

Short-Range-Order Minerals and Dominant Accessory Properties Controlling P Sorption in Tropical Tephra Soils of the Cameroon Volcanic Line

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Abstract

Knowledge on soil properties likely to influence P sorption in tephra soils is very important for sustainable management of available P. Sorption studies on six tephra soils were conducted to relate P sorption to soil characteristics in order to identify those with potential influence on P sorption. Four equilibrium-based sorption models commonly encountered in soil studies (Langmuir, Freundlich, Temkin, and Van Huay) were used to describe P sorption in the soils. P sorption was determined by measuring the residual P content of a clarified equilibrating solution of 0.02 N KCl containing varying concentrations (0, 5, 10, 15, 30, 40, 50, 60, 80, and 100 mg/L) of P as KH₂PO₄ after mixing with 1 g of soil in duplicates for 16 hours at 25°C. Maximum amount of P sorbed for the varying P concentrations used ranged from 2080 to 5402 mg/kg with a potential for greater P sorption maxima at higher P solution concentrations. P sorption in these soils was best described by the Langmuir and Freundlich models. Allophane and ferrihydrite are the principal species controlling the high P sorption in these soils. pH-NaF proved to be a potentially reliable test for assessing the presence of allophanic materials and thus for estimating P sorbed. This work would guide both effective and efficient P fertilizer management with economic implications for both the study area and similar environments.

Keywords

Allophane, Ferrihydrite, Mount Kupe, Mount Manengouba, Sorption Isotherms

1. Introduction

Adsorption is the accumulation of a substance at an interface between the solid surface and the bathing solution [1]. It is one of the most important processes in soils that affect transport of nutrients and contaminants as it determines the quantity of crop nutrients, metals, pesticides, and other organic chemicals retained on soil surfaces [1]. Phosphorous is a major element which plays a fundamental role in agronomy and biogeochemical cycles, but is unfortunately not very abundant in soils [2]. Phosphorous is capable of forming innumerable covalent organo-phosphorous compounds and to bind to C, N, O, Al, Fe, and Ca.

In tephra soils characterized by high organic matter contents and allophanic minerals, this element can become very unavailable as it is easily adsorbed by the latter. Tephra soils, or better still soils with andic soil properties are usually classified as variable charge soils with unique properties that make them respond in a particular manner to different management [3]. These soils are known to have a high P-retention capacity thereby posing a problem of P deficiency for crop production; thus requiring heavy applications of P fertilizers [4]. However, despite the acidic nature of some volcanic soils, such as the Bokwango Andosols on the slopes of Mt. Fako in Cameroon, with pH-H₂O ranging between 4.9 and 5.5, at which high concentrations of exchangeable aluminium (0.1 - 0.3 meg/100 g)soil) were observed [5] and susceptible to fix phosphorus, crops like cocoyams (Colocascia esculenta) and plantains (Musa spp.) still perform well with very good yields. The mechanism which enables these soils to continue to produce very well despite their acidic nature and hence the high P sorption of such soils has been puzzling, requiring in-depth studies. P sorption is known to be mostly associated with Fe and Al oxides, extractable Ca and Mg, pH, soil texture, and carbon content [6]. This phosphorus adsorption depends on many factors such as concentration, crystallinity, specific surface area, and the configuration and concentration of hydroxyl groups on the surface of iron oxides, which in turn are affected by the formation route, parent material, degree of weathering, soil solution composition, drainage conditions and pH [7]. In P sorption experimental studies, an adsorptive solution of a known composition and volume is equilibrated with a known amount of adsorbent at a constant temperature and pressure for a period of time such that equilibrium (adsorption reaches a steady state or no longer changes after a period of time) is attained [1]. This can be achieved following a variety of methods. One common and easiest method usually employed in studying P sorption in soils is the batch method [8]. In this method, the solid or adsorbent (soil) is shaken in the solution or adsorbate (e.g., KH₂PO₄ solution) until the adsorption equilibrium is reached, after which the remaining solute concentration is measured. However, this method has numerous disadvantages. For example, the solid/solution ratio is often too high or too low compared to the natural conditions in soils [8]. This is one among many factors that render P sorption studies very challenging and so most often limited to qualitative rather than quantitative appreciation.

In this study, P sorption was conducted on six representative tephra soils (five Andosols and one aluandic Cambisol) using four sorption models commonly applied in soil P sorption studies [9] [10] [11] [12] with the aim of comparing these models and identifying soil characteristics likely to influence proper P sorption assessment. The effectiveness of these models in describing P sorption as observed in prior investigations [1] dictated their choice.

2. Materials and Methods

2.1. Description of Study Area (Geological and Environmental Setting)

The study area covers two massifs in the south-west region of Cameroon; Mts. Kupe and Manengouba (Figure 1).

Morphologically and geologically, the Kupe massif consists of two very different parts: a syenitic horst on the one hand, and a basaltic cover on the other [13], which are the sites of many recent monogenic volcanoes [14]. The lavas



Figure 1. (a) Topographic map of study area showing sampling sites; (b) Cameroon map showing study area; (c) Africa map showing location of Cameroon.

that cover the area and especially the ashes spread over the greater part of the mountain are believed to have resulted from these craters [13].

On the slopes and foot of Mt. Kupe lie many small cones of ash and lapilli, ranging between 50 and 150 m in height. The proportion of pyroclastic products (blocks, bombs, lapilli and ashes, with many syenite and gneiss enclaves) is much higher than that of the lavas. These pyroclastics are of Quaternary origin [14].

Previous studies by [15] showed that most of the soils, especially those located on the western slopes of Mt. Kupe, are of two Reference Soil Groups; Andosols and Cambisols with dominant parent materials being pyroclastics (mainly block and lapilli tephra).

The soils are generally stratified and present erratic variations in most of the physico-chemical properties. Mean annual rainfall around Mt. Kupe stands at 3096 mm, while mean annual temperature and relative humidity stand at 25°C and 86%, respectively.

The Manengouba massif is of volcanic origin and harbours Mt. Manengouba (2396m). Its volcanic story is related to four chronological stages: 1) forming of the early Manengouba shield volcano between 1.55 and 0.94 Ma; 2) building of the Eboga strato-cone between 0.94 and 0.89 Ma; 3) caldera collapse and silicic extrusions of the Elengoum Complex between 0.89 and 0.70 Ma; and 4) intra-caldera and flank activity between 0.45 and 0.11 Ma [16]. The volcanic rocks are attributed to two magmatic events. The first and main magma emitted produced the shield volcano, the strato-cone, and the syn- to post-caldera extrusions, displaying a complete series from basanites to trachytes (magmatic Group 1). The second magma emitted, is limited to the late and flank activity and evolved from basanites to trachy- phonolite materials. Both magmatic groups belong to the under-saturated alkaline sodic series [16].

The climate on Mt. Manengouba and environs is equatorial, with heavy rainfall fairly well distributed throughout the year. Mean annual rainfall is 2316 mm, while mean annual temperature and relative humidity are 20.3°C and 84%, respectively.

Six sites, representative of the study area were selected for the study. On Mt. Manengouba, dominated by grassland vegetation, two sites were selected on old (P1) and more recent (P2) volcanic ejecta. At the foot of Mt. Manengouba, dominated by forest vegetation on the old basement, a third profile was identified (P3). This site is situated on a more stable geomorphic surface subject to higher water infiltration and thus more intense weathering. It constitutes an older tephra flow parent material which has not been influenced by the recent flows of sites 1 and 2.

On Mt. Kupe, dominated by forest vegetation, three profiles were selected following a toposequence at altitudes of 1030 (P5) m, 583 m (P4) and 465 m (P6). The characteristics of the sites are summarized in **Table 1**. The soil profiles were described following the FAO recommendations [17]. Soil samples were collected per horizon and stored in polythene bags. Samples for bulk density were collected in duplicates to evaluate the consistency of analytical results in order to minimize measurement errors.

Profile number (site)	Location	Land use/Vegetation	Physiography	Relief/ Elevation (m)	Parent material	Classification (IUSS Working Group WRB, 2015)
Profile 1 Lake Manengouba series.	Lat. 5°02'14.6"N, Long. 9°49'34.4"E	Herbaceous (short grassland vegetation) with patches of shrubs. Dominant grass species is the "cow grass".	25% - 30% (Moderately steep). General gradient into the lake is very steep (60% - 70%) marked by intermediate V-shaped valleys. Good internal and external drainage. Signs of geologic erosion (slight).	Highland 1964	Block tephra	Eutric silandic Andosol (colluvic, loamic)
Profile 2 Top of the rim of the first caldera (external caldera) on Mount Manengouba.	Lat. 5°02'44.1"N, Long. 9°48'53.4"E	Herbaceous and shrubs. Grassland vegetation with "cow grass" as dominant species. Touristic site, sightseeing, grazing land for cattle.	Highland, undulating landscape with varying slopes from 0% - 1% (flat to nearly level) to about 70% (very steep) slopes. Rim of caldera composed of intermittent hills and valleys, and micro-relief of beds about 2 × 2 m in size.	Highland 1935	Lapilli tephra	Eutric skeletic silandic Andosol (fragic, hyperhumic, loamic)
Profile 3 Bangem series, cultivated farmland	Lat. 5°05'27.7"N, Long. 9°45'58.5"E	Farmland used for cultivation of coffee (Coffea spp.), plantain and banana (Musa spp.), plum (Dacryodes edulis), African oil palm (Elaeis guineensis), taro (Colocascia esculenta) and cassava (Manihot esculenta).	Mountainous and undulating landscape, 10% - 15% slope (Strongly sloping).	Highland 1155	Block tephra	Dystric aluandic Cambisol (humic, loamic, tephric)
Profile 4 Kupe series (at foot of mount Kupe)	Lat. 4°45'05.4"N, Long. 9°41'32.1"E	Cultivated farmland: Cocoa (Theobroma cacao) farm with presence of the African oil palm (Elaeis guineensis), cocoyam (Colocasia esculenta), plum (Dacryodes edulis), variety of herbs, and some forest tree species.	Mountainous and undulating landscape. 10% - 15% slope (Strongly sloping). Good drainage, no signs of erosion.	Graben 583	Block and lapilli tephra	Eutric skeletic silandic Andosol (fragic, loamic)
Profile 5 Essossong series, virgin forest	Lat. 4°51'25.0"N, Long. 9°43'32.3"E	Montane forest with a variety of forest trees, marantaceae, herbs, etc.	Mountainous and undulating landscape. Good drainage. No signs of erosion. 10% - 15% slope (strongly sloping).	Highland 1030	Block and lapilli tephra	Eutric Akroskeletic silandic Andosol (colluvic, hyperhumic, loamic)
Profile 6 Loum forest reserve	Lat. 4°43'53.2"N, Long. 9°42'06.2"E	Protected forest. Variety of forest trees. Protected forest under exploitation for farming.	Undulating lowland with patches of rock outcrops, 15% - 20% slope (moderately steep).	Graben 465	Block and lapilli tephra	Eutric silandic Andosol (colluvic, loamic).

Table 1. Summary of site characteristics harboring the six soil profiles.

2.2. Laboratory Methods

Soil samples were air-dried, crushed and sieved on a 2 mm sieve. The < 2 mm fractions were used for the analyses.

Soil physico-chemical analyses were conducted following standard methods. Soil organic carbon (OC) content was determined following the Walkley and Black method with prior determination of a recovery factor, while OM was obtained from the equation $OM = OC \times 1.724$ (based on the recovery factor) [18]. Bulk density (BD) was determined in duplicates as the oven dry ($105^{\circ}C$) mass of each undisturbed core sample per unit volume [19]. A 1:2.5 soil-H₂O and 1:2.5 soil-KCl solutions were used for pH-H₂O and pH-KCl determinations, respectively. pH-NaF was determined after agitating 1 g of soil in 50 ml of 1 N NaF for two minutes. Texture was determined by the pipette method [19]. Acid ammonium oxalate extractable (Al_o, Fe_o, Si_o and Mn_o), dithionite citrate bicarbonate (DCB) extractable (Al_d, Fe_d, Si_d, and Mn_d), and pyrophosphate extractable (Al_p) were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES).

Calculation of the allophane content was done according to the method of [20] as follows:

$$\%$$
 allophane = $\%$ Si \times (100/y)

where *y* is the % Si in allophane, calculated using the equation y = 23.4 - 5.1x, where $x = (Al_o - Al_p)/Si_o$ atomic ratio.

Calculation of the ferrihydrite content was done using the equation of [21] as follows:

% ferrihydrite =
$$1.7 \times \text{Fe}_{o}$$

The subscripts $_{o}$ and $_{p}$ in the equations above represent oxalate and pyrophosphate extractions, respectively.

Phosphorus sorption was conducted following the procedures according to [22]. The P sorption was determined by measuring the residual P content of a clarified equilibrating solution of 0.02 N KCl (to maintain the ionic strength) containing varying concentrations (0, 5, 10, 15, 30, 40, 50, 60, 80, and 100 mg/L) of P as KH₂PO₄ after mixing with 1 g of soil in duplicates for 16 hours at 25°C. The solution was decanted into centrifuge tubes and centrifuged at 4000 rpm for 30 minutes using an HRT 20 MM model Multifunctional Intelligent Centrifuge. The remaining P in the solution after equilibration was determined colorimetrically based on the reaction with ammonium molybdate. In the procedure, 1 ml aliquote of the centrifuged solution was pipetted into a test tube and 10 ml of a mixture of ammonium molybdate, sulphuric acid, potassium antimonyl tartrate, and ascorbic acid added with subsequent development of the molybdenum blue colour [22]. The absorbance, which is directly proportional to the remaining P content in solution, was measured at 882 nm using a Searchtech 722 N model visible spectrophotometer. The amount of P sorbed was then calculated as the difference between the initial concentration in the equilibrating solution and the remaining P using (1).

$$P \text{ sorbed}(mg/kg) = \frac{(C_i - C_f) \times V}{w}$$
(1)

where C_i is the initial P concentration in the equilibrating solution, C_f is the P concentration after adsorption, V is the volume of equilibrating solution used, and w is the oven-dry (105°C) equivalent mass of the soil sample.

2.3. P Sorption Description

To describe P sorption in the six soils, four equilibrium-based models commonly used for soils were used viz: Langmuir, Freundlich, Temkin, and Van Huay.

The linear form of the simple Langmuir equation [9] is defined by (2) as follows:

$$\frac{C}{q} = \frac{1}{kb} + \frac{C}{b} \tag{2}$$

where q is the amount of adsorption (adsorbate per unit mass of adsorbent) in g·kg⁻¹, C is the equilibrium or final adsorptive concentration, k is a constant related to the binding strength, and b is the maximum amount of adsorptive that can be adsorbed (monolayer coverage). The Langmuir equation is based on some assumptions which are not valid for the heterogeneous surfaces found in soils [1]. Plotting C/q vs. C produces the slope equal to 1/b and the intercept equal to 1/kb.

The Freundlich equation [10] is defined as follows (3):

$$q = K_d C^{1/n} \tag{3}$$

where *q* is the amount of adsorption (adsorbate per unit mass of adsorbent) in $g \cdot kg^{-1}$, *C* is the equilibrium or final adsorptive concentration, K_d is the distribution coefficient, and *n* is a correction factor. The linear form of the Freundlich Equation (4) is as follows:

$$\log q = \frac{1}{n} \log C + \log K_d \tag{4}$$

The slope is the value of 1/n and the intercept is equal to $\log K_{d}$.

One of the major disadvantages of the Freundlich equation is that it does not predict an adsorption maximum. The single K_d term in the Freundlich equation implies that the energy of adsorption on a homogeneous surface is independent of surface coverage.

The Temkin adsorption isotherm [11] is defined by (5) as follows:

$$X = a + b \ln C \tag{5}$$

where *b* is the buffer capacity (mL/g), *X* is the amount of P adsorbed (mg/kg), *C* is the equilibrium solution concentration (mg/L). A plot of *X* against $\ln C$ gives a slope equal to *b* and an intercept equal to *a*.

The Van Huay isotherm [12] is defined as follows (6):

$$\frac{x}{m} = m + n\sqrt{C} \tag{6}$$

where x is the amount of phosphate adsorbed (mg/kg), C is the concentration of fluid phase (mg/L), n is the Van Huay adsorption coefficient (L/kg), and m is the Van Huay constant parameter. A plot of x against $C^{1/2}$ gives a gradient equal to mn and an intercept equal to m^2 .

2.4. Statistical Analysis

The Pearson's correlation test was conducted to assess the association between P

sorbed, soil properties and sorption parameters of the various equilibrium-based models, while multiple linear regression analysis was conducted on soil properties to explain possible relationships between them. All statistical analyses were facilitated using Microcal Origin Version 6.0 [23], Microsoft Excel 2007 [24] and SPSS for Windows Version 17.0 [25].

3. Results and Discussion

3.1. Physico-Chemical Properties

From the physico-chemical properties (**Table 2**), profiles 1, 2, 4, 5 and 6 have texture classes [17] ranging between loam, silty loam, loamy sand, and sandy loam. Profile 3 alone has a clay loam texture in some of its horizons with higher clay contents compared to the others indicative of a more advanced stage of development. The soils are slightly acidic to basic, except for profile 3 which has pH-H₂O values less than 5.5. Organic carbon contents are generally high in the surface horizons and decrease with depth. Bulk density is generally low (less than 0.9 Mg/m³ in most of the soils), typical of Andosols except for profile 3, all soils have allophane within some of their horizons.

3.2. Description of Sorption Isotherms

Figures 2(a)-(f) present the adsorption isotherms of selected soil horizons for the six soils studied. The isotherm generally described by sorption in soils is the L (Langmuir) shaped isotherm, in which the slope of the curve decreases with increasing concentration. This implies that vacant adsorption sites for P decrease as the concentration of adsorbate (KH_2PO_4) increases. This is explained by the high affinity of the adsorbent (soil) for the adsorptive (P) at low concentrations, which then decreases as concentration increases [1].

For profile 1, all three horizons (A, AC, and Cr) follow the L-shaped isotherm. At low concentrations, soils have a high affinity for P and at these low concentrations; the gradient of the isotherm is very steep. As binding sites become occupied due to increase in concentration, affinity for P reduces with corresponding decrease in gradient of the isotherm. For profile 2, the A and AB horizons with very high OC contents follow the H-type (high-affinity) isotherms indicative of strong adsorbate-adsorptive interactions with the adsorbent. The 2C and 4C horizons follow the C-type isotherm whereby adsorptive ions are distributed between the interfacial phase and the bulk solution phase without any specific bonding between the adsorbent and adsorbate [1]. That is, it describes partitioning, which suggests interaction between a generally hydrophobic adsorbate with a hydrophobic adsorbent [26]. In profile 3, all horizons follow the L-shaped isotherm in all horizons.

Generally, in sorption studies, equilibrium is seldom attained especially in soils which have multi-component systems [26]. Furthermore, variability in soils

Table 2. Selected physico-chemical properties of the six soils studied.

Horizon/ depth (cm)	Clay (%)	Silt (%)	Sand (%)	Textural class	BD (Mg/m³)	Alloph (%)	Ferrih (%)	Al/Si	pH-H₂O	pH-KCl	pH-NaF	OC (%)
Profile 1												
A (0 - 65)	16	45	39	L	0.86	6.0	4.5	1.34	6.6	5.1	11.7	3.06
AC (65 - 95)	17	58	25	SiL	0.99	5.0	4.5	1.54	6.5	5.0	11.4	2.64
Cr (95 - 170)	17	36	47	L	0.79	3.9	4.6	1.31	6.8	5.1	11.0	1.29
Profile 2												
A (0 - 40)	32	13	55	SCL	0.50	11.0	6.7	2.00	6.1	4.4	12.4	5.29
AC (40 - 50)	21	43	36	L	0.62	21.2	9.3	2.10	6.6	5.1	12.5	4.76
1C (50 - 100)	6	12	82	LS	0.69	nd	nd	nd	7.1	5.5	11.6	2.60
2C (100 - 130)	5	25	70	SL	0.69	nd	nd	nd	7.3	6.0	11.2	0.49
3C (130 - 170)	2	16	82	LS	0.68	nd	nd	nd	7.0	6.1	11.2	0.40
4C (170 - 205)	2	15	83	LS	0.67	nd	nd	nd	7.3	6.1	10.9	0.47
Profile 3												
Ap (0 - 20)	18	49	33	L	0.96	0.4	1.9	-1.52	7.0	5.6	10.2	2.79
AB (20 - 46)	30	25	45	SCL	1.10	0.2	1.6	-9.80	5.6	4.3	10.2	1.57
Bw ₁ (46 - 82)	30	37	33	CL	1.12	nd	nd	nd	5.3	4.2	10.5	1.03
Bw ₂ (82 - 123)	29	47	24	CL	1.17	0.5	1.2	-0.52	5.1	4.2	10.4	0.66
BC (123 - 180)	17	58	25	SiLS	1.18	nd	nd	nd	5.3	4.0	10.4	0.49
Cr (180 - 220)	17	48	35	L	1.16	0.6	1.0	1.56	5.4	3.9	10.4	0.31
Profile 4												
A (4 - 27)	21	43	36	L	0.70	18.8	5.8	1.75	6.2	4.6	11.5	6.37
Bw (27 - 50)	21	44	34	L	0.87	24.0	6.0	1.82	6.4	5.0	11.4	4.37
BC (50 - 67)	19	26	55	SL	0.86	19.5	6.3	1.54	6.8	5.7	11.3	1.73
1C (67 - 86)	3	2	95	S	0.92	nd	nd	nd	7.0	5.5	10.9	0.20
2C (86 - 100)	10	13	77	SL	0.86	15.6	6.5	1.21	7.1	5.9	11.0	0.92
3C (100 - 122)	3	2	95	S	0.95	nd	nd	nd	7.3	5.7	10.6	0.44
4C (122 - 130)	7	9	84	LS	1.08	8.7	4.3	1.12	7.1	6.0	10.8	0.70
5C (130 - 180)	2	3	95	S	0.90	nd	nd	nd	7.3	6.0	10.1	0.12
Profile 5												
A _c (8 - 47)	9	24	67	SL	0.57	15.9	6.9	1.30	6.1	4.5	10.4	5.57
Cr ₁ (47 - 132)	8	26	67	SL	0.93	16.8	6.9	1.43	6.3	5.0	11.0	3.56
Cr ₂ (132 - 220)	6	26	68	SL	0.90	33.8	9.2	1.44	6.6	5.3	11.0	0.99
Profile 6												
A (0 - 45)	12	31	57	SL	0.65	20.5	7.8	1.41	7.3	6.0	10.6	5.70
Cr (45 - 60)	12	19	69	SL	0.85	nd	nd	nd	7.1	6.2	10.3	0.62
2Bw (90 - 130)	15	40	45	L	0.86	10.8	8.8	0.85	7.2	6.2	10.3	1.64
2Cr ₂ (130 - 180)	9	9	82	LS	0.91	7.7	7.7	0.56	7.2	6.2	10.1	0.32

nd = not determined, Alloph = allophane, Ferrih = ferrihydrite.

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Figure 2. Adsorption isotherms of selected horizons for the six soils studied; (a) profile 1, (b) profile 2, (c) profile 3, (d) profile 4, (e) profile 5, (f) profile 6.

especially when very small quantities of soil samples are used for laboratory analysis is easily observed. Further, when carrying out equilibration studies over long durations (between 16 and 24 hours) and for several days (such as in kinetics studies), often temperatures are not constant throughout. The above observations explain in part the irregular variations in sorption isotherms.

3.3. Relationship between P Sorption, Clay Content, OM Content, pH-NaF, and pH-H₂O

Correlations between the soil characteristics and adsorbed P are summarized in **Table 3**. The selection of these properties was based on their relevance in such studies in prior investigations [27].

Table 3. Correlations between soil p	properties and P sorbed.
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	pH-H ₂ O	pH-KCl	pH-NaF	BD (Mg/m³)	Sand (%)	Silt (%)	Clay (%)	OM (%)	P sorbed (mg/kg)	Alloph (%)	Ferrihy (%)	Al/Si
pH-H ₂ O	1											
pH-KCl	.934**	1										
pH-NaF	0.069	-0.132	1									
BD (Mg/m ³)	-0.454	-0.225	-0.518*	1								
Sand (%)	0.449	0.462	-0.283	-0.326	1							
Silt (%)	-0.240	-0.271	0.171	0.347	-0.886**	1						
Clay (%)	-0.542*	-0.517*	0.309	0.095	-0.599*	0.160	1					
OM (%)	0.129	-0.084	0.505*	-0.785**	-0.016	-0.010	0.054	1				
P sorbed (mg/kg)	0.103	0.026	0.506*	-0.509*	0.345	-0.321	-0.179	0.476	1			
Alloph (%)	0.425	0.373	0.327	-0.489*	0.360	-0.190	-0.437	0.440	0.820**	1		
Ferrihy (%)	0.764**	0.701**	0.269	-0.669**	0.552*	-0.374	-0.529*	0.374	0.637**	0.764**	1	
Al/Si	0.371	0.251	0.422	-0.436	0.045	0.182	-0.412	0.287	0.330	0.424	0.469	1

**. Correlation is significant at the 0.01 level (2-tailed), P≤0.01; *. Correlation is significant at the 0.05 level (2-tailed), P ≤ 0.05.

Maximum amount of P sorbed ranged from 2080 to 5402 mg/kg (**Table 4**) for the P equilibrium concentrations established.

However, the adsorption curves (**Figure 2**) indicate that these soils would adsorb more P if the concentrations of the equilibrating solution were increased.

pH-NaF is an indication of the presence of amorphous materials or allophanes in volcanic ash soils if the pH-NaF test gives a value of 9.5 or more [28]. pH-NaF values indicate that all soils might contain allophane. Profile 3 (aluandic Cambisol), with the lowest pH-NaF values and an average of 10.4, is the most weathered of all the soils with very low concentrations of allophane (less than 1%). Pooled data for the soils show that there is a positive and significant correlation between P sorbed and pH-NaF. This behaviour indicates that allophane is likely a dominant component of these soils and is responsible for the adsorption of P. However, from the phosphate-binding groups in soils, such as, Al-O-Si, R-COO-Al

Coloria Cl	P sorbed	d Langmuir		Freur	dlich	Van	Huay	Temkin		
horizons	с	b (mg/kg)	<i>k</i> (L/mg)	1/ <i>n</i> (L/kg)	Kd	<i>n</i> (L/kg)	<i>m</i> (mg²/kg²)	<i>a</i> (mg/kg)	b (mL/g)	
А	2080	2018	0.124	0.333	462	12.0	22.9	231	194	
AC	2479	2606	0.192	0.436	486	36.4	15.3	324	255	
Cr	2350	2428	0.206	0.458	415	29.7	16.5	286	273	
А	4799	4476	2.169	0.236	2070	13.1	50.0	959	782	
AC	4767	4435	3.263	0.128	2931	8.0	54.7	760	1050	
2C	2690	2014	0.062	0.357	334	16.9	16.4	210	45	
4C	2025	2976	0.011	0.59	89	-	-	180	-192	
Ар	1686	2360	0.040	0.467	229	-	-	361	31	
AB	2367	2224	0.250	0.283	676	13.4	18.9	349	631	
Bw_1	2663	2662	0.529	0.287	927	15.0	22.4	414	994	
Bw ₂	2361	2100	0.366	0.259	752	11.5	20.8	317	747	
BC	2197	1691	0.282	0.22	659	9.3	19.3	241	620	
Cr	2143	1600	0.231	0.467	231	10.0	17.5	262	462	
А	3578	3784	0.189	0.437	719	34.7	15.2	748	526	
Bw	4261	4373	0.548	0.355	1334	28.2	24.0	734	1553	
BC	3382	3339	0.267	0.368	826	25.0	18.4	591	798	
2C	2575	2270	0.112	0.431	368	24.1	11.2	496	-7	
4C	1883	2919	0.024	0.723	92	-	-	630	911	
Ac	3699	3580	0.148	0.436	627	34.1	13.7	732	297	
Cr_1	4893	4843	1.507	0.262	2138	29.5	29.5	789	2225	
Cr_2	5402	5102	3.791	0.15	3133	31.8	31.9	463	3417	
А	3261	2772	0.157	0.411	532	23.8	14.7	561	260	
Cr	2725	2381	0.122	0.43	400	21.0	13.3	511	47	
2Bw	2638	1958	0.153	0.232	617	15.3	14.7	193	737	
2Cr	2445	1760	0.070	0.332	330	24.1	7.7	237	279	

I abic 4. Farameters of various equinorium-based mou	Tabl	le 4. Paramet	ers of variou	as equilibrium	i-based	mode
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(organic ligands), and Al-OH groups [29], and given that exchangeable aluminium values would be low as indicated by the pH-H₂O values that are greater than 5.5, phosphate groups in these soils could thus be largely attributed to organic ligand binding groups. This probably explains why P sorption also correlates with organic matter (OM). Organic matter and allophane are known to be the key colloids in Andosols which have a high affinity for elements mainly through sorption processes [30] [31].

No correlation was observed between clay content and P sorption, though reports by [22] indicate that the amount of P sorbed increases with increases in clay content. Kaolinite, a major phyllosilicate clay mineral, is reported to contribute to P sorption at low pH [32]. The mechanism for such behaviour has been explained by pH-dependent charge sites at crystal edges in kaolinite, where A1(OH)H₂O groups are exposed, and at low pH, become positively charged and adsorb P [32]. pH-H₂O values in these soils vary from 6.5 - 6.8 (Profile 1), 6.1 - 7.3 (profile 2), 5.1 - 7.0 (profile 3), 6.2 - 7.3 (profile 4), 6.1 - 6.6 (profile 5), and 7.1 - 7.3 (profile 6). Only profile 3 has low pHs less than 5.5 at which exchangeable aluminium would be observed. This is the only profile in which P sorbed correlates best with clay content (r = 0.75), though not significant.

P sorption has been reported to be more closely related to the content of oxalate-extractable aluminium (corresponding to poorly ordered inorganic and organic Al compounds that release considerable amounts of OH to NaF solution) than to any other soil constituent [33]. The concentration of these compounds in soil could be estimated by measuring the pH of a NaF extract. Equally, other studies by the latter authors on some west Australian soils indicate that well crystalline aluminium and iron oxides, clay minerals and other soil constituents are of secondary importance in determining P sorption and that most P sorption is associated with poorly ordered and organically complexed forms of Al.

This may also explain why P sorption of these soils significantly correlates with pH-NaF and OM but does not with clay content.

In a review on the relationship between P availability and iron oxides and OM, in some highly weathered Brazilian Ferralsols, [7] reported that iron oxides and OM are the soil constituents most strongly affecting the reactions and rate of phosphorus adsorption and desorption of P. Given that OM is an important influential factor on chemical, physical and biological soil properties, [7] observed that adsorption of organic functional groups onto iron oxides can promote anion (phosphate) adsorption through cation bridges (Al³⁺ and Fe³⁺). Though the soils in this study are relatively less weathered, they occur in environments (humid tropics) which have similar soil chemical processes, and similar properties associated with their variable charge nature. This is in agreement with the significant correlation between P sorption and OM in this study. In view of the foregoing, [7] assert that fertilizer recommendations based on soil buffering categories established in terms of clay contents alone may be erroneous.

Observations in this study of a positive correlation between phosphate adsorption and OM content are in agreement with reports by [34].

Reference [35], in their study, "Organic matter effects on phosphorus sorption in sandy soils" in west and south west Poland, also observed that removal of OM from soil reduced phosphate adsorption. The effect of OM on phosphate adsorption is indirect; the interactions between OM and oxides of iron and aluminium inhibit their crystallization thereby increasing their phosphate adsorption capacity [34]. The high pH-NaF indicates that active aluminium is present, but because the pH-values of most of the soils are within the ranges for which aluminium is not soluble (except profile 3), it is probable the large surface area of allophane exposes considerable amounts of aluminium on its surface, capable of fixing high P [36] [37]. Correlations between pH-H₂O and P sorbed, for profiles 1, 2, 4, 5, and 6, which have pHs greater than 6 indicate that OM can increase P sorption. This is in agreement with results of [37] who reported that, at a soil pH > 6.0, soil OM increases P sorption.

3.4. Relationship between P Sorbed, Allophane Content, and Ferrihydrite Content

Influence of amorphous materials in soils notably allophane and ferrihydrite has been reported [38]. **Table 2** shows that all profiles contain allophane and ferrihydrite, except profile 3. Allophane and ferrihydrite correlate positively and significantly with amount of P sorbed indicating that these amorphous species greatly contribute to P sorption. Allophane has a higher affinity for phosphate compared to ferrihydrite [38] and the higher concentration of allophane content compared to that of ferrihydrite in the studied soils indicates that its effect on P sorption is greater. This high P sorption is probably due to its high surface area [36].

The net positive charge of amorphous silicates at prevailing soil pH causes a strong adsorption of phosphate ions and the phosphate adsorption capacity increases with the Al/Si ratio of allophane [29]. This Al/Si molar ratio, computed as $(Al_{o}-Al_{p})/(Si_{o})$ molar ratio, where $_{o}$ and $_{p}$ refer to oxalate and pyrophosphate extractions, respectively, which is an indication of the type of allophane (silicon or aluminium rich) [39], indicates that aluminium in allophane is more responsible for P sorption than silicon. The high positive and significant correlation between P sorbed and Al_o+½Fe_o ratio is in agreement with observations of [40], and indicates that P sorption will increase with increasing andic properties generally characterized by presence of short-range-order minerals, such as allophane and ferrihydrite. The high positive and significant correlation between allophane content and P sorbed (r = 0.806, P < 0.01) and between P sorbed and ferrihydrite content (r = 0.669, P < 0.01) compared to OC (r = 0.476, P > 0.05) clearly indicates that these amorphous substances are the principal soil components responsible for P sorption. This confirms the assertion earlier made with respect to pH-NaF as an indication of the presence of amorphous substances notably allophane [33] in these soils. Though there is no significant correlation between allophane and pH-NaF, the fact that pH-NaF correlates with P sorbed and because pH-NaF values reflect the presence or absence of allophane in the soils, pH-NaF can be used as a fast tool to estimate P sorbed in these soils using the following simple linear regression Equation (7).

P sorbed =
$$782.7(pH-NaF) - 5277$$
, $r = 0.506^*$ (7)

The rationale for using pH-NaF for estimating P sorbed is that this parameter can be easily measured in the laboratory or in the field.

However, because allophane and ferrihydrite correlate with P sorbed better than pH-NaF, they remain better estimators of P sorbed in these soils compared to pH-NaF.

3.5. Equilibrium-Based Models for P Sorption Description

Plots of P sorption data following the Langmuir, Freundlich, Temkin and Van-Huay equilibrium-based models for the soil profiles and horizons studied (**Figures 3-8**) indicate that all four models show very good fits.



Figure 3. Equilibrium-based models for profile 1: (a) Langmuir, (b) Freundlich, (c) Temkin, and (d) Van Huay.





Figure 4. Equilibrium-based models for profile 2: (a) Langmuir, (b) Freundlich, (c) Temkin, and (d) Van Huay.



Figure 5. Equilibrium-based models for profile 3: (a) Langmuir, (b) Freundlich, (c) Temkin, and (d) Van Huay.



Figure 6. Equilibrium-based models for profile 4: (a) Langmuir, (b) Freundlich, (c) Temkin, and (d) Van Huay.





Figure 7. Equilibrium-based models for profile 5: (a) Langmuir, (b) Freundlich, (c) Temkin, and (d) Van Huay.



Figure 8. Equilibrium-based models for profile 6: (a) Langmuir, (b) Freundlich, (c) Temkin, and (d) Van Huay.

Generally, the Langmuir model presents the best fit, though the coefficients of determinations are very similar for all the models. The fact that all the curves in all horizons within the profiles do not systematically follow the L-shaped type of isotherm (Figure 2) suggests that the other three models would be better indicated for some of the soils than the Langmuir model.

3.6. Relationship between P Sorption Parameters, P Sorbed, and Selected Soil Properties

Sorption parameters for the four models used are presented in **Table 4. Table 5** indicates that, b, the maximum amount of P that can be sorbed increases with increase in pH-NaF, OM, allophane content, ferrihydrite content, Al/Si molar ratio, and $Al_0+\frac{1}{2}Fe_0$ ratio. These are the same parameters that correlate with P sorbed. This indicates that the Langmuir equation perfectly describes P sorption in these soils. The constant k, related to the binding strength, increases with pH-NaF, allophane content, ferrihydrite content, and $Al_0+\frac{1}{2}Fe_0$ ratio. This implies that active aluminium as predicted by the pH-NaF values contributes to this binding energy.

The distribution coefficient of the Freundlich model (K_d) significantly increases with increase in pH-NaF, allophane content, ferrihydrite content, and $Al_0+\frac{1}{2}Fe_0$ ratio.

The amount of P sorbed in the Temkin model increases with pH-NaF, OM, allophane content and the $Al_o+\frac{1}{2}Fe_o$ ratio. This can equally be explained by the amount of active Al present.

In the Van Huay model, the adsorption coefficient (*n*) doesn't significantly correlate with any of the soil properties, while the constant, *m*, increases with pH-NaF and $Al_0+\frac{1}{2}Fe_0$ ratio.

	<i>c</i> (mg/kg)	<i>b</i> (kg/L)	<i>k</i> (L/mg)	1/ <i>n</i> (L/kg)	Kd	<i>n</i> (L/kg)	<i>m</i> (mg²/kg²)	<i>a</i> (mg/kg)	<i>b</i> (mL/g)
c (mg/kg)	1	0.972**	0.812**	-0.540*	0.898**	0.232	0.689**	0.806**	0.751**
pH-H ₂ O	0.103	0.050	0.015	-0.027	0.019	0.301	-0.130	-0.068	-0.019
pH-KCl	0.026	-0.056	-0.036	-0.149	-0.016	0.205	-0.228	-0.206	0.050
pH-NaF	0.506*	0.573*	0.523*	-0.275	0.547*	-0.091	0.773**	0.578*	0.127
Sand (%)	0.345	0.243	0.194	-0.140	0.197	0.291	-0.076	0.172	0.273
Total Silt (%)	-0.321	-0.223	-0.192	0.237	-0.201	-0.052	-0.088	-0.282	-0.161
Clay (%)	-0.179	-0.129	-0.082	-0.112	-0.071	-0.529*	0.316	0.122	-0.303
OM (%)	0.476	0.531*	0.106	0.093	0.211	0.240	0.310	0.783**	-0.101
Allophane (%)	0.820**	0.798**	0.587*	-0.333	0.662**	0.416	0.324	0.574*	0.666**
Al/Si	0.331	0.315	0.198	0.118	0.193	0.266	0.178	0.281	0.097
Ferrihydrite (%)	0.637**	0.547*	0.499*	-0.426	0.535*	0.280	0.301	0.383	0.375
Al _o +½Fe _o (%)	0.913**	0.885**	0.701**	-0.441	0.777**	0.291	0.558*	0.733**	0.604*

Table 5. Summary of correlations between P sorption parameters and soil characteristics.

**Correlation is significant at the 0.01 level (2-tailed), $P \le 0.01$; *Correlation is significant at the 0.05 level (2-tailed), $P \le 0.05$.

These correlations show that model parameters that directly explain or inform on adsorption are better observed for the Langmuir, Freundlich, and Temkin models.

Because the amount of P sorbed in the Temkin model has values that are very different from the actual P sorbed values, the Temkin model would not be considered a good model for evaluating P sorption in these soils. Thus, following the relationships between sorption parameters and soil properties, the Langmuir and Freundlich equilibrium-based models best explain P sorption in these soils.

3.7. Estimation of P Sorbed Using Multiple Linear Regression and Applications

Based on the fact that P sorbed is related to pH-NaF, OM, allophane content, and ferrihydrite content, two multiple regression equations have been proposed for the estimation of P sorbed in these soils; the first Equation (8) relates OM and pH-NaF to P sorbed.

P sorbed =
$$103(OM) + 649(pH-NaF) - 4447$$
, $R^2 = 0.371$ (8)

The rationale for using these two parameters (OM and pH-NaF) is based on their ease of determination in soils.

Estimated P sorbed using this equation significantly correlates with the experimentally determined P sorbed (Figure 9).

Paired sample t-test performed on the data sets showed that the means are statistically equal (t = 0.017, p = 0.986 at the 95% confidence level).

The second multiple regression Equation (9), relates allophane (Alloph) and ferrihydrite (Ferrih) contents to P sorbed:

P sorbed =
$$92.4$$
 (Alloph) + 11.2 (Ferrih) + 2107 , $R^2 = 0.67$ (9)

Estimated P sorbed using this equation significantly correlates with the experimentally determined P sorbed (Figure 10).

Paired sample t-test performed on the data sets show that the means are statistically equal (t = -0.834, p = 0.415 at the 95% confidence level).







Figure 10. Correlation between experimentally determined P sorbed and estimated P sorbed using allophane and ferrihydrite contents (Equation (9)).

The higher coefficient of determination and correlation coefficient obtained for correlation between the experimental and theoretical P sorbed values (Equation (9)) as compared to the first equation (Equation (8)) indicates that the latter equation is more appropriate for estimation of P sorbed.

These regression equations can be used as a tool for quick assessment of P sorbed in soils of similar environments from data found in soil survey reports and soil laboratories. This will guide effective and efficient P fertilizer application and management.

3.8. Oxalate and DCB Extractable Al, Fe, Si, and Mn in Relation to P Sorption

A second group of soil parameters (Al_o, Fe_o, Si_o, Mn_o, Al_d, Fe_d, Si_d and Mn_d) (**Table 6**) were also related to P sorption, to complement and or confirm some of the relationships earlier observed in this study.

From **Table 7**, it can be observed that P sorbed increases with Oxalate extractable Al, Fe, Mn, and Si. This indicates that amorphous materials in these soils are the principal factors explaining P sorption. The highest correlation is observed for oxalate extractable aluminium indicating that active aluminium is the principal cause of high P sorption in these soils. The positive and significant correlation between this oxalate extractable aluminium and pH-NaF (r = 0.566, P < 0.05) confirms that the latter component in these soils indicates the presence of amorphous materials, especially allophane, and hence could be conveniently used to estimate P adsorption. The positive and significant correlation between OM and oxalate extractable aluminium (r = 0.598, P < 0.05) suggests the formation of organo-metallic complexes in these soils indicating that OM is a good indicator for P adsorption as there exists a co-correlation between OM and oxalate extractable aluminium through pH-NaF data.

The fact that the amount of P sorbed correlates more with oxalate extractable Al, Fe, Si, and Mn than DCB extractable forms, suggests that amorphous materials are the most important components responsible for P sorption. Studies by [41] have shown that these amorphous materials, especially iron, have high sur-

face areas, which make them efficient sorbents for inorganic anions such as phosphates, biocides, etc. From the relationships between various forms of Al, Fe, Si, and Mn, parameters of sorption isotherms, and other selected physico-chemical characteristics (Table 7), the order of correlation of amorphous species is $Al_o > Si_o > Fe_o > Mn_o$. Aluminium and silicon are the dominant elements in allophanes.

In contrast to the first set of regression Equations, (8) and (9), where the accuracy of the dependent variable increases with the amorphous character of variables introduced, these second set of regression equations indicate that the

Table 6. Acid oxalate extractable Al, Fe, Mn, Si (Al_o,Fe_o,Mn_o,Si_o) and DCB extractable Al, Fe, Mn, Si (Al_d, Fe_d, Mn_d, Si_d) of selected soil horizons.

Horizon	Al₀	Fe₀	Mn₀	Si₀	Ald	Fed	Mnd	Sid
depth (cm)				9	6			
Profile 1								
A (0 - 65)	1.62	2.64	0.11	0.99	0.93	4.23	0.14	0.66
AC (65 - 95)	1.55	2.67	0.13	0.77	1.02	5.07	0.17	0.66
Cr (95 - 170)	1.01	2.68	0.14	0.65	0.65	4.96	0.19	0.75
Profile 2								
A (0 - 40)	5.44	3.92	0.17	1.45	3.62	6.05	0.17	0.52
AC (40 - 50)	7.65	5.47	0.16	2.69	3.91	7.89	0.16	0.58
Profile 3								
Ap (0 - 20)	0.46	1.10	0.14	0.13	0.49	4.63	0.17	0.26
AB (20 - 46)	0.58	0.97	0.09	0.12	0.80	6.26	0.16	0.30
Bw ₂ (82 - 123)	0.49	0.72	0.09	0.12	0.50	4.37	0.14	0.36
Cr (180 - 220)	0.42	0.59	0.09	0.10	0.39	3.31	0.14	0.38
Profile 4								
A (4 - 27)	5.42	3.39	0.10	2.72	2.26	5.99	0.12	0.74
Bw (27 - 50)	6.50	3.50	0.08	3.39	2.78	7.04	0.12	0.94
BC (50 - 67)	4.80	3.71	0.08	3.03	2.07	5.56	0.10	1.01
2C (86 - 100)	3.34	3.85	0.07	2.69	1.40	4.74	0.08	1.01
4C (122 - 130)	1.79	2.51	0.05	1.54	0.70	2.78	0.05	0.68
Profile 5								
A _c (8 - 47)	4.47	4.08	0.15	2.66	2.81	10.66	0.21	1.14
Cr ₁ (47 - 132)	5.19	4.06	0.16	2.71	4.16	11.78	0.23	1.11
Cr ₂ (132 - 220)	8.07	5.42	0.17	5.43	3.23	11.29	0.23	1.28
Profile 6								
A (0 - 45)	4.88	4.58	0.12	3.32	1.43	7.00	0.14	0.99
Cr (45 - 60)	1.90	5.19	0.12	2.06	0.68	6.38	0.13	1.10
2Cr ₂ (130 - 180)	0.94	4.55	0.12	1.59	0.42	5.38	0.13	1.12

	%Al。	%Fe。	%Mn。	%Si。	%Al _d	%Fed	%Mn _d	%Sid
С	0.930**	0.637**	0.608**	0.768**	0.953**	0.775**	0.464	0.409
<i>b</i> (kg/L)	0.922**	0.547*	0.546*	0.734**	0.960**	0.751**	0.466	0.361
<i>k</i> (L/mg)	0.710**	0.499*	0.685**	0.532*	0.721**	0.555*	0.516*	0.132
1/ <i>n</i> (L/kg)	-0.414	-0.426	-0.427	-0.313	-0.456	-0.398	-0.243	-0.063
K_d	0.794**	0.535*	0.641**	0.602*	0.834**	0.654**	0.501*	0.199
<i>n</i> (L/kg)	0.274	0.280	0.171	0.461	0.203	0.433	0.323	0.609**
$m (mg^2/kg^2)$	0.594*	0.301	0.550*	0.212	0.719**	0.278	0.281	-0.224
<i>a</i> (mg/kg)	0.784**	0.383	0.368	0.485*	0.886**	0.527*	0.203	0.137
<i>b</i> (mL/g)	0.628**	0.375	0.380	0.672**	0.607**	0.697**	0.516*	0.418
pH- H ₂ O	0.250	0.764**	0.250	0.478	0.038	0.153	-0.100	0.687**
pH- KCl	0.145	0.701**	0.094	0.451	-0.078	0.127	-0.201	0.705**
pH- NaF	0.566*	0.269	0.339	0.196	0.603*	0.013	-0.001	-0.196
Sand (%)	0.242	0.552*	0.454	0.454	0.276	0.559*	0.386	0.696**
Silt (%)	-0.177	-0.374	-0.350	-0.251	-0.267	-0.375	-0.234	-0.385
Clay (%)	-0.209	-0.529*	-0.360	-0.535*	-0.125	-0.540*	-0.416	-0.817**
OM (%)	0.598*	0.374	0.260	0.367	0.598*	0.336	0.036	0.102
Alloph content (%)	0.933**	0.764**	0.338	0.986**	0.719**	0.691**	0.192	0.678**
Ferrih content (%)	0.698**	1.000**	0.594*	0.784**	0.564*	0.601*	0.200	0.764**
Al _o +½Fe _o (%)	0.985**	0.810**	0.507*	0.901**	0.862**	0.698**	0.249	0.551*

 Table 7. Correlations between parameters of various sorption isotherms, selected physico-chemical properties, and various forms of Al, Fe, Si, and Mn.

Alloph = allophane, ferrih = ferrihydrite, Al/Si = $(Al_o - Al_p)/(Si_o)$ molar ratio where $_o$ and $_d$ refer to oxalate and DCB extraction, respectively. **Correlation is significant at the 0.01 level (2-tailed), $P \le 0.01$; * Correlation is significant at the 0.05 level (2-tailed), $P \le 0.05$.

simple linear Equations (10) and (11) would be more accurate in P sorption assessment.

P sorbed =
$$392(Al_o) + 1942$$
, $R^2 = 0.864$ (10)

P sorbed =
$$799(Al_d) + 1860, \quad R^2 = 0.908$$
 (11)

P sorbed =
$$458(Al_o) - 135(Si_o) + 1979$$
, $R^2 = 0.854$ (12)

P sorbed =
$$455(Al_o) - 163(Si_o) + 36(Fe_o) + 1915$$
, $R^2 = 0.843$ (13)

P sorbed =
$$713(Al_d) + 61(Si_d) + 1612$$
, $R^2 = 0.905$ (14)

The developed regression Equations (10)-(14) indicate that P sorption is more associated with DCB extractable species compared to the oxalate extractable species. DCB extractable species includes crystalline, amorphous and organic forms. The difference between DCB and oxalate extractable species generally gives an idea of the crystalline forms of the corresponding species. In these soils, the concentrations of DCB extractable Al and Si (which are the dominant components of allophane) are lower than the oxalate extractable forms (a common observation in tephra soils) [42], indicating that DCB extractable Al and Si is dominated by amorphous forms and so the high correlation coefficients in Equations (10) and (11) are evident.

As observed above, the sorption parameters of the various sorption isotherms correlate with the various forms of DCB and acid oxalate extractable Al, Si, Fe, and Mn. The Langmuir parameters correlate with Al_o , Fe_o , Mn_o , Si_o , Al_d and Fe_d . The k_d parameter of the Freundlich equation shows the highest degree of association as it correlates with all parameters except Si_d . The fact that P sorbed correlates with amorphous forms of Al, Fe, Si, and Mn compared to the free forms of the latter elements suggests that in these soils amorphous materials are the dominant species responsible for P sorption.

4. Conclusions

P sorption studies showed that P sorption capacity of the six tephra soils varied from 2080 to 5402 mg/kg. However, these values do not constitute the sorption maxima for these soils as higher P equilibrium concentrations were not introduced. The soil parameters that relate to P sorption in these soils are OM, pH-NaF, allophane content, ferrihydrite content, %Al_o, %Fe_o, %Mn_o, %Si_o, %Al_d, %Fe_d, but also Al_o+½Fe_o. Presence of amorphous materials can be assessed through pH-NaF tests in these tephra soils as confirmed through the high and significant correlation established among them and constitutes the dominant species influencing P sorption.

All four equilibrium based models used for the description of P sorption in these soils fit the data satisfactorily. However, based on the parameters of the models, the Freundlich and Langmuir models best describe P sorption. Multiple linear regression equations can be used to estimate P sorption capacity of similar soils if data is available.

The results of this study are in agreement with those of [43] and [32] who reported that pH-NaF can be used in Andosols and sesquioxidic soils to estimate P sorption. Because soils in this stud*y* belong to two main Reference Soil Groups (Andosols and Cambisols with few andic properties), it can be generalised that for variable charged soils, or soils developed from volcanic parent materials, pH-NaF can be used as a reliable parameter for estimating P sorption.

P sorption studies to be effective require much time, high concentration, are costly, and often not affordable to most users. Assessment of P sorption and P requirements from parameters found in soil survey reports and other sources would minimize P fertility management costs. The confirmed relationship that exists between pH-NaF and amorphous components as determined through DCB and oxalate extractable Al, Fe and Si and their relationship to P sorption provides a possible pathway for estimation of P sorption directly using pH-NaF which is much less expensive than long established procedures. This is very important for the Andosols of the humid tropics where a paucity of such studies exist.

The continued high crop performance observed in some tephra soils having low pHs (pH \leq 5.5), where exchangeable Al would be present and fix P, a major plant element had been puzzling. The mechanism for Al adsorption on the allophane-OM complex is inherent in these systems, thus liberating P for plant use required elucidation. The mechanism for Al-adsorption to OM on the allophane-OM complex outlined in this study explains in part the on-going process in these tephra soils.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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