

MECHANISTIC PATHWAYS FOR MOBILISING LEGACY PHOSPHORUS IN CALCAREOUS SOILS: A COMPREHENSIVE REVIEW

Ajibala. S¹, Guru. G^{1*}, Raju. M¹, Ravichandran. V², Suganya. S³

¹Department of Agronomy, Tamil Nadu Agricultural University, Coimbatore - 641 003, Tamil Nadu, India.

² Department of Crop Physiology, Tamil Nadu Agricultural University, Coimbatore - 641 003, Tamil Nadu, India.

³ Department of Soil Science & Agri. Chemistry, Tamil Nadu Agricultural University, Coimbatore - 641 003, Tamil Nadu, India.

Ajibala. S¹ (sajibala719@gmail.com), ORCID ID: 0009-0009-9425-0169

Guru. G^{1*} (guru.g@tnau.ac.in), ORCID ID: 0000-0002-3202-378X,

Raju. M¹ (raju.m@tnau.ac.in), ORCID ID: 0000-0001-9026-5106,

Ravichandran. V² (ravi.v@tnau.ac.in), ORCID ID: 0000-0002-6447-6417,

Suganya. S³ (suganssac2010@tnau.ac.in), ORCID ID: 0000-0003-2716-7591

*Correspondence Author: Guru. G, Email: guru.g@tnau.ac.in

ABSTRACT

Calcareous soils contain substantial reserves of legacy phosphorus (P) accumulated from long-term fertilizer use, yet most of this P remains unavailable because of fixation by calcium carbonate minerals (Sharma *et al.*, 2019). Under alkaline pH conditions, soluble phosphate reacts with Ca²⁺ and precipitates as stable calcium-phosphate compounds, limiting plant uptake despite high total soil P (Penn and Camberato 2019). Plants mobilize this Ca-bound phosphorus through rhizosphere acidification caused by proton release during nutrient absorption (Gupta *et al.*, 2022). Roots also release low-molecular-weight organic acids such as citrate, malate and oxalate into the rhizosphere (Gupta *et al.*, 2022). These carboxylates chelate calcium and displace phosphate from mineral surfaces via ligand-exchange reactions, increasing phosphate concentration in soil solution (Penn and Camberato 2019). Soil microorganisms and their phosphatase enzymes further mineralize organic phosphorus into plant-available orthophosphate (Gupta *et al.*, 2022). Enhanced root-microbe interactions improve phosphorus acquisition beyond the root-depletion zone (Sharma *et al.*, 2019). Overall, integrated plant, microbial and soil chemical processes convert legacy phosphorus into available forms and improve phosphorus use efficiency in calcareous agroecosystems (Penn and Camberato 2019).

KEYWORDS: phosphorus mobilization, legacy phosphorus, calcareous soils, phosphate-solubilizing microorganisms, rhizosphere acidification, phosphatase enzymes, organic acids, organic amendments, phosphorus use efficiency, sustainable agriculture, eutrophication, microbial inoculants, mycorrhizal fungi

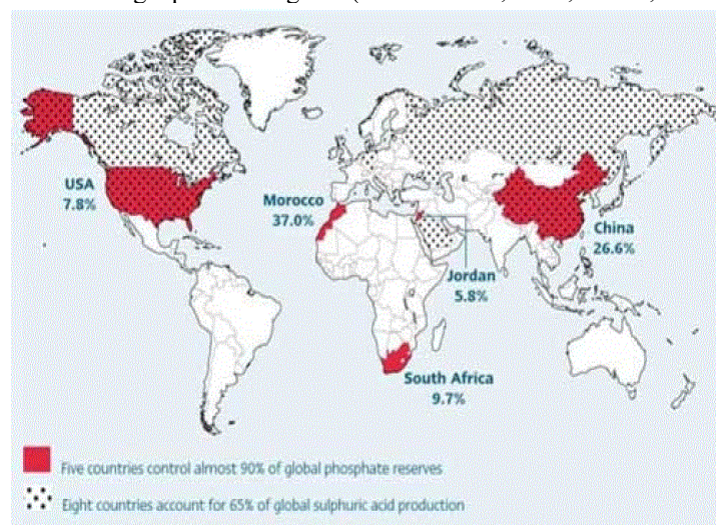
INTRODUCTION:

Phosphorus (P) is one of the most essential macronutrients required for plant growth and development and plays a fundamental role in sustaining agricultural productivity worldwide. It is involved in numerous physiological and biochemical processes that regulate plant metabolism and energy transfer. Phosphorus forms a major component of adenosine triphosphate (ATP), which functions as the primary energy currency of plant cells and is indispensable for processes such as photosynthesis, respiration, and active nutrient transport (Taiz *et al.*, 2015). In addition, phosphorus is a structural component of nucleic acids (DNA and RNA), phospholipids, and several coenzymes, making it critical for cell division, genetic information transfer, and protein synthesis. Because of these functions, phosphorus plays a central role in regulating plant growth, development, and productivity (Marschner, 2012). Apart from its biochemical roles, phosphorus has a significant influence on plant morphology and crop performance. Adequate phosphorus nutrition stimulates early root development, enhances root branching, and improves root architecture, allowing plants to explore a larger soil volume for water and nutrients. This improved root system contributes to better nutrient acquisition and overall plant vigor. Phosphorus also accelerates crop maturity, promotes flowering and seed formation, and improves grain quality in many crops. Furthermore, adequate phosphorus supply increases plant tolerance to environmental stresses such as drought, low temperature, and nutrient imbalances (Hinsinger, 2001). In contrast, phosphorus deficiency results in poor root growth, delayed maturity, reduced photosynthetic activity, and ultimately lower crop yields. Despite its importance for plant growth, phosphorus availability in soils is often limited due to its strong chemical interactions with soil minerals. When phosphorus fertilizers are applied to soil, a large proportion of the added phosphorus becomes rapidly immobilized through fixation reactions. In acidic soils, phosphorus reacts with iron and aluminium oxides to form insoluble Fe-P and Al-P compounds, whereas in alkaline and calcareous soils, it precipitates with calcium to form calcium phosphate minerals such as dicalcium phosphate, octacalcium phosphate, and hydroxyapatite (Penn and Camberato, 2019). These reactions significantly reduce the concentration of soluble phosphorus in the soil solution, which is the form directly available for plant uptake. As a result, only a small fraction of applied phosphorus fertilizer is utilized by crops during the growing season.

Studies have shown that typically less than 20–30 percent of applied phosphorus fertilizer is recovered by crops in the first year of application, while the remaining portion accumulates in the soil in less available forms (Withers *et al.*, 2018). The issue of phosphorus availability is particularly important in many agricultural regions of the world where soils have low phosphorus availability or high phosphorus fixation capacity. In India, the problem is further intensified by the heavy dependence on imported phosphatic fertilizers. Domestic phosphate rock reserves are limited and of relatively low grade, making the country highly reliant on imports to meet its fertilizer demand. Currently, India imports more than 90 percent of its phosphatic fertilizer requirement from countries such as Morocco, Jordan, China, and the United Arab Emirates (USGS, 2024). The rising cost of phosphorus fertilizers and fluctuations in global fertilizer markets place a significant financial burden on the agricultural sector. Consequently, improving phosphorus use efficiency and reducing fertilizer dependency have become critical objectives for achieving sustainable agricultural production. One promising approach to address this challenge is the effective utilization of legacy phosphorus accumulated in agricultural soils. Over decades of intensive agriculture, repeated applications of phosphorus fertilizers and organic manures have resulted in the accumulation of large quantities of phosphorus in soil pools that are not immediately available to plants. This accumulated phosphorus is referred to as legacy phosphorus. Recent estimates indicate that global agricultural soils contain more than 400 million tonnes of legacy phosphorus, which represents a substantial nutrient reserve capable of supporting crop production for many years if effectively mobilized (Rowe *et al.*, 2016; Withers *et al.*, 2018). In many cropping systems, the accumulation of phosphorus in the topsoil can exceed 1000–1500 kg P ha⁻¹, indicating a significant buildup of phosphorus resources within the soil profile. Although legacy phosphorus represents a valuable nutrient reserve, its utilization by crops is limited due to the strong chemical and physical processes that stabilize phosphorus in soil. Therefore, understanding the mechanisms that control phosphorus mobilization is essential for improving phosphorus use efficiency. Various processes contribute to the release of legacy phosphorus from soil pools, including biochemical mechanisms involving root exudation of organic acids, biological mechanisms mediated by soil microorganisms, and physicochemical processes such as redox reactions and colloid transport. These processes influence the transformation and mobilization of phosphorus in the soil–plant system and determine its availability to crops. Exploring the mechanistic pathways that control legacy phosphorus mobilization can provide new opportunities for sustainable nutrient management. Strategies such as the use of phosphorus-mobilizing crops, application of organic amendments, and inoculation with phosphate-solubilizing microorganisms can enhance phosphorus availability in soils and improve crop productivity. By harnessing these processes, it may be possible to utilize existing phosphorus reserves in soils more efficiently, thereby reducing fertilizer requirements, lowering production costs, and minimizing environmental risks associated with excessive phosphorus accumulation.

The Global Phosphorus Crisis

Phosphorus (P) is an essential macronutrient required for plant growth and agricultural productivity, but unlike nitrogen, it has no atmospheric source and must be mined primarily from phosphate rock. Phosphate rock is a finite and non-renewable geological resource, formed over millions of years through sedimentary processes. The global reserves of phosphate rock are unevenly distributed, with a large proportion concentrated in a few countries, particularly Morocco, China, Jordan, and the United States. Among these, Morocco and the Western Sahara region together hold more than 70% of the world's known phosphate reserves, making global fertilizer supply highly dependent on a limited number of geopolitical regions (Cordell *et al.*, 2009; USGS, 2023).



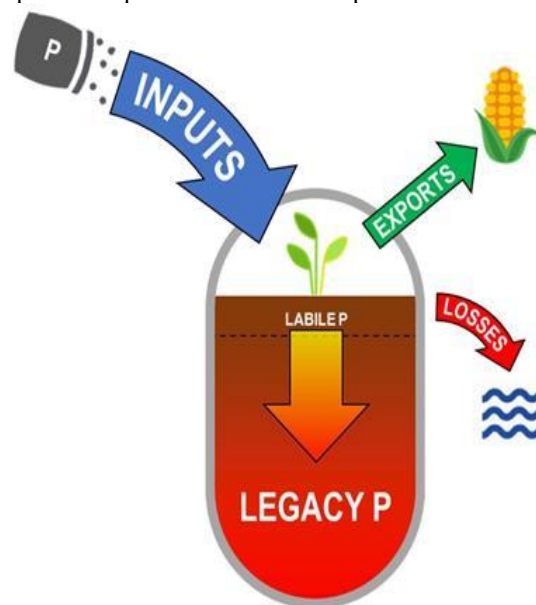
Source: U.S. Geological Survey, Mineral Commodity Summaries, 2024

The global demand for phosphorus fertilisers has increased dramatically over the last five decades due to rapid population growth, agricultural intensification, and the need to achieve higher crop yields. Modern agricultural systems rely heavily on phosphorus fertilizers to maintain soil fertility and ensure food production. According to the Food and Agriculture Organization, global fertilizer consumption continues to rise as countries attempt to meet the food requirements of a growing population expected to reach nearly 9.7 billion by 2050 (FAO, 2022). This

increasing demand has intensified concerns about the long-term sustainability of phosphate rock reserves and the potential for a future “phosphorus scarcity” or “phosphorus crisis” if efficient nutrient management strategies are not adopted. Another major concern is that phosphorus use efficiency in agriculture remains relatively low. Studies estimate that only 15–25% of applied phosphorus fertiliser is taken up by crops in the year of application, while the remainder becomes immobilised in the soil through chemical reactions with calcium, iron, or aluminium compounds, depending on soil type. Over time, these reactions lead to the accumulation of legacy phosphorus in soils, which is not immediately available to plants but represents a potentially valuable nutrient reserve (Sharpley *et al.*, 2013). For countries with limited domestic phosphate resources, dependence on fertilizer imports creates economic and strategic challenges. India, for example, has relatively small phosphate rock reserves and therefore depends heavily on imports of rock phosphate and finished phosphorus fertilizers such as Diammonium Phosphate and Single Super Phosphate. It is estimated that India spends nearly ₹50,000 crores annually on phosphorus fertilizer imports. Fluctuations in global fertilizer prices, supply chain disruptions, and geopolitical tensions can therefore directly influence fertilizer availability, production costs, and ultimately the profitability of farmers in the country (FAI, 2023). In addition to economic concerns, inefficient phosphorus use also has environmental implications. Excess phosphorus from agricultural fields can be lost through runoff and erosion into rivers, lakes, and reservoirs, leading to eutrophication and the degradation of aquatic ecosystems. This dual challenge—finite phosphorus resources and environmental pollution—highlights the urgent need for more sustainable phosphorus management practices (Elser & Bennett, 2011). To address the global phosphorus crisis, improving phosphorus use efficiency (PUE) in agricultural systems has become a major research and policy priority. Strategies include the development of phosphorus-efficient crop varieties, use of biofertilizers such as phosphate-solubilizing microorganisms, recycling of organic wastes, precision nutrient management, and the mobilization of legacy phosphorus already accumulated in soils. Efficient utilization of existing soil phosphorus reserves can reduce dependence on imported fertilizers while sustaining crop productivity and ensuring long-term food security (Cordell *et al.*, 2009; Withers *et al.*, 2015).

Legacy Phosphorus

Legacy phosphorus refers to the residual phosphorus accumulated in agricultural soils due to repeated fertilizer and manure applications over long periods of time. When phosphorus fertilizers are applied to soil, only a portion of the applied phosphorus is immediately taken up by crops. A large fraction becomes fixed or adsorbed by soil minerals such as iron, aluminium, and calcium compounds, forming relatively stable pools that remain in the soil for years or even decades. As a result, continuous fertilizer use often leads to the gradual buildup of phosphorus in soils beyond the immediate requirements of crops. Global studies indicate that agricultural soils contain large reserves of residual phosphorus, commonly referred to as legacy phosphorus. It is estimated that more than 400 million tonnes of legacy phosphorus have accumulated in agricultural soils worldwide, mainly due to decades of fertilizer overuse and inefficient phosphorus management (Sharpley *et al.*, 2013; Sattari *et al.*, 2012). In many intensive cropping systems, the phosphorus stored within the top 50 cm of soil may exceed 1000–1500 kg P ha⁻¹, far greater than the annual phosphorus requirement of most crops.



(Gatiboni *et al.*, 2020)

Legacy phosphorus exists in different forms in soil, including adsorbed phosphorus, mineral-bound phosphorus, and organic phosphorus associated with soil organic matter. Although these forms are not immediately available to plants, they can slowly become available through processes such as mineralization, desorption, and microbial activity. Because of this, legacy phosphorus can act as a long-term nutrient reserve, potentially supporting crop growth for several years even with reduced fertilizer inputs. However, excessive accumulation of phosphorus in soils also creates serious environmental concerns. When soils become saturated with phosphorus, the risk of

phosphorus loss through surface runoff, soil erosion, and leaching increases significantly. This lost phosphorus can enter rivers, lakes, and reservoirs, contributing to eutrophication, which leads to excessive algal growth, oxygen depletion, and deterioration of water quality (Withers *et al.*, 2014). Therefore, effective management of legacy phosphorus has become an important strategy for improving phosphorus use efficiency and reducing environmental risks. Approaches such as soil testing, precision nutrient management, use of phosphorus-solubilizing microorganisms, and reduced fertilizer application rates can help utilize existing soil phosphorus reserves while minimizing further accumulation.

Calcareous Soils and Phosphorus Dynamics

Calcareous soils are soils that contain significant amounts of calcium carbonate (CaCO_3) and generally exhibit alkaline pH conditions ranging from 7.5 to 8.8. These soils are widely distributed in arid and semi-arid regions of the world, including large parts of Asia, the Middle East, North Africa, and Mediterranean regions. In India, calcareous soils are common in dryland regions where low rainfall and high evaporation result in the accumulation of carbonates in the soil profile (Lindsay, 1979; Havlin *et al.*, 2017). Phosphorus management in calcareous soils is difficult because the soil chemical environment promotes rapid phosphorus fixation. When soluble phosphorus fertilizers such as diammonium phosphate (DAP) or single superphosphate (SSP) are applied, the released phosphate ions quickly react with calcium ions present in the soil solution. This reaction leads to the formation of insoluble calcium phosphate compounds, which significantly reduces the availability of phosphorus for plant uptake (Hinsinger, 2001; Syers *et al.*, 2008). Another important characteristic of calcareous soils is their high buffering capacity due to the presence of calcium carbonate. The carbonate system neutralizes acids and maintains alkaline conditions in the soil. Because of this buffering effect, even when acidifying fertilizers or organic amendments are applied, the soil pH remains relatively high. The persistent alkaline environment favors the precipitation of calcium phosphates and limits the dissolution of phosphorus into the soil solution (Lindsay, 1979). Calcareous soils also generally contain low organic matter content, typically ranging from 0.2 to 1.0%. Low organic matter reduces microbial activity and the production of organic acids, which otherwise could help dissolve calcium-bound phosphorus. Consequently, biological processes that normally enhance phosphorus availability in soils are less effective in calcareous environments (Havlin *et al.*, 2017). The clay mineral composition of calcareous soils, often dominated by illite and smectite, further influences phosphorus dynamics. These clay minerals possess surface charges that allow them to adsorb phosphate ions, thereby reducing their mobility and availability to plant roots (Syers *et al.*, 2008).

Characteristics of Calcareous Soils Affecting Phosphorus Availability

Property	Typical Range	Implication for P
Soil pH	7.5–8.8	Promotes precipitation of Ca–P compounds
Free CaCO_3	5–30%	High buffering capacity and Ca interaction with P
Organic matter	0.2–1.0%	Low microbial activity and limited P mineralization
Clay minerals	Illite, smectite	High adsorption capacity for phosphate

Under alkaline conditions, phosphate ions react with calcium to form a sequence of calcium phosphate minerals with decreasing solubility. Initially, phosphorus may precipitate as brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), which gradually transforms into octacalcium phosphate ($\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$) and eventually into hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$], a highly stable and poorly soluble mineral (Lindsay, 1979). Because these compounds dissolve very slowly in alkaline soils, the phosphorus they contain becomes largely unavailable for plant uptake. As a result, phosphorus use efficiency in calcareous soils is typically low, often less than 20% of applied fertilizer phosphorus being utilized by crops during the first growing season, while the remaining phosphorus accumulates in the soil as fixed or residual phosphorus (Syers *et al.*, 2008; Hinsinger, 2001).

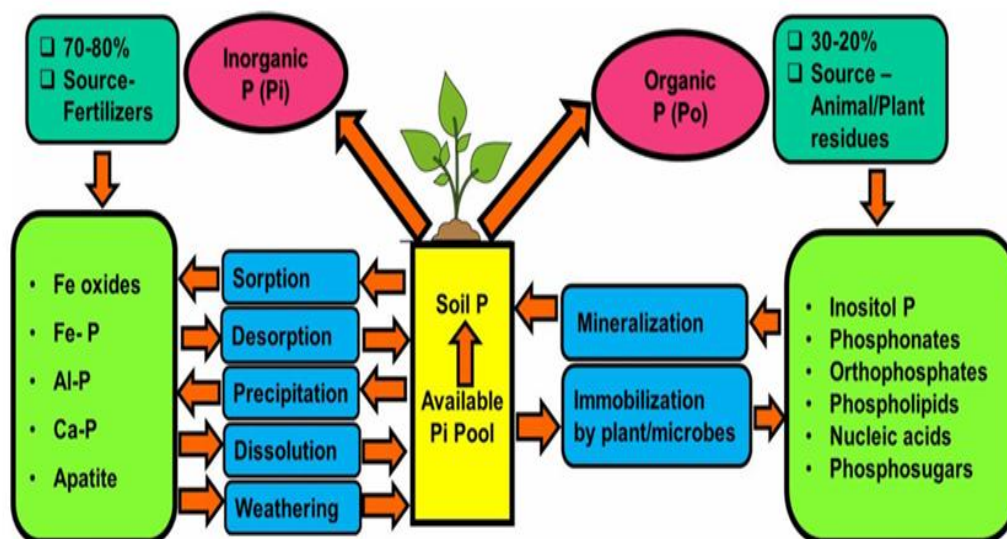
Forms and Pools of Soil Phosphorus

Phosphorus in soil exists in several chemical fractions that differ in their solubility and availability to plants. These fractions form a dynamic equilibrium where phosphorus continuously moves between different pools through processes such as adsorption, desorption, precipitation, dissolution, mineralization, and immobilization. Even though soils may contain relatively large amounts of total phosphorus, only a very small fraction is present in the soil solution and is immediately available for plant uptake (Syers *et al.*, 2008; Havlin *et al.*, 2014).

P Fraction	Percentage of Total Soil P	Availability
Solution P	<0.1%	Immediately available
Labile P	1–3%	Rapidly available
Ca-bound P	60–80%	Poorly available
Fe/Al-bound P	5–15%	Low availability
Organic P	10–20%	Requires mineralization
Occluded P	5–10%	Practically unavailable

Solution phosphorus consists mainly of orthophosphate ions (H_2PO_4^- and HPO_4^{2-}) dissolved in the soil solution, which are the forms directly absorbed by plant roots. However, this fraction usually represents less than 0.1% of the total soil phosphorus and must be continuously replenished from other phosphorus pools (Brady and Weil, 2017). Labile phosphorus includes weakly adsorbed phosphorus associated with soil particles such as clay

minerals, calcium carbonate, and metal oxides. This fraction serves as a readily exchangeable reservoir that helps maintain phosphorus concentration in the soil solution as plants absorb phosphorus (Havlin *et al.*, 2014). Calcium-bound phosphorus (Ca-P) is the dominant form in calcareous and alkaline soils. In these soils, phosphate ions react with calcium to form relatively insoluble compounds such as dicalcium phosphate, octacalcium phosphate, and hydroxyapatite, which reduces phosphorus solubility and plant availability (Syers *et al.*, 2008). Iron- and aluminium-bound phosphorus (Fe-P and Al-P) are more common in acidic soils, where phosphate ions become strongly adsorbed onto iron and aluminium oxides and hydroxides. These forms are less soluble and therefore contribute limited phosphorus to plant uptake (Brady and Weil, 2017).



(Penn & Camberato, 2019)

Organic phosphorus originates from plant residues, microbial biomass, and soil organic matter. This fraction becomes available only after microbial decomposition and mineralization convert organic phosphorus compounds into inorganic phosphate forms (Havlin *et al.*, 2014). Occluded phosphorus refers to phosphorus that becomes trapped within mineral structures or coated by iron and aluminium oxides. This form is highly stable and generally unavailable for plant uptake over short time periods (Syers *et al.*, 2008). In calcareous soils, calcium-bound phosphorus constitutes the largest proportion of the total phosphorus pool because high soil pH and the presence of calcium carbonate promote precipitation of phosphate as stable Ca-P minerals, thereby limiting phosphorus availability to crops (Havlin *et al.*, 2014).

Constraints to Phosphorus Availability

Phosphorus availability in soil is often limited due to several chemical, biological, and physical factors. These constraints reduce the efficiency of applied phosphorus fertilizers and limit the amount of phosphorus that plants can absorb for growth and development.

Chemical Constraints

Chemical reactions in soil strongly influence phosphorus availability. In alkaline and calcareous soils, high soil pH favours the precipitation of phosphorus with calcium to form insoluble calcium phosphate minerals such as dicalcium phosphate, octacalcium phosphate, and hydroxyapatite. These compounds are poorly soluble and therefore not readily available for plant uptake. As a result, a large portion of applied phosphorus fertilizers becomes fixed in the soil and unavailable to crops within a short period after application. In acidic soils, phosphorus can react with iron and aluminum oxides to form Fe-P and Al-P compounds that are also poorly available to plants. Because of these fixation reactions, only a small fraction of applied phosphorus fertilizer (often less than 20–30%) is taken up by crops during the first growing season (Havlin *et al.*, 2014; Brady & Weil, 2016).

Biological Constraints

Soil microorganisms play a dual role in phosphorus availability. Microbial biomass can temporarily immobilize phosphorus by incorporating it into microbial cells during the decomposition of organic matter. This immobilized phosphorus becomes unavailable to plants until microbial cells die and release it back into the soil. In addition, a significant portion of soil phosphorus exists in organic forms such as phytates, nucleic acids, and phospholipids. These organic compounds cannot be directly absorbed by plants and must undergo enzymatic mineralization through microbial activity and phosphatase enzymes before being converted into inorganic orthophosphate forms that plants can utilize. Therefore, the rate of microbial activity and enzyme production strongly influences phosphorus availability in soil (Richardson *et al.*, 2009; Shen *et al.*, 2011).

Physical Constraints

The physical movement of phosphorus in soil is extremely limited compared with other nutrients, such as nitrogen. Phosphorus reaches plant roots mainly through diffusion rather than mass flow. Diffusion is a slow process that depends on the concentration gradient of phosphorus in soil solution and is strongly affected by soil moisture, soil texture, and root density. When soil moisture is low or when phosphorus becomes strongly adsorbed onto soil particles, the diffusion rate decreases significantly. Consequently, the supply of phosphorus to plant roots becomes

restricted, particularly in dry soils or soils with high phosphorus fixation capacity. This limitation often results in phosphorus deficiency even when the total phosphorus content in soil is relatively high (Barber, 1995; Havlin *et al.*, 2014).

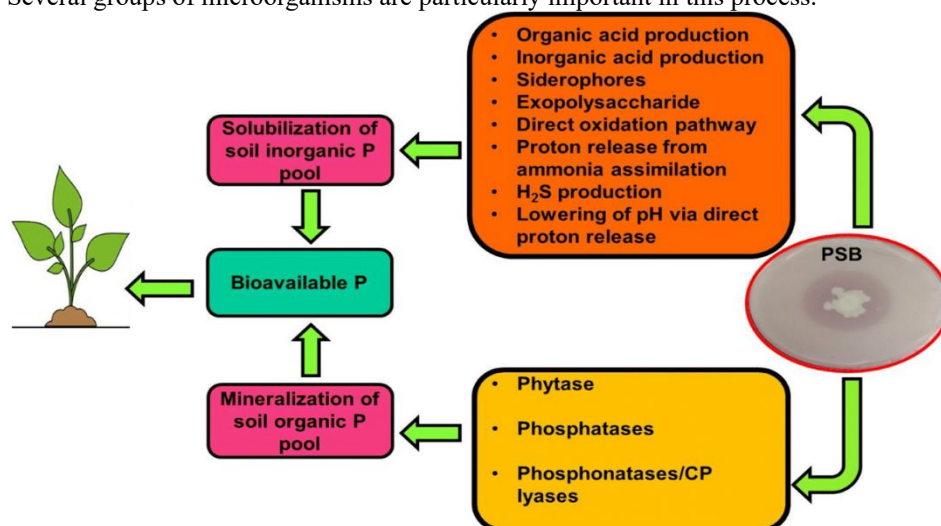
Mobilization Mechanisms of Legacy Phosphorus

Biochemical Mobilization of Legacy Phosphorus

Biochemical mobilization is an important mechanism through which plants and soil microorganisms access legacy phosphorus that has accumulated in soils over long periods of fertilizer and manure application. Much of this legacy phosphorus exists in relatively insoluble mineral forms such as calcium phosphates, iron phosphates, and aluminium phosphates, particularly in calcareous and highly weathered soils. Since these forms are not readily available for plant uptake, plants and microbes employ biochemical strategies to solubilize and mobilize this phosphorus pool (Hinsinger, 2001). One of the primary mechanisms involved in biochemical mobilization is the release of low-molecular-weight organic acids (LMWOAs) from plant roots and soil microorganisms. These organic acids are also called carboxylates because they contain carboxyl functional groups capable of interacting with soil minerals. Root exudation of organic acids is a well-documented adaptive response to phosphorus deficiency and is especially pronounced in crops such as lupin, chickpea, and sorghum under low-phosphorus conditions (Richardson *et al.*, 2011). Common organic acids involved in phosphorus mobilization include citrate, malate, oxalate, malonate. These compounds mobilize phosphorus through several biochemical processes. The most important mechanisms include ligand exchange, chelation, and mineral dissolution. In ligand exchange reactions, organic acid anions replace phosphate ions that are bound to soil minerals such as iron and aluminium oxides. This process releases phosphate into the soil solution, making it available for plant uptake (Jones, 1998). In calcareous soils, where phosphorus is predominantly associated with calcium phosphate minerals, organic acids play an additional role through calcium chelation. Organic acids such as citrate and oxalate can form stable complexes with calcium ions (Ca^{2+}). By binding calcium, these acids reduce the stability of calcium phosphate minerals and promote their dissolution, thereby releasing phosphate ions into the soil solution (Hinsinger *et al.*, 2003). Another important effect of organic acid exudation is the local reduction of rhizosphere pH. The release of protons along with organic acids acidifies the immediate soil environment around roots, which further enhances the dissolution of phosphate-containing minerals. This localized acidification can significantly increase phosphorus availability in otherwise phosphorus-fixing soils (Richardson *et al.*, 2009). In addition to plant roots, phosphate-solubilizing microorganisms (PSMs) such as species of *Pseudomonas*, *Bacillus*, and *Aspergillus* also produce organic acids that contribute to the mobilization of legacy phosphorus. These microorganisms enhance phosphorus availability by secreting gluconic acid and other organic acids that dissolve mineral phosphates and convert them into plant-available forms (Sharma *et al.*, 2013). Overall, biochemical mobilization through organic acid exudation represents a key natural process that enables plants and microorganisms to access the large reserves of legacy phosphorus present in soils. Understanding and enhancing this mechanism is increasingly recognized as an important strategy for improving phosphorus-use efficiency and reducing dependence on mineral phosphorus fertilizers in sustainable agricultural systems.

Biological Mobilization of Legacy Phosphorus

Biological mobilization of legacy phosphorus refers to the transformation of accumulated and poorly available phosphorus in soil into plant-available forms through the activity of soil microorganisms and their enzymes. In many agricultural soils, a substantial portion of phosphorus exists either as insoluble inorganic phosphates or as complex organic phosphorus compounds that plants cannot directly absorb. Soil microorganisms play a crucial role in converting these forms into soluble orthophosphate ions (H_2PO_4^- and HPO_4^{2-}), which can be taken up by plant roots. Several groups of microorganisms are particularly important in this process.



(Alori *et al.*, 2017)

Phosphate-solubilizing bacteria (PSB) such as *Bacillus*, *Pseudomonas*, and *Rhizobium* species can solubilize insoluble phosphate minerals by producing organic acids and releasing protons that lower the pH in the

rhizosphere. These reactions dissolve calcium, iron, and aluminium phosphates and release phosphate ions into the soil solution. Similarly, phosphate-solubilizing fungi (PSF), including *Aspergillus* and *Penicillium* species, are highly effective at secreting organic acids such as citric, oxalic, and gluconic acids that enhance phosphorus solubilization (Richardson *et al.*, 2009). Another important biological mechanism involves arbuscular mycorrhizal fungi (AMF). These fungi form symbiotic associations with plant roots and extend their hyphae into the surrounding soil, thereby increasing the effective root surface area. AMF hyphae can access phosphorus from soil micropores that are otherwise inaccessible to plant roots and transport it back to the plant. In addition, AMF can release enzymes and organic compounds that mobilize phosphorus from both inorganic and organic pools (Smith & Read, 2008). Actinomycetes, which are filamentous soil bacteria, also contribute to phosphorus mobilization by decomposing organic residues and releasing phosphorus during mineralization. Many actinomycetes produce extracellular enzymes that break down complex organic phosphorus compounds present in plant residues and soil organic matter. Microorganisms also produce several key enzymes involved in phosphorus cycling. Phosphatases catalyze the hydrolysis of organic phosphate esters, releasing inorganic phosphate, while phytases specifically degrade phytate, a common form of organic phosphorus found in plant residues and soils. These enzymatic reactions are essential for converting organic phosphorus into forms available for plant uptake (Hinsinger *et al.*, 2011). Overall, biological mobilization is an important mechanism for utilizing legacy phosphorus in soils. Enhancing microbial activity through practices such as organic amendments, reduced soil disturbance, and microbial inoculants can improve phosphorus availability and reduce dependence on mineral phosphorus fertilizers.

Physicochemical Mobilization

Physicochemical processes also contribute significantly to the mobilization and redistribution of legacy phosphorus in soils. These processes involve changes in soil chemical conditions and physical transport mechanisms that influence the stability and movement of phosphorus compounds. Among the important mechanisms are redox reactions and colloid-facilitated transport, both of which can release phosphorus from previously stable soil pools.

Redox Reactions

Redox reactions play an important role in regulating phosphorus availability, particularly in soils that experience periodic waterlogging or flooding. Under aerobic conditions, phosphorus is often strongly adsorbed onto iron (Fe^{3+}) and manganese (Mn^{4+}) oxides and hydroxides present in the soil. However, when soils become anaerobic, such as during flooding or prolonged saturation, microbial respiration consumes oxygen and causes the reduction of iron and manganese oxides. During this reduction process, ferric iron (Fe^{3+}) is converted to ferrous iron (Fe^{2+}), which leads to the dissolution of iron oxide minerals. As these minerals dissolve, the phosphorus that was previously bound to their surfaces is released into the soil solution, increasing phosphorus availability. This mechanism is commonly observed in paddy soils and wetland ecosystems, where fluctuating redox conditions frequently control phosphorus dynamics (Reddy and DeLaune, 2008; Hinsinger, 2001).

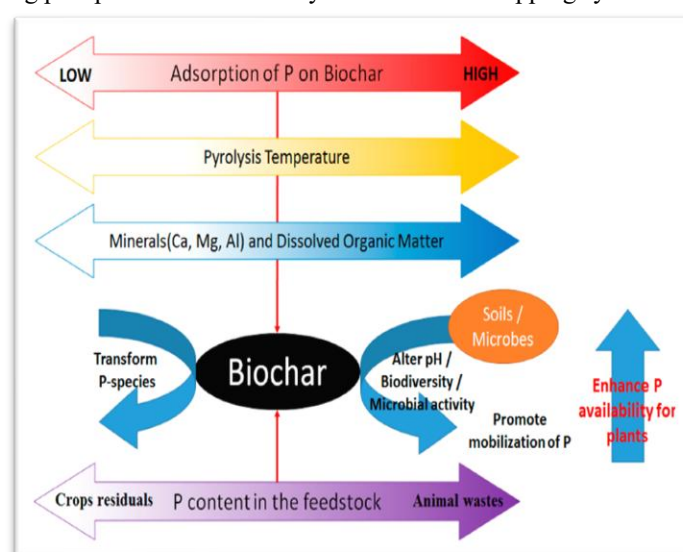
Colloid Transport

Another important physicochemical mechanism is the transport of phosphorus attached to soil colloids. Soil colloids are extremely small particles of clay minerals, organic matter, and metal oxides that possess a high surface area and strong adsorption capacity. Phosphorus can bind to these colloidal particles through adsorption or precipitation reactions. During rainfall, irrigation, or subsurface water flow, these colloids may become suspended and move through soil pores. As a result, colloid-facilitated transport can move phosphorus within the soil profile and sometimes even into drainage water or groundwater systems. This mechanism plays a key role in the redistribution of legacy phosphorus, particularly in soils with high clay content or in landscapes experiencing erosion and preferential flow pathways (Sharpley *et al.*, 2013; Sposito, 2008). Overall, physicochemical mobilization processes influence both the availability and mobility of legacy phosphorus, affecting nutrient cycling, crop nutrition, and the risk of phosphorus loss to surrounding water bodies.

8. Role of Organic Amendments

Organic amendments such as farmyard manure (FYM), compost, green manure, humic substances, and biochar play an important role in improving phosphorus availability in soils, particularly in soils where phosphorus is strongly fixed by calcium, iron, or aluminium compounds. Application of organic materials enhances soil microbial activity, which stimulates the growth of phosphate-solubilizing microorganisms. These microorganisms release organic acids (such as citric, oxalic, and malic acids) and protons that help dissolve insoluble phosphate minerals and convert them into plant-available forms. In addition, microbial decomposition of organic matter releases enzymes such as phosphatases, which mineralize organic phosphorus compounds into inorganic phosphate that plants can absorb (Richardson *et al.*, 2009). Organic amendments also reduce phosphorus fixation by competing with phosphate ions for adsorption sites on soil minerals. Organic molecules can coat the surface of iron and aluminium oxides, thereby blocking fixation sites and preventing newly applied phosphorus from becoming unavailable. Furthermore, the gradual decomposition of organic matter releases carbon dioxide and organic acids, which slightly lower soil pH and promote the dissolution of calcium phosphate minerals in calcareous soils (Hinsinger, 2001). Another important effect is the improvement of soil physical properties, including soil structure, aggregation, and water-holding capacity. These improvements enhance root growth and increase the volume of soil explored by roots, thereby improving phosphorus uptake by crops. Therefore,

integrating organic amendments with mineral fertilizers is considered an effective strategy for mobilizing legacy phosphorus and improving phosphorus use efficiency in sustainable cropping systems.



(Awad *et al.*, 2024)

Management Strategies

Efficient management of legacy phosphorus (P) aims to increase the availability of previously accumulated soil P while reducing the need for additional fertilizer inputs. Several agronomic and biological strategies can enhance the mobilization and utilization of this residual phosphorus.

Crop Rotation with Phosphorus-Mobilizing Crops
Crop rotation involving species with strong phosphorus-mobilising capacity can improve the utilization of legacy P. Crops such as legumes, lupin, and certain cover crops release organic acids and protons from their roots, which help solubilize calcium, iron, and aluminium-bound phosphates. Deep-rooted crops can also access phosphorus from deeper soil layers and recycle it to the surface through plant residues (Richardson *et al.*, 2009).

Intercropping Systems
Intercropping systems enhance phosphorus mobilization through complementary root interactions between different crop species. Some plants release organic acids or phosphatase enzymes that mobilize soil phosphorus, which can then be utilized by neighboring plants. Legume–cereal intercropping systems are particularly effective in improving phosphorus acquisition and overall nutrient use efficiency in low-P soils (Li *et al.*, 2014).

Application of Organic Amendments
Organic amendments such as farmyard manure, compost, green manure, and biochar can increase the availability of legacy phosphorus. These materials improve soil microbial activity and produce organic acids during decomposition, which help dissolve insoluble phosphorus compounds. In addition, organic matter can reduce phosphorus fixation by forming complexes with calcium, iron, and aluminum in soil (Syers *et al.*, 2008).

Use of Microbial Inoculants
The application of beneficial microorganisms such as phosphate-solubilizing bacteria (PSB), phosphate-solubilizing fungi (PSF), and arbuscular mycorrhizal fungi (AMF) can significantly enhance the mobilization of legacy phosphorus. These microorganisms release organic acids, protons, and phosphatase enzymes that convert insoluble phosphorus into plant-available forms. Mycorrhizal fungi also extend the root absorption zone through their hyphal networks, improving phosphorus uptake efficiency (Shen *et al.*, 2011).

Improved Fertilizer Placement Techniques
Efficient fertilizer placement methods such as band placement, localized placement, and deep placement, can improve phosphorus availability by reducing contact between fertilizer and soil particles that cause fixation. These techniques create localized zones with higher phosphorus concentration near the root system, which enhances phosphorus uptake efficiency and allows crops to utilize both applied and legacy phosphorus more effectively (Hinsinger *et al.*, 2011).

Overall, integrating these management strategies can improve phosphorus use efficiency, enhance crop productivity, and promote the sustainable utilization of accumulated soil phosphorus reserves.

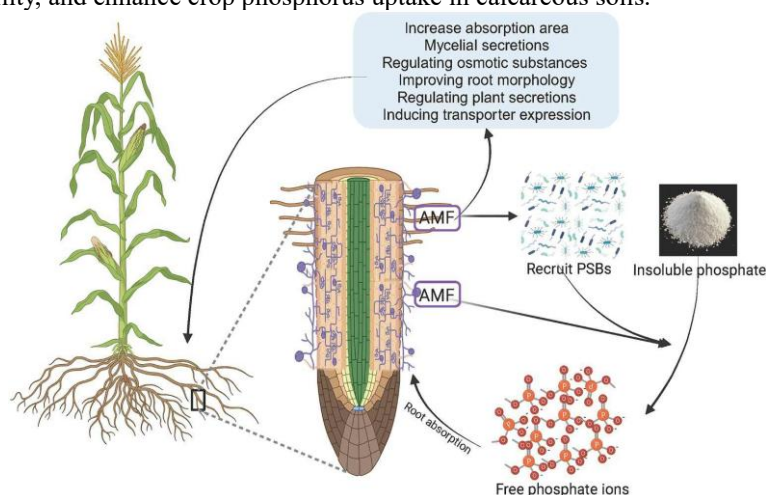
Environmental Implications

Mobilization of legacy phosphorus can significantly improve phosphorus availability for crops and reduce the need for additional fertilizer inputs. However, if the release of this stored phosphorus exceeds plant uptake capacity, it can contribute to environmental problems. One of the major concerns is eutrophication, a process in which excessive phosphorus enters surface water bodies such as lakes, rivers, and reservoirs. Elevated phosphorus concentrations stimulate the rapid growth of algae and aquatic plants, leading to algal blooms that reduce water quality and disrupt aquatic ecosystems. During eutrophication, dense algal blooms limit light penetration into the

water, affecting submerged vegetation and altering the ecological balance. When these algae die and decompose, microbial respiration consumes dissolved oxygen in the water, creating hypoxic or anoxic conditions that can lead to fish kills and biodiversity loss. In agricultural landscapes, legacy phosphorus accumulated in soils can be transported to water bodies through surface runoff, erosion, and subsurface drainage, particularly during heavy rainfall events or improper soil management practices (Sharpley *et al.*, 2013). In addition, long-term accumulation of phosphorus in soil increases the risk of phosphorus saturation, where soils can no longer retain additional phosphorus effectively. Under such conditions, even small disturbances in soil chemistry or hydrology can trigger the release of phosphorus into surrounding water systems. Therefore, strategies aimed at mobilizing legacy phosphorus must be carefully managed to ensure that mobilized phosphorus is efficiently utilized by crops rather than lost to the environment (Withers *et al.*, 2014). To minimize environmental risks, integrated nutrient management practices such as balanced fertilizer application, soil testing, erosion control, and buffer strips near water bodies should be adopted. These measures help maintain a balance between improving phosphorus use efficiency in crops and protecting surrounding ecosystems from nutrient pollution.

Case Studies

Several experimental studies have demonstrated the effectiveness of phosphorus activators and organic amendments in mobilizing legacy phosphorus and improving plant uptake in calcareous soils. A field experiment conducted on maize hybrid COH(M) 6 in calcareous soil evaluated different combinations of phosphorus activators such as farmyard manure (FYM), humic acid, phosphate-solubilizing bacteria (PSB), and phytase along with recommended soil-test phosphorus levels. The treatments included FYM + humic acid (PA1), PSB + phytase (PA2), and phytase + humic acid (PA3) combined with 100%, 75%, and 50% of the recommended phosphorus fertilizer dose. The results indicated that the combined application of FYM and humic acid produced the highest plant phosphorus concentration and uptake. Grain phosphorus concentration increased from 0.171% in the control to 0.272% under FYM + humic acid treatment with 100% recommended phosphorus. Similarly, phosphorus uptake increased from 3.62 kg ha⁻¹ to 9.98 kg ha⁻¹ in grain and from 5.06 kg ha⁻¹ to 12.67 kg ha⁻¹ in stover, demonstrating significant improvement in phosphorus utilization. The study also revealed that reducing phosphorus fertilizer application by 25% still maintained high phosphorus uptake, indicating that phosphorus activators enhanced the mobilization of native and fixed calcium-bound phosphorus in calcareous soils (Aswitha *et al.*, 2022). Long-term fertilization experiments have also highlighted the importance of organic amendments in improving soil phosphorus dynamics. Continuous application of organic manure significantly increased Olsen-P levels in the surface soil (0–20 cm) from approximately 55 mg kg⁻¹ to 86 mg kg⁻¹ over five years, whereas chemical fertilizer alone produced comparatively smaller increases. Organic manure application also increased total soil phosphorus and enhanced the concentration of different inorganic phosphorus fractions, demonstrating its role in gradually mobilizing legacy phosphorus pools and improving nutrient availability to crops (Song *et al.*, 2017). Another study examining the long-term application of dairy manure reported that organic inputs can promote the accumulation and mobility of legacy phosphorus in calcareous soils. The results indicated that manure amendments not only increase phosphorus availability but also influence phosphorus transformation processes and microbial activity, thereby enhancing phosphorus cycling within the soil system (Hu *et al.*, 2024). Research on arbuscular mycorrhizal fungi (AMF) has further demonstrated their role in improving biological activity and biochemical properties of calcareous soils. Different AMF inoculation treatments such as *Glomus intraradices*, *G. constrictum*, and *Gigaspora* species increased soil biological activity and enhanced phosphorus acquisition by plants through extended hyphal networks that explore soil volumes beyond the root zone (Burak *et al.*, 2024). Overall, these case studies highlight that integrated approaches combining organic amendments, microbial inoculants, and optimized fertilizer management can effectively mobilize legacy phosphorus, increase soil phosphorus availability, and enhance crop phosphorus uptake in calcareous soils.



Future Research Directions

Future research should focus on:

- ✓ Development of efficient microbial consortia

- ✓ Identification of phosphorus-mobilizing crop varieties
- ✓ Integration of biological and chemical approaches
- ✓ Long-term monitoring of phosphorus dynamics in soils

CONCLUSION

Legacy phosphorus represents a large but underutilized reserve of nutrients accumulated in agricultural soils as a result of many years of continuous fertilizer application and low phosphorus use efficiency by crops. In most agricultural systems, only a small portion of the applied phosphorus fertilizer is immediately absorbed by plants, while the remaining portion becomes fixed in the soil through chemical reactions with calcium, iron, and aluminium compounds. These reactions convert soluble phosphorus into relatively stable mineral forms that are not easily available for plant uptake. Over time, this leads to the buildup of legacy phosphorus in soils, creating a substantial nutrient pool that can potentially support crop production if it is properly mobilized. Mobilizing this stored phosphorus is an important strategy for improving phosphorus use efficiency in modern agriculture. Several mechanisms contribute to the release of legacy phosphorus, including biochemical, biological, and physicochemical processes. Plant roots and soil microorganisms release organic acids and other compounds that help dissolve mineral-bound phosphorus and convert it into forms that plants can absorb. Soil microorganisms also play a critical role by producing enzymes and other substances that break down organic phosphorus compounds. In addition, certain soil conditions such as changes in pH, redox reactions, and the movement of soil colloids can help release phosphorus from mineral surfaces and redistribute it within the soil profile. Effective management practices are essential to enhance the mobilization and utilization of legacy phosphorus. Integrated nutrient management approaches that combine organic amendments, microbial inoculants, balanced fertilizer application, and improved cropping systems can significantly increase the availability of phosphorus to plants. Practices such as crop rotation, intercropping, and the use of crops with strong phosphorus-mobilizing abilities can further enhance nutrient cycling and improve soil fertility. Organic materials such as farmyard manure, compost, and biochar also contribute to improved phosphorus availability by stimulating microbial activity and reducing phosphorus fixation in the soil. Utilizing legacy phosphorus efficiently offers several important benefits. It can reduce the dependence on chemical phosphorus fertilizers, lower production costs for farmers, and conserve limited global phosphate resources. At the same time, better management of soil phosphorus can help reduce environmental problems associated with excessive fertilizer use, particularly the contamination of water bodies through phosphorus runoff and leaching. In the long term, sustainable phosphorus management requires a balanced approach that focuses not only on the application of fertilizers but also on the efficient use of existing soil phosphorus reserves. By combining biological processes, improved soil management practices, and appropriate cropping strategies, it is possible to transform legacy phosphorus into a valuable nutrient source for crops. This approach will play a crucial role in improving agricultural sustainability, enhancing nutrient use efficiency, and ensuring stable crop production for future food security.

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