Chemistry and the Nitrogen Cycle

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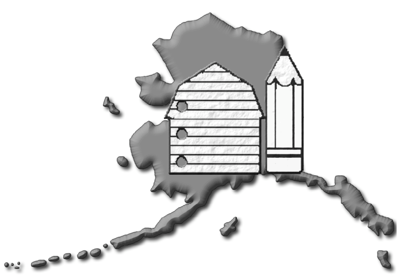
Objectives
Apply the science of chemistry to the nitrogen cycle and plant growth.

Suggested grade levels
11-12

Alaska Content Standards
Science, D1,D3

Terms to Define
oxidation
methemoglobinemia
eutrophication
valence
mineralization
proteolysis
aminization
biotic
assimilation



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A. Background Info

• Nutrient most often limiting plant growth
• Most money is spent on Nitrogen (N) fertilizer
• Important environmental impacts
 -- Methemoglobinemia-“blue baby” syndrome
 -- Groundwater contamination-nitrate (NO3-) leaching-very mobile in soil because nitrate does not absorb to the soil particles
 -- Eutrophication of surface waters-increase in nutrient content of rivers, lakes, ponds, or oceans results in algal blooms which depletes the oxygen and kills all fish and other organisms
 -- Acid rain
 -- Ozone depletion and climate change

• Exist in nature in a number of different forms and valence states. Most N transformations involve the oxidation (loss of electrons) or reduction (gain of electrons) of the N atom by biological (microbial) or chemical means.

NO_3^-, NO_2^-, N_20, N_2, NH_4^+, NH_3
Valence = +5 +3 0 0 -3 -3

B. Plant N Nutrition

Major roles of N- component of a number of plant constituents including chlorophyll, DNA, RNA, amino acids, vitamins, and hormones. N is essential for carbohydrate metabolism

Deficiency symptoms in plants- chlorosis-absence of chlorophyll that causes yellowing of plant leaves

C. Soil Nitrogen Cycle

1. Nitrogen pools in the soil
• Nitrogen in organic matter (OM)- OM contains about 5% N largely as NH_2 groups
• Mineral (inorganic) N in the soil solution and on soil exchange sites
• Nitrogen in fresh plant residues
• Ammonium (NH_4^+) fixed in clay minerals
• Gaseous N_2 in the soil atmosphere

2. Nitrogen Transformation Processes-N is capable of being transformed both biologically and chemically
• Mineralization- refers to the process of converting organic forms (organic forms are generally not plant useable) to mineral or inorganic forms
 -- Proteolysis and Aminization: Biotic reaction carried out by bacteria

$$\text{Organic N} \rightarrow R\text{-}NH_2$$

 -- Ammonification: Biotic reaction carried out by bacteria

$$R\text{-}NH_2 \longrightarrow NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$$

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Peter Bierman, UAF Cooperative Extension Service Land Agent in Palmer, contributed to this lesson.

-- Factors influencing mineralization

- Temperature: 20-40C might be better) is the optimal temperature range; even in mid-summer, soil temperatures below the surface few inches seldom reach 20C in Alaska and this limits mineralization
- Amount of water: too much water and there is not enough O_2 to carry out the reactions
- Amount of O_2: low oxygen means less mineralization and less OM breakdown
- Amount of organic matter (OM)
- The carbon:nitrogen (C:N) ratio in the OM: optimal range is a C:N ratio of 5:1 to 10:1. A ratio greater than 30:1 results in immobilization and a ratio less than 20:1 results in mineralization

- Immobilization — the opposite of mineralization. General term used to describe conversion of inorganic N to organic N. Assimilation of inorganic N (NO_3^-, NO_2^-, NH_4^+, NH_3) by soil micro-organisms and transformation into organic compounds. The C:N ratio in OM greatly influences the net balance between mineralization and immobilization reactions.

- Nitrification- two step microbial process in which NH4+ is oxidized to NO3-

$$2\ NH_4^+ + 3\ O_2 \longrightarrow 2\ NO_2^- + 2\ H_2O + 4H^+ + \text{energy}$$

$$2NO_2^- + O_2 \longrightarrow 2\ NO_3^-$$

To some degree, this is the end point for N though it can be further cycled.

General Nitrification Info

Nitrate is generally the principle form of N in the soil; hence it is the form most absorbed by plants in the field. Ammonium-N is higher in Alaska soils than many other areas, because cool soil temperatures frequently limit nitrification.

Autotrophic bacteria (obtain C from the sun) are the main nitrifying bacteria

Nitrate leaching- nitrate can be transported from the soil into groundwater and surface water by leaching, erosion, or runoff.

Nitrification inhibitors and slow release fertilizers help prevent nitrate leaching.

Factors Affecting Nitrification

- Supply of NH4+- depends on C:N ratio in OM and the ammonification process to supply the NH4+
- Soil aeration and moisture- NO_2^- cannot be produced in the absence of O_2; nitrification must occur under aerobic conditions because the bacteria are aerobic. Water logged soils have low O_2 levels and bacteria are sensitive to high soil moisture. Field capacity is the optimum soil moisture level.
- Soil temperature- biological reactions are affected by temperature. The optimum temperature is 25 to 35 degrees Celsius.
- Soil pH — optimum level is 6.6 to 8.0

Presence of nitrifying bacteria

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• Ammonia volatilization

Refers to the gaseous loss of N as NH3 from the soil

$NH_4^+ + OH^- \rightleftharpoons NH_3$ (g)

Alkaline conditions push reaction to the right

Normally associated with surface applications of ammonium fertilizers and organic wastes (animal manure, municipal biosolids)

Volatilization can be substantial if the soil or organic waste is alkaline in nature

This process occurs naturally in soils, but typically is associated with surface applications of ammonium-based fertilizers

Reducing volatilization and the loss of NH3 as gas is done by incorporating the fertilizer in the soil using tillage, injection, or irrigation

Factors affecting volatilization

pH — high soil pH results in higher volatilization rates

Temperature — Since high temperature results in higher volatilization rates, cool soil temperatures in Alaska may limit volatilization losses

• Denitrification- reduction of nitrate and nitrite to gaseous forms of N (NO, N2O, and N2); predominantly a microbial process

NO = nitric oxide
N_2O = nitrous oxide
N_2 = dinitrogen

Denitrification has to occur under anaerobic conditions. Very saturated or wet soils or wetlands meet this criterion.

Denitrification results in a loss of N from the system which may lead to a lack of nitrogen for plant uptake and nutrition.

Denitrification is an economic problem because it costs money to replace the nitrogen to meet the plant's needs (buying and spreading fertilizer)

Denitrification is a benefit as a wastewater treatment component because it converts the nitrate to a gas so it does not leach into the groundwater, etc.

The major denitrifiers are heterotrophic bacteria (get C from OM). Bacteria responsible for denitrification are actually aerobic but under anaerobic conditions they use NO_3^- instead of O_2 as an acceptor of electrons. The NO_3^- is consequently reduced.

Factors affecting denitrification

Amount of decomposable OM as the bacteria need a carbon source

Soil water content and aeration status- denitrification occurs in saturated soils where O_2 levels are too low to meet the biological requirements of bacteria

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Presence of nitrate or nitrite

Soil pH- bacteria responsible for denitrification are sensitive to low pH. A pH less than 5 stops denitrification. The optimum pH range is 6 to 8.

Soil temperature- optimum temperature is 30 degrees C

Nitrogen Cycle Problem Solutions (Problems on separate student sheet)

1. a. True b. False c. True

2. Nitrification is the biochemical oxidation of ammonium to nitrate predominantly by autotrophic bacteria.

$$NH_4^+ \longrightarrow NO_2^- \longrightarrow NO_3^-$$

Autotrophic bacteria are responsible for driving this process.

3. a. (2100 lbs/acre) x (51% C or 0.51) = 1071 lbs C/acre
(1071 lbs C/acre) x (35% in the microbes or 0.35) = 374.8 lbs C/acre going into the microbes

$$\frac{1\ N}{8\ C} = \frac{374.8\ lbs\ C/acre}{x\ lbs\ N/acre}$$

x lbs N/acre = 374.8 lbs C/acre / 8 C

x = 46.9 lbs N/acre needed by the microbes

b. (2100 lbs/acre) x (51% C or 0.51) = 1071 lbs C/acre

Need to find the amount of N in the organic residue

$$\frac{1\ N}{50\ C} = \frac{1071\ lbs\ C/acre}{x\ lbs\ N/acre}$$

x lbs N/acre in residue = 1071 lbs C/acre / 50 C

x = 21.4 lbs N/acre in residue

The amount immobilized = lbs N/acre needed by the microbes minus the lbs N/acre in the residue

46.9 lbs N/acre – 21.4 lbs N/acre = 25.5 lbs N/acre being immobilized

c. Decreases

4. a. Beginning: (8% OM) x (2 x 10^6 lbs/acre) = 160,000 lbs OM/acre
(160,000 lbs OM/acre) x (5%N) = 8,000 lbs N/acre
(8,000 lbs N/acre) x (4% mineralization rate) = 320 lbs N/acre-year being mineralized

End: (3% OM) x (2 x 10^6 lbs/acre) = 60,000 lbs OM/acre
(60,000 lbs OM/acre) x (5%N) = 3,000 lbs N/acre
(3,000 lbs N/acre) x (2.1% mineralization rate) = 63 lbs N/acre-year being mineralized

b. 320 lbs N/acre-year / 8% OM = 40 lbs N/ % OM

63 lbs N/acre-year / 3% OM = 21 lbs N/ % OM

c. Mineralization rate has decreased over this period. Some potential problems associated with a decreased mineralization rate is a lack of nitrogen for crop uptake and nutrition, spending money on nitrogen fertilizer to meet the needs of the crop, and a decrease in OM that supplies the carbon needed for mineralization. Some ways to solve the problems are to convert to no-till farming which will leave more residue on the field and gradually increase the OM which will lead to more mineralization, rotate the crops with legumes (alfalfa, peas, beans) which create their own nitrogen of which some is returned to the soil. Similar trends in OM loss occur in Alaska soils following cultivation, although the rates are reduced by cool soil temperatures. Solutions to this problem are also complicated by temperature. Leaving more residue on the soil surface insulates the soil and restricts soil warming in the spring. And many legumes, such as alfalfa and beans, are not well adapted for growth in Alaska's climate or soil conditions

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Nitrogen Cycle Problems

1. Circle True or False

a. During denitrification, nitrate and nitrite are reduced to gaseous forms of N by bacteria. T or F

b. Mineralization refers to the conversion of nutrients from inorganic to organic forms. T or F

c. Incorporation of N fertilizer materials is one way to minimize ammonia volatilization. T or F

2. Briefly define nitrification and complete the reaction below (stoichiometry is not important; just indicate the nitrogen form in the reactant, intermediate, and product). Indicate which microorganisms (nitrifying bacteria) drive this two step process.

$\longrightarrow$ $\longrightarrow$

3. An organic residue with a 50:1 C:N ratio is added to the soil at a rate of 2100 lbs/acre.

Assumptions: The residue contains 51% C; 35% of the C is incorporated into the microbial cells, the remainder (65%) is respired as CO_2; C:N ratio of microbes is 8:1

a. What would be the amount of N used or required by the microbes to digest this residue?

b. What is the net amount of N immobilized from the soil?

c. What happens to the C:N ratio of this residue over time (i.e. increases, decreases, remains the same)?

4. A farmer purchased some native grassland with 8% organic matter (OM) in Montana early during the 20th century. The native grass was plowed under and the land is cultivated. During the first few years, OM is mineralized at a rate of 4% per year. One hundred years later, the farmer's great great granddaughter is now farming the land. The OM content has now diminished to 3% and the rate of mineralization is only 2.1% per year.

Assumptions: Top 6" of soil = 2 x 106 lbs/acre; Organic matter contains 5% N throughout the entire century

a. Calculate for this soil (top 6" only) the N mineralization rate at the beginning and end of the 100 year period (units of lbs of N/acre-year)

b. Express the N mineralization rate in units of lbs of N / % OM.

c. What has the mineralization rate done over the last 100 years (i.e. increased, decreased, stayed the same)? What are some problems related to what the mineralization rate has done? What are some ways to solve the problems?