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Chapter

Processes and Factors Affecting Phosphorus Sorption in Soils

Samuel Kwesi Asomaning

Abstract

The subject of this chapter is soil chemistry. The chapter is entitled Processes and Factors Affecting Phosphorus (P) Adsorption in Soils. The chapter aims to give an overview of the major mechanisms responsible for phosphate sorption (i.e., adsorption and absorption of phosphate) in soils, particularly of acid soils. According to studies conducted by some soil scientists, the major soil factors affecting P sorption are time, soil pH, soil organic matter, and iron and aluminium oxides of soils. Studies conducted indicated that adsorption of the P increases as the P ages in the soil. Soil pH affects phosphate adsorption but the effect is limited for adsorption by soils in the pH range of 4–8. Organic matter may affect P adsorption in two ways: indirectly by inhibiting iron oxide crystallisation and directly by competing for adsorption sites. On per mole basis, oxalate extractable aluminium oxides adsorb nearly twice as much P as oxalate extractable iron oxides due to poorer crystallinity (higher specific area) of the aluminium oxides compared to the iron oxides and also to a higher charge of the former. The chapter also highlights the pedotransfer functions (PTFs) of Borggaard, which can be used to calculate for the P adsorption in highly weathered acid soils.

Keywords: sorption, adsorption, adsorbent, adsorbate, specific adsorption, amorphous oxides, pedotransfer functions

1. Introduction

With increasing demand of agricultural production and as the peak in global production will occur in the next decades, phosphorus (P) is receiving more attention as a non-renewable resource [1, 2]. One unique characteristic of P is its low availability due to slow diffusion and high fixation in soils. Few unfertilized soils release P fast enough to support the high growth rates of crop plant species. In many agricultural systems in which the application of P to the soil is necessary to ensure plant productivity, the recovery of applied P by crop plants in a growing season is very low, because in the soil more than 80% of the P becomes immobile and unavailable for plant uptake because of adsorption, precipitation, or conversion to the organic form [3]. All of this means, that P can be a major limiting factor for plant growth.

Phosphate in soils tends to react with soil components to form relatively insoluble compounds, many of which have limited availability to plants [4]. Major factors which influence these reactions include: phosphorus concentration in solution, amount of free oxides of iron and aluminium, type and amount of clay, soil pH, and organic matter [5].

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Aluminium oxides, iron oxides and clay silicates are well known phosphate adsorbents in soils [6]. According to Borggaard et al. [7], aluminium and iron oxides are the main phosphate adsorbents in sandy soils. Close correlations have been found between a soil's capacity to adsorb phosphate and the content of aluminium and iron oxides, in the soil suggesting these oxides to be the main phosphate adsorbents in soils [8].

In acidic soils, P can be dominantly adsorbed by Al/Fe oxides and hydroxides, such as gibbsite, haematite, and goethite [9]. P can be first adsorbed on the surface of clay minerals and Fe/Al oxides by forming various complexes. The nonprotonated and protonated bidentate surface complexes may coexist at pH 4–9, while protonated bidentate innersphere complex is predominant under acidic soil conditions [10]. Clay minerals and Fe/Al oxides have large specific surface areas, which provide large number of adsorption sites. The adsorption of soil P can be enhanced with increasing ionic strength.

Phosphate is strongly adsorbed by the number of adsorption sites, which vary greatly among soils [11]. With further reactions, P may be occluded in nanopores that frequently occur in Fe/Al oxides, and thereby become unavailable to plants [10].

Therefore, the availability of soil phosphate as well as the soil solution concentration of phosphate will depend on the degree of phosphate saturation, rather than on the total phosphate content [12]. Phosphate saturation is the proportion of adsorption sites occupied by phosphate, which is normally taken as the ratio between adsorbed phosphate and the phosphate adsorption capacity (PAC) of the soil [13].

2. Mechanism of phosphorus adsorption in soils

2.1 Specific adsorption of phosphorus by aluminium and iron oxides

Phosphate sorption is a term used to describe all the processes resulting in the removal of phosphate from soil solution, mainly by surface adsorption and precipitation [14]. Important soil factors that determine its capacity to retain phosphorus (P) are the presence of amorphous aluminium and Iron oxides compounds [15]. The process of adsorption of the phosphate by these compounds (i.e. aluminium and Iron oxides) which are also known as adsorbents is known as specific adsorption. The phosphate molecule or ion which is adsorbed is then known as adsorbate. Specific adsorption of ions can occur unto uncharged adsorbents and sometimes even unto surfaces bearing charge of the same sign as the adsorbent. Thus phosphate can be adsorbed unto surfaces of variable-charge minerals such as aluminium and iron oxides even at alkaline pH, where these adsorbents are negatively charged. Specific adsorption is characterised by formation of inner-sphere complexes, where no water molecules are interposed between the adsorbent and the adsorbate. The most important variable-charge minerals in the soil that adsorb P include aluminium oxides and iron oxides. The poorly ordered ("amorphous") iron and aluminium hydroxides possess very large specific surface area (SSA) which can be as high as 800 $m^2\ g^{-1}$, and 10 times larger than the SSA of corresponding crystalline forms. Additionally, these sesquioxides have high singly coordinated surface hydroxyl density [16]. The reactive sites of these amphoteric AlOH and FeOH minerals are the hydroxyl groups exposed on the mineral surfaces. The kind of hydroxyl (OH) groups in which the oxygen of the OH is coordinated to one structural Iron (111) (Fe^{3+}) ion (single – coordinated), are found to protonate and deprotonate in response to solution pH.

The single–coordinated OH groups are those surface hydroxyl groups onto which specifically adsorbable anions are adsorbed [7]. The single–coordinated hydroxyl groups can be quantitatively replaced or exchanged by the phosphate anions. This results in the formation of a binuclear or surface complex for the phosphate iron oxide system, where one phosphate ion occupies two surface sites. This is accompanied by a release of hydroxyl (OH^-) and H_2O groups (**Figure 1**).

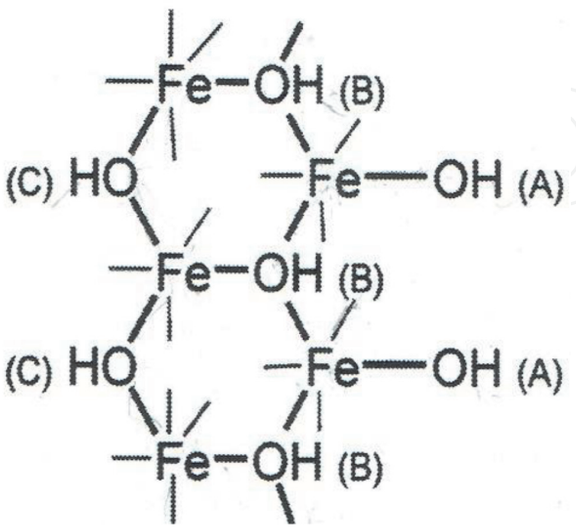


Figure 1.
The three kinds of hydroxyl groups occurring on the goethite surface denoted (A) single-coordinated, (B) triple - coordinated and (C) double-coordinated. Source: Borggaard and Elberling [6].

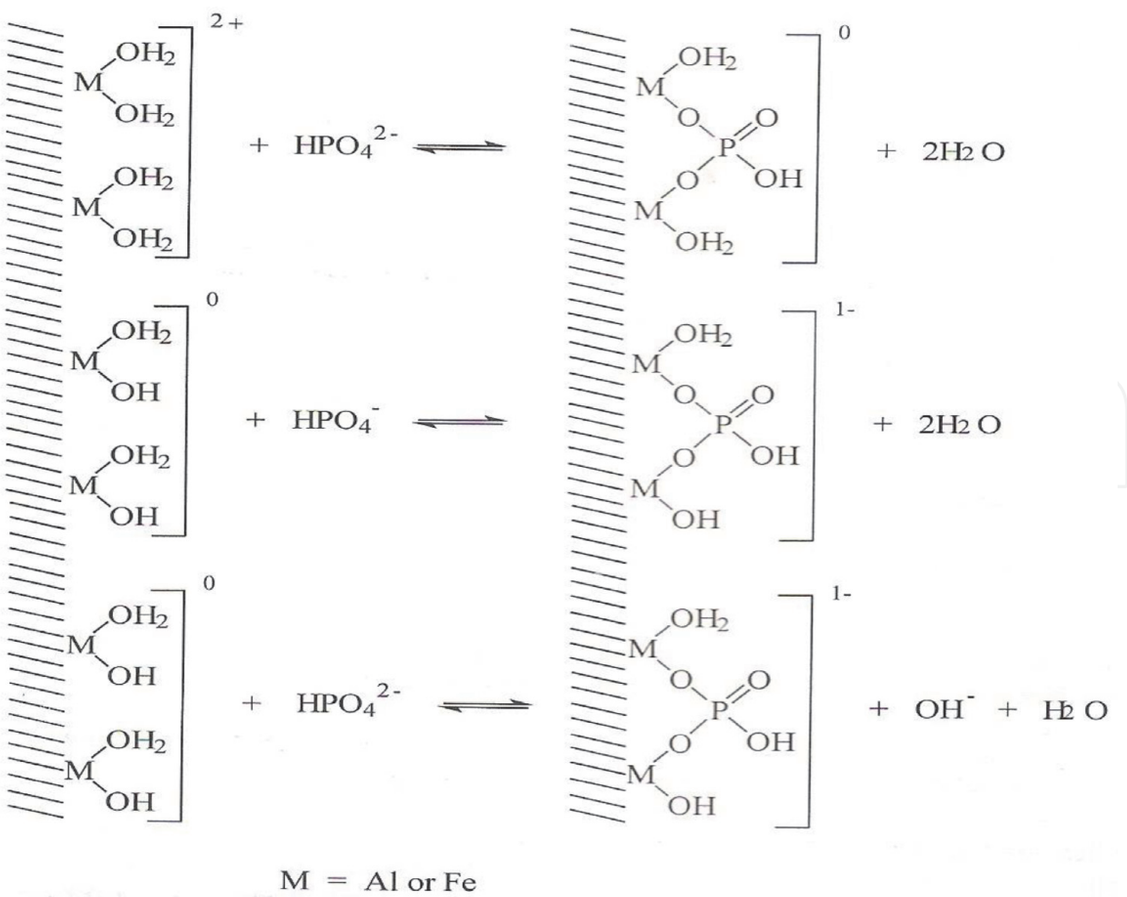


Figure 2.
Examples of phosphate adsorption mechanisms. Source: Syers and Cornforth [17].

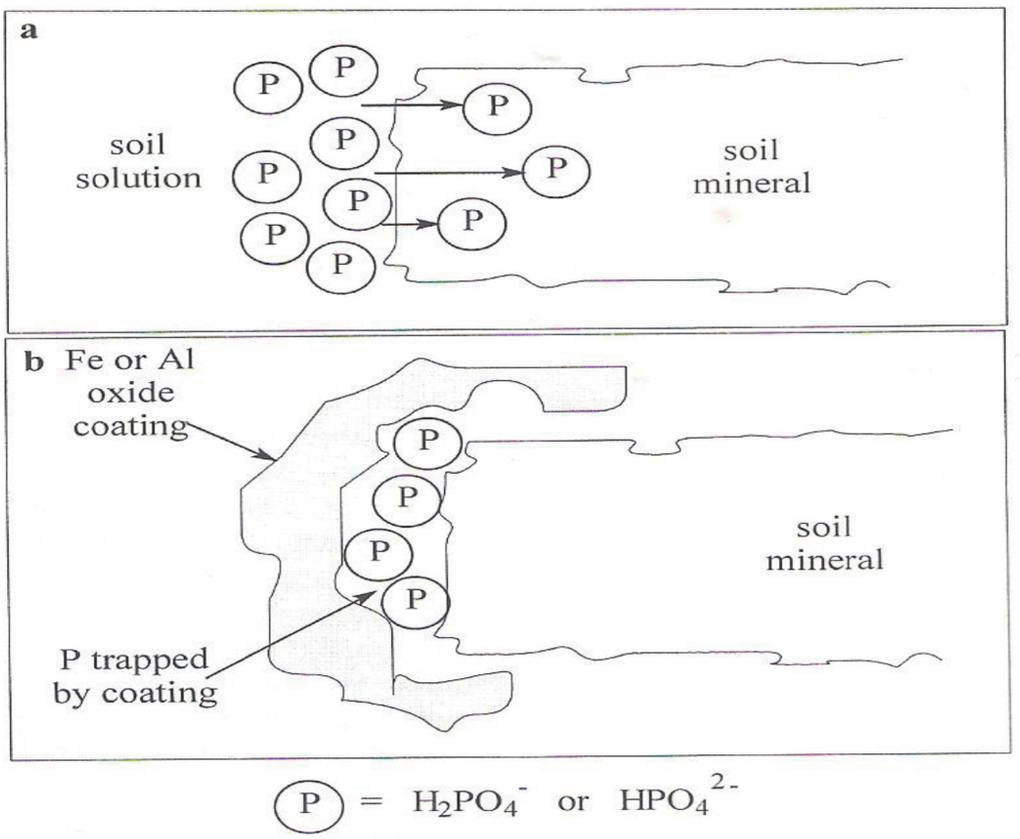


Figure 3.
The inner sphere formation of P in soil minerals (a) and the subsequent occlusion of adsorbed P (b). Source: Syers and Cornforth [17].

The precise nature of these reactions depends on pH which influences the proportions of hydroxyl (OH^-) and OH_2^+ groups on the solid surface and hence its surface charge.

If the adsorbed phosphate ions then diffuse into the solid, then they are "absorbed". Sorption covers the combined processes. Adsorbed phosphate may become trapped on the surface of soil minerals if any Fe or Al oxide coating is precipitated on the mineral. The trapped phosphate is then described as occluded (**Figures 2** and **3**).

3. Factors affecting phosphate adsorption in soils

3.1 Time

Adsorption of phosphate by soils increases with increasing reaction time, first rapidly and then slowly, but without reaching a true equilibrium [18]. Increasing phosphate concentration increases with the equilibrium time.

The slow reaction of phosphate with oxides has been attributed to formation of iron phosphate, with a surface coating on the oxides [19]. The porous structure often observed in goethite may similarly not only account for slow phosphate adsorption but also for slow desorption and thus irreversibility [20]. Accordingly, adsorption of phosphate by well crystallised goethite having few pores was complete after 3 days and remained constant up to 260 days [21]. According to Schwertmann [22], aluminium substituted goethite crystals are generally smaller and less porous than non-substituted goethite crystals therefore the former should adsorb phosphate faster and reach equilibrium faster than the latter. Furthermore,

self-aggregation (clustering) and porosity seem to be important factors in controlling adsorption/desorption (irreversibility) of phosphate by iron oxides and thus by soils. Formation of iron phosphate coatings has, however, been rejected by others [9], who considered migration (diffusion) of phosphate into aggregated iron oxides, particularly ferrihydrite, to cause the slow reaction.

3.2 Soil pH

Several investigations have shown the effect of pH on phosphate adsorption by soil and synthetic iron oxides [6, 23]. The pH effect on soil iron oxide adsorption seems to be less pronounced than on pure iron oxide adsorption. According to Borggaard [24], pH affects phosphate adsorption but the effect is limited for adsorption by soils in the pH range 4–8 in contrast to adsorption by pure iron oxides. For soils, increasing pH has been shown to either increase or decrease and to have no effect on phosphate adsorption [25]. Nwoke et al. [26] found that sorption of P decreased with increasing soil pH and this was attributed to increased negative charge on variable-charge colloids which cause electrostatic repulsion of the ionic P species from the surface. In contrast, Agbenin and Mokwunye [27, 28] reported an increase in sorption with increasing pH for some savannah soils. Agbenin [27] attributed this trend to the chemistry and retention of Ca^{2+}, the predominant cation in savannah soils. Nevertheless, the pH effect on phosphate adsorption should not be exaggerated, since this effect is fairly small, particularly, over the pH range covering most soils, and ancillary effects may therefore appear relatively important [29].

3.3 Organic matter

Organic matter may affect phosphate adsorption in two ways: Indirectly by inhibiting iron oxide crystallisation and directly by competing for adsorption sites [24]. Dissolved organic matter (fulvic and humic acids) has been shown to decrease phosphate adsorption by iron oxides and by soils, particularly at acid pH, indicating that dissolved organic matter can compete with phosphate for adsorption sites [30]. In the study by Sibanda [30], organic matter which was isolated from soils as humic and fulvic acids, was added in solution, and the background electrolyte was sodium chloride. Of seven naturally occurring organic compounds tested, only phytic acid reduced soil phosphate adsorption significantly [31].

In contrast, the results of the study of influence of organic matter on phosphate adsorption by aluminium and iron oxides in sandy soils clearly showed that organic matter has no direct influence on adsorption of phosphate by these soils [24]. According to these workers, the phosphate adsorption capacity changes with the amount of extractable aluminium and iron, irrespective of the organic matter content; even removal of the organic matter does not alter phosphate adsorption. In the study mentioned, there was no addition of organic matter, and calcium acetate was used as background electrolyte. Calcium flocculates organic matter, while sodium tends to disperse it. The interpretation of the results, therefore, could be that to act as a competitor, organic matter must be in solution; otherwise it has no direct effect on phosphate adsorption. In limed soils and in many cultivated soils the concentration of dissolved organic matter is considered to be very low. Interactions are known to occur between organic matter and the aluminium and iron oxides inhibiting their crystallisation, and thereby increasing their phosphate adsorption capacity [22, 32]. Soil organic matter, can indirectly affect soil phosphate adsorption capacity (PAC) by retarding crystal growth of poorly crystalline aluminium and iron oxides, which because of high specific surface areas have very high PACs [33, 34].

Iron oxides and probably also aluminium adsorb phosphate and other anions of weak acids, including organic matter, by ligand exchange. Factors which affect the development of aluminium and iron oxides crystals (crystallisation) may influence adsorption, due to a change in the specific surface area of the adsorbent. In soils, organic matter acts as a factor [32], although its effects are complicated and it appears to affect aluminium and iron differently.

The formation of crystalline iron oxides may be inhibited in the presence of certain organic acids, and the ratio of poorly crystalline to well-crystallised forms (or Fe_{ox}: Fe_{dcb}) increases as the soil organic matter content increases [22]. However, the interaction between organic matter and iron seems weak. Borggaard [24] found that although most Fe_{ox}:Fe_{dcb} ratios were rather high in some Danish sandy soils, the correlation between Fe_{ox}:Fe_{dcb} and organic matter was not significant which suggests that there is no inhibition of adsorption sites for phosphate. Also they found that the crystallinity of the aluminium oxides seems very poor, in as much as extractable Al_{ox} was similar to Al_{dcb} probably because of strong interaction between aluminium and organic matter. Hydrogen peroxide – treated soil, to remove organic matter, did not change amounts of phosphate adsorbed which strongly suggests that, organic matter affects phosphate adsorption indirectly by decreasing aluminium oxide crystallinity, but not directly by competing for adsorption sites.

Aluminium oxides are found to be more effective adsorbents of phosphate than are the iron oxides [24]. On per mole basis oxalate extractable aluminium oxides (Al_{ox}) adsorb nearly twice as much phosphate as oxalate-extractable iron oxides. This may be due to poorer crystallinity (higher specific surface area) of the aluminium oxides compared to the iron oxides and also to, a higher charge on the former [35]. For synthetic oxides, the amounts of phosphate adsorbed per m^2 seem to be higher for aluminium oxides than for iron oxides, although the trend is weak [35]. This suggests that differences in crystallinity are the main reason for the observed differences in adsorption capacity [24]. This may explain, at least partly, the observed positive correlations between phosphate adsorption capacity and organic matter content.

3.4 Phosphate sorption as a function of the iron and aluminium oxides of soils

The reactivity of Al and Fe oxides is determined by the conditions under which the soil is formed. Thus, under cold, humid and nutrient-poor conditions, which result in organic matter accumulation, poorly crystalline oxides of small particle size are favoured, while under well-aerated tropical conditions larger, more well developed crystals are formed [7, 36]. Since the reactivity depends on the specific surface areas the poorly crystalline Al and Fe oxides with smallest particle size will be the most reactive.

On the basis of laboratory measurements of P sorption, Borggaard [24] found that the P sorption capacity of some Danish Spodosol or Spodosol-like samples was a function of amorphous Al and Fe and crystalline iron. For 43 samples from Canadian Spodosols, the P sorption capacity was, however, found to be a linear function of the sum of amorphous Al and Fe but independent of the crystalline Fe oxides [37]. A similar relationship was found for some German soils [11]. According to these workers, the total P sorption measured was predominantly related to amounts of amorphous Fe and Al. Similarly, Van der Zee [38] reported that P sorption in different acid soils from Netherlands was linearly related to the sum of oxalate-extractable Fe and Al of the soils. For some tropical and subtropical soils, Loganathan [39] found that P sorption was positively correlated with the contents of amorphous Fe and Al. In Ghana, a study of P sorption in relation to Al and Fe oxides of Oxisols by Owusu-Benoah et al. [40] indicated that the P sorption capacity

(Pmax) of the soils significantly correlated with oxalate extractable Fe and Al but not with crystalline Fe and Al.

On the contrary, Pena and Torrent [41] described P sorption in Mediterranean soils as being strongly affected by crystalline Fe. Crystalline Fe oxides were also reported to be the most important P sorption compounds in some Spanish clay samples [18] and of great importance for the P sorption in some strongly weathered, tropical soil samples from Australia [42]. However, Pmax of 97 soil samples of some South-Western Australian soils was closely related to crystalline Al while amorphous and crystalline extractable Fe gave low or no relationship [43].

4. Adsorption isotherms

When an adsorbent (a soil sample or a soil component) is shaken with a solution containing an adsorbate, the amount of adsorbate adsorbed by the adsorbent depends on the experimental conditions including adsorbate concentration, adsorbate:adsorbent ratio, pH, shaking time and temperature. At fixed adsorbate:adsorbent ratio, pH, shaking time and temperature, the amount adsorbed adsorbate, q, increases at increasing adsorbate concentration, C_{eq} following a curve (isotherm) like that in **Figure 4**. C_{eq} denote the equilibrium concentration of the adsorbate, i.e. the initial concentration less adsorbed adsorbate.

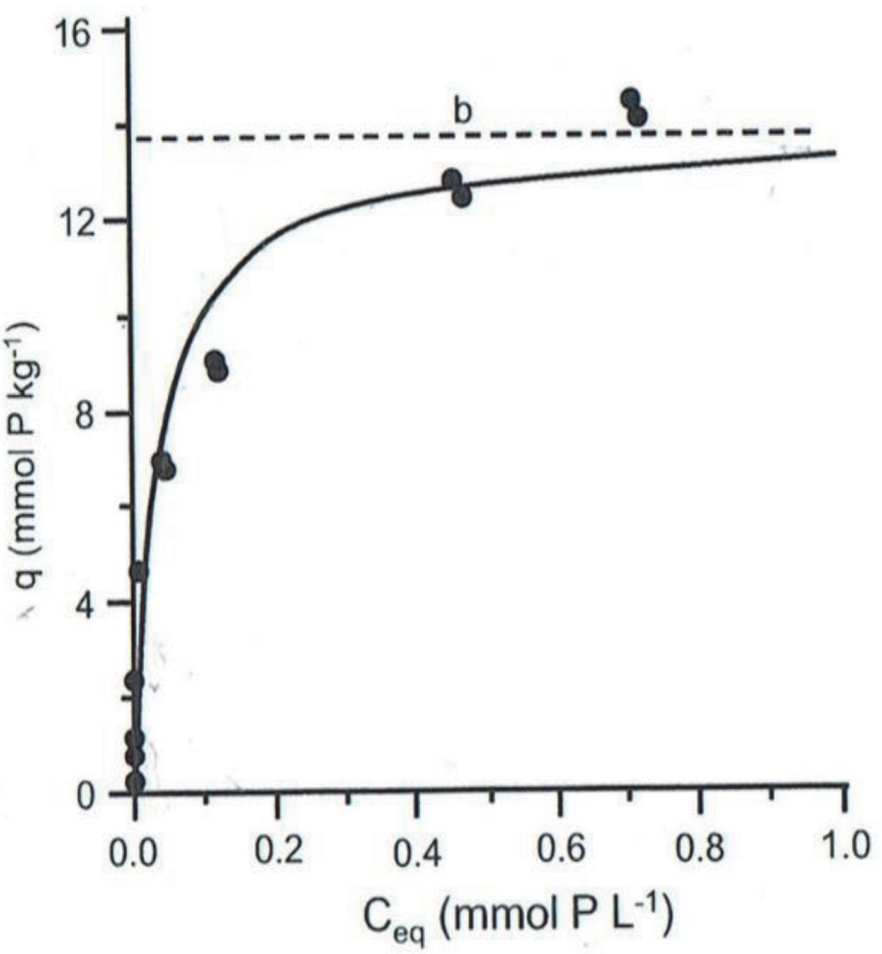


Figure 4.
A plot of adsorbed phosphate, q, against the equilibrium phosphate concentration, C_{eq}. The adsorbent is a sample from the A horizon of an Oxisol (Typic Hapludalf) from Ghana. The curve is fitted to the experimental points (dots) by the Langmuir equation (Eq. 1) the dashed line (b) indicates the adsorption maximum (modified) from Owusu-Bennoah et al. [40].

An isotherm like that shown in **Figure 4**, which is a L-curve isotherm because it can be fitted by the Langmuir equation (see subsequent Eq. 1), is often seen, particularly when soil is the adsorbent. In some cases an extreme version of the L-curve isotherm is seen; the H-curve isotherm, where q increases sharply for a small increase in C_{eq} until q achieves an upper value, where upon q is virtually independent of C_{eq}. The initial very high slope of the H-curve isotherm indicates a very high affinity (hence the designation H for high) between adsorbate adsorbent On the other hand, if q is proportional to C_{eq}, a straight-line isotherm is obtained. It can be noticed that a straight line or almost straight line relation between q and C_{eq} can also be obtained if only an initial small part of the curve in **Figure 1** is included in the plot, e.g. the part of the curve where $C_{eq} < 0.05$ mM. Adsorption of organic compounds such as most pesticides by soil organic matter-containing soil often follows a straight line. For straight line adsorption, the adsorbate-adsorbent affinity is independent of the amount adsorbed, in contrast to the initially very high and then deceasing affinity for adsorptions following the L-and H-curves.

4.1 Phosphorus sorption isotherms and equations

The relationship between the amounts of P sorbed per unit weight of soil (q) and the equilibrium P concentration in solution (C) bathing the soil at a constant temperature has been described by several sorption isotherms. The main motivations for describing curves were to (1) identify the soil constituents involved in the sorption [39], (2) predict the amount of fertiliser needs of soils to meet the demand of plant uptake for optimum yield and (3) study the nature of the sorption process to learn more about the mechanism of the process [25].

The Langmuir, Freundlich and Temkin equations are common models for describing P sorption when input data are limited [44].

4.1.1 Langmuir equation

Langmuir equation may be written as:

$$q = \frac{b\,KC_{eq}}{1 + K\,C_{eq}} \tag{1}$$

where b and K are fitting parameters. The parameter b represents the value of q that is approached asymptotically as C_{eq} becomes arbitrarily large. Accordingly b has been taken as a measure of maximum adsorption, the upper limit of adsorbate that can be adsorbed by the adsorbent. The b parameter is, therefore, commonly used in comparison of soils and soil components. K determines the initial slope of the isotherm and has sometimes been considered a measure of the affinity of the adsorbate and the adsorbent; a binding constant. By rearrangement, Eq. (1) can be expressed in linear forms such as:

$$\frac{Ceq}{q} = \frac{Ceq}{b} + \frac{1}{bK} \tag{2}$$

Eq. (2) which is the linearized form of Eq. (1) is often used to estimate the adsorption (b), affinity index (k) and buffer capacity of soils. The straight line resulting from plotting C_{eq}/q against C_{eq} will have slope equal to 1/b and an intercept equal to 1/(bk).

4.1.2 Freundlich equation

Freundlich equation has the form:

$$q = aC_{eq}b \tag{3}$$

where a and b are fitting parameters. The linearized form of the equation is

$$\log\ q = \log\ a + b\ \log\ C_{eq}$$

A plot of log q against log C_{eq} result in a straight line with slope equal to b and an intercept equal to log a.

4.1.3 Temkin equation

Temkin equation is in the form:

$$\frac{x}{b} = \frac{RT}{B} \ln\ ACeq \tag{4}$$

where x is the amount of P adsorbed, and A and B are the Temkin isotherm constants. A represents the equilibrium binding constant ($dm^3\ g^{-1}$). R is the universal gas constant.

The linearized form of the equation is

$$x = a + b\ \ln\ C_{eq} \tag{5}$$

where a and b are constants obtained from the intercept (a) and the slope (b). Eq. (5) indicates that a plot of x against ln C should yield a straight line but such plots for soils in many cases yielded curves rather than straight lines The b value of Temkin equation is taken as the P buffering capacity (retention capacity of adsorbed P) of soils (ug P g^{-1}).

4.2 Pedotransfer functions (PTFs) for estimation of phosphate adsorption capacity

Apart from the solution concentration, the amount of phosphate to be adsorbed depends on phosphate loading (content) and the content and reactivity of phosphate adsorbents, such as aluminium and iron oxides in sandy soils [24]. The maximum phosphate adsorption capacity (Pmax), corresponding to adsorption at high (infinite) phosphate concentrations, can be calculated by applying the Langmuir adsorption equation to the measured data. The limitation of the Langmuir equation is indicated by the deviation of points corresponding to the highest equilibrium of P concentration. Langmuir equation is restricted to a limited concentration range [45, 46].

Again, due to the discrepancies of phosphate adsorption in relation to aluminium and iron oxides in different soils, various models have been proposed for predicting P sorption [18, 24].

Aluminium and iron oxides are the main phosphate adsorbent in soils, especially in Spodosols and other sandy soils [15, 47]. Accordingly, close relationships have been found between amounts of adsorbed phosphate of some forms of soil aluminium and iron, which have resulted in creation of pedotransfer functions for predicting adsorbed phosphate from aluminium and iron oxide contents quantified

by selective extractions. Thus, for a range of soils, which have received high amounts of fertiliser P, phosphate adsorption (in mmol kg^{-1}) was found to be well predicted by the simple pedotransfer function of Van der Zee and Riemsdijk [48]:

$$P_{adsorbed} = \alpha \times (Al_{ox} + Fe_{ox}) \quad (6)$$

Where Al_{ox} and Fe_{ox} are the soil contents of aluminium and iron (mmol kg^{-1}) that can be extracted by means of the oxalate method [49]. The fitting constant was found to be between 0.14 and 0.48, depending on phosphate concentration and equilibrium time in the adsorption experiments [50]. With α = 0.5, this pedotransfer function is commonly used for estimating phosphate adsorption capacity in phosphate pollution assessment.

For strongly weathered soils enriched in Al and Fe oxides with different degree of ordering, a model that is able to account for different oxide fractions such as that of [24] will be a logical choice. This model was based on studies of Danish sandy soils (Spodosols and podzolised Entisols) low in adsorbed phosphate. Therefore, the phosphate adsorption maximum may be calculated from the content of poorly crystalline aluminium and iron oxides (Al_{OX}, Fe_{OX}) and well crystallised iron oxides (Fe_{CBD} - Fe_{OX}) according to the equation [24]:

$$\begin{aligned} P_{calc} = {} & (0.22 \pm 0.02)\ \text{x}\ Al_{OX} + (0.12 \pm 0.02)\ \text{x}\ Fe_{OX} \\ & + (0.04 \pm 0.03)\ (Fe_{CBD} - Fe_{OX}) + (0.3 \pm 0.5) \end{aligned} \quad (7)$$

Where Al_{OX} and Fe_{OX} denote oxalate extractable aluminium and iron and Fe_{CBD} is citrate-bicarbonate-dithionite extractable iron. Phosphate adsorption maximum calculated using the pedotransfer model of [24] (P_{calc}), $Al_{OX,}$ $Fe_{OX,}$ and Fe_{CBD} are in mmol kg^{-1}. According to the function, 0.22 mmol P is adsorbed by 1 mmol Al_{OX} kg^{-1}, 0.12 mmol P is adsorbed by 1 mmol Fe_{OX} kg^{-1} and 0.04 mmol P is adsorbed by 1 mmol (Fe_{CBD} - Fe_{OX}) kg^{-1}. On a per mole basis the aluminium oxides (Al_{OX}) adsorb nearly twice as much phosphate as the oxalate-extractable iron oxides. This may be caused by poorer crystallinity (higher specific surface area) of the aluminium oxides compared to the iron oxides, but it could also be attributed to a higher charge on the former [24].

Apart from other coefficients to $Al_{OX,}$ and Fe_{OX}, the main difference between the two pedotransfer functions is that the function of [24] accounts for crystalline (Fe_{CBD} - Fe_{OX}) as well as amorphous iron (Fe_{OX}) and aluminium (Al_{OX}), while only amorphous oxides are considered by Van der Zee [38]. According to Szilas et al. [51], amorphous aluminium and iron oxides are undoubtedly the dominating phosphate adsorbents, especially on heavily fertilised non-calcareous soils and sandy soils of humid temperate regions such as parts of Canada and Western Europe. However, crystalline iron oxides corresponding to (Fe_{CBD} - Fe_{OX}) can be important phosphate adsorbents in more tropical upland soils and some clayey soils of drier climates [24]. Therefore, application of the pedotransfer function of [38] should be restricted to temperate, non-calcareous soils as pointed out by [11], while the pedotransfer function of [24] is expected to have a wider application range.

The pedotransfer function of [24] was, however, found to overestimate PAC of Ghanaian and Tanzanian soils (mainly Oxisols and Ultisols) enriched in well-crystallised iron oxides corresponding to (Fe_{CBD} - Fe_{OX}) [47]. This is because the coefficient (0.04) to the term (Fe_{CBD} - Fe_{OX}) was found to be too high. In fact, this coefficient is very uncertain and insignificant as is the intercept, whereas the $Al_{OX,}$ and Fe_{OX} coefficients were highly significant [24].

In order to widen its applicability, the following linear expression was used with data from a wide range of soils including Danish Entisols, Inceptisols, and Spodosols [24]

together with strongly developed Ghanaian and Tanzanian Alfisols, Inceptisols, Oxisols, and Ultisols [7]:

$$P_{calc} = x\ Al_{OX} + \beta\ x\ Fe_{OX} + \gamma\ x\ (Fe_{CBD} - Fe_{OX}) \quad (8)$$

The regression analysis resulted in the following pedotransfer function with P_{calc} Al_{OX}, Fe_{OX}, and Fe_{CBD} in mmol kg^{-1}:

Where x β γ are the coefficient of Al_{OX}, Fe_{OX} and Fe_{CBD} - Fe_{OX} respectively.

$$P_{calc} = (0.22 \pm 0.03)\ x\ Al_{OX} + (0.12 \pm 0.03)\ x\ Fe_{OX} + (0.02 \pm 0.01)\ (Fe_{CBD} - Fe_{OX}) \quad (9)$$

The three parameters were found to be significant at 0.1% level [47]. The calculated PAC was plotted against experimentally determined values of the phosphate adsorption isotherms based on phosphate adsorption data. The linear regression line for this plot has R^2 = 0.87, indicating that 87% of the variation in PAC of the soils is accounted for by oxalate-extractable aluminium and iron together with dithionite-citrate-bicarbonate-extractable iron. Furthermore, the slope of the regression line is indistinguishable from 1, and the intercept is 0 [47].

4.2.1 Predictability of the PTF of Borggaard et al.

The PTF of Borggaard [24] has been tested on a wide range of soils. Soil samples were from Denmark, Canada, Ghana and Tanzania representing non calcareous Alfisols, Entisols, Histosols, Inceptisols, Mollisols, Oxisols, Spodosols and Ultisols. While the Danish soils covered several soil groups, the Ghanaian and Tanzanian soils were restricted to strongly weathered soils, mainly Acrisols and Ferralsols and the Canadian soils were Podzols. Despite the great variability of the soil samples, the investigation clearly demonstrated the very close relationship between phosphate adsorption capacity (PAC) and contents of Al and Fe oxides, and hence the fairly good predictability of PAC by means of Al and Fe oxide-based PTF [47]. This was in general agreement with results of previous studies carried out, however, on fewer and considerably less different soil samples [11, 24].

In Ghana, Owusu-Benoah et al. [40] evaluated P sorption characteristics of the ploughed layer of six natural Ghanaian Oxisols. Except for one soil in which phosphate adsorption capacity calculated (Pcalc.) using the PTF was more than twice that for phosphate adsorption capacity (Pmax) determined from the Langmuir's adsorption isotherm, measured (P_{max}) and modelled (Pcalc) P sorption capacities were in fair agreement.

Further testing of this PTF was performed by data from two Tanzanian Andisols. The results demonstrated, however, that PAC of these soils is substantially overestimated by the function. The poor predictability of PAC of soils developed on volcanic materials compared to that of the other soils is probably due to differences of the main phosphate adsorbents. While poorly crystalline aluminium silicates (allophane and imogolite) with very high specific surface area, and hence, PAC can dominate phosphate adsorbents in Andisols, the other soils adsorb most phosphate onto more or less crystallised aluminium and iron oxides [7, 8]. Consequently, the pedotransfer function Pcalc = 0.22 x Al_{OX} + 0.12 x Fe_{OX} + 0.02 x (Fe_{CBD} - Fe_{OX}) is not recommended to be used for PAC estimation of Andisols. Hopefully, future testing will more precisely delineate the kinds of soils in which the suggested PTF can be used as well as those in which it would give unacceptable PAC estimates.

5. Conclusion

Phosphorus adsorption in soils account for the low P availability for plant uptake.

The Langmuir, Freundlich and Temkin equations are common models for describing P sorption when input data are limited.

The review indicated that, in acid soils amorphous Al and Fe oxides compounds are the important factors that determine the soils' capacity to retain P.

For strongly weathered soils enriched in Fe and Al oxides, with different degree of ordering, a model that is able to account for the different oxide fractions and which can be used to predict the adsorption P capacity of these soils is the pedotransfer model of Borggard et al. [7].

However in alkaline soils, calcium carbonate may determine the amount of P sorbed by the soils.

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