

Environmental Chemistry

Laboratory exercise

Available nitrogen and phosphorus in soil

GENERAL CONSIDERATION

The compounds of nitrogen (N) and phosphorus (P) are of great interest to environmental engineers because of their importance both in the atmosphere and in the life processes of all plants and animals. Due to latter one N and P are called biogenic substances. Lately a need for better understanding of the role and fate of N and P in crop production systems has increased, because of economic and environmental issues. Deficit of biogenic elements in crop production results in poor harvest. Therefore, the delivery of them results in substantial economic return for farmers. However, when N and P inputs to the soil system exceed crop needs, there is a possibility that excessive amounts of nitrates (NO_3^-) and phosphates (PO_4^{3-}) may enter either ground or surface water, thus leading to eutrophication.

Managing N and P inputs to achieve a balance between profitable crop production and environmentally tolerable levels of NO_3^- and PO_4^{3-} in water supplies should be every grower's goal. The behavior of N and P in the soil system is complex, yet an understanding of these basic processes is essential for a more efficient N and P management program.

NITROGEN CYCLE

Nitrogen exists in the soil system in many forms and transforms from one form to another very easily. The route that N follows in and out of the soil system is collectively called the "nitrogen cycle" (fig. 1) and is biologically influenced. Biological processes, in turn, are influenced by prevailing climatic conditions along with the physical and chemical properties of a particular soil. Both climate and soils vary greatly across the world and affect the N transformations for the different areas.

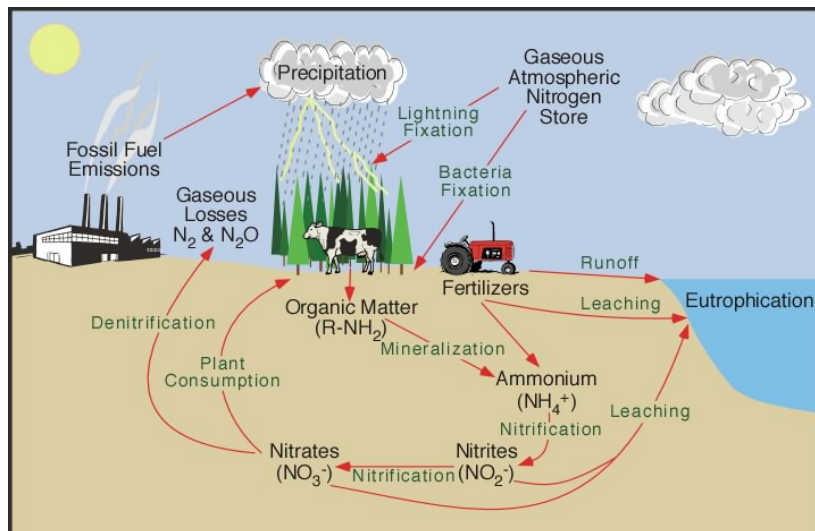


Fig. 1. Nitrogen cycle.

Sources of Nitrogen Compounds for Plant Growth

Nitrogen (N) is easily available to plants in two mineral forms, either as ammonium-nitrogen ($N-NH_4^+$, available at low rates) or as nitrate-nitrogen ($N-NO_3^-$, available at high rates). Nitrogen of organic origin (e.g. proteins) can also become available, just after conversion into inorganic forms.

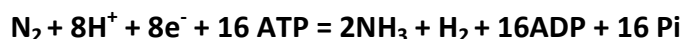
There are several sources of N supply for plant growth:

- ❖ The atmosphere
 - Biological fixation
 - Atmospheric fixation
 - Precipitation
- ❖ Commercial fertilizers
- ❖ Soil organic matter
- ❖ Crop residues
- ❖ Animal manures

Nitrogen from the atmosphere

Nitrogen from the atmosphere is the main reservoir for N in the N cycle. Although unavailable to most plants (due to being very inert), large amounts of N_2 can be used by leguminous plants via process called N fixation. N Fixation is a process of N_2 conversion to ammonia, which is available for the plants. When the fixation is performed by plants or microorganisms then the process is called biological N fixation. For example, nodule-forming *Rhizobium* bacteria in symbiosis with roots of leguminous plants (inhabited by them) convert

1 mole of atmospheric N_2 to 2 moles of ammonia at an expense of 16 moles of adenosine triphosphate (ATP):



Even though being very inert, nitrogen dimolecules can be broken by the enormous energy of lightening. This enables N atoms to combine with oxygen and thus form nitrogen oxides NO_x (atmospheric fixation). Then after reaction with moisture in the air they fall down the ground in a form of precipitation.

Commercial fertilizers

Commercial N fertilizers are also derived from the atmospheric N pool. The major step is to combine N_2 with hydrogen (H_2) to form ammonia (NH_3). Then anhydrous ammonia is used as a substrate for other nitrogen fertilizers manufacturing. Both, anhydrous ammonia and other N products derived from NH_3 can supplement soil in nitrogen.

Animal manure

Animal manures and other organic wastes can be important source of N for plant growth. Both the amount and the form of N supplied by manure vary with the type of livestock, way of handling, rates and methods of application. Therefore, an analysis of the manure before an application is recommended to improve N management.

Crop residues

Crop residues (e.g. roots and nodules) are also a source of N for plants, especially residues from leguminous plants (non-leguminous contain relatively small amounts of N as compared with leguminous). However, N in crop residues is present in a complex organic forms, which are unavailable to plants. Therefore, the residues must decay (then N becomes available), what takes up to several years.

Soil organic matter

Soil organic matter (SOM) is an organic component of soil and also a major source of N used by crops. SOM is composed of animal and plant residues at different stages of decomposition, as well as of humus. Humus is a stable material formed out of substances that are quite resistant to decomposition (e.g. lignin, cellulose). Humus provides physical and chemical fertility to the soil.

Nitrogen Transformations

Nitrogen, present or added to the soil, is subjected to several changes (transformations) that dictate its availability to plants and influence the potential movement of NO_3^- to adjacent water supplies.

Organic N that is present in SOM, crop residues, and manure is converted to inorganic forms through the process called **mineralization**. In this process, bacteria digest organic material and release ammonium-nitrogen (N-NH_4^+). Formation of NH_4^+ increases as microbial activity increases. In turn, bacterial growth is directly related to soil temperature and water content.

N-NH_4^+ has properties that are of practical importance for N management. Primarily it is easily absorbed by plants. Secondly, it has a positive charge and, therefore, is attracted or held by negatively charged soil and soil organic matter. Therefore, NH_4^+ does not migrate in soils thus being relatively safe for environment. However, NH_4^+ that was not taken up by plants is subjected to other transformations in the soil system, thereby becoming more mobile.

Nitrification is a conversion of N-NH_4^+ to N-NO_3^- . Nitrification is a biological process and proceeds rapidly in warm, moist, and well-aerated soils. Nitrification slows down at soil temperatures below 10°C . Thus, the general recommendation is that ammoniacal (NH_4^+ forming) fertilizers should not be applied until soils are below 10°C .

As nitrates are negatively charged ions, in contradiction to NH_4^+ they are not attracted to soil particles or soil organic matter. N-NO_3^- is also water soluble and mobile, therefore can easily move below the crop rooting zone and contaminate adjacent water reservoirs.

Denitrification is a process by which bacteria convert N-NO_3^- to gaseous N_2 , that is released to the atmosphere. Denitrifying bacteria use NO_3^- instead of oxygen in their metabolic processes. Denitrification usually takes place in waterlogged soil, if there is an ample organic matter to provide energy for bacteria. For these reasons, denitrification is generally limited to topsoil. Denitrification proceeds rapidly when soils are warm and become saturated for at least 2 or 3 days.

Immobilization is a temporary reduction of available N in soil. When bacteria decompose high carbon-low nitrogen residues (e.g. corn stalks, small grain straw), they need more N to digest the material. If there is no sufficient amount of N in residue, they uptake nitrates and/or ammonium present in the soil. Therefore, some part of soil N becomes organic again, what means it becomes temporarily unavailable for plants.

Nitrogen Loss From the Soil System

Nitrogen is lost from the soil system in several ways:

- ❖ Leaching
- ❖ Denitrification
- ❖ Volatilization
- ❖ Crop removal

❖ Soil erosion and runoff

In contrast to the biological transformations previously described, loss of nitrate by **leaching** is a physical phenomenon. Leaching is the loss of soluble NO_3^- as it moves with soil water (usually excess water) below the root zone. Nitrates that move below the root zone have a potential to enter either groundwater or surface water through tile drainage systems.

Coarse-textured soils have a lower water-holding capacity and, therefore, a higher potential to loose nitrates due to leaching when compared with fine-textured soils. Nitrates can be leached from any soil if rainfall or irrigation moves water through the root zone.

Denitrification can be a major loss of NO_3^- mechanism when soils are saturated with water for 2 or 3 days. Nitrogen in the NH_4^+ form is not subjected to this loss. Management alternatives are available if denitrification losses are a potential problem.

Significant losses from some surface-applied N sources can occur also due to **volatilization**. In this process, N is lost as the ammonia (NH_3) gas. This concerns especially manure and fertilizer products containing urea. Ammonia is an intermediate form of N during the process in which urea is transformed to NH_4^+ . Incorporation of these N sources would virtually eliminate volatilization losses. Loss of N from volatilization is greater when soil pH is higher than 7.3, the air temperature is high, the soil surface is moist, and there is a lot of residues in soil.

Nitrogen can be lost from agricultural lands also through soil **erosion and runoff**. Losses through these events do not normally account for a large portion of the soil N budget, but should be considered for surface water quality issues.

PHOSPHORUS CYCLE

Phosphorus is widely distributed in nature, however it does not exist there in its elemental form. Being extremely reactive it immediately combines with oxygen after exposure to air. Therefore its most common form are orthophosphates. P cycle is similar to the cycles of other mineral compounds.

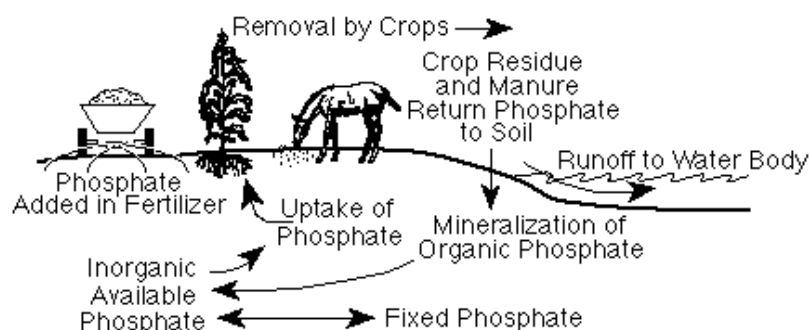


Fig. 2. Phosphorus cycle.

Forms of phosphorus in soils

Although phosphorous exists in many different forms in soil, in practical terms only three of them are crucial – P in solution, so called “active P” and fixed P.

Solution P

The term “solution P” covers mainly orthophosphates, but also small amount of organic P. The amount of solution P in soil is very small, however very important because it P in a solution is available for plants, and additionally is also mobile. After being taken up by plants P solution is replenished by active P. On the other hand, addition of P solution to the crop in excess results in its transformation into fixed P.

Active P

The active P is P in the solid phase. It comprises of inorganic phosphates attached (or adsorbed) to small particles in the soil, phosphates that reacted with elements such as calcium or aluminum to form somewhat soluble solids, and organic P that is easily mineralized. Being relatively easily released to the soil solution (the water surrounding soil particles), serves as the supply of P solution, therefore is considered to be the main source of available P for crops.

Fixed P

The term “fixed P” corresponds to inorganic phosphate compounds that are very insoluble and organic compounds that are resistant to mineralization by microorganisms in the soil. Fixed P may remain in soils for years without being made available to plants and may have very little impact on the fertility of a soil. Fixed P is less soluble than active P, however a slow conversion between both forms occurs in soils.

Sources of phosphorus compounds for plant growth

Plants uptake P only in the orthophosphate form (PO_4^{3-} , HPO_4^{2-} , H_2PO_4^-). There are several sources of P supply for plant growth:

- ❖ Commercial fertilizers
- ❖ Animal manures
- ❖ Crop residues
- ❖ Weathering of phosphate rocks

Commercial fertilizers and manure

The phosphate in fertilizers and manure is initially quite soluble and available. Most phosphate fertilizers have been manufactured by treating rock phosphate (the phosphate-bearing mineral that is mined) with acid to make it more soluble. Manure contains soluble phosphate, organic phosphate, and inorganic phosphate compounds that are quite available. When the fertilizer or manure phosphate comes in contact with the soil, various reactions begin occurring that make the phosphate less soluble and less available. The rates and

products of these reactions are dependent on such soil conditions as pH, moisture content, temperature, and the minerals already present in the soil.

Crop residues

The crop residues serve as a source of organic P. Organic P becomes available to plants after mineralization. In the case of P mineralization is the microbial conversion of organic P to H_2PO_4^- or HPO_4^{2-} , PO_4^{3-} .

Weathering of phosphate rocks

There are two types of weathering involved in the P cycle – chemical weathering and physical weathering. In chemical weathering P rocks break down and release P due to chemical reaction induced by acid rain or chemicals released by lichen. In physical reaction P rocks break down due to rain, wind or freezing. Then, P gets to the soil in the form of small particles of rocks.

Phosphorus loss from the soil system

Phosphorus can be lost from the soil due to: crop uptake, runoff and leaching.

Runoff is a major cause of P loss from farms. Both particulate P (soil-bounded) in eroded sediment and dissolved P (from manure and fertilizer) are carried away by water.

Leaching is responsible for the loss of dissolved P from soil by vertical water movement. The process concerns to soils relatively rich in P (near or at P saturation), especially where preferential flow or direct connections with tile drains exist.

Sustainable soil fertilization

The results of a precise soil analysis for the N and P content (but also K and Mg) are the basis of sustainable crop fertilization. The analysis are run in the agro-chemical laboratories. They include the determination of soil pH (pH in KCl) and liming needs, as well as soil fertility by determination of available phosphorus and potassium (with Egner-Riehm's method), and magnesium content. The precise determination of local soil requests for biogenic substances is a key to prevent overfertilization, thus helping to minimize agricultural costs and possibilities of adjacent water reservoirs contamination.

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Determination of nitrates by sodium salicylate method

Nitrates in the acidum medium react with sodium salicylate to form nitrosalicylic acid. Nitrosalicylic acid after alkalizing convert into yellow ionized form. A yellow color is formed proportionally to the nitrates concentration.

1. Weigh 2 g of soil
2. Add 100 ml distilled H₂O
3. Filter
4. Measure 3 ml of filtrate into evaporating dish
5. Add 2-3 drops NaOH and 1 ml of sodium salicylate
6. Evaporate the solution to dryness on the water bath
7. Pour to solid residue 1 ml H₂SO₄ covering all dry residue
8. After 10 min. add 20 ml distilled H₂O and 7 ml of potassium-sodium tartrate
9. Transfer **quantitatively** the solution into measuring flask a'50 ml and refill distilled H₂O to the line. Invert several times to mix.
10. Pour solution into a sample cell. Place the prepared sample into the cell holder. Close the light shield.
11. Read the concentration of nitrates (in the sample) from the display (m)
12. Calculate the concentration of N-NO₃ [mg/L]:

$$X = m \cdot 1000/V$$

m - concentration of nitrates in investigated sample

V – volume of sample used for examination, mL

Determination of soluble (available) phosphorus in soil by the Egner-Riehm method

Method is based on the extraction of phosphorus from the soil with calcium lactate buffer at pH of approx. 3.6. It is assumed, that the forms of phosphorus extracted from soil with this reagent are forms available for plants. The method is used by Agrochemical Stations to set boundary values of P, which describe the degree of soil fertility.

Phosphorus content in the extract is determined colorimetrically, after turning into blue phosphoro-molibdenate in the reaction with ammonium molybdate, metol solution (fotorex) and tin chloride (SnCl_2) as a reducing agent.

Stage I Extraction

1. Weight 2,00 g of dry soil and place in the plastic bottle with a capacity of at least 120 mL
2. Add 100 mL of freshly prepared 0.04 M calcium lactate (pH 3.55 ± 0.05). Prepare also the blank sample.
3. Shake for about 20 min.
4. Filter through an average filter (through away first few mL of filtrate so as to achieve a clear filtrate)
5. Take 25 mL of clear filtrate and analyse for the phosphorous content

Stage II Phosphorous content assessment

6. Measure 25 mL of clear filtrate and pour into a 50 mL beaker
7. Add 2 mL of the mixture of ammonium molibdenate and metol solution (fotorex)
8. Add 1 mL of SnCl_2 solution
9. Leave the sample for 30-45 minutes in a dark place. Within this time a blue phosphoro-molibdenate complex is formed. The color is stable for up to few hours.
10. Analyze the sample in a spectrophotometer.
11. The value from the display is expressed directly in $\text{mgP}_2\text{O}_5/100\text{g}$ of soil.

REPORT

Report should include: introduction about sustainable fertilization practices and methods of runoff control, results obtained during the exercise, all the calculations needed, and (above all) discussion of results (*i.a.* basing on Tab. 1) and conclusions.

Tab. 1. Evaluation of the content of phosphorus in the mineral soil, based on the extraction with Egner-Riehm's method.

Class of soil	Content	mg P_2O_5 / 100g soil
V	very low	<5.0
IV	low	5.1-10.0
III	moderate	10.1-15.0

II	high	15.1-20.0
I	very high	>20.0

Tab.2 Classification of soil according to N content

Type of soil	N content, %
Mineral soil	0.04-0.4
Soil made of low peat	1-4