Agri Articles
(e-Magazine for Agricultural Articles)
Volume: 06, Issue: 04 (JULY-AUG, 2026)
Available online at http://www.agriarticles.com
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Nutrient Transformation – N, P, S; Trace Metal Interaction with Humic Substances, Significance of Chelation Reaction in Soils

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Soil is a dynamic natural system where nutrients continuously undergo physical, chemical and biological transformations that regulate their availability to plants and microorganisms. Among the essential plant nutrients, Nitrogen (N), Phosphorus (P), and Sulfur (S) are fundamental for plant growth, crop productivity, and ecosystem functioning. These nutrients exist in various organic and inorganic forms and are transformed through processes such as mineralization, immobilization, oxidation, reduction, nitrification, denitrification, and biological fixation. Soil microorganisms play a central role in driving these transformations, thereby maintaining nutrient cycling and soil fertility.

Transformations of Nitrogen

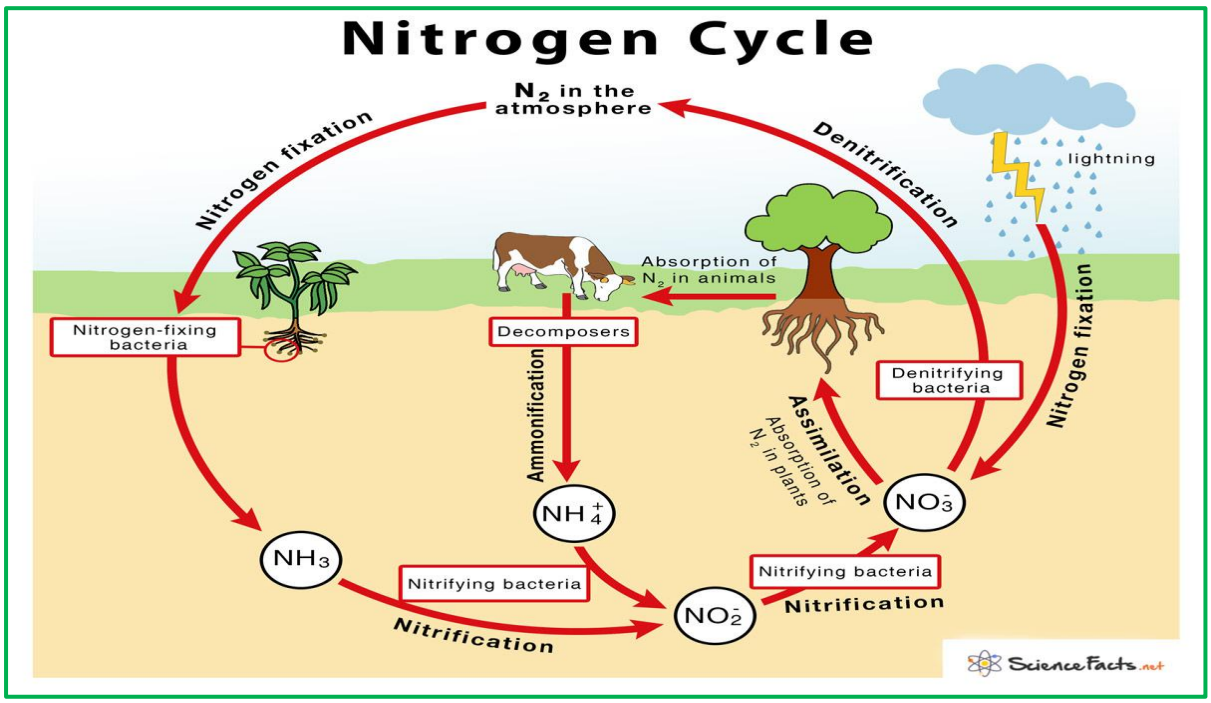
Nutrient transformation of nitrogen refers to the various biological and chemical processes through which nitrogen changes from one form to another in soil, plants, atmosphere, and microorganisms. These transformations are essential for maintaining soil fertility and plant nutrition.

This element is the key building block of the protein molecule upon which all life is based on, it is an indispensable component of the protoplasm of plants, animals and microorganism. Molecular N_2 constitutes about 78% of the earth's atmosphere but it is chemically inert and cannot be utilized by more living organism, plant animals and microorganism therefore depend on a source of combined N such as ammonia, nitrate or organic N compounds for their growth.

Nitrogen undergoes a number of transformations that involve organic, inorganic and volatile forms of nitrogen. A small part of the large reservoir of N_2 in the atmosphere is converted to organic compounds by certain free-living microorganism or by plant microbe association that makes the element available to plant growth.

The nitrogen present in the proteins or nucleic acids of plant tissue is used by animals. In the animal body, the N is converted to other simple and complex compounds. Upon the death, plants and animals undergo microbial decay and organic N is released as ammonium, which is then utilized by vegetation or is oxidized to nitrate by microorganisms. The nitrate from of N is mostly used by the plants or may be lost by bacteria reduced to gaseous N_2, which escapes to atmosphere, there by completing the cycle. The Nitrogen cycle mainly includes transformations such as;

1. **Nitrogen mineralization:** In which N containing organic complexes are decomposed and converted into inorganic compounds for use by plants.
2. **Nitrogen Immobilization**: In which N containing inorganic compounds are assimilated.



Major Transformations of Nitrogen

1. Nitrogen Fixation

Conversion of atmospheric nitrogen (N_2) into usable forms like ammonia (NH_3).

Types:

- **Biological fixation**; Done by microorganisms such as:

✓ *Rhizobium* in legumes

✓ *Azotobacter*

✓ Cyanobacteria

Reaction; $N_2 + 8H^+ + 8e^- \rightarrow 2NH_3 + H_2$

- **Industrial fixation**; Haber–Bosch process for fertilizer production.
- **Atmospheric fixation**; Lightning converts N_2 into nitrates.

2. Ammonification (Mineralization)

Conversion of organic nitrogen from plant and animal residues into ammonia/ammonium by decomposer microbes.

$$\text{Organic N} \rightarrow NH_3 \rightarrow NH_4^+$$

Example:

Proteins → amino acids → ammonium.

Importance:

- Supplies available nitrogen to plants.
- Increases soil fertility.

3. Nitrification

Biological oxidation of ammonium into nitrate under aerobic conditions.

Step I:

$$\boldsymbol{NH_4^+ \rightarrow NO_2^-}$$

By *Nitrosomonas*

Step II:

$$\boldsymbol{NO_2^- \rightarrow NO_3^-}$$

By *Nitrobacter*

Overall:

$$\boldsymbol{NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-}$$

4. Immobilization

Conversion of inorganic nitrogen into microbial biomass.

$$NO_3^- \text{ or } NH_4^+ \rightarrow \text{Organic microbial N}$$

5. Denitrification

Reduction of nitrate to gaseous nitrogen forms under anaerobic conditions.

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

Microorganisms:

- *Pseudomonas*
- *Bacillus*

6. Volatilization

Loss of nitrogen as ammonia gas.

$$\boldsymbol{NH_4^+ \rightarrow NH_3 \uparrow}$$

7. Leaching

Downward movement of nitrate with water.

$$\boldsymbol{NO_3^- \downarrow}$$

Importance:

- Causes nitrogen loss.
- May contaminate groundwater.

Summary Table

Process	Conversion	Main Microorganisms	Condition
Nitrogen fixation	$N_2 \rightarrow NH_3$	Rhizobium, Azotobacter	Biological
Ammonification	Organic N $\rightarrow NH_4^+$	Decomposers	Aerobic/anaerobic
Nitrification	$NH_4^+ \rightarrow NO_3^-$	Nitrosomonas, Nitrobacter	Aerobic
Immobilization	Inorganic N $\rightarrow$ Organic N	Soil microbes	High C: N residues
Denitrification	$NO_3^- \rightarrow N_2$	Pseudomonas	Anaerobic
Volatilization	$NH_4^+ \rightarrow NH_3$ gas	Chemical process	High pH
Leaching	NO_3^- loss	—	Excess rainfall

Phosphorus Cycle

Phosphorus is only second to N2 as an inorganic nutrient required by both plants and micro-organisms. Phosphate constitutes nearly 0.1% of the earth crust. They occur in soil in inorganic and organic forms.

The inorganic forms are derived from parent rocks or through fertilizers application and manuring with bone meal. They are soluble in water when present as phosphates of Na, K, Ca, Mg etc.

Key Forms of Phosphorus in the Environment

1.Inorganic phosphorus:

Includes phosphate ions (e.g., orthophosphate- **$H_2PO_4^-$**, **HPO_4^{-2}**), which are readily available for biological uptake.

2. Organic Phosphorus:

Found in organic molecules such as inositol phosphate, nucleic acids, phospholipids and phytates. In soil, from15-85% of the total P is organic. Soils rich in organic matter contain abundant organic P.

3. Mineral Phosphorus:

Found in insoluble mineral forms like **Apatite** or as part of iron and Aluminum compounds.

Microbial Processes in Phosphorus Transformation

1. Mineralization (Organic to Inorganic P): Microorganisms break down organic phosphorus compounds, converting them into inorganic phosphate (PO_4^{-3}), which is bioavailable. Enzymes involved: **Phosphatases, phytases**

Example: Decomposition of organic matter by soil bacteria like *Bacillus* or fungi like Aspergillus.

2. Immobilization (Inorganic to Organic P): Microorganisms assimilate inorganic phosphate into their biomass, converting it into organic phosphorus.

3. Solubilization (Mineral P to Soluble P): Microorganisms solubilize insoluble phosphate minerals by releasing organic acids making phosphorus more available for plants and other microbes.

Example organisms: *Pseudomonas*, *Bacillus*, *Penicillium*, *Aspergillus niger*.

Mechanisms: Production of acids like gluconic acid or chelating compounds.

C:P inorganic ratio	**Process operates**
➢ 200:1 or less	Mineralization
➢ 300:1 & above	Immobilization
➢ Above 200:1 but less 300:1	Neither net mineralization nor net immobilization

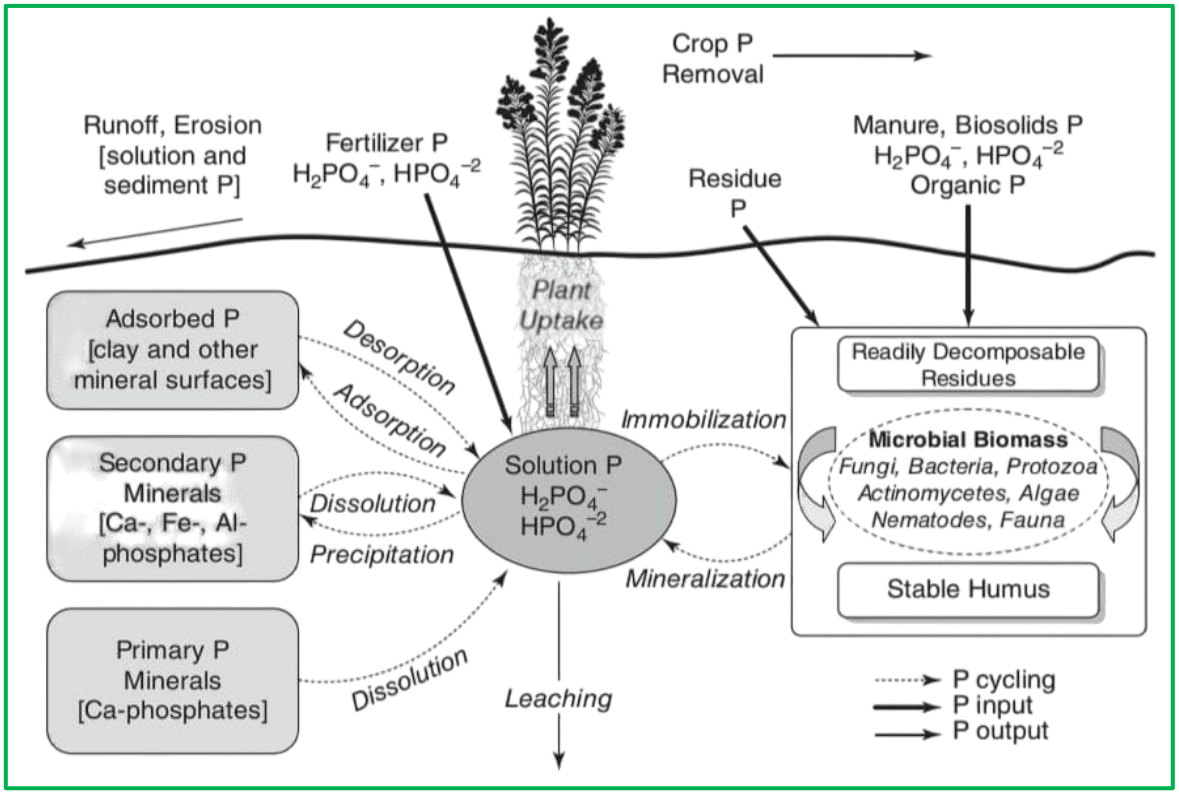


Fig.: Phosphorus Cycle

Transformations in the Sulfur Cycle

The sulfur cycle is often compared to the nitrogen cycle because both are heavily regulated by microbial activity and involve atmospheric components.

1. **Mineralization**

This is the conversion of **organic sulfur** (found in organic matter and plant residues) into inorganic sulphate.

Process: Microorganisms break down complex organic compounds (like proteins containing cysteine and methionine).

Significance: This is the primary way sulfur becomes available to plants, as plants mainly absorb sulfur in the sulfate form.

2. Immobilization

The reverse of mineralization, where inorganic sulfate is converted back into organic forms by soil microbes.

3. Oxidation

Sulfur in reduced forms (such as elemental sulfur or sulfides) is converted into sulfate. The oxidation process supports the population of chemolithotrophs like Beggiatoa, Thiothrix, Thermothrix (thermophile).

Chemical Impact: This process produces sulfuric acid, which can significantly lower soil pH (acidification).

4. Reduction

Under anaerobic (waterlogged) conditions, sulfate is reduced to hydrogen sulfide or other sulfides.

Process: Facultative and obligate anaerobic bacteria (e.g., *Desulfovibrio*) use sulfate as an electron acceptor in the absence of oxygen.

➢ Sulphur is present in three forms in the biosphere:

1. Elemental Sulphur – Which is available as Sulphur deposits and Sulphide ores.

2. Inorganic Sulphur – Which is available as sulphate in aerobic soil environment and as sulphide in anaerobic soil environment.

3. Organic Sulphur – Is present in the form of amino acids and plants/animal residues.

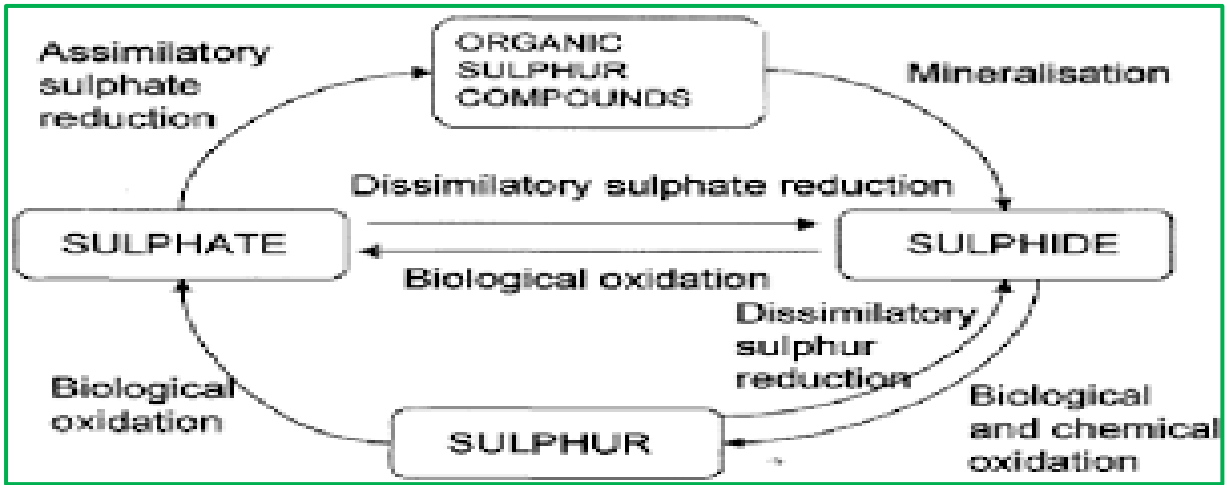


Fig.: Sulphur Cycle

Trace Metal Interaction with Humic Substances and Significance of Chelation Reactions in Soils

Humic substances are the major components of soil organic matter formed during decomposition and humification of plant and animal residues. They include:

- Humic acids (HA)
- Fulvic acids (FA)
- Humin

These substances are chemically active and possess large numbers of functional groups capable of interacting with metal ions present in soil.

Trace metals such as Fe, Zn, Cu, Mn, Co and Mo are essential micronutrients for plants, whereas Cd, Pb, Hg and As may become toxic at higher concentrations. The interaction of these metals with humic substances controls their availability, mobility and toxicity in soil.

Humic Substances in Soil

Defination

Humic substances are dark colored, amorphous and colloidal organic compounds produced during humification. They are highly reactive due to the presence of many functional groups.

➢ **Types of Humic Substances**

Humic Fraction	Solubility	Characteristics
1.Fulvic acids	Soluble in acid and alkali	Low molecular weight, highly reactive
2.Humic acids	Soluble in alkali, insoluble in acid	High CEC and strong metal binding
3.Humin	Both Insoluble	Stable and less reactive

Functional Groups Responsible for Metal Binding

Humic substances contain several reactive functional groups:

- Carboxyl (-COOH)

- Phenolic hydroxyl (-OH)
- Alcoholic groups
- Carbonyl groups
- Amino groups
- Amide groups
- Sulphydryl groups

These groups dissociate in soil solution and produce negatively charged sites capable of binding metal cations.

Mechanisms of Trace Metal Interaction

1. Adsorption

Metal ions are adsorbed onto the negatively charged surfaces of humic colloids.
Example:

- Cu^{2+}, Zn^{2+}, Fe^{2+}

Humic substances possess very high cation exchange capacity (CEC); therefore, they can retain large amounts of metals.

2. Ion Exchange

Metal cations replace H^+ or other exchangeable ions attached to humic substances.
Example:

$$2R - COOH + Cu^{2+} \rightarrow (R - COO)_2Cu + 2H^+$$

3. Complexation

Metal ions combine with functional groups of humic substances forming coordination complexes. Carboxyl and phenolic groups mainly participate in this process.

Effects

- Stabilizes metal ions
- Alters metal mobility
- Controls bioavailability

4. Chelation

Chelation is a special type of complexation in which one metal ion binds with two or more donor groups of the same organic molecule forming ring-like structures.
Example

$$\text{Humic acid} + Fe^{3+} \rightarrow \text{Fe-humate complex}$$

- **Chelating Functional Groups**

Carboxyl groups, Phenolic groups, Amino groups and Sulphydryl groups.

❑ **Significance of Chelation Reactions in Soils**

i.) Increases Micronutrient Availability

- Chelation keeps micronutrients like Fe, Zn, Cu and Mn in soluble and plant-available forms.
- Without chelation, these nutrients may precipitate and become unavailable.

ii.) Reduces Heavy Metal Toxicity

Chelation binds toxic metals such as: Cd, Pb, Hg
This decreases free ionic concentration and lowers toxicity to plants and microorganisms.

iii.) Prevents Nutrient Leaching

Chelated metals remain retained in upper soil layers and are not easily washed away.

Result

- Better nutrient conservation
- Reduced fertilizer loss

iv.) Improves Soil Buffering Capacity

Humic substances regulate:
Soil pH, Redox reactions, Soil solution concentration
Chelation contributes to soil chemical stability.

v.) Enhances Plant Growth

Chelated micronutrients are slowly released and readily absorbed by plants.

This supports:
Chlorophyll synthesis, Enzyme activation, Root growth and Crop yield

vi.) Role in Soil Remediation
Humic substances are useful in remediation of contaminated soils because they immobilize toxic metals and reduce environmental pollution.

vii.) Maintains Metal Mobility
Fulvic acids may form soluble metal chelates that increase movement of metals in soil solution.
This may:

- Improve nutrient transport
- Increase heavy metal mobility under some conditions

Conclusion

The transformation of Nitrogen, Phosphorus and Sulfur in soils is a complex process governed largely by microbial activity and environmental conditions. These transformations regulate nutrient availability, influence soil fertility, and determine crop productivity. Efficient management of these nutrient cycles is essential for sustainable agriculture and minimizing nutrient losses to the environment. Humic substances significantly affect the behavior of trace metals through adsorption, complexation, ion exchange, and chelation reactions. Chelation enhances the availability of essential micronutrients while reducing the toxicity and mobility of harmful heavy metals.

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