NITROGEN IN SOIL AND FERTILIZERS

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Nitrogen influences turf health and quality more than any other nutrient. Nitrogen is present in grass plants in greater quantities than any other essential nutrient other than carbon, oxygen, and hydrogen. Nitrogen is an integral component of amino acids that make up the protein and enzymes in all living organisms including turfgrass. Nitrogen surrounds the magnesium atom in chlorophyll, which captures the sun's energy and allows sugars to be created from carbon dioxide and water. The cycling of nitrogen through the air, soil, and water is highly complex. Understanding the nitrogen cycle, nitrogen transformations, and the movement of nitrogen is critical for optimum management of turfgrass.

Nitrogen is present in soils in organic and inorganic forms. There is a wide variation in the types of organic compounds that contain nitrogen. Organic compounds can be small and easily degraded by microorganisms like amino acids, or large complex molecules that are quite resistant to microbial decay. The most resistant of these soil organic materials are typically referred to as humus. Inorganic forms of nitrogen are nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), and ammonia (NH_3). Nitrate and ammonium are readily taken up by plants and beneficial for plant growth. Nitrite and ammonia are toxic to plants.

NITROGEN REACTIONS IN SOIL

The quantity and forms of nitrogen in soils is constantly changing due to biological, chemical, and physical processes. Hopefully, understanding these changes and the effects of environmental factors on their progression will help you to manage nitrogen more efficiently and produce a healthier, higher quality turf.

Mineralization

The microbial transformation of organic nitrogen to inorganic forms is referred to as mineralization. Common organic nitrogen substances are; soil humus, plant leaf clippings and root tissue, and sludge and manure based fertilizers. Generally, a complex and large molecule containing nitrogen is broken down into a simpler and smaller molecule and then into ammonium. Sometimes this process is referred to in two parts with the first part termed aminization and the second part ammonification.

$$\text{organic N} \xrightarrow{\text{aminization}} \text{amino N} \xrightarrow{\text{ammonification}} \text{ammonium N}$$

Many different types of organisms can perform these reactions, some can do both steps while others can only perform one reaction or the other. Fungi and bacteria carry on most of the mineralization in soils. Because many different organisms can mineralize nitrogen the conditions necessary for mineralization to occur are not highly specific. Warm, wet conditions, and soil pH greater than 5.5 enhance mineralization. Good soil aeration promotes mineralization, so water contents greater than field capacity tend to reduce the rate of nitrogen mineralization. One factor that can be altered by the turfgrass manager and greatly affects how fast nitrogen is released from an organic nitrogen source is the C:N ratio of the material.

Carbon:Nitrogen ratio

The rapidness of nitrogen mineralization from organic compounds is a function of the carbon:nitrogen ratio (C:N) of the material. In substances with low C:N ratio, less than 15:1, the nitrogen content is relatively high and the microorganisms rapidly release nitrogen when they decompose the material. On the other hand, if the C:N ratio of the material is high (greater than 30:1), indicating a low nitrogen content, then mineralization is slow. In order for the organisms to break down a high C:N material inorganic nitrogen is removed from the soil solution. This process is called immobilization and occurs frequently when high C:N substances (for example: sawdust, some compost, types of sludge) are added to soil. If the material has a high enough C:N ratio all of the inorganic nitrogen can be removed from the soil for a considerable amount of time. The growth of grass plants will then be halted. Microorganisms are much more competitive for soil nitrogen then plants so they consume the inorganic nitrogen first before the plants.

Fumigation can eliminate mineralization

The microbial populations necessary for mineralization to occur are essentially eliminated by fumigation for a period of time. Therefore, organic nitrogen sources will not be made available to the plant by mineralization to inorganic nitrogen forms. Only inorganic nitrogen sources will be successful in providing the grass with nitrogen shortly after fumigation. Mineralization will eventually take place after some time that is determined by the thoroughness of the fumigation and the movement of organisms from adjacent areas into the fumigated areas.

Nitrification

Nitrification refers to the conversion of ammonium to nitrate. This conversion is a two step reaction performed by two distinct and specific microorganisms. The first step is the conversion of ammonium to nitrite by *Nitrosomonas* and the second step is the conversion of nitrite to nitrate by *Nitrobacter*. Luckily this reaction is tightly coupled so that nitrite in soils rarely accumulates. Nitrite is highly toxic to plants.

$$\text{Ammonium} \xrightarrow{\textit{Nitrosomonas}} \text{Nitrite} \xrightarrow{\textit{Nitrobacter}} \text{Nitrate}$$

Since only two microorganisms are involved in this reaction the conditions that alter the reaction rate are relatively narrow and well understood.

Temperature

Nitrification occurs in soils at temperatures above freezing. The warmer the temperature the faster the rate of nitrification. For example: ammonium sulfate was mixed with soil and kept moist at different temperatures for 24 days. At 40 ^{o}F, 29% of the ammonium had been nitrified, at 60 ^{o}F, 59% was nitrified, and at 80 ^{o}F, 100% was converted to nitrate. Thus temperature has a substantial effect on the form of nitrogen available to the turfgrass plant. Fertilization with an ammonium source in cool weather may supply substantial amounts of ammonium to the plant, but at high temperatures most of the nitrogen available to the plant will be nitrate.

Soil pH

Nitrification occurs in soils at pHs between 5.5 and 10. The optimum pH is around 7.

Moisture

Moisture contents between field capacity and the wilting point have little effect on the rate of nitrification. However, nitrification in soils wetter than field capacity is substantially reduced. In wet soils oxygen limits nitrification. Maximum nitrification rates occur in soils when the oxygen percentage is greater than 10% (20% is the natural concentration in the air).

Nitrification inhibitors

Dicyandiamide (65%N, $C_2H_4N_4$, sold as DCD) is a nitrification inhibitor. A nitrification inhibitor is a chemical that prevents the conversion of ammonium to nitrate. These chemicals affect the activity of *Nitrosomonas* so that no nitrite appears in the soil. There is interest in keeping nitrogen in the ammonium form because it is less mobile than nitrate and therefore is not readily leached from the soil. Also, ammonium is thought to have a desirable physiological effect on plant growth. Dicyandiamide is mobile in soil. Dicyandiamide can be placed on the soil surface and watered into the root zone with irrigation. In this manner it can be incorporated into the soil with minimal disturbance of the turf. However, because DCD is mobile in soils it can also be leached from the soil profile by excessive rainfall and/or irrigation.

Dicyandiamide effects on nitrification do not last forever because it is broken down by microorganisms as well as leached from the root zone. Generally, inhibition of nitrification lasts only four to six weeks. High temperatures and moist conditions hasten breakdown of the DCD. Dicyandiamide may be included in nitrogen fertilizers at 2 to 10% of the total nitrogen content. The breakdown of the DCD (65% N) thus contributes to soil inorganic nitrogen. Therefore, DCD is considered a slow release form of nitrogen as well as a nitrification inhibitor.

Dicyandiamide and urea can be co-granulated into a stable urea-like fertilizer particle with identical properties to urea. The material can be applied as a solid to the turf surface and watered into the root zone with irrigation water. The mobility of urea and DCD in soil is the same, so the DCD accompanies the urea into the rootzone and inhibits nitrification of the ammonium released from the urea. However, once the urea hydrolyzes to the ammonium form it is no longer mobile, but the DCD remains mobile. If leaching removes DCD from the rootzone, then nitrification resumes again. Repeated applications of DCD are necessary to inhibit nitrification in the rootzone when leaching conditions exist.

<u>Plant uptake and use of ammonium and nitrate</u>

When evaluated in solution culture, most plants can take up ammonium and nitrate by the roots equally as well. In soils, however, the movement of nitrate and ammonium to the root surface can alter the uptake of the nitrogen forms. Nitrate primarily arrives to the root surface in the flow of water that is transpired by the plant. Since none of the nitrate is adsorbed to soil particles it is abundant in the soil water and the movement of the nitrate to the root rarely limits its uptake. Ammonium, however, is attracted to the soil particles so only a portion of the ammonium is in the soil water at any one time. Ammonium concentrations at the root surface can limit plant uptake in certain situations. In soils of high cation exchange capacity or high fixation capacity (prevalent clay minerals are vermiculite, mica, and hydrous mica) the amount of ammonium in solution is insufficient to support optimum nitrogen uptake by the plant. Under dry conditions soil moisture may also limit the movement of ammonium to the root and plant uptake may be hindered. In irrigated turfgrass, especially in sandy soils, the movement of ammonium to the root surface should not limit plant uptake. However, in soils with high quantities of ammonium fixing clays or when dry soil conditions are prevalent, ammonium will be inferior to nitrate in providing nitrogen to the plant.

Nitrate and ammonium may alter plant growth even under conditions where total nitrogen supply and movement to the root does not favor either nitrate or ammonium. Much research has been conducted examining the physiological effects of ammonium and nitrate on the growth of grasses. Most of the grasses examined have been crop plants, corn, sorghum, wheat , but some studies have been conducted with ryegrass and bentgrass. Surprisingly the effects of ammonium on plant growth and development have been fairly consistent across species. Ammonium grown plants, in comparison to nitrate grown plants, produce greater dry matter, more tillers, and have more branched root systems. Generally, maximum increases in these factors are obtained by providing and maintaining no more than half of the total nitrogen supply in the ammonium form.

Urea hydrolysis

Urea hydrolysis is the conversion of urea ($CO(NH_2)_2$) to ammonia/ammonium by the enzyme urease. Urease is everywhere and can function outside of living organisms. This reaction is important because many of the fertilizer materials utilized in turfgrass contain substantial amounts of urea as the nitrogen carrier. Although urea can be taken into the plant by roots, this mode of nitrogen uptake is not important, as the amount accumulated is small compared to the uptake of nitrate and ammonium. However, the foliar adsorption of urea can occur at a high rate and contribute substantially to plant nitrogen accumulation.

Urease inhibitors

Several compounds have been isolated that inhibit urea hydrolysis for a short period of time. Generally, the effects have been short-lived and erratic. The purpose of the inhibitors has been to delay hydrolysis and increase the probability that rainfall could occur and move the urea into the soil where the potential for ammonia volatilization is significantly lower than on vegetative or soil surfaces (discussed below). Since irrigation is generally available and utilized frequently to water fertilizers into the turf, urease inhibitors are not that useful in turfgrass systems.

Ammonia volatilization

Ammonia volatilization is the loss of nitrogen to the atmosphere as ammonia gas. Ammonia production and loss is typically associated with urea hydrolysis in soils. Upon hydrolysis of urea the pH around the urea particle is increased drastically and the proportion of nitrogen in the ammonium form is shifted towards ammonia. Ammonia is then released into the atmosphere and no longer available to the plant. Ammonia loss may be as great as 60% of the nitrogen applied as urea. Several factors affect the volatile loss of ammonia.

The capacity of the soil to restrict the increase in soil pH (buffering capacity) upon urea hydrolysis is important in decreasing losses of ammonia from urea. Soils that are high in clay and organic matter have a high buffer capacity. Therefore, soil pH increases and ammonia volatilization losses are minimized. Sandy soils generally have low buffer capacity, therefore, pH increases and ammonia volatilization can be substantial.

The cation exchange capacity of the soil is correlated with the soil buffering capacity. Soils with high buffering capacity usually have a high cation exchange capacity. Ammonium generated by urea hydrolysis can be absorbed to the cation exchange sites in the soil and prevent the loss by ammonia volatilization. Leaf and stem surfaces and thatch have essentially no soil buffering capacity or cation exchange capacity. When urea hydrolyzes on these surfaces, soil pH increases are substantial and much of the nitrogen added as urea may be lost to ammonia volatilization.

Movement of urea into the soil prior to hydrolysis is an effective way to minimize ammonia volatilization. Incorporation of urea a couple of inches into the soil eliminates ammonia loss. High temperatures increase the loss of ammonia. Volatilization losses are generally minimal below 50 ^{o}F.

Leaching

Leaching is the downward movement of nitrogen with water percolation through the soil profile. How much nitrogen is lost from the rootzone is dependent on the nitrogen form present, soil type, the amount of rainfall in relation to evapotranspiration, and the depth of the rootzone.

Most soils do not have much anion exchange capacity within the turfgrass rootzone. Anion exchange capacity is the amount of positive charges that develop on the edges of soil clay and organic matter that attract negatively charged ions such as nitrate. Since there is little anion exchange capacity in the soil, nitrate moves with the percolating water. Often times this movement can be rapid and leads to loss of nitrate from the rootzone.

Cations, such as ammonium, are retained by the soil's cation exchange capacity. Cation exchange capacity is the quantity of negative charge that develops on the faces and edges of soil clay and organic matter. In most soils there is enough cation exchange capacity to greatly retard the leaching of ammonium with percolating water. In some cases, greens mixes constructed of sand may have limited cation exchange capacity and some leaching of ammonium can occur. Ammonium competes with potassium, calcium, and magnesium for adsorption to the cation exchange sites. Calcium and magnesium are held more tightly than ammonium and potassium to the cation exchange sites. Abundance of these other essential nutrients can limit the adsorption of ammonium and enhance its leaching.

Urea is a molecule without charge. It is neither attracted to the cation or anion exchange sites occurring in soil. Urea moves with the percolating water until it is hydrolyzed to ammonium. This mobility of urea in soil can be used to the turfgrass manager’s advantage by watering the urea into the rootzone, thereby eliminating volatile losses of ammonia and maximizing nitrogen supply in moist soil.

Nitrogen fertilizer affects soil pH

Nitrogen fertilizers affect soil pH in two ways. First, the reaction of the fertilizer, including the hydrolysis reaction of urea and the nitrification of ammonium, can alter bulk soil pH. Bulk soil is that soil that is not directly adjacent to the turfgrass roots. The form of nitrogen entering the plant can also alter the pH of the rhizosphere soil. Rhizosphere soil is that in intimate contact with the plant root system.

<u>Direct effects on bulk soil pH</u>

Nitrogen in the ammonium form generates acidity when the ammonium is nitrified to nitrate and lowers bulk soil pH. The initial reaction of urea is to increase soil pH through the hydrolysis reaction. However, after nitrification of the ammonium soil pH is eventually lowered. Decreases in soil pH resulting from application of ammonium containing or forming fertilized will occur in the absence of plants.

Nitrogen form effects on rhizosphere pH

The repeated application of nitrate containing fertilizer materials generally increases rhizosphere soil pH. The plant causes the increase in pH itself as nitrate is taken into the root and hydroxyl ion (OH^-) is released into the soil. However, when ammonium is the primary form of nitrogen accumulated by the plant, the plant releases acid and the pH adjacent to the root decreases. Rhizosphere pHs can be as much as 2 pH units different than bulk soil pH. Soil pH can substantially alter the population of microorganisms inhabiting the rhizosphere.

NITROGEN FERTILIZER MATERIALS

High quality turfgrass requires nitrogen throughout the time that the weather is suitable for growth. The level of nitrogen supply needed to produce a suitable turf is dependent on the turfgrass, soil, time of the growing season, and weather. Turfgrass will require and can utilize more nitrogen at certain times of the year than others. Color, texture, and recuperative potential are all highly dependent on the level of nitrogen supply available to the turfgrass. Inadequate nitrogen results in thin turf of light green color that has little ability to repair damage. Excessive nitrogen supply causes the turf to be succulent, have a high water and mowing requirement, reduce root growth, and be susceptible to injury, such as scalping.

Providing the proper supply of nitrogen can be achieved by frequent applications of soluble fertilizers or by infrequent applications of slow release materials. Generally, the best approach is to use combinations of fast and slow release fertilizers to fine-tune nitrogen supply during the growing season.

Fast Release Nitrogen Fertilizers

Fast release, or soluble nitrogen fertilizers, are mostly inorganic nitrogen salts. The exception is urea, which is considered a synthetic organic compound. The inorganic salts become plant available when they dissolve. Urea must undergo a hydrolysis reaction prior to becoming plant available, but in most situations this reaction is quite rapid and does not constitute a slow release material.

The characteristics of the fertilizer material are determined by the form of nitrogen in the fertilizer and the accompanying cation or anion. Two characteristics that are important to turfgrass production are the salt index and the residual acidity/basicity of the fertilizer. The higher the salt index the greater the potential for burn. Differences in acidity/basicity of the fertilizers will also alter the liming needs of soil (Table 1).

Table 1. The acidity or basicity of common nitrogen fertilizer materials. Negative numbers indicate acid creating fertilizers and positive numbers represent fertilizers that are basic in reaction.		
Fertilizer material	Nitrogen concentration	Acidity (-) or basicity (+) created after reaction
	% nitrogen	lb $CaCO_3$/lb nitrogen
Ammonium nitrate	34	-1.74
Ammonium sulfate	21	-5.24
Calcium nitrate	15	+1.33
Milorganite	7	-1.70
Potassium nitrate	13	+2.00
Sodium nitrate	16	+1.81
Sulfur coated urea	37	-3.19
Urea	46	-1.83
Ureaformaldehyde	38	-1.79

Slow or Controlled Release Nitrogen Fertilizers

A number of slow or controlled release fertilizer materials exist. Some of these materials are natural, but many are manufactured. The mechanism by which a controlled release of nitrogen is achieved differs among the fertilizers. The influence of temperature, soil moisture, and pH on release is also fertilizer specific. Understanding the processes that govern nitrogen release from each material is important to select the correct fertilizer for each situation.

<u>IBDU - Isobutylidene diurea - 31% N</u>

Reacting urea and isobutyraldehyde form Isobutylidene diurea. The particle size and hardness of IBDU is important to determining the release rate of nitrogen from the particle. The release of nitrogen from small particles of IBDU can be identical to that of urea. For larger particles, soil moisture and temperature influence the release rate of IBDU. Microbial activity is not required for the release of nitrogen from IBDU.

Moisture is critical for the release of nitrogen from IBDU. Release can be greatly delayed if IBDU particles remain in the thatch where dry conditions often exist. The nitrification of IBDU nitrogen is much greater at low pH than at high pH. Release of nitrogen from IBDU at pH 7.7 was only 50% of that at pH 5.7. Phytotoxicity, likely due to ammonia, can occur when IBDU is applied to soils with pH greater than 7.0.

Ureaformaldehyde - 38% N

Ureaformaldehyde is produced by reaction of urea and formaldehyde in the presence of a weak acid. The resulting substance is a mixture of several components, including unreacted urea, methylene urea, and numerous complex urea-containing compounds. The rate of nitrogen release from a preparation of ureaformaldehyde is dependent on the relative proportion of the components. Urea is available as ammonium within days of application. The slow release nature of ureaformaldehyde is due to the complex urea-containing compounds that must be degraded by microorganisms before the nitrogen is made available to the turfgrass. Because of the microbial involvement in nitrogen release, the release rate of ureaformaldehyde is dependent on conditions such as temperature and moisture, which affect the activity of the microbes. The rates of release of some commercial preparations of ureaformaldehyde are 6 to 7% of the total nitrogen content per month.

Since nitrogen availability from ureaformaldehyde is relatively low, substantial quantities must be applied to supply the turfgrass nitrogen requirement if ureaformaldehyde is the sole source of nitrogen. Accumulations in excess of 15 lb N/1000 sq. ft. are required to provide 1 lb of available N/1000 sq. ft. per month. Generally, ureaformaldehyde is utilized as a component of a fertilizer program to provide only a portion of the nitrogen requirement.

Plastic-coated nitrogen sources

Nitrogen release from plastic-coated fertilizer particles depends on moisture diffusing through the coating and into the particle, dissolving the nitrogen source inside the particle, and diffusion of the nitrogen solution out of the particle. Varying the thickness of the particle coating as well as mixing particles of different coating thickness controls the rate of nitrogen release. The type of fertilizer material inside the particle also influences the rate of nutrient release.

Increasing temperature from 50 to 68 ^{o}F doubles the release rate of nitrogen from plastic coated particles. Beyond 68 ^{o}F there is a smaller effect of temperature on release rate. Moisture is required for nitrogen release from plastic-coated materials, but the rate of release is not altered by soil moisture between field capacity and the permanent wilting point. When plastic-coated fertilizers are applied to the turf surface, moisture could be limiting at times. Soil pH and the absence of microorganisms, from fumigation for example, have no effect on the release of nitrogen from plastic-coated fertilizers.

Sulfur-coated urea

Sulfur-coated urea consists of a urea particle coated with elemental sulfur and then sealed with wax. A microbicide may also be included in the wax to delay biological degradation of the sealant. The thickness and integrity of the coating determine the rate of nitrogen release from the fertilizer. Nitrogen release in the first seven days after application is thought to arise from damaged particles where there is no coating between urea and the soil. Otherwise, the microorganisms first degrade the wax sealant, the urea diffuses through the sulfur into the soil solution, hydrolyzes, and is then made available to the plant. Turf mowers may damage larger sulfur-coated urea particles, enhancing the release of urea. Increased temperature and moisture increase the release rate of nitrogen from sulfur coated urea, but soil pH does not have an affect. Ammonia loss from surface-applied sulfur-coated urea is less than that for surface-applied urea.

Processed organic fertilizers

Many different types of organic fertilizers are available. Base materials for organic fertilizers include animal and human manure and waste products from the processing of crop plants, trees, and animals. Seaweed provides the basis for some organic fertilizers. Treatment generally includes composting which transforms readily available nitrogen into more slowly available forms and kills disease organisms. Grinding or screening of materials is often done to reduce particle size and provide a uniform range of particle sizes.

The rate of nitrogen release from processed organic fertilizers is highly dependent on the type of material. Since there are so many different products available it is difficult to generalize as to whether release rates are fast or slow. Since biological decay of the organic fertilizer is required to release the nitrogen it is certain that a healthy microbial population is required and that temperature and moisture will greatly affect the rate of release.

Fertilizer quality

The performance of many of the slow release nitrogen sources is highly dependent on the quality of their manufacture. The particle size distribution of IBDU is critical to determining the release rate of nitrogen. The uniformity of coating thickness and mixtures of particles with varied coating thickness determines the rate of release of plastic coated nitrogen sources. The relative proportions of urea, dimethylene urea, and ureaformaldehyde determine the nitrogen release of ureaformaldehyde based nitrogen fertilizers. Consistent manufacturing of these fertilizers is essential for repeatable performance and beneficial use by the turfgrass manager.

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