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The Effect of Clay Minerals on Phosphorus Fixation and Release Reactions /Review

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Annotation: Phosphorus is considered one of the most essential macronutrients required for plant growth; however, its availability in soil is often limited and insufficient to meet plant demands due to fixation and precipitation reactions. These processes are significantly influenced by the soil's pH level. In acidic soils, the dominance of iron and aluminum oxides both in crystalline and amorphous forms contributes to the reduced solubility of inorganic phosphorus. This occurs as phosphorus becomes fixed on positively charged surfaces or forms low-solubility compounds with iron and aluminum. Moreover, interactions with kaolinite minerals further limit phosphorus mobility in such soils. Conversely, in alkaline soils, phosphorus tends to react with calcium ions, resulting in the formation of slightly soluble calcium phosphates. These chemical interactions reduce the efficiency of phosphorus fertilization and its subsequent availability to plants. Accordingly, this article aims to investigate the influence of various clay mineral types on the mechanisms of phosphorus fixation and its subsequent release in soils.

Keywords: Phosphorus, fixation, release.

Introduction

Phosphorus is one of the primary essential nutrients required for plant development, playing a vital role in numerous physiological and biochemical processes such as cell division, metabolic regulation, nucleic acid (DNA and RNA) synthesis, nutrient transport, redox reactions, and respiration [1]. Although phosphorus is abundantly present in the Earth's rocky crust, the bioavailable form inorganic phosphate (Pi) exists in limited concentrations in soil, primarily due to its low solubility and restricted mobility, resulting in phosphorus deficiency in plants [2].

As reported by [3], the primary sources of phosphorus in soil systems are mineral weathering and organic matter decomposition. Plants predominantly absorb phosphorus in the form of dihydrogen phosphate ($H_2PO_4^-$) and hydrogen phosphate (HPO_4^{2-}) ions. However, a significant portion of soil phosphorus becomes adsorbed onto clay minerals or is fixed by free oxides and hydroxides of iron and aluminum, forming insoluble complexes, especially in acidic soils. In alkaline conditions, phosphorus tends to react with calcium compounds, particularly calcium carbonate, forming sparingly soluble calcium phosphates, further limiting its availability to plants [4].

These fixation mechanisms reduce the effectiveness of phosphorus in supporting plant growth, thereby diminishing crop productivity. In response, agricultural practices have often relied on the excessive application of chemical phosphorus fertilizers to mitigate the resulting deficiency [5, 6]. Nevertheless, only 15–25% of the applied phosphorus fertilizers are absorbed by plants, while the remainder is subject to leaching or fixation, leading to soil degradation and environmental contamination [7].

Due to the critical role of phosphorus and its complex behavior in soil, recent years have seen a growing body of research focused on understanding its dynamics, mobility, and interaction with soil components. This trend is illustrated in Figure 1, which reflects the increasing scientific interest in phosphorus-related studies.

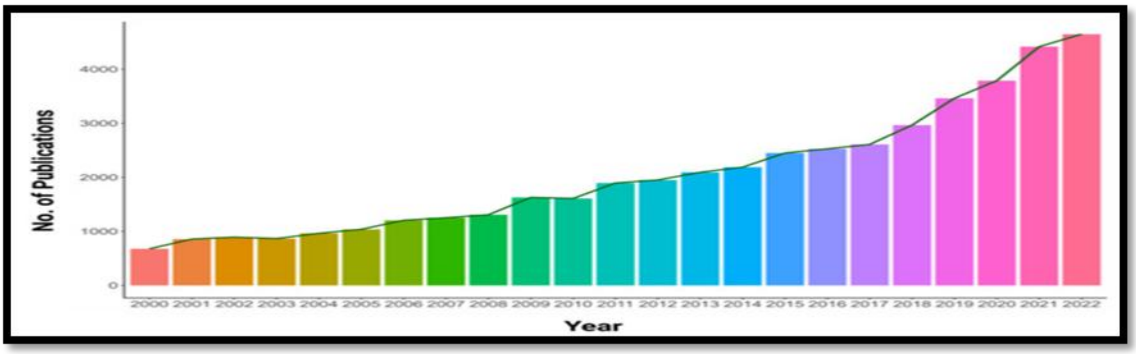


Figure 1 shows the number of studies conducted on the element phosphorus from 2000-2022 [8]

Factors affecting phosphorus availability

Several studies have indicated that the key factors influencing phosphorus availability, adsorption, and deposition include soil pH, texture, ionic strength, mineral composition, ion types, organic matter content, and salinity [9, 10]. However, the present article specifically focuses on the influence of different types of clay minerals on the processes of phosphorus fixation and subsequent release in soils.

The effect of clay minerals on phosphorus fixation and release processes

Phosphorus fixation is strongly influenced by soil clay content, exhibiting a positive correlation with increasing clay percentage due to the larger specific surface area associated with finer particles. As soil texture becomes finer, the capacity for phosphorus fixation increases, and consequently, fine-textured soils tend to contain higher levels of total phosphorus compared to coarse-textured counterparts. When the concentration of phosphorus in the soil solution declines, adsorption processes are favored; in contrast, precipitation reactions dominate when phosphorus levels exceed the solubility product (Ksp) of the relevant mineral phase [11, 12]. In calcareous soils, phosphorus fixation involves both adsorption and precipitation mechanisms. At low phosphorus concentrations, phosphate ions may replace carbonate (CO_3^{2-}) on the surfaces of calcium carbonate ($CaCO_3$), leading to surface adsorption. However, when phosphorus levels rise, insoluble calcium-phosphate minerals begin to precipitate on $CaCO_3$ surfaces, further reducing phosphorus availability [11, 12].

According to [13], the presence of clay minerals significantly enhances the soil's capacity to fix phosphorus, particularly 1:1 clay mineral such as kaolinite, which exhibit a greater ability to retain phosphate ions compared to 2:1 clay mineral like montmorillonite. This difference is primarily attributed to the structural characteristics and surface charge properties of these mineral types.

Kaolinite group of minerals (1:1)

Phyllosilicate clay minerals are divided into two groups, 1:1 and 1:2, depending on the number of tetrahedral and octahedral layers, In 1:1 minerals it consists of one layer of tetrahedra followed by one layer of octahedra, The tetrahedral layer is linked to the octahedral layer by oxygen atoms (tops of tetrahedral units), including the kaolinite group of minerals [14],[15], as shown in Figure 2.

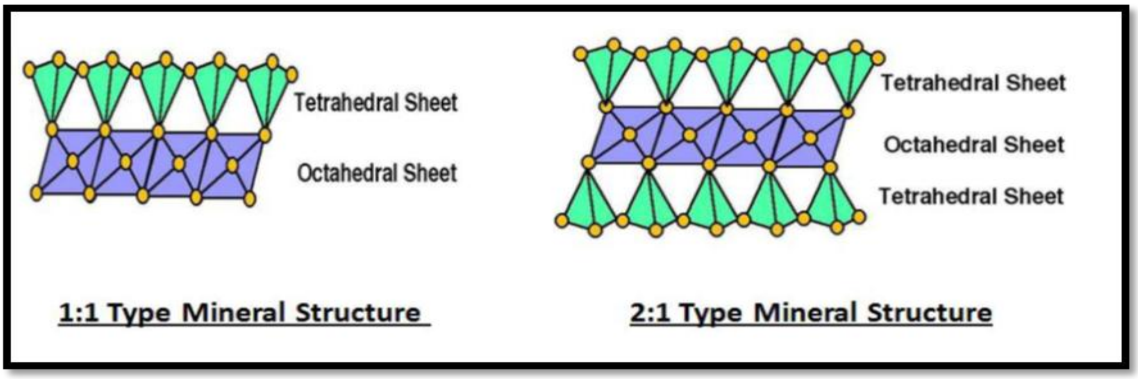


Figure 2 shows the structural composition of silicate clay minerals 1:1, 1:2

Kaolinite has a low surface area and a low Cation and anion exchange capacity of 5-15 Cmol kg^{-1},This is due to the non-occurrence of the isomorphic replacement process within the crystal layers of the kaolinite mineral, Kaolinite is one of the most common minerals in soil, especially in humid and warm climates, and it is a product of acid weathering [16],[15]. [17] showed that the phosphorus fixation process increases with the increase of clay minerals especially a 1:1 mineral such as kaolinite, which has a greater ability to stabilize than a 2:1 mineral such as Montmorillonite, due to it containing iron and aluminum oxide groups associated with kaolinite, It contains exposed hydroxyl groups in the octahedra layer, The type of charges for the kaolinite mineral depends on the degree of soil reaction, which is found on the edges of the mineral and absorbs phosphorus. A study conducted by [18] showed that clay containing kaolinite or Halloysite fixes 75% of the added phosphorus, while Montmorillonite fixes about 45%.

Smectite group of minerals (2:1)

The structural composition of the 2:1 group of minerals consists of two layers of tetrahedra (the silica layer) and between them a layer of octahedra (the aluminum layer), The silica layer is connected to the aluminum layer by the apical oxygen atoms, which share the hydroxyl groups of the aluminum layer to form a common layer, Figure 2, The 2:1 mineral group is characterized by its large surface area, which leads to the creation of negative surfaces that absorb nutrients, These minerals are also characterized by a high exchange capacity of 110Cmol kg^{-1} [16]. Many studies have shown that fine-textured soils contain higher total phosphorus than coarse-textured soils, The higher the clay content, the greater the surface area and thus the greater the surface area exposed to the bonding between the phosphorus in the soil solution and the clay minerals, which causes the phosphate to be fixed and retained in the soil, That is, the higher the clay content of the soil, the greater the adsorption and fixation of phosphorus compared to sandy soils [19].

Phosphorus dynamics in soil

Phosphorus dynamics in soil depend on several factors, including the degree of soil reaction, high concentrations of toxic elements, and salinity, Total phosphorus concentration, leaching, surface runoff, organic matter, mineral composition, and others [20] . The main source of phosphorus is the weathering of primary minerals such as apatite, the weathering of sedimentary, igneous and metamorphic rocks, plant remains, fertilizers and agricultural waste, Apatite's, Strangite, and variscite are stable primary phosphorus minerals, as phosphorus is released into the soil after weathering, and this process takes place in acidic soils, As for secondary phosphorus minerals such as calcium, iron and aluminum phosphates, their solubility varies depending on the size of the mineral particles and the degree of soil reaction, As the acidity of the soil increases and the degree of soil reaction decreases, the solubility of iron and aluminum phosphates increases, The solubility of calcium phosphate decreases as the soil reaction temperature increases above 8 [21] .

Mechanisms of phosphorus fixation and adsorption in soil

Precipitation and adsorption reactions contribute to the retention and fixation of phosphorus in the soil. When the phosphate concentration is low, the predominant process is the adsorption of phosphate ions onto the surfaces of more crystalline clay minerals or carbonates, In the case of high phosphate concentration, the dissolved phosphorus precipitates in the form of aluminum and iron phosphate in acidic soil, in basic soils, it precipitates in the form of calcium and magnesium phosphates [22]. The term phosphorus fixation refers to the process of fixing inorganic phosphorus by means of iron, aluminum, and calcium oxides and forming phosphorus-containing compounds with low solubility, this process occurs when fertilizers are added to the soil. This process includes a series of reactions that remove phosphorus from the soil solution so that it is not available to the plant, which leads to a decrease in its efficiency to only 15-20%, permanently or temporarily, depending on the time and stage of the chemical fixation reactions [23] . Phosphorus fixation increases in acidic soils, due to the dominance of goethite and gypsite minerals in these soils. Kaolinite 1:1 has a lower capacity to absorb phosphorus due to its small surface area [24],[25],[26]. Another factor responsible for the low phosphorus adsorption capacity of kaolinite compared to iron and aluminum oxides is the PZC (point zero charge) which ranges for kaolinite (2-3.1) [27]. The limiting factor for phosphorus availability in alkaline soils is due to the solubility of calcium phosphate compounds in the soil, as dissolved H_2PO_4 reacts directly with calcium , for example, adding mono-calcium phosphate $(CaH_2PO_4)_4$ as a fertilizer reacts with calcium carbonate to form di-calcium phosphate, which reacts again to form tri-calcium phosphate, which has decreasing solubility.

$CaH_2PO_2 + CaCO_3 \leftrightarrow Ca_2(H_2PO4)_2 + CO_2 + H_2O$

Monocalcium-P Ca-carbonate Dicalcium

Phosphate (Less soluble)

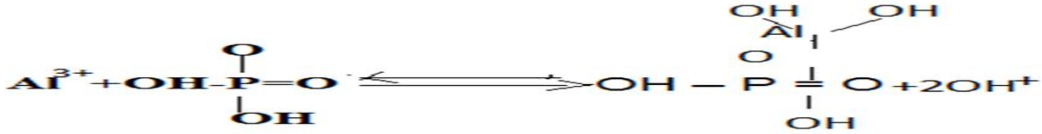
$Ca_2(H_2PO_4)_2 + CaCO_3 \leftrightarrow Ca_3(PO_4)_2 + CO_2 + H_2O$

Tri-calcium phosphate (Least soluble)

[23], [28] showed that most of the phosphorus fixation occurs in acidic soils, as H_2PO_4 reacts with the surfaces of iron, aluminum, and manganese oxides, which are insoluble. This process involves a series of chemical fixation reactions, as shown by the chemical equations

a-Precipitation reaction

In this reaction, the hydroxyl phosphate formed is slightly soluble, due to the presence of a large surface area exposed to the soil solution. Therefore, the phosphorus is available to the plant, but with the passage of time it becomes less soluble and not available to the plant.



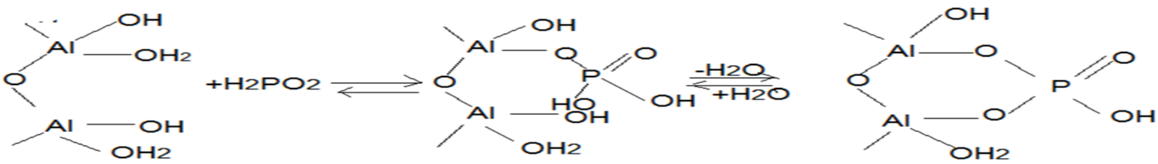
Precipitated hydroxyl phosphate (Insoluble) Dissolved P ion (Soil solution)

b- Anion exchange reaction (outer sphere)

In this reaction, negatively charged phosphate ions are attracted to the positive charges on the surfaces of iron and aluminum oxides and the broken edges of kaolinite clay. This process occurs under acidic conditions.

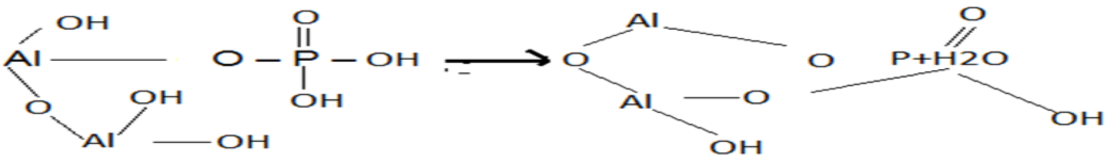
c- Reaction with Al or Fe oxide surfaces (inner sphere)

The specific adsorption process occurs when the phosphate ion replaces the hydroxyl groups present on the surfaces of iron and aluminum oxides and hydroxides, or on clay surfaces in the presence of strong covalent bonds.



d-Formation of stable binuclear bridge (inner sphere)

Phosphate penetrates the metal surface further by forming a more stable di-nuclear bridge.



Mechanisms of phosphorus release in soil

To understand the adsorption-desorption process in soil, we must study the mechanisms that occur in the soil for phosphate adsorption, which can be classified into two types: specific and non-specific adsorption, Specific adsorption involves the fixation of the phosphate ion H_2PO_4 in exchange for the OH or H_2O bond at the soil surface, Non-specific adsorption is the adsorption of free phosphate ions in the soil solution by electrostatic force on the soil surface[29] . The process of desorption of phosphorus in the soil is a reverse process. The mechanisms of desorption include diffusion, competition, and dissolution[30] Phosphorus is released into the soil to be absorbed by plants through several processes

- Chemical processes (precipitation and dissolution of primary and secondary minerals)
- Physicochemical processes (adsorption and desorption of phosphorus from clays, oxides, and minerals)
- Biological processes (immobilization and mineralization of phosphorus in organic materials to inorganic forms [31].

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