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Phosphorus Adsorption and Its Relation with Soil Properties in Acid Soils of Western Kenya

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Authors' contributions

This work was carried out in collaboration between all authors. Author EMM designed the study, wrote the protocol and wrote the first draft of the manuscript. Authors JPM, ES and CKG guided on data collection, evaluated and interpretations while author MKN was involved in data collection, data analysis, interpretation and review. All authors read and approved the final manuscript.

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ABSTRACT

Low available phosphorus (P) is one of the major hindrances to crop production in acid soils of western Kenya. Although considerable work has been done to establish P levels in the region, there is paucity of information on which to base fertilizer recommendations due to potential crop production differences caused by different soil types and climate. Phosphorus adsorption capacity and its relationship with some soil properties were evaluated in acid soils from nine locations of western Kenya. Adsorption data was obtained by equilibrating the nine soil samples with 30ml of KH_2PO_4 in 0.01 M $CaCl_2$, containing 0, 80, 150 and 300 µg ml^{-1} for 48 hours with shaking for 30 minutes at intervals of 8 hours. Langmuir, Freundlich and Tempkin adsorption models were fitted to the test results and relationship between P adsorption and soil properties determined by correlations. The result of this study showed that the soils were strongly to extremely acidic (pH 4.83 - 3.76), had high exchangeable Al^{3+} (>2 cmol Al kg^{-1}), Al saturation of (> 20% Al) and

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calculated maximal phosphorous adsorption varied from 770.83 to 1795.83 mg kg^{-1} soil. Comparing the models, Freundlich linear model showed a better fit to the tested soils compared to Langmuir and Tempkin models. The regression coefficients (R^2) for the fitted Freundlich P adsorption isotherms was highly significant ranging from (0.995- 1.000) for all tested soils. Analysis of relationship between adsorption maximum and soil attributes revealed that adsorption maximum positively correlated with clay content, exchangeable P, exchangeable acidity and Aluminium saturation and negatively correlation with organic matter and electrical conductivity. Due to differences in maximal P sorption capacities within the tested area, blanket P fertilizer recommendation may affect crop productivity in some sites. There is therefore need for further research to determine optimal Phosphorus requirements for soils in each research site.

Keywords: Adsorption; acid soils; phosphorus; Western Kenya.

1. INTRODUCTION

Adsorption is the net accumulation of chemicals at the interface between solid phase and aqueous solution phase which determines availability of native soil nutrients and the rate of nutrients to be applied to soil as fertilizers. Phosphate adsorption is the process in which phosphate ions are held on active sites of soil particle surfaces [1]. The adsorption by oxides of iron and aluminium, and amorphous materials in soils affects the fate of applied P and availability of P to plants [2,3]. As of today, many researchers have studied and proposed diverse techniques for evaluation of phosphorus status in the soil. Adsorption isotherm is an important criterion which has been used to estimate: phosphorous concentration in aqueous phase of soil, energy of phosphorous adsorption, maximal value of its adsorption by soil, buffer strength of soil against phosphorous concentration variations in solution and equilibrium state between phosphorous in aqueous and solid phases and their relationship [4,5]. The isotherms can be described as the equilibrium relationship between amount of adsorbed and dissolved phosphate at constant temperature in quantitative terms. They are explained by fitting of the isotherms and their mathematical descriptions using Langmuir, Freundlich, Tempkin, Linear or Van Huay isotherm models among other models [1,6]. However, Freundlich model have been reported to give the best fit in many areas of the world [7].

Although adsorption isotherm equations can be used to predict fertilizer requirement for crops [8], the nutritional element in soil solution is closely linked to adsorption processes through the physico- chemical characteristics of the soil. This eventually governs the availability of nutrient ions to growing plants. Among the soil properties affecting P sorption capacity are texture, organic matter, soil pH, Aluminium saturation, CEC and $CaCO_2$ content. Knowledge of the relationship of these soil properties with adsorption capacity is therefore necessary in understanding sorption behavior of varied soils. Several research carried out on this have reported varied conclusions with [9] reporting a Statistical significant relations between parameters of Langmuir equation and soil properties such as clay percentage, organic carbon, Fe and Al contents while [10] recognized free iron as the only factor significantly correlating with maximal phosphorus adsorption in the Langmuir's model.

The Kenyan soils, similar to other agricultural soils of the tropics are generally low in available P. Several authors have reported that the available P in western Kenya- acid soils is deficient, ranging between 2 to 5mg Pkg^{-1} soil [11-13]. Many local experimental results also indicate that these soils have high P – fixation capacity that makes about 80% of the inorganic added P become unavailable for crop use [12,14,15]. However, limited work has been carried out to understand the relationship between the P sorption capacity and specific soil properties in the research area. The objectives of this study were therefore: (i) To quantify and compare the applicability of Langmuir, Freundlich, and Tempkin equations in describing the sorption of P in acid soils in western Kenya, (ii) To evaluate the relationship between P sorption and soil properties in acid soils in Western Kenya.

2. MATERIALS AND METHODS

2.1 Location of the Study Sites

Sites were selected to represent major agro-ecological environments with acid soils where staple food crop, maize is widely grown in the western kenya [16]. Selected sites were, Barondar, Yenga, Sega, Fumbire, Bukhahala, Umala, Uboro, Mois Bridge and Kamgut.

Barondar, Sega and Yenga had Orphic Acrisols, Bhukhahala, Umala and Uboro had Orphic Ferrasols while Moi bridge and Kamgut had Chromic Acrisols [17]. All the sites were under continuous crop cultivation and lies between (00°13'N to 00°17'N) and (34° 10'E to 34° 14'E).

2.2 Soil Sampling, Preparation and Characterization

Surface soil samples (0-15cm) were collected from cultivated farmers' fields from the nine locations, air-dried, ground and passed through a 2 mm sieve. Soil pH was measured in 1:2.5 soil to liquid ratio in 0.01 M $CaCl_2$ [18] while electrical conductivity (1: 2.5, soil: water), organic carbon (% C), total N (% N), CEC, exchangeable bases and exchangeable acidity were analyzed according to procedures described by [19]. Extractable P was determined by Bray I method and particle size analysis by the pipette method as described by [20].

2.3 Phosphate Sorption Isotherms

Three replicate 3.0g, air-dried and milled (<2 mm), soil samples were equilibrated with 30ml of KH_2PO_4 in 0.01M$CaCl_2$ containing 0, 80,150, 300µg P/ml for 48 hours with shaking for 30 minutes at intervals of 8 hours. Three drops of toluene were added to each container to inhibit microbial activity. Following equilibration, the soil suspensions were centrifuged at 3000 rev min^{-1} for 10 minutes and filtered through Whatman No. 5 filter paper to obtain a clear solution. Phosphorus in the supernatant was then determined colorimetrically by [21] method. The amount of P sorbed was calculated as the difference between the amount of P added and that remaining in solution [22] then P-adsorption isotherms developed from the concentrations of P in the soil 0.01M $CaCl_2$- filtrates. The P adsorbed data for the soils used in this study were fitted into the linearized form of the Langmuir, Frendlich, and Tempkin equations proposed by [23-25]. The equations described in its linear form are: $C/X = 1/ K_Lb_L + C/b$ [26]; $X = K_fC^{1/n}$ [27] and $X = a + b \ln C$ [28].

Where

- C = Equilibrium concentration of phosphorus in solution (mg P L^{-1})
- X = mg of P adsorbed (mg P kg^{-1})
- b_L = Adsorption maximum for Langmuir model (mg P kg^{-1})
- K_L = Bonding energy constant of Langmuir model (L mg^{-1} P)
- n = Empirical constant related to bonding energy of soil for phosphate
- K_f = Proportionality constant for Freundlich model (mg kg^{-1})
- a = Amount of P adsorbed of Tempkin model (mg P kg^{-1})
- b = Buffer capacity of Tempkin model (mL g^{-1})

2.5 Statistical Analysis

Relationships between P sorption parameters, and P sorbed at equilibrium with 0.2 mg P L^{-1} ($P_{0.2}$), with selected soil chemical properties were done with simple regression and correlations and tested for significance at p = 0.05 using the GenStat statistical software [29].

3. RESULTS AND DISCUSSION

3.1 Physico- Chemical Properties of Soils from Nine Sites

The tested soils were acidic with pH ($CaCl_2$) ranging from 3.76 to 4.83 (Table 1). Umala soils had the highest percentage Aluminium saturation (34.32%) and Uboro soils the lowest (22.38%). Likewise, Umala soils had the highest exchangeable acidity and Aluminium and Yenga the least. Kamgut soils had the highest percent organic matter with Moi bridge having the lowest. All the three soils contained low amount of soluble salts with a mean electrical conductivity of 0.07mS cm^{-1} and base saturation ranging from 43.76 to 71.33 %. The soil exchangeable P was found deficient in all the sites except in Sega and the % clay ranged from 20-32.

3.2 Phosphate Adsorption Isotherms

The Phosphate adsorption isotherms of soils in the nine study sites were determined by plotting the equilibrium concentration of phosphate (C) against the amount of phosphate adsorbed (X). Comparing the highest amount of P adsorbed, it is evident that soils in each site had different capacities to adsorb P (Fig. 1). The result of the study showed that Barondar soil had the highest value of maximum adsorption 1795.83mg kg^{-1} and Sega soils had the lowest value with maximum P adsorbed 770.83mg kg^{-1}. The graphic representation of the adsorption isotherms of the soils showed that Umala soils had the highest level of Sorbed P, followed by Barondar soils while Sega soils had the lowest.

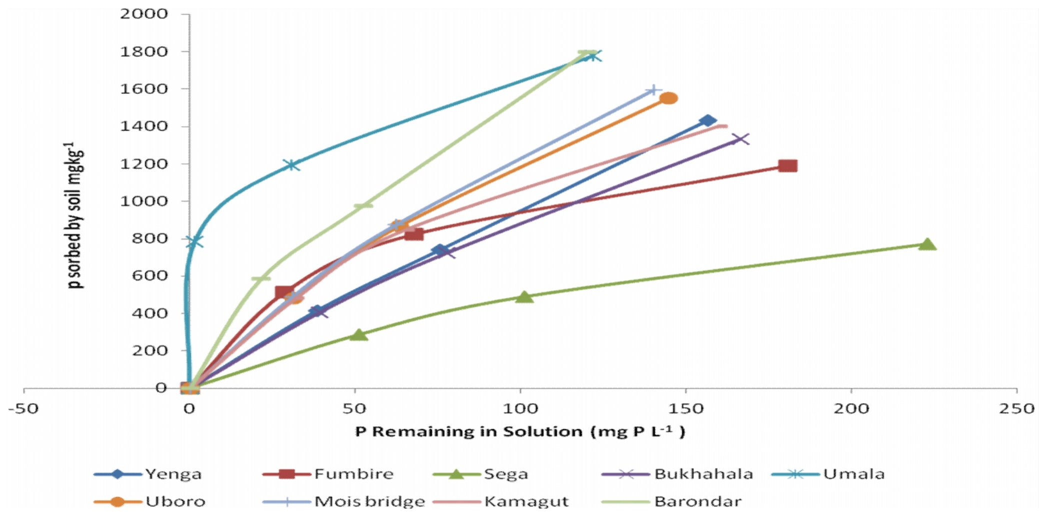

Fig. 1. Phosphate adsorption isotherm of soils from nine sites

Table 1. Physico-chemical properties of soils from the nine sites

Site	Barondar	Yenga	Sega	Uboro	Bukhahala	Umala	Fumbire	Moi bridge	Kamgut
pH	4.83	4.46	4.08	4.22	4.48	4.02	3.90	4.45	3.76
Al Saturation (%)	24.24	23.17	27.8	22.38	27.35	34.32	31.22	24.92	26.00
Exch. Acidity	3.55	3.35	3.60	3.90	4.65	5.50	4.22	4.30	3.60
Al (cmol kg^{-1})	2.80	2.65	2.95	3.60	3.25	3.9	2.9	3.4	2.95
EC($mScm^{-1}$)	0.04	0.09	0.06	0.07	0.05	0.07	0.07	0.03	0.17
OM (%)	1.76	2.38	3.97	2.49	3.64	2.75	3.75	1.53	4.55
P ($mgkg^{-1}$)	3.28	6.32	35.15	5.92	2.49	1.88	2.54	2.80	7.91
CEC ($cmolkg^{-1}$)	12.60	12.20	20.00	19.40	20.80	33.20	17.80	21.60	19.20
BS (%)	68.40	61.20	57.06	71.33	43.76	43.95	50.07	64.47	62.98
Clay (%)	30.00	32.00	31.00	27.00	29.00	32.00	30.00	22.00	20.00

3.3 Fitting the Adsorption Data to Different Equations

The sorption isotherms were examined according to the linear form of the Langmuir, Freundlich and Tempkin equations. Langmuir adsorption isotherms were plotted by taking C/X against C (Fig. 2).

Regression coefficients (R^2) for the fitted Langmuir P adsorption isotherms were significant for soils from all sites except Fumbire (Table 2). The R^2 values were highest (0.984) in Umala and lowest in Yenga (0.583). The slope of the plot ($1/K_2$) was found less than 0.01 for all the soils. The binding energy was highest in Umala 0.021 L (mg P)$^{-1}$ and lowest in Fumbire 0.001L (mg P)$^{-1}$ soils. It was also observed that Sega soils had the lowest adsorption maxima while Moi bridge, Uboro and Barondar had the highest.

The adsorption isotherm was examined by the linear form of the Freundlich equation by plotting log C against log X. The equation showed a good linear fit to the data of the nine sites (Fig. 3).

The Tempkin equation was obtained by plotting X against ln C (Fig. 4). The equation did not show a good linear fit for all tested soils except Umala.

Regression coefficients (R^2) for the fitted Freundlich P adsorption isotherms were significant for all tested soils (0.995- 1.000) while R^2 was significant for eight soils in both Langmuir and Tempkin equations (Table 3). The exponent (b) was found high in all soils for Tempkin equation than for the other equations with maximum value of (252.11) while the other equations had exponent (b) values of less than 1.5. The three linear equations fitted very well in Umala soils.

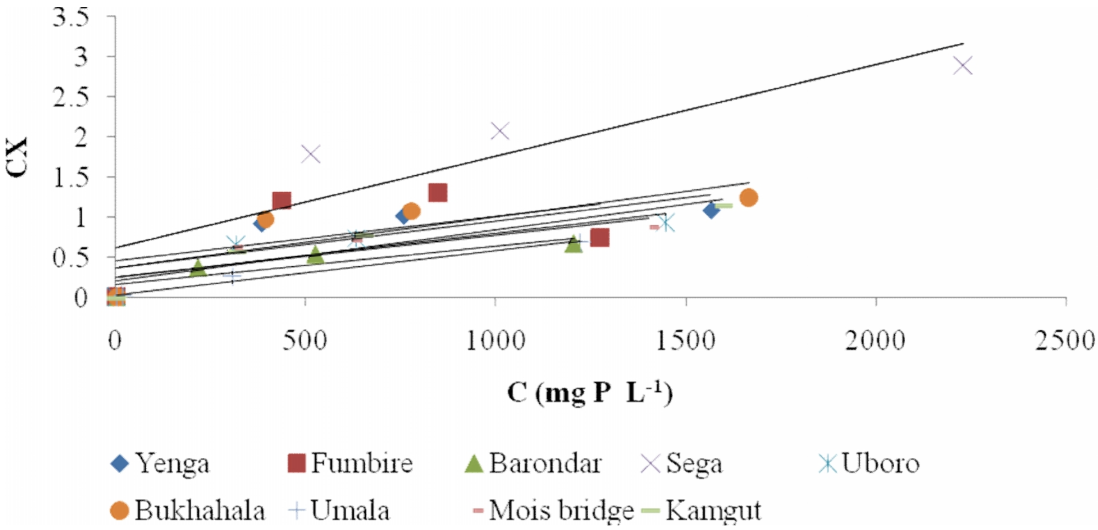

Fig. 2. Langmuir equation for soils in the nine sites

Table 2. Parameters of the fitted langmuir adsorption equations

Site	b_L	K_L	R^2
Yenga	1666.667	0.002	0.583*
Fumbire	1666.667	0.001	0.260 NS
Barondar	2000.000	0.003	0.773**
Sega	909.091	0.002	0.803**
Uboro	2000.000	0.002	0.702*
Bukhahala	1666.667	0.002	0.645*
Umala	1666.667	0.021	0.984***
Moi bridge	2000.000	0.002	0.682*
Kamgut	1666.667	0.002	0.804**

*bl- adsorption maxima (mg/kg); kl- constant related to binding energy; not significant, *- significant at p=.05 level; ***- significant at p≤.001 level*

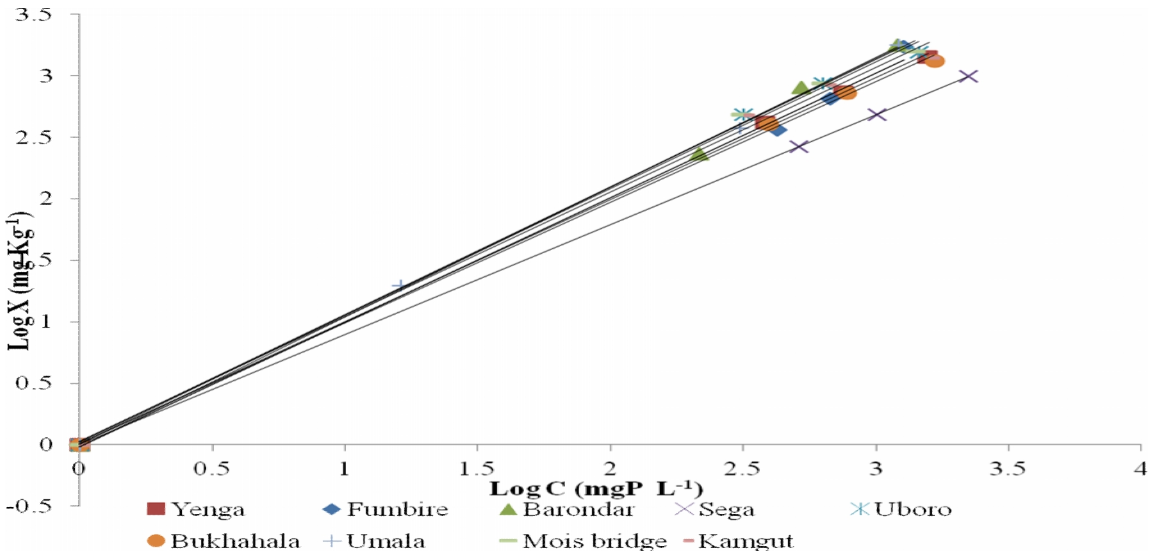

Fig. 3. Freundlich equation for soils in the nine sites

3.4 Relationship between Adsorption and Soil Properties

A significant correlation was observed between maximal adsorbed P, clay content and soil P (Bray I) for all the added P concentrations and soils (Table 4). A positive correlation between the soil pH, Aluminium saturation, Exchangeable acidity and Calcium with maximal P was also observed. Organic matter and electrical conductivity was negatively correlated with maximal adsorbed P.

4. DISCUSSION

Accuracy of adsorption isotherms slightly declined in predicting phosphorous adsorption from Freundlich isotherm to Tempkin and Langmuir equations. Freundlich model showed a better fit to the data compared to Langmuir model. Phosphorous calculated through different adsorption isotherms also yielded varied results. The results are similar to work reported by other authors [1,6,30,31,32,33]. The high conformity of the obtained adsorption data with the modified Freundlich model have been reported by [34]. Tempkin equation was found to be of limited value in determination of P adsorption in western Kenyan soils. This is because although the adsorption energy decreases linearly with increasing surface coverage, the relationship between amounts of P adsorbed and the logarithm of concentrations of P did not give a straight line. These results agree with [26,35,34].

As observed in Table 4, the significant correlation between maximal P adsorption and clay content , and the total amount of phosphorous adsorbed into the soil can be attributed to presence of sorptive sites. This could be related to the relatively large number of positive charges that can react and strongly bind the negatively charged phosphate ions in the solution. [6,31] also reported that maximal adsorption value increases with increasing values of clay content and phosphorus of soil. Negative correlation between adsorbed P with organic matter content and pH has also been reported by several researchers. [6,35] reported that presence of organic matter reduces P sorption capacity due to occupation of adsorption spaces by organic anions. The organic matter may also have reduced P- sorption capacity through direct competition for sorption sites between phosphate and organic ligands in the highly weathered soils [36]. The positive correlation of Phosphate adsorption with Aluminium saturation and exchangeable acidity is in agreement with findings by [6,37]. The negative relationship between soil electrical conductivity and phosphorous adsorption in soils was also observed by [6].

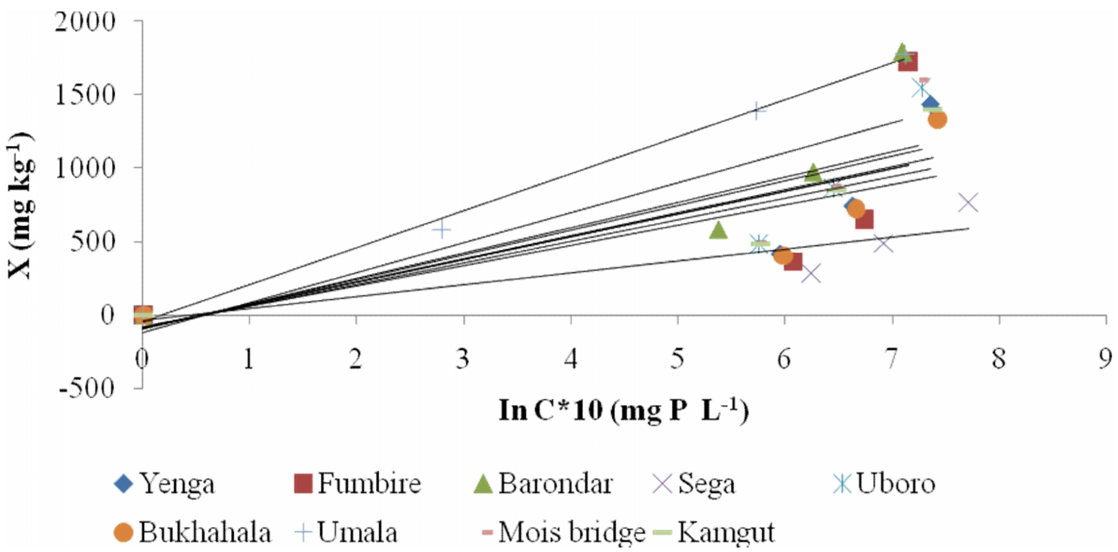

Fig. 4. Tempkin Equation for soils in the nine sites

Table 3. Regression equations with R^2 value for soils in the nine sites

Site	Langmuir		Freundlich		Tempkin	
	R^2	Y	R^2	Y	R^2	Y
Yenga	0.583	Y =0.0006x+0.3646	1.000	Y=0 .995x+0.0073	0.672	Y = 147.21x+86.134
Fumbire	0.260	Y =0.0006x+0.4561	0.997	Y=1.0134x-0.0166	0.494	Y = 155.45x-90.923
Barondar	0.773	Y = 0.0005x+0.7729	0.997	Y=1.0648x-0.0134	0.752	Y = 204.22x-117.77
Sega	0.803	Y = 0.0011x+0.6131	0.999	Y= 0.8864x+0.0104	0.783	Y = 81.537X-38.599
Uboro	0.702	Y = 0.0005x+0.7021	0.998	Y= 1.0317x+0.0207	0.725	Y = 168.67x-96.017
Bukhahala	0.645	Y = 0.0006x+0.375	0.999	Y= 0.9819x+0.0107	0.699	Y = 138.59x-79.074
Umala	0.984	Y = 0.006x+0.0284	1.000	Y = 1.0454x+0.007	0.996	Y= 252.11x-45.67
Moi bridge	0.682	Y = 0.0005x+0.2486	0.998	Y = 1.0381x+0.0195	0.715	Y = 172.89x-99.424
Kamgut	0.860	Y = 0.0006x+0.2079	0.995	Y = 1.0132x+0.0304	0.774	Y= 156.07x-83.177

Table 4. Relationship between Phosphorus adsorption maximum and some soil Properties

Soil property	Maximal adsorbed phosphorus
Organic Matter	-0.94*
Electrical Conductivity	-0.83*
pH	0.87**
Aluminium saturation	0.79**
Exchangeable Acidity	0.78**
Calcium	0.76*
Exchangeable Phosphorous	0.83*
Clay	0.90**

Correlation is significant at p=.05 level (two tailed)

5. CONCLUSION

The results depicted that Freundlich adsorption model is the most precise in predicting P adsorption in the soils of the tested region. The results also revealed differences in P adsorption among soils from the study sites. The differences in the P adsorption maxima of the studied sites indicate that use of blanket P fertilizer rate recommendations for the whole western Kenya may affect crop yields in some sites.

Additionally, the study identified soil pH, organic matter, aluminium and bases like calcium as some of the factors that influence P availability. There is therefore, need for more intensive studies to understand the role and interactions of soil properties on P availability in the study area.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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