Chapter 9

BIOCHEMICAL TRANFORMATIONS OF PHOSPHORUS

Phosphorus is critical to all life forms because of the role it plays in many important biomolecules such as DNA (deoxyribonucleic acid), phospholipids, and ATP (adenosine triphosphate). The amount of total phosphorus found in a surface soil can vary greatly, ranging from <100 μg P g^{-1}(200 kg ha^{-1}) in a very sandy soils to > 1,000 μg g^{-1} (200 kg ha^{-1}) in soils derived from basic rocks. The primary mineral form of phosphorus is rock phosphate, or *apatite*. The chemical weathering of apatite results in the release of orthophosphate ($H_2PO_4^-$ is the dominant species at pH values below 7.2; HPO_4^{2-} dominates above pH 7.2). Very little orthophosphate is present in the soil solution at any one time, usually <1% of the total phosphorus.

Forms of Phosphorus in soil

Solution phosphorus concentrations of 0.1 to 1 mg L^{-1} are common in soil. Of this, more than half may be in the form of soluble organic compounds released by dead cells or in colloidal organic compounds. Addition of soluble phosphate fertilizers or mineralization of organic phosphorus results in the release of orthophosphate into the soil solution, followed by precipitation as iron and aluminum phosphates in acid soils or calcium phosphates in alkaline soils (stable-inorganic phosphorus) or by adsorption to iron and aluminum oxides (labile-inorganic phosphorus). These reactions result in low orthophosphate concentrations in the soil solution. The optimum availability of orthophosphate occurs at a soil pH of about 6.5 because precipitation as both aluminum and calcium phosphates is minimized. One practical aspect of liming acid soils or acidifying alkaline soils is the improved availability of orthophosphate.

Many organic forms of phosphorus are also found in soils. As plant and animal remains or waste products are returned to the soil, readily mineralized organic phosphorus compounds are introduced. Microorganisms also produce organic phosphorus compounds as organic materials which are transformed in soil. Organic phosphorus in most soils may account for as little as 3 and as much as 90% or more of the total soil phosphorus but usually represents 30 to 50% of total phosphorus in most soils. The total amount of organic phosphorus in a soil is usually strongly correlated with total organic carbon; organic phosphorus decreases with depth in the soil profile, as does organic carbon. The chemical nature of the soil organic phosphorus fraction is not well known. There are many different forms of organic phosphorus in soil. Of these compounds, inositol phosphates, often called phytins or phytic acids, are typically present in the greatest quantity, comprising 10 to 50% of the total organic phosphorus. Phospholipids and nucleic acids may account for 1 to 5% of the organic phosphorus. Other identifiable organic phosphorus compounds are typically present in trace amounts only.

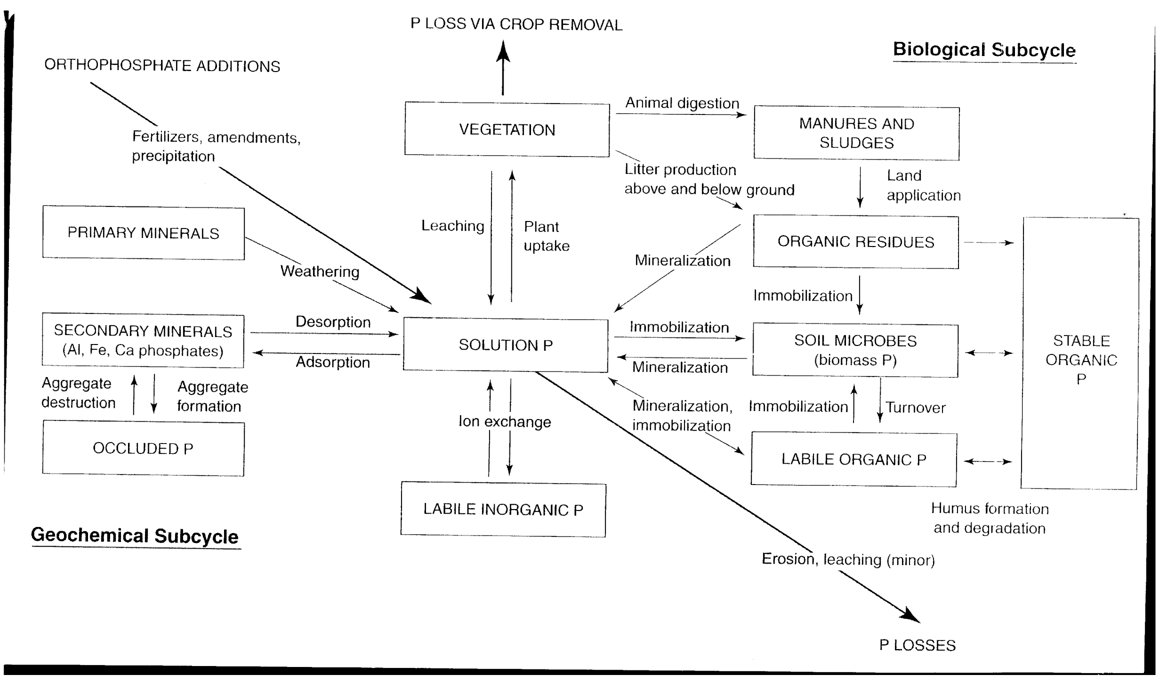
Another important pool of organic phosphorus is the soil microbial biomass. This fraction represents the actively cycling pool of organic phosphorus in the soil environment and is part of the labile, or readily available, organic phosphorus. Through this pool, the active mineralization and immobilization of phosphorus in soil occurs. Concentrations of 5 to 75 μg biomass P g^{-1} soil are common. Cultivation of soil results in a reduction of soil organic matter and total organic phosphorus and reduces the proportion of biomass phosphorus to total organic phosphorus. Therefore, tillage depletes the labile organic phosphorus pool more rapidly than the stable organic phosphorus fraction.

The Phosphorus Cycle

A model of the phosphorus cycle, illustrated in Figure shows the various compartments of phosphorus in the terrestrial environment. Phosphorus is affected by both biological and chemical reactions. This model divides the phosphorus cycle into a geochemical subcycle and a biological subcycle, with the solution phosphorus pool serving as the central point in the overall cycle. Solution phosphorus is the source of orthophosphate for plant and soil microorganisms.

In the biological phosphorus subcycle, orthophosphate can be taken up by plants or immobilized into microbial biomass. As plant residues and animal remains and wastes are returned to soil, the organic phosphorus may be directly incorporated into stable humus, mineralized to orthophosphate, or immobilized into the microbial biomass. Biomass phosphorus is subject to incorporation into humic substances and mineralization and immobilization reactions. The turnover or cycling of the biomass contributes significantly to the labile organic phosphorus pool, crop removal and erosion are two mechanisms for loss of organic phosphorus.

In the geochemical phosphorus subcycle, orthophosphate is solubilized from primary and secondary minerals by chemical and biochemical weathering processes. Dissolution of these compounds in the soil solution or solubilization through microbially produced organic acids releases orthophosphate to the soil solution for plant and microbial uptake. Orthophosphate can adsorb to aluminum and iron oxides (labile inorganic phosphorus) or precipitate as aluminum, iron, or calcium phosphates (secondary minerals).



The Phosphorous cycle, showing inputs, losses, and major transformations in the soil environment

Mineralization and Immobilization of Phosphorus

Phosphorus availability is controlled by mineralization and immobilization through the organic fraction and the solubilization and precipitation of phosphate in inorganic forms. As the remains of plants, animals, and microbes are returned to the soil, they are actively decomposed by soil microorganisms. Phosphorus in these organic residues must be released if it is to be available to plants and microorganisms.

Phosphorus mineralization is an enzymatic process. As a group, the enzymes involved, called *phosphatases*, catalyze a variety of reactions that release phosphate from organic phosphorus compounds to the soil solution. Phosphatases are released by microorganisms extracellularly into the soil solution to catalyze these hydrolytic mineralization reactions:

- *Phosphomonoesterases* hydrolyze the phosphate from monoester forms of phosphorus, such as those in nucleotides or phospholipids.
- *Phosphodiesterases* hydrolyze phosphate from diester of phosphorus, such as in nucleic acids.
- *Phytases* hydrolyze phosphate from inositol phosphates.

Once phosphorus is mineralized, it can be taken up by plants or immobilized back into microbial cells, or it can form insoluble inorganic complexes. The microbial biomass can affect phosphorus availability through immobilization, the incorporation of orthophosphate ions into organically bound forms in the organisms. For example, orthophosphate reacts with ADP (adenosine diphosphate) and a suitable input of energy to form ATP. The extent of immobilization is affected by the carbon to phosphorus ratio of the organic materials being decomposed and the amount of available phosphorus in the soil solution.

The carbon to phosphorus ratio of an added residue can determine the extent to which inorganic phosphorus is mineralized or immobilized. If insufficient phosphorus is available in the residue for assimilation of the added carbon, then inorganic phosphorus from the soil solution must be used and net immobilization occurs. Conversely, if more phosphorus is present in the residue than is needed for carbon assimilation, net mineralization of orthophosphate occurs. Generally, a C/P ratio <200/1 results in mineralization, while a C/P ratio > 300/1 results in immobilization. Ratios between 200 to 300 results in little net change in solution phosphorus concentrations. These processes are similar to those for nitrogen and sulfur mineralization and immobilization. In addition to the phosphorus content of residue, other soil and environmental variables (e.g., pH, temperature, aeration, and soil moisture) affect microbial activity and phosphorus mineralization. The element that is most limiting controls the overall mineralization rate of a residue. If rapid carbon mineralization of a phosphorus-limited residue is occurring, then immobilization of phosphorus from the soil results. As mineralizable organic carbon disappears, a portion of the phosphorus-rich microbial biomass will be mineralized as well, resulting in the eventual release of the previously immobilized phosphorus.

Solubilization of Inorganic Phosphorus

Inorganic phosphorus minerals are generally found as aluminum and iron phosphates in acidic soils, while calcium phosphates dominate in alkaline soil. These slightly soluble compounds provide orthophosphate to soil solution to the extent allowed by the soluble compound. Solubility products provide a relative measure of solubility in pure water; however, these compounds are also affected by soil pH. Orthophosphate is supplied to the roots primarily by diffusion. Thus chemical equilibria between orthophosphate, adsorbed orthophosphate, and inorganic phosphates minerals are important in supplying phosphorus to plants and microorganisms. As phosphorus is taken up, it is replenished from these sources.

Plant roots and soil microorganisms can enhance the dissolution of phosphate compounds by the release of carbon dioxide and organic acids to the soil solution. Carbonic acid can promote the acid dissolution of calcium and magnesium phosphate compounds. Similarly, the acidity produced by the nitrifying bacteria and sulfur-oxidizing bacteria promotes solubilization of insoluble phosphate salts. A wide range of organic acids is produced by microorganisms and plants, and many act as **chelating agents** to solublize aluminum, iron, calcium, and magnesium phosphates, resulting in the release of orthophosphate into the soil solution. One group of organisms that may be important in this regard is the mycorrhizal fungi, which form symbioses with plant roots and enhance the uptake of phosphorus and other nutrients. Under water-logged conditions, hydrogen sulfide, produced by sulfate-reducing bacteria or other processes, can also displace metal cations from insoluble phosphates, with the release of phosphate.

Environmental Aspects of Phosphorus Cycling

Phosphorus can cause environmental damage if applied in excess to soils. Phosphorus is the most limiting nutrient for primary productivity in many ecosystems, particularly aquatic systems. If a large amount of phosphorus is applied to soil, it may move to waters with runoff water and eroded soil particles that bind phosphorus. The major consequence is a process called **eutrophication.** Eutrophication can occur in surface waters when excessive phosphorus or nitrogen accumulates. The process occurs most noticeably in relatively still bodies of water such as ponds and lakes. If phosphorus is the limiting nutrient in the pond, excess phosphorus additions can result in rapid growth of algae in the water. This algal bloom is often noticeable as a green “scum” or film on the water surface. As the algae die, they settle to the bottom, where bacterial decomposition of the nutrient-rich algae occurs. The decomposition of the algae results in oxygen depletion. If the process continues, the lake slowly becomes anaerobic, resulting in a poor environment for many forms of aquatic life.

Nonpoint sources of phosphorus, such as agricultural activities, are often associated with increased phosphorus in surface water. For example, runoff from cropland and soils receiving animal manures can lead to significant phosphorus inputs into surface waters. In industrialized countries, nonpoint sources are the major source of phosphorus. In nonindustrialized countries with limited sewage treatment capacity, raw sewage discharge into surface water (a point source) is a significant source of phosphorus polution.

The natural ability of soils to adsorb phosphorus from solution removes phosphorus from treated wastewater. Natural and constructed wet-lands can serve as a sink for the removal of phosphorus from wastewater before their release to river to lake.