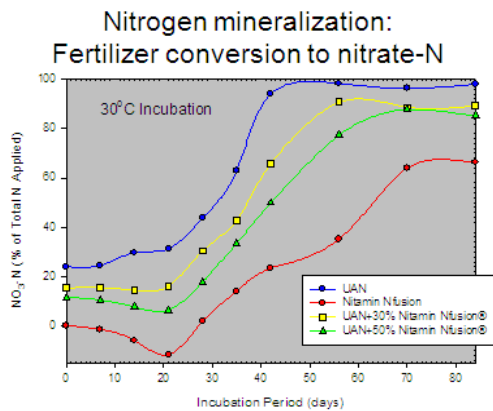
Table 5. **Controlled and slow release N products**

N Source	Base Compound	Common Name(s)	N Content	Inhibition Duration
			--%--	--weeks--
S-coated urea	urea	SCU	30-42	4-12
		Enspan	39	
Polymer/S coated urea	urea	PolyPlus Poly-S TriKote	38-42	6-16
		XCU	41-43	
Polymer-or resin-coated urea	urea	Polyon, Osmocote,	38-44	8-14
		Meister Agriform Multicote Escote Prokote ESN Nutrisphere	25-46	
Urea-formaldehyde	ureaforms	Nitroform	38	10-30+
		FLUF	18	6-10
		Folocron	29	
		GP-4340	30	
	methylene urea	Nutralene Hydrolene Nitamin	40	7-12
	methylol urea	Resi-Grow	30	6-10
polymethylene urea	CoRoN	12 or 28	7-9	
Isobutylidene diurea	isobutylidene urea	IBDU	31	10-16
Triazone	triazone/urea	N-Sure, Nitamin TriSert, Formolene	28-33	6-10
Crotonylidene Diurea	urea/crotonaldehyde	Crotodur, CDU, Triabon	34	6-12

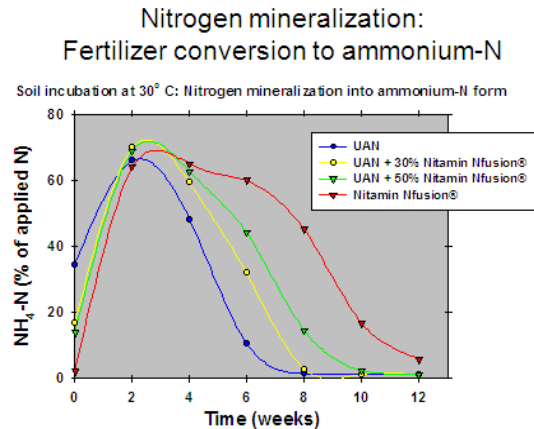
found to date offered for sale in the Idaho. The chemistry and physical behavior of the coated fertilizers are reasonably to understand, the additive products are a little more difficult to understand and predict.

The theory behind polymer coatings is that they control penetration of moisture and therefore, the solubility of the fertilizer contained within the polymer. Sulfur coated products are controlled by microbial action on the element sulfur coating.

The newest technology is production of products that are a chemical mixture of additives. Several of the products are a combination of Triazone, Methylene Urea, and Ammonium Nitrate. The data supplied by the manufacture shows the delayed ammonification of urea by the additive. The data also shows no synergistic effect of the additive on UAN, which is made up of liquid urea (50%) and liquid ammonium



Source: International Fertilizer Development Center



Source: International Fertilizer Development Center

(25%) nitrate (25%). The data suggests that after two weeks, the UAN urea is converted to ammonium, with nitrification inhibited for 20 days, this inhibitory effect is either the elevated pH and/or free ammonia, known to be toxic to nitrification bacteria. The nitrate-N data is reflective of the ratio of the additive to UAN, with that ratio mix maintained throughout the incubation period. As a side note, the data also suggests the led time that a producer has to consider in applying a fertilizer product like UAN. Upon application, 25% of the nitrogen is available immediately to the crop with the remaining becoming available over the next 40 day period. As a topdress material for small grains applied at GS 10-20 makes UAN by itself a potentially very effective top-dress fertilizer for winter small grains and an effective material for pre-plant on spring grains.

Table 6. lists the current Fertilizer additives that have been develop of the years for reducing the potential for N losses through leaching, volatilization, and denitrification. These chemical additives either reduce the biological population of the application zone thus impeding the natural biological process or form a chemical boundary that prevents the nitrogen source from interacting with the natural chemistry in the soil.

Table 6. **Fertilizer additives used to reduce potential N losses (leaching, volatilization, and denitrification)**

Additive	Base Compound	Common Name(s)	N Content	N Process	Inhibition Duration
			--%--		--weeks--
<i>Nitrification Inhibitors</i>					
Nitrapyrin	2-chloro-6-trichloromethyl pyridine	N-Serve Stay-N 2000	–	nitrification denitrification	2-6
DCD	dicyandiamide	DCD Ensan	1.6		4-8
DMPP	3,4-dimethylpyrazole phosphate	DMPP	–		6-8
		ENTEC	12-26		
<i>Urease Inhibitors</i>					
NBPT	n-butyl-thiophosphoric triamide	Agrotain	–	volatilization	2-3
		SuperU	46		
Thiosulfate	Ammonium or Calcium thiosulfate	ATS CaTs	12	volatilization nitrification	2-3
<i>Combination Products</i>					
DCD + NBPT	dicyandiamide + n-butyl-thiophosphoric triamide	Agrotain Plus HYDREXX	–	volatilization nitrification denitrification	6-8
		UMAXX	47		8-12
DCD + NBPT + urea		UFLEXX SuperU	46		6-8
polymer	maleic-itaconic copolymer	Nutrisphere	–		6-12
polymer + urea		SSN	46		

In summary

Nitrogen is found throughout the environment. It is an essential element for life, however, because of the quantity, cultural practices, climatic conditions, crop uptake timing, economics of fertilizer sources and nitrogen form required by crops, nitrogen use efficiency is often low in Idaho's crop production. Nitrogen management is an environmental concern due to changes in nitrogen form as nitrogen fertilizers go through various transformations within the Nitrogen Cycle. Some of the nitrogen transformations are difficult to predict due to difference in cultural practices, fertilizer forms used and the uncertainties of weather. Ammoniacal forms of nitrogen fertilizer are subject to ammonia loss through volatilization with urea, the solid form of ammoniacal nitrogen, subject to ammonia volatilization through the activity of the urease enzyme. Ammonium nitrogen with its positive charge is adsorbed to the negative charge surfaces of organic matter and soil particles, and is transformed to nitrate nitrogen through nitrification, a biological process involving the activities of specific soil bacteria and a process that generates acidity in the soil. The nitrate nitrogen form with its negative charge is subject to leaching and under low soil oxygen levels is subject to denitrification. Both conditions are dependent on the water content of the soil and water movement through the soil. Denitrification, a process in which soil microbes strip oxygen from the nitrate molecule, results in the formation of nitrogen dioxide, a Green House Gas.

Conservation practices and EQIP and CSP programs are designed to assist the producer in managing nitrogen in crop production. In many of our cultural practices nitrogen is often applied to crops before planting, a practice that can lead to nitrogen loss. For many of our crop the first growth period after planting requires only a small amount of nitrogen, however, once the crop starts growing, whether a grain, forage or row crop then a large proportion of its nitrogen uptake is required as the plant in its vegetative stage matures in preparation for harvest. Nitrogen management and timing of nitrogen application is required to match this nitrogen uptake pattern, however, cultural practices, soil conditions and weather often dictates when nitrogen can be applied in the production of a crop. To increase nitrogen use efficiency and thereby increase yields or decrease N rates, a number of products have been developed as nitrogen stabilizer, urease, nitrification and denitrification inhibitors, or containing slow or controlled release chemical, that delay the nitrogen transformation processes so that the period of time in which the N source is available for uptake is closer to the time the crop needs the available N.

REFERENCES

- Bremner, J.M. 1965. Inorganic forms of nitrogen. In C.A. Black et al. (ed.) Methods of soil analysis, Part 2. Agronomy 9:1179-1237. Am. Soc. of Agron., Inc., Madison, WI.
- Cabrera, M., J. Molina, and M. Vigil. 2008. Modeling the nitrogen cycle. p. 695-730. In Nitrogen in Agricultural Systems. Agronomy Monograph No. 49. J.S. Schepers and W.R. Raun, eds. ASA-CSSA-SSSA, Madison, WI.
- Coyne, M.S. 2008. Biological denitrification. p. 201-254. In Nitrogen in Agricultural Systems. Agronomy Monograph No. 49. J.S. Schepers and W.R. Raun, eds. ASA-CSSA-SSSA, Madison, WI.
- Ferguson, R. G. Slater, and D. Krull. 2009. Encapsulated nitrapyrin study, 2009. University of Nebraska Report.
- Franzen, D. 2009. Studies on slow-release liquid fertilizers applied at low rates as a foliar application on North Dakota spring wheat/winter wheat. North Dakota State University, Fargo, ND.
- Franzen, D.W., R.J. Goos, R.J. Norman, T.W. Walker, T.L. Roberts, N.A. Slaton, G. Endres, R. Ashley, J. Staricka, and J. Lukach. 2010? Field and laboratory studies comparing Nutrisphere®-N with urea in North Dakota, Arkansas and Mississippi. Journal of Plant Nutrition. Accepted for publication, June, 2010.
- Goos, R.J. and B.E. Johnson. 1999. Performance of two nitrification inhibitors over a winter with exceptionally heavy snowfall. Agronomy Journal 91:1046-1049.803-806.
- Goos, R.J. 2008. Evaluation of Nutrisphere-N as a soil nitrification and urease inhibitor. p. 89-96. In Proceedings of the North Central Extension-Industry Soil Fertility Conference, 12-13 November, 2008, Des Moines, IA. International Plant Nutrition Institute, Brookings, SD.
- Grant, C.A. 2004. Potential uses for Agrotain and polymer-coated products. p. 76-86. Canada Soil Science Conference Proceedings, 2004.

- Hendrickson, L.L., L.M. Walsh, and D.R. Keeney. 1978. Effectiveness of nitrapyrin in controlling nitrification of fall and spring-applied anhydrous ammonia. *Agronomy Journal* 70: 704-708.
- Hergert, G.W., and R.A. Wiese. 1980. Performance of nitrification inhibitors in the Midwest (west). p. 89-105. In *Nitrification Inhibitors-Potentials and Limitations*. ASA-SSSA, Madison, WI.
- Huber, D.M., H.L. Warren, D.W. Nelson, C.Y. Tsai, and G.E. Shaner. 1980. Response of winter wheat to inhibiting nitrification of fall-applied nitrogen. *Agron. J.* 72:632-637.
- Karow, R.S., E.L. Klepper, R.W. Richman, and R.R. Toll. 1993. *Early Growth and Development of Cereals*. Oregon State University Extension Service. EM 8542
- Kissel, D.E., M.L. Cabrera, and S. Paramasivam. 2008. Ammonium, ammonia and urea reactions in soils. p. 101-156. In *Nitrogen in Agricultural Systems*. Agronomy Monograph No. 49. J.S. Schepers and W.R. Raun, eds. ASA-CSSA-SSSA, Madison, WI.
- Norton, J.M. 2008. Biological denitrification. p. 173-200. In *Nitrogen in Agricultural Systems*. Agronomy Monograph No. 49. J.S. Schepers and W.R. Raun, eds. ASA-CSSA-SSSA, Madison, WI.
- Randall, G.W., J.A. Delgado, and J.S. Schepers. 2008a. Nitrogen management to protect water resources. p. 911-946. In *Nitrogen in Agricultural Systems*. Agronomy Monograph No. 49. J.S. Schepers and W.R. Raun, eds. ASA-CSSA-SSSA, Madison, WI.
- Schmidt, E.L. 1982. Nitrification in soil. p. 253-288. In *Nitrogen in Agricultural Soils*-Agronomy Monograph No. 22. F.J. Stevenson, ed. ASA-CSSA-SSSA, Madison, WI.
- Schwab, G.J., and L.W. Murdock. 2009. Nitrogen transformation inhibitors and controlled release urea. University of Kentucky Cooperative Extension Service circular AGR-185.
- R.L. Westerman, Editor. 1990. *Soil Testing and Plant Analysis*, Third Addition, SSSA Book Series 3.
- Stark, J. 2008. Evaluation of Nutrisphere-N as a nitrogen source for spring malt barley. 2008 Report. Montana State University.
- Stark, J. 2009. Evaluation of Nutrisphere-N as a nitrogen source for spring malt barley. 2009 Report, Montana State University
- Sullivan, D.M., J.M. Hart and N.W. Christensen, 1999, *Nitrogen Uptake and Utilization by Pacific Northwest Crops*. A Pacific Northwest Extension publication, PNW 513.
- Touchton, J.T., R.G. Hoefl, and L.F. Welch. 1978a. Nitrapyrin degradation and movement in soil. *Agronomy Journal* 70:811-816.
- Touchton, J.T., R.G. Hoefl, and L.F. Welch. 1978b. Effect of nitrapyrin on nitrification of fall and spring-applied anhydrous ammonia. *Agronomy Journal* 70: 805-810.

Touchton, J.T., R.G. Hoelt, and L.F. Welch. 1979a. Effect of nitrapyrin on nitrification of broadcast-applied urea, plant nutrient concentrations, and corn yield. *71:787-791*.

Touchton, J.T., R.G. Hoelt, L.F. Welch, D.L. Mulvaney, M.G. Oldham, and F. E. Zajicek. 1979b. N uptake and corn yield as affected by applications of nitrapyrin with anhydrous ammonia. *Agronomy Journal 71:238-242*.

Warncke, D. and M. Nagelkirk. 2008. Nitrogen management for winter wheat in Michigan. *Crop and Soil Sciences Information Series, CSSIS #S*, Michigan State University Extension Publication, East Lansing, MI.