Understanding Soil Phosphorus

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Author's contribution

The author designed, analysed, interpreted and prepared the manuscript.

Review Article

ABSTRACT

Phosphorus is the second most important crop nutrient after Nitrogen. It is an essential macronutrient that plays important role in all crop biochemical processes such as photosynthesis, respiration, energy storage, transfer, cell division, cell enlargement and nitrogen fixation. It is also important in seed germination, seedling establishment, root, shoot, flower and seed development. Despite its importance in crop nutrition, availability of the nutrient in soils for plant uptake is limited by several soil factors. The factors include: soil pH levels, clay mineralogy, organic matter, free iron and aluminium, calcium carbonate, soil temperatures and availability of other nutrients among other factors. Availability of phosphorus for plant uptake can be managed by adoption of practices such as liming acidic soils, application of organic amendments in both alkaline and acidic soils, tillage practices and regulation of time and method of P fertilizer application.

1. INTRODUCTION

Phosphorus is a chemical element with the symbol P and atomic number 15. It exist in approximately 23 isotopes [1] ranging from 25P to 47P [2] and has several allotropes ranging from white, red, violet to black [3,4]. The various allotropes exhibit striking different properties. White and red forms are the most common forms but white is the most important form because it is the least stable, most reactive, most volatile, toxic, least dense, soft, waxy solid containing

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tetrahedron P4 molecules in which each atom are attached to the other three atoms by a single bond [5] The white form also exists in alfa and beta crystalline forms. Alfa form is stable and common at room temperature but it transforms to beta forms at temperatures exceeding -78°C [6]. Presence of light and heat however gradually transforms the white P to red P and because it is highly reactive, P is never found as a free element on earth.

The phosphorus content of rocks within continental crust is typically assumed to be between 500-1400 ugP/g, depending on parent rock [7,8]. Of the Igneous rocks, basalts are usually at the upper end with apatite containing higher concentrations while granites and most sedimentary rocks are at the lower end [9]. Typical total P contents in soils range from 150ug -700ugP/g [10] with soils from very old land masses such as Africa and Australia often containing low total P content compared to some other parts of the world. The reduction in the concentration of P occurs as rocks weather, probably because apatite dissolves and the P is lost, before the formation of Al and Fe oxide minerals which would adsorb the P.

1.1 Role and Importance of Phosphorus in Plants

Next to nitrogen, phosphorus (P) is the second most important macronutrient as an essential plant nutrient [11]. It is a key nutrient for higher and sustained agricultural productivity [12] and which limits plant growth in many soils. Phosphorus forms an important component of the organic compound adenosine triphosphate (ATP), which is the energy currency that drives all biochemical processes in plants [13]. It is also an intergral component of nucleic acids, coenzymes, nucleotides, phosphoproteins, phospholipids and sugar phosphates as well as intermediates of signal transduction events [14, 15,16]. It is also involved in an array of processes in plants such as photosynthesis, respiration, nitrogen fixation, flowering, fruiting, and maturation [13,15,17] Plant dry matter may contain up to 0.5% phosphorus [13].

Despite the important role played by soil P in plants, however, phosphorus deficiency in soil is the most common nutritional stress in many regions of the world, affecting 42% of the cultivated land in the world [18]. The P deficiency is caused either by low P content in the soils parent materials or by transformations of P added to soils to forms not available to plants. The P deficiency results in poor plant root formation, slow development, poor seed set and fruit formation hence, low and poor crop yields [13,19].

1.2 Forms of Phosphorus in Soils

Soil P exists in various chemical forms including inorganic P (Pi) and organic P (Po). These P forms differ in their behaviour, fate in soils [20,21] and availability to plants [13].

1.2.1 Organic phosphorus in soils

The amounts of organically held phosphorus (Po) vary greatly among soils. It occurs from traces in aridisols to several hundred mg kg^{-1} in histosols. It is estimated to range from 7 to 1056 P mg kg^{-1} of soil or 20-80% of P in soils worldwide [22,23]. Decomposing plant and animal products, along with the soil microflora and fauna, provide a significant store and source of Po in agricultural systems [24]. It is generally assumed that soil Po is derived directly or after biochemical transformations of organic matter both among soils and within the soil profile [25,26] Added P from phosphate fertilizers can also be converted to organic forms (immobilized) [13,27,28] especially where there is no enough P in the soil, whereby microorganism convert the Pi to Po to incorporate it into their living cells.

Soil Po exists mainly in stabilized forms as inositol phosphates and phosphonates, and active forms as orthophosphate monoesters, and organic polyphosphates [15,29,30]. The Po can be released when roots or phosphate secretions undergo decomposition and mineralization [31, 32,33] mediated by soil microorganisms. As proposed by [34] mineralization can be divided into two processes: a) biochemical mineralization in which inorganic phosphorus (Pi) is released from organic compounds through phosphatase exoenzymes, regulated by P demand; and b) biological mineralization, which is the release of Pi from organic materials during carbon oxidation by soil organisms, regulated by energy demand. These processes are highly influenced by the soil moisture status, soil temperature regime, surface soil physical and chemical properties [21].

1.2.2 Inorganic phosphorus in soils

Inorganic phosphorus (Pi) occurs mainly as $H_2PO_4^-$ and HPO_4^{2-} adsorbed onto the surfaces of oxides and hydroxides of Fe or Al, organic

matter or bound to Ca [34]. The adsorption of P in soils depends on soil pH and clay minerals [35]. However, most Pi occurs in the clay fraction as salts of orthophosphoric acid. Phosphorus forms insoluble compounds with iron and aluminium at low pH, more soluble compounds with calcium and magnesium at pH values near neutrality, and insoluble compounds with calcium at higher pH values [13,36,37]. There is a wide range of solubility of these various phosphate compounds and their availability to crops is optimal within the soil pH range of about 6.0 to 6.5 for most agricultural soils. The Pi compounds are grouped as calcium or magnesium-bound and iron and aluminium-bound [13].

1.2.2.1 Calcium and magnesium phosphates

Calcium or magnesium phosphate compounds are not found in soils at low soil pH but are stable, insoluble and dominant in neutral or alkaline soils [13,37] They occur in soils in several forms and the most important forms are:

a) Ca $(H_2PO_4)_2.H_2O$, monocalcium phosphate, which is the water-soluble component of superphosphate that is transformed to less soluble products.
b) $CaHPO_4.2H_2O$ and $CaHPO_4$, dicalcium phosphate, both hydrated and the unhydrated forms that are slightly soluble in water.
c) Ca_8H_2 $(PO_4)_6.5H_2O$, octacalcium phosphate.
d) Ca_3 $(PO_4)_2$, tricalcium phosphate.
e) Ca_{10} $(PO_4)_6.$ $(OH)_2$ (hydroxyapatite) and Ca_{10} $(PO_4)_6F$ (fluorapatite), and
f) $MgNH_4PO_4.$ $6H_2O$ (struvite) which is alkaline and water-soluble [36,38,39].

Dicalcium phosphate $(CaHPO_4.$ $2H_2O)$, octacalcium phosphate $(Ca_8H_2$ $(PO_4)_6.$ $5H_2O)$ and hydroxyapatite $(Ca_{10}$ $(PO_4)_6.$ $(OH)_2)$ are the principal crystalline phosphates which have been identified in soils [36]. The native phosphorus in soils originated largely from disintegration and transformation of rocks containing the mineral apatite, Ca_{10} $(PO_4)_6(F.Cl.OH)_2$. Apatite has also been reported as a common soil mineral by Hagin and Tucker [40]. However, the apatite in its primary form does not supply phosphate to plants, because of its low solubility and rate of solubilization [13]. On the contrary, hydroxyapatite $(Ca_{10}$ $(PO_4)_6.$ $(OH)_2)$ has been reported to be a stable form of Pi over a wide range of soil pH values [36], hence its ability to supply phosphate to plants.

The phosphorus found in calcareous soils does not correspond to any one mineral species [40]. It may be controlled by octacalcium phosphate in some soils or by hydroxyapatite in other soils [40,41]. The hydroxyapatite in soil invariably contains some carbonate ions while the presence of octacalcium phosphate has been reported in soils limed or fertilized with phosphates [41]. Baifan and Yichu [42] classified Pi in calcareous soils as follows: calcium phosphate in the form of dicalcium phosphate, octacalcium phosphate and apatite types. On the contrary, [43,44] suggested the fractionation of inorganic phosphorus in calcareous soils as a series of calcium phosphates with complex physico-chemical reactions and varying availability to plants for growth.
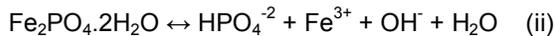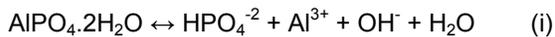
The availability of P from various inorganic compounds was further compiled by Tisdale et al. [36]. It was revealed that struvite $(MgNH_4PO_4.6H_2O)$ had the highest P availability as compared to mono or dicalcium phosphates. In soils containing large quantities of magnesium, a number of insoluble magnesium phosphate compounds such as dimagnesium phosphate trihydrate $(MgHPO_4.3H_2O)$, trimagnesium phosphate $(Mg_3$ $(PO_4)_2$ and/or struvite $(MgNH_4PO_4.6H_2O)$ may form (36,41]. However, these magnesium phosphates are more soluble than dicalcium phosphate and octacalcium phosphate, hence results in greater availability of P for plant uptake.

1.2.2.2 Iron and aluminium phosphates

A number of aluminum and iron phosphate minerals occur in soils [36]. The most common aluminum phosphates in soils are wavellite $[Al_3(PO_4)(OH)_3.5H_2O]$ and variscite $(AlPO_4.2H_2O)$ [13,38,45]. Although variscite is dominant in slightly acidic soils, it dissolves incongruently at high pH values, leading to formation of a more basic solid phase of aluminum hydroxy phosphate [46]. The aluminium hydroxyl phosphates so formed controls phosphorus concentration in solution in acid soil by forming a surface complex on variscite. However, in pure systems, where the pH of the equilibrium solution is less than 3.1, the solubility product of variscite controls the phosphorus concentration in solution [47].

Although variscite $(AlPO_4.2H_2O)$ and strengite $(FePO_4.2H_2O)$ are the least soluble compounds at low soil pH (36,38], strengite is the most common iron phosphate in soils. According to [47], strengite coexists with hydrated iron oxide

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($Fe_2O_3.2H_2O$) at pH 3.8 to 6.7 in the tropics and in the pH range of 3.8 to 4.2 in temperate soils. Strengite also crystallizes rapidly when iron phosphate is formed. Less crystalline aluminium phosphate has greater surface area which is favorable for release of phosphorus into the soil solution. Therefore, under very acid conditions minerals of the variscite and strengite groups are precipitated from their soluble forms [13] according to the reactions shown in equations (i and ii).

$$AlPO_4.2H_2O \leftrightarrow HPO_4^{-2} + Al^{3+} + OH^- + H_2O \qquad (i)$$

$$Fe_2PO_4.2H_2O \leftrightarrow HPO_4^{-2} + Fe^{3+} + OH^- + H_2O \quad (ii)$$

1.2.2.3 Soil solution P

Soil solution P refers to the phosphorus fractions or phosphate ionic species dissolved in the soil solution and it is always in equilibrium with the labile P [48]. Phosphorus concentrations in the soil solutions are low, normally ranging from 0.001 to about 1 mg P L^{-1}, with an average of about 0.05 mg P L^{-1} [49]. The phosphorus taken up by plant roots and mycorrhizal hyphae are mainly the $H_2PO_4^{4-}$, HPO_4^{2-} or PO_4^{3-} , depending on the pH of the soil [50,51]. The dominant inorganic P species in the soil solution below pH 7.2 is the $H_2PO_4^{4-}$ while HPO_4^{2-} and PO_4^{3-} are dominant at pH values between 7.2 and 12.1, and 10.0 and 14.0, respectively [51].
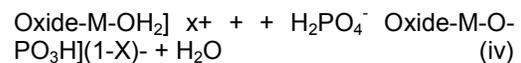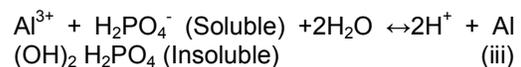
1.3 Phosphorus Dynamics in Soils

Primary P minerals like apatites, strengite and variscite are very stable and the release of P in soil solution from these minerals by weathering in acid soils is generally low [37]. In contrast, secondary P minerals including calcium (Ca), iron (Fe), and aluminium (Al) phosphates vary in their dissolution rates, depending on the size of the mineral particles and soil pH [45,52,53]. With increasing soil pH, solubility of Fe and Al phosphates increases but solubility of calcium phosphates decreases until pH values above 8 where it starts to increase [54]. The parent material of soil P is primarily calcium phosphates, mostly the fluorapatite [Ca_5 $(PO_4)_3F$], with chloride (Cl), hydroxyl (OH^-), or carbonate (CO_3^{2-}) sometimes replacing the F. This $Ca_5(PO_4)_3(OH,F,Cl)$ is the raw material used in the manufacture of P fertilizers [54]. Weathering processes cause bases, silicates and carbonates to be lost from the soil, concentrates

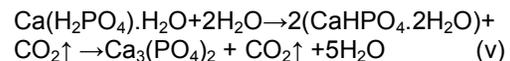the Fe and Al and releases P into the soil solution [52].

The released P can be availed to the soil solution as soluble inorganic P and/or reverted back to organic P through immobilization by living organisms in the soil. The soluble P can also be sorbed onto surfaces of secondary minerals and become part of the soil P pool referred to as labile P [29] Additionally, the labile P can be desorbed, returned to the soil solution or transformed into more thermodynamically stable forms of P referred to as non-labile P [55,56].

1.3.1 Phosphate retention by soils

The types of reactions that are responsible for P retention by soils differ from soil to soil and are closely related to soil pH [13]). In acid soils, these reactions involve mainly Al, Fe and Mn oxides, or their ionic forms or hydrous oxides [13,57]. The aforementioned soil components retain P through ligand exchange, adsorption and precipitation reactions as shown in equations (iii) and (iv) [57,58]. In alkaline and calcareous soils, the reaction involves precipitation of calcium phosphate minerals (Equation v) or adsorption onto iron impurities on surfaces of carbonates and secondary clay minerals [13,58,59].

$$Al^{3+} + H_2PO_4^- \text{ (Soluble) } +2H_2O \leftrightarrow 2H^+ + Al(OH)_2 H_2PO_4 \text{ (Insoluble)} \qquad (iii)$$

$$\text{Oxide-M-OH}_2] \text{ x+ } + + H_2PO_4^- \text{ Oxide-M-O-}PO_3H](1-X)- + H_2O \qquad (iv)$$

where M = Al or Fe .

$$Ca(H_2PO_4).H_2O+2H_2O \rightarrow 2(CaHPO_4.2H_2O)+CO_2\uparrow \rightarrow Ca_3(PO_4)_2 + CO_2\uparrow +5H_2O \qquad (v)$$

Where: Monocalcium phosphate is soluble and tricalcium phosphate is insoluble.

1.3.1.1 Phosphate adsorption by soils

In acid soils, adsorption of P occurs principally via the formation of an inner-sphere complex between orthophosphate anions (such as $H_2PO_4^{2-}$) and a metal cation or metal oxyhydroxide (such as Fe and Al) [60,61,62]. The orthophosphate ion then undergoes ion exchange with OH- or H_2O groups on the soil particle surface, with a coordinate covalent bond formed between the P atom and the metal cation [60,61].

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The afore mentioned reactions or transformations lead to decreased point of zero charge (PZC). According to Reddy et al. [63] once all surface sites are occupied by P adsorption, the P begins to diffuse into the particle via absorption. The adsorption processes are temperature dependent, pH controlled and process rates decrease with time [62,64]. The Al and Fe oxides occur as amorphous Al and Fe in flooded soils and/or as crystalline terrestrial soils [65,66]. However, the amorphous oxides of Al and Fe often exhibit greater reactive surface areas than crystalline forms for P sorption [59,67]. This makes oxalate extractable Fe and Al tests useful in extraction of poorly crystalline oxyhydroxides of Fe and Al rather than the crystalline forms which are not associated with P sorption [68].

1.3.1.2 Precipitation

Precipitation processes involve the removal of P from solution through the reaction of the P with Al (Equation vi), Fe and Ca cations to form new solid precipitates [13,60]

$$Al^{3+} + PO_4{}^{3-} = AlPO_4 \qquad (vi)$$

Reactions with calcite surfaces involve initial adsorption of small amounts of P, which can be followed by precipitation of Ca-bound P [69]. Cations such as Na, K, and Mg can also affect P adsorption, as they can displace Ca, from the exchange complex thereby freeing up Ca to sorb P [69]. Precipitation of P as insoluble Ca-bound P (Equation vii) is the dominant transformation reaction in wetland soils and sediments at pH values greater than 7 [70,71].

$$Ca^{2+} + HPO_4{}^{2-} = CaPO_4 \qquad (vii)$$

1.4 Phosphate Adsorption Isotherms

A phosphate adsorption isotherm is a graphical presentation for describing the adsorption of P by, or desorption of P from the soil solid phase as a function of the P equilibrium concentration in the soil solution at constant temperature and pressure [39,71,72]. According to [73,74] an isotherm from a plot of phosphate retained against different equilibrium P concentrations can be divided into three regions. The regions correspond to three distinct stages in soil - phosphate interactions. The first region corresponds to low phosphate addition, resulting in practically complete adsorption or a negligible fraction of the added phosphate remaining in the equilibrium solution; the adsorption isotherm rises steeply and remains close to the Y-axis. The second region is a strongly curved portion of the isotherm which is convex to the Y-axis and adsorption varies logarithmically with the equilibrium phosphate concentration. The third portion occurs at medium to high phosphate concentrations (precipitation), where, the adsorption varies linearly with the amounts of P in the equilibrium solution. At higher level of this region, the slope of the line is small and, for most soils, the isotherms tend to be more or less parallel to the X-axis.

The adsorption reaction between phosphate and soils has been described mathematically using several adsorption equation models. They include: Langmuir equation [75,76], Freundlich equation [75,76], Temkin equation [38,79] and Elovich equation [73,80,81]. Among these equations, the Langmuir and Freundlich equations are the most commonly used to describe the relationship between equilibrium P and P sorbed by tropical soils [38,79]. Sorption parameters derived from these equations can predict the maximum P sorption capacity (Kmax) and the P adsorption energy and are, therefore, useful in the evaluation of soil fertility and other P management parameters [80] in relation to P.

1.4.1 The Langmuir equation

The Langmuir equation was developed by Langmuir in 1916 on the assumption that gas-molecules are sorbed onto solid surfaces as a monolayer, with a constant and specific energy of adsorption. It was first used by Olsen and Watanabe [71] to describe phosphate adsorption in soils. In its linear form, the Langmuir equation can be written as shown in equation (viii below):

$$C/X = 1/ Kb + C/b \qquad (viii)$$

where, C = equilibrium concentration of phosphate in solution (μg P/ml), X= mass of phosphate adsorbed (μg)/ mass of soil (g) K= adsorption maximum (μg P g-1 soil), b is a constant related to the binding energy of the soil. A plot of C/X against C should give a straight line, from which the adsorption maximum, K, the inverse of the slope and the constant b, can be calculated. The equation follows three principles, namely (i) the energy of adsorption is constant, hence uniform sites of adsorption and lack of interaction between adsorbed molecules for the gases but for soil ions; (ii) adsorption is on localized sites, which implies no translational

motion of adsorbed ions in the plane of the surfaces, and (iii) the maximum adsorption possible corresponds to a complete mono ionic layer [84].

The Langmuir equation was derived based on theoretical grounds and it contains parameters which have physico-chemical significance [71,81] representing the extensive (adsorption capacity) and intensive (affinity) properties of the adsorbent for the adsorbate [82]. However, deviations from the expected linearity (curvilinearity) have been reported at high phosphate additions [71]. This problem was resolved by assuming that the type of adsorption occurred at low equilibrium concentration where a mono ionic layer can be expected [71,83]. However, the development of a multi-surface Langmuir-type equation by [81,83] under higher equilibrium concentrations has somewhat overcome these deviations [85,86] used the two-term Langmuir relationship to obtain improved fit and understanding of the P –adsorption and soil-phosphate interaction. This has been considered appropriate for phosphate adsorption studies since P is retained in soils by surfaces with different affinities for phosphate. According to [81], the two-surface Langmuir equation gives meaningful estimates of phosphate adsorption capacity compared to the simple Langmuir equation. However, the only parameters considered in all the models are the equilibrium concentration "C" and the retained phosphate "X", either in the original form or in the modified form by taking into account the phosphate already adsorbed, as suggested by [71,87,88,89]. The multi-surface Langmuir equation model has the form shown in equation (ix):

$$X= [K_1b_1P/ (1+b_1P)] + [K_2b_2P/ (1+b_2P)] + …. [K_nb_nP/ (1+b_nP)] \qquad (ix)$$

where, X= mass of phosphate adsorbed (µg)/ mass of soil (g) K= adsorption maximum (µg P g-1 soil), b is a constant related to the binding energy of the soil, P is the equilibrium gas pressure.

1.4.2 The Freundlich equation

Freundlich equation was the first model to be used in describing phosphate retention in soil [90,91]. Barrow [92] advocated that the adsorption data from dilute solution could be fitted to the Freundlich equation of the form (equation x):

$$x/m = aCb \qquad (x)$$

It was later modified to (equation xi): $x/m = K_fC^{(1/n)}$ (xi)

Where, x/m is the amount of P adsorbed / sorbed (mg kg^{-1} soil), C is the concentration of P in soil solution at equilibrium (EPC) (mg L^{-1}), Kf is the proportionality constant (mg kg^{-1}), that is extent of sorption = antilog (Y-intercept). The constant Kf is also interpreted as the amount of sorbed P that would sustain a unit P concentration in equilibrium solution [79]. The 1/n is the slope of the curve when log(x/m) vs. logC is plotted; while "a" and "b" are constants which represent the intercept (P sorption maximum) and slope (bonding energy) of sorption isotherms, respectively [79]. The equation is normally used in its logarithmic form (equation xii):

$$Log X = 1/n Log C + Log a \qquad (xii)$$

hence, a plot of log X against log C should give a straight line.

The equation was originally empirical, without any theoretical physico-chemical foundation and no significance could be attached to the adsorption coefficients [71,82,93]. This implied that the energy of adsorption decreased exponentially as the fraction of covered surface is increased (amount of adsorption) and because of this it has not been possible to compare quantitatively adsorption data for soils obtained from plots of the Freundlich equation because the equations were assumed to be empirical and treatments assumed to be theoretical [93]. However, some workers suggested that the intercept and slope of a linear Freundlich plot could be used to compare phosphate adsorption in soils, but it has a limitation in that it does not predict the maximum adsorption capacity [82,94]. Despite its limitations, the equation gives better fit to phosphate adsorption isotherms in most soils than the most widely used Langmuir equation and the more complex two-surface Langmuir equation [88,95].

1.4.3 The Temkin adsorption equation

The derivation of the Temkin isotherm assumes that the reduction of the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation [96].

According to Anghiononi et al. [97] the Temkin equation has generally been applied in the form (equation xiii):

$$X/m = a + B \ln C \qquad (xiii)$$

where X/m = mass of adsorbed P (µg g^{-1} soil), C = the equilibrium P concentration (µg ml^{-1}), B- P-buffering capacity (µg g^{-1} soil) and "a" = Temkin constant. A plot of X/m against ln C gives a straight line if the adsorption process fits the model. The values of "a" and B are obtained from the intercept (a) and the slope (B), respectively.

1.5 Factors Affecting P Sorption by Soils

Phosphorus sorption by soils is influenced by soil pH, ionic species in the soil solution, clay mineralogy, organic matter content, free iron and aluminium, soil calcium carbonate, temperature and time of equilibration (contact) among other factors [13,98,99,48,100].

1.5.1 Soil pH

Soil pH has a profound effect on the amount and manner in which soluble phosphates become adsorbed. Phosphorus adsorption occurs at very low and very high soil pH. The dominant P ion species present in acid soils are $H_2PO_4^-$ and PO_4^{3-} in alkaline soils [51,101]. Adsorption of phosphorus by iron and aluminium oxides also declines with increasing pH [13,48,100] due to reduced solubility of Fe and Al ions. At lower pH, adsorption results from the reaction with iron and aluminium (reaction equation xiv) and their hydrous oxides while above pH 7.0, ions of calcium, and magnesium and their carbonates cause P precipitation (reaction equation xv) [13,48,102]. Gibbsite (Al (OH)$_3$) adsorbs high amount of phosphate between pH 4 and 5 while adsorption by goethite (an-FeOOH) decreases steadily between pH 3 and 12 [173] This is because Al^{3+} is more dominant and soluble between pH 4 and 5 while Fe^{3+} is dominant and soluble at pH levels below 3. Therefore, maximum P availability is attainable in most soils at the pH range 6.0 to 6.5 [36].

$Al^{3+} + H_2PO_4^- + 2H_2O \leftrightarrow 2H^+ + Al (OH) 2H_2PO_4$ (xiv)
(Soluble)   (Insoluble)

Ca (H$_2$PO$_4$)$_2$ [Soluble] + 2Ca^{2+} ↔ Ca$_3$ (PO$_4$)$_2$ [Insoluble] + 4^{H+} (xv)

1.5.2 Ionic strength and composition of the soil solution

Both organic and inorganic anions in the soil solution compete with phosphate for adsorption sites to varying extents. This results in either adsorption of added phosphate or desorption of retained phosphate in conformity to the anion exchange mechanisms. Weakly held inorganic anions such as nitrate and chloride are of little significance, whereas specifically adsorbed anions like hydroxyl, sulphate and molybdate are competitive. The strength of bonding of the anions with the adsorption surface determines the competitive ability of that anion. For example, sulphate, even though considered to be a specifically adsorbed anion, is unable to desorb much phosphate [103] because of the affinity for colloidal surfaces. Additionally, divalent cations enhance P sorption more than monovalent cations [104]. For example, clays saturated with Ca^{2+} retain greater amounts of P than those saturated with monovalent cations like Na+ [105].

1.5.3 Organic matter

There are two principal mechanisms by which organic matter may affect the adsorption and hence availability of phosphorus in soils: (a) negatively charged organic matter adsorbs or complexes cations such as Al and Fe in acid soils and Ca in calcareous soils [13,106] and hence reduces their activities in solution and their role in P sorption and/or precipitation or (b) presence of organic acids such as humic acid, fulvic acid and citric acid on the surface of (hydr)oxides could inhibit phosphate adsorption through site competition, electrostatic effects, and steric hindrance [107].

According to [36,108], the existing correlation between phosphate and organic matter. This increase is attributed to the ability of humic molecules to adhere to sorbing surfaces and masking of fixation sites hence preventing them from interacting with phosphate ions in solution [13]. Organic acids produced by plant roots and microbial decay can also serve as organic anions which compete with P for positively charged sites. Other organic compounds can also entrap reactive Al and Fe in stable organic complexes called chelates hence their unavailability for reaction with phosphorus [13].

1.5.4 Clay mineralogy

Numerous studies show that aluminosilicate clay minerals play an important role in P sorption by soils [77,109]. Generally, clay minerals possessing high anion exchange capacity have a high affinity for phosphate ions. The clay content of a soil also has great impact on phosphate adsorption. Soils containing large quantities of clay would adsorb more phosphate than those

with less clay content. Generally, the layer silicate clay minerals of the 1:1-type minerals (kaolinites) are made up of one tetrahedral (silica) sheet and one octahedral (alumina) sheet, while 2:1 type minerals (montmorillonite) are characterised by an octahedral sheet sandwiched between two tetrahedral sheets [13]. The 1.1 clays with low SiO_2/R_2O_3 (sesquioxide) ratios have therefore higher phosphate adsorption capacity than 2.1 clays (montmorillonite) with high SiO_2/R_2O_3 (sesquioxide) ratios [13,36]. The high amount of P fixed by 1:1 clays is probably due to the higher amounts of hydrated oxides of iron and aluminium associated with kaolinitic clays [36]. Kaolinite has large number of exposed hydroxyl groups in the gibbsite layer that can be exchanged for P [36,110]. In addition, kaolinite develops pH dependent charges on its edges which can enter into adsorption reactions with P [110].

1.5.5 Free iron and aluminium

Oxides and hydroxides of Al and Fe play a significant role on P availability and sorption properties. According to [109,111] oxides of Fe and Al positively correlate with P adsorption maxima. The high value of P adsorption maxima in cases of soil containing high contents of oxides of Fe and Al might be due to formation of their respective metal phosphates [13,62]. The sorption of inorganic phosphate of soils with pH less than 7.0 is closely related to the amount of reactive Fe and Al compounds [112]. It has also been reported that about 1 cmol Al kg^{-1} soil, when completely hydrolyzed, can sorb up to 102 mg P L^{-1} from the soil solution [114]. The amorphous hydrous metal oxides of Fe and Al have, however, been reported to sorb relatively greater amounts of P than their crystalline counterparts [113]. This is because the amorphous hydrous metal oxides have more exposed sites for reaction as compared to the crystalline metal oxides.

1.5.6 Soil calcium carbonate

Availability of P in soil solution in calcareous soils is dictated by both adsorption and precipitation mechanisms [114]. According to Cole and Olsen [115], solubility of P in calcite suspensions is controlled by a dicalcium phosphate solid phase. The initial attachment involves chemisorption of P onto dicalcium phosphate [116] followed by octacalcium phosphates which are of low energy [117]. The initial process is relatively rapid,

followed by approximately a two - hour induction period, then precipitation [118]. Phosphorus sorption on all carbonates is, however, dictated by surface characteristics, especially surface area and zeta potential [115]. According to Woodruff and Kamprath [119] the possible reactions leading to P fixation in calcareous soils are: (a) Precipitation of relatively insoluble calcium phosphate such as octacalcium phosphate, hydroxyl apatite and carbonate apatite, favoured by high calcium activity and high pH. (b) Fixation of P by clays saturated with calcium.

1.5.7 Effect of temperature

Temperature affects the equilibrium between phosphate solution and adsorbed P and the rate of transfer from adsorbed, to firmly adsorbed phosphate [120]. High temperatures slightly increase the molar solubility of compounds such as apatite, hydroxyapatite, octacalcium phosphate, variscite and strengite. It may also stimulate biological activity which enables phosphate to be released from organic residues [95,122]. This can be attributed to increased mobility and rate of chemical reactions.

1.5.8 Effect of time

Phosphorus adsorption by soils and many soil components follows an initial fast reaction followed by a much slow reaction [62]. The adsorption reaction involving exchange of phosphate for anions and ligands on the surfaces of iron and aluminum oxides are extremely rapid [36,62]. The slower continuing adsorption reactions involve either a diffusive penetration or chemisorption of surface - adsorbed phosphorus into micropores or aggregates of soil particles [123] or precipitation of a phosphorus compounds for which the solubility product has been exceeded [124]. The slow reaction also involves a shift in the forms of phosphorus held at the surface from more loosely bound to more tightly bound forms, which may take months or years.

1.6 Fate of P in Acid Soils

In acidic soils, P can be adsorbed dominantly by Al/Fe oxides and hydroxides, such as gibbsite, hematite and goethite [125]. Phosphorus is first adsorbed on the surface of clay minerals and Fe or Al oxides by forming various complexes. The non - protonated and protonated bidentate surface complexes may coexist at pH 4 to 9,

while the protonated bidentate inner sphere complex is predominant under acidic soil conditions [126,127]. Clay minerals and Fe / Al oxides have large specific surface areas, which provide large numbers of adsorption sites. The adsorption of soil P can be enhanced with increasing ionic strength of the soil solution. Phosphorus may also be occluded in nanopores that frequently occur in Fe/Al oxides and thereby become unavailable to plants [127].

As a result of adsorption, precipitation and / or conversion to organic forms, only 10-30% of the phosphate mineral fertilizer applied to soils can be recovered by the crop grown after fertilization [27,28]. The remaining P stays in the soil and may be used by crops in the subsequent years depending on the dynamic equilibrium between the adsorbed P level and P in the soil solution. Because of the low P solubility and desorption, only a small proportion of phosphate ions exists in the soil solution for plant uptake even under optimum fertilization. This makes P recovery from P fertilizer to be lower compared to other nutrient containing fertilizers [27].

1.7 Strategies and Approaches to Manage Acid Soils

Crop production in acid soils with Al toxicity and low soil available P can be improved by use of lime, fertilizers with a liming effect, organic materials, crop germplasms tolerant to Al toxicity and /or low soil available P, and modified tillage practices [128,129,130,131].

1.7.1 Liming

Liming modifies the physical, chemical and biological characteristics of soil through its direct effect on amelioration of soil acidity [132,133]. It also plays an indirect role of mobilization of plant nutrients, immobilization of toxic heavy metals and improvement of soil structure [134]. Physical amelioration of lime occurs through flocculation of colloid particles which leads to changes in surface potential and charge densities [135].

The chemical amelioration of lime entails reduction of chemical problems associated with soil acidity [135]. Use of agricultural lime containing Ca and /or Mg compounds such as $CaCO_3$ and $CaCO_3.MgCO_3$ respectively to acid soils increase Ca^{2+} and /or Mg^{2+} ions in the soil solution. It also increases the soil pH, thereby reducing the activities / concentrations of Al^{3+} and Fe^{3+}, H^+, Mn^{4+} and Fe^{3+} ions in the soil

solution. Aluminium in soils is bound in the form of Al-hydroxy compounds like $AlOH_2^+$ and $Al(OH)_2^+$, which tend to polymerise to species such as $Al_6(OH)_{153}+$ [136]. As the pH increases, the surface becomes increasingly negative hence increasing electrostatic repulsion and decreasing electrostatic potential [137], thus reducing P sorption and increasing the concentration of HPO_4^{2-} in the soil solution [133, 148,149] leading to increased available P for plant uptake [130,132].

In addition to neutralization of soil acidity, lime enhances root development, water and nutrient uptake, which are necessary for improved crop yields [133,139,140]. Studies conducted worldwide have shown that liming improves crop yields in acid soils. For example, [141] evaluated the potentials of some cement byproducts as liming materials for acid soils in Cameroon and found that they increased maize yields by 67.2%. Similarly, [142] observed that liming acid soils and the subsequent residual effects of lime significantly increased maize and beans yields. However, [143] reported that the efficiency of lime depends on soil type and level of acidity, hence the need to critically study the lime - soil components interactions.

Several studies have shown that lime reduces Al toxicity, increases soil pH, Ca, Mg, uptake of N and P, thus improving crop productivity in Kenyan acid soils [130,132,145,146]. Nekesa et al. [147] reported increased soil pH and available P in western Kenya acid soils by agricultural lime containing 21% calcium oxide (CaO). In a four - year experiment, [130] reported increased soil pH, maize grain yield, P use efficiency and reduction in exchangeable Al^{3+} in acid soils of the highlands of Kenyan Rift Valley. Higher rates of lime (4 and 6 tonnes ha^{-1}) increased and maintained higher soil pH, available P and grain yield compared to lower rates (2 tonnes ha^{-1}). [148] also reported maize grain yield increase of 0.77 to 6.18 tonnes ha-1 per tonne of applied lime.

1.7.2 Application of organic soil amendments

Use of organic amendments such as manure has been proposed as a good alternative to liming to reduce Al toxicity in acid soils [106,149]. The Organic materials (OMs) interact with P in soils in a variety of ways that potentially influences P sorption and release reactions. Direct and indirect mechanisms have been proposed for the increase of soil available P as a result of the

addition of OM [150]. It is hypothesized that organic acids produced during decomposition of crop residues prevent precipitation of phosphates by iron (Fe) and aluminium (Al) oxides out of the soil solution [151] and, as a result, P concentration in the equilibrium solution increases. Competition for P-sorption sites between P and the released organic acids as well as complexation of Fe and Al oxides/ hydroxides by organic acids have been suggested as the key factors controlling the reduction of soil P sorption capacity and increasing P availability [106,152]. Ch'ng et al. [149] further indicated that some organic amendments have affinity for Al and Fe which enables long term chelation of Al and Fe, instead of P, hence availing P for plant use.

Many researchers have documented the effects of organic matter (OM) on soil acidity, Al toxicity and increase in soil available P in acid soils. In western Kenya, Opala et al. [145] demonstrated that *Tithonia diversifolia* (tithonia) green manure was effective in increasing maize yield due to its ability to reduce exchangeable Al in soils without necessarily increasing the soil pH. This was attributed to the ability of tithonia manure to form complexes with Al. However, in the same study, farmyard manure (FYM) increased the soil pH but it was less effective in decreasing the exchangeable Al^{3+} as compared to tithonia. It was, therefore, concluded that the ability of an organic material to reduce Al toxicity was related to its ability to complex the Al through organic acids produced during its decomposition. The tithonia green manure was, therefore, more effective because of its ability to release large quantities of organic acids like oxalic and tartaric acids, as compared to the well decomposed FYM which had lost most of the organic acids. [153] in Tanzania also reported large quantities of organic acids in soils treated with tithonia as compared to soils treated with FYM. Similary, on testing the effects of a range of organic materials of diverse composition commonly found on smallholder farms on maize dry matter production on two acid soils in Kericho, Kenya, [154] reported that manures of high quality increased maize dry matter yields above the control and were generally superior to lime applied alone or in combination with TSP. This confirmed earlier observations by Opala et al. [155] that some organic materials such as tithonia could substitute lime as an amendment for soil acidity.

Apart from decreasing Al and Fe ions, soil organic matter can increase plant P uptake by

decreasing bulk density and increasing porosity, thereby improving root growth and prorification hence exploration and effective nutrient uptake [156]. Organic P pool increases with increasing organic matter. Organic P compounds such as inositol phosphates, nucleic acids, and phospholipids present in organic matter can be decomposed, resulting in P mineralization, thereby increasing P availability and acting as a P source for subsequent crops.

There are, however, some challenges in the use of OM to manage acid soils and replenish soil fertility. Plant P availability does not always increase following incorporation of plant residues [157]. This is because the magnitude of the effect of plant residues on soil P availability depends on the organic residues' quality, especially the C: P ratio [158], as well as on the soil characteristics [159]. Due to their low P contents, large amounts of organic residues have to be applied, thus increasing labour costs [160,161]. Additionally, the cost incurred by use of nutrient - rich organic materials like tithonia, Calliandra, or maize stover cannot be offset by the subsequent crop yield increases [145,146,160,162].

1.7.3 Tillage

Tillage practices can significantly influence the productivity and sustainability of modern farming systems. [163,164] argued that tillage practices could alter nutrient dynamics via three processes: (a) mixing nutrients through the soil matrix and altering their availability to crop (b) changing the soil physical environment and, (c) affecting soil biological activity. No till or minimum tillage systems allow the accumulation of organic materials on the surface, which supply energy, carbon skeletons and electrons for growth and development of microorganisms [128] hence increase in biomass and eventually microbial P. Accumulated Po in the undisturbed rhizosphere may also result in high microbial activity; hence build-up of more stable Po fractions [165]. Additionally, minimal soil disturbance may promote increased populations of microorganisms and plant roots, thereby increasing synthesis and exudation of phosphatase enzymes and leading to enhanced transformation of Po into plant - available Pi [166].

The effect of tillage practices on soil P dynamics within the soil profile has been explained differently by different authors. Rosolem et al. [166] attributed accumulation of P in the surface

soil under zero-tillage to lack of physical disturbance that mixes fertilizer P thoroughly within the plough layer. On the other hand, Bolland and Brennan [168] argued that tillage practices which mix the topsoil increase availability through mixing the previously applied P, and thus improving the effectiveness of P fertilizer for subsequent crops. There are, therefore, no consistent reports on the effect of tillage on the availability of soil P.

Although incorporation of lime into soil ameliorates soil acidity, the lime applied in the surface soil layer has little impact on subsurface acidity. This is because vertical mobility of lime is limited to only about 13 mm per year on fine - textured soils, hence taking several years to reach a considerable depth [169]. Since soils with subsurface acidity require liming down to 30 cm depth or deeper, thus, deep tillage to incorporate lime in the subsurface layers of acid soils may be appropriate in the alleviation of the subsurface acidity problem which, so far, has received little attention.

1.7.4 Time and method of application of P-fertilizers

Efficient plant use of phosphorus from P - fertilizers is important from an economic view point and the conservation of the world's phosphate resources. Phosphorus recovery from P fertilizer by crops can be improved through proper method of P fertilizer placement. In soils that have high P fixing capacities, band application enhances P recovery as compared to broadcasting [170]. Banding below the level of seed placement at the time of planting has the added advantage of placing the fertilizer in immediate contact with the emerging radical and seminal roots during seedling establishment [171]. This concentrates the P fertilizer in a small soil volume and saturates the P binding sites, lowering the buffering capacity of the soil, thereby increasing concentration of phosphate ions in the soil solution and furthering diffusion toward the root. Rudd and Barrow [172] reported that the combination of drilling in bands and application at sowing gives the best yield responses from single super phosphate (SSP) [Ca $(H_2PO_4)_2$].

Although the timing application of P fertilizer may not influence P uptake and efficiency as much as it does with nitrogen fertilizer, the longer the phosphorus is in contact with soil, the greater the fixation that occurs. For annual crops, P application at planting time is important but top dressing is not usually effective. Unlike annual crops, top - dress application of P to perennial crops is very important. This is because annual crops will complete their life cycle without full utilization of the top - dressed P, unlike the perennial ones.

2. CONCLUSION

Phosphorus is an essential macro nutrient in the life of all living organisms. It plays vital direct role in metabolic activities such as energy generation, photosynthesis, and respiration, formation of nucleotides, germination and seed formation in plants among other functions. Despite its importance, availability for plant uptake by plants or living organisms within the soil is limited. The un availability of soil P for uptake is attributable to poor agronomic practices which leads to inherent nutrient mining without adequate replenishment, soil acidification, salinization among other practices. Presence of oxides and hydroxides of iron and Aluminium in acid soils adsorb P making it unavailable for uptake. Carbonates and bi carbonates of calcium on the other hand adsorb P in alkaline conditions rendering it unavailable. Phosphorus is also sorbed by some highly weathered and leached clay minerals hence becoming unavailable for uptake. This means that Phosphorus is only available for uptake at a defined narrow pH range. Management of soil P entails application of P rich fertilizers, organic matter that buffers soil pH change and also regulates soil physical, chemical and biological properties, liming, tillage practices as well as modification of other agronomic practices such as planting time and fertilizer application methods.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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