EVALUATION OF PHYSICO-CHEMICAL PROPERTIES AND P SORPTION CHARACTERISTICS OF SOIL WITH DIFFERENT LAND USE IN TIGONI, KIAMBU COUNTY, CENTRAL KENYA †

[EVALUACIÓN DE PROPIEDADES FÍSICO-QUÍMICAS Y CARACTERÍSTICAS DE SORPCIÓN DE P DE SUELOS CON DISTINTOS USOS DE SUELO EN TIGONI, CONDADO DE KIAMBU, KENIA CENTRAL]

Kiplangat Rop[1*], George N. Karuku[2] and Caroline W. Nduhiu[2]

[1]Department of Chemistry, University of Nairobi, P.O. Box 30197-00100, Nairobi, Kenya, E-mail kiplangatrop@uonbi.ac.ke
[2]Department of Land Resource and Agricultural Technology, University of Nairobi, P.O. Box 29053-00625, Kangemi, Nairobi, Kenya
**Corresponding author*

SUMMARY

Background: Phosphorous is a limiting crop nutrient in highly weathered tropical soils due to fixation, and its availability for plants' uptake is influenced by soil physico-chemical characterics, land use type and management practices. **Objective:** To evaluate the relationship between selected physico-chemical properties and phosphorous sorption characteristics of a humic nitisol (Alfisol) from Tigoni, Kiambu County, central Kenya. **Methodology:** The soil was sampled from the same area with different land uses that include tea plantation, maize field and natural forest at 0-25, 25-50 and 50-75 cm depths. P solution at the rates of 50, 100, 150, 200 mg P L^{-1} in a 24 h contact time were used in the study for maximum sorption. The data was analysed by simple regression and Pearson correlation analysis. **Results:** The adsorption data was fitted more to Langmuir model (R^2 = 0.9100-0.9994) compared to Freundlich (R^2 = 0.6815-0.9971). The values of P sorption maxima (Q_{max}) determined by Langmuir model ranged from 3,333-5,000 mg kg^{-1} and bonding energies (k) ranged from 0.2308-1.5385 L mg^{-1}. The buffering capacity of soil ranged from 769-5000 L kg^{-1} and the external P requirement at 0.2 mg kg^{-1} ($EPR_{(0.2)}$) ranged from 147-1176 mg P kg^{-1} both increasing with soil depth. P sorption maxima were negatively and significantly correlated with organic carbon (r^2 = -0.700*) and Ca^{2+} (r^2 = -0.703*) contents. The pH of soil and clay content were negatively correlated with adsorption parameters (Q_{max}, k, K_f, $EPR_{(0.2)}$) while Al content was positively correlated though none of them was statistically significant. **Implication**: The data revealed a highly P-sorbing soil particularly tea plantation, a situation that can be alleviated by management practices such as liming and enhancing soil organic matter content. Field experiments are however, recommended to validate the findings of this study. **Conclusion:** Land use type influences P-sorption capacity of soil hence, fertilizer recommendations should be based on soil physico-chemical characteristics besides crop nutrient requirements.

Key words: p-sorption; pH; land use; soil physico-chemical properties; humic nitisol.

RESUMEN

Antecedentes: El fósforo es un nutriente limitante para los cultivos en suelos tropicales muy meteorizados debido a que la fijación, y su disponibilidad para la absorción por las plantas está influenciada por las características fisicoquímicas del suelo, el tipo de uso de la tierra y las prácticas de manejo. **Objetivo:** Evaluar la relación entre las propiedades fisicoquímicas seleccionadas y las características de sorción de fósforo de un nitisol húmico (Alfisol) de Tigoni, condado de Kiambu, Kenia central. **Metodología:** El suelo fue muestreado de la misma área con diferentes usos de suelo que incluyen plantación de té, campo de maíz y bosque natural a 0-25, 25-50 y 50-70 cm de profundidad. En el estudio se utilizó solución de P a razón de 50, 100, 150, 200 mg P L^{-1} en un tiempo de contacto de 24 h para obtener la máxima sorción. Los datos fueron analizados por regresión simple y análisis de correlación

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de Pearson. Resultados: Los datos de adsorción se ajustaron más al modelo de Langmuir (R^2 = 0.910-0.999) que al de Freundlich (R^2 = 0.681-0.997). Los valores máximos de sorción de P (Q_max) determinados por el modelo de Langmuir oscilaron entre 3.333 y 5.000 mg kg^{-1} y las energías de enlace (k) oscilaron entre 0.2308 y 1.5385 L mg^{-1}. La capacidad amortiguadora del suelo osciló entre 769 y 5000 L kg^{-1} y el requerimiento externo de P a 0.2 mg kg^{-1} (EPR_((0.2))) osciló entre 147 y 1176 mg P kg^{-1}, ambos aumentando con la profundidad del suelo. Los máximos de sorción de P se correlacionaron negativa y significativamente con los contenidos de carbono orgánico (r2 = -0.70*) y Ca_2+ (r^2 = -0.703*). El pH del suelo y el contenido de arcilla se correlacionaron negativamente con los parámetros de adsorción (Q_max,k,K_f,EPR_((0.2))) mientras que el contenido de Al se correlacionó positivamente aunque ninguno de ellos fue estadísticamente significativo. **Implicaciones:** Los datos revelaron un suelo altamente absorbente de P, particularmente plantaciones de té, una situación que puede aliviarse con prácticas de manejo como el encalado y la mejora del contenido de materia orgánica del suelo. Sin embargo, se recomiendan experimentos de campo para validar los hallazgos de este estudio. **Conclusión:** El tipo de uso de la tierra influye en la capacidad de absorción de fósforo del suelo, por lo tanto, las recomendaciones de fertilizantes deben basarse en las características fisicoquímicas del suelo además de los requisitos de nutrientes de los cultivos.

Palabras clave: sorción de P; pH; uso del suelo; propiedades fisicoquímicas del suelo; nitisol húmico.

INTRODUCTION

The overall productivity and sustainability of agricultural sector are functions of fertile soils and therefore, the application of phosphorous (P) to the soil is essential for optimal crop yields. The limited availability of P is a major constraint in crop production particularly in highly weathered tropical soils such as the oxisols and ultisols (Moazed *et al*., 2010; Campos *et al*., 2016; Getie *et al*., 2021). This is attributed to low activity clays and inherent P content, high weathering incidence and soil reactions, and the situation could be aggravated by improper anthropogenic P management such as intensive cultivation without adequate supply of external P, among others (Moazed *et al*., 2010; Getie *et al*., 2021).

The initial growth stages of plants predominantly depend on P due to its role in cell division and root development and hence, retarded growth as deficiency symptom for P may be too late to salvage (Grant *et al*, 2001). It is estimated that > 80% of P applied to the soil is immobile and unavailable for plant uptake, a phenomenon ascribed to P adsorption/fixation (Muindi *et al.,* 2014; Rop *et al*., 2018). The degree of P sorption and availability in soil vary from soil to soil due to differences in their physico-chemical properties and management (Moazed *et al*., 2010; Muindi *et al* 2014; Ayenew *et al*., 2018). Therefore, understanding P sorption characteristics is essential in the design of appropriate management strategies and prediction of fertilizer requirements for a particular soil (Ayenew *et al*., 2018) and crop(s). Physico-chemical properties that influence P sorption include soil texture, organic carbon, soil pH, porosity, clay content, Fe and Al contents, cation exchange capacity (CEC), exchangeable bases, hydraulic conductivity, among others (Moazed *et al*., 2011; Muindi *et al*., 2014; Sun *et al*., 2016). For instance, crop response to P application is often erratic in acidic soil due to formation of insoluble compounds with Al and Fe at low pH values particularly in Luvisols and Nitisols which are deep, well drained, and with high clay content (Getie *et al*., 2021). High affinity for P sorption in such highly weathered soils is attributed to the clay fraction that is dominated by 1:1 silicate mineral, and oxides, hydroxides and oxyhydroxides of Al, Fe, Mn (Campos *et al*., 2016). Land use type is also among the factors influencing P-sorption capacity of soil (Moazed *et al*., 2010).

Up to date, many workers have carried out extensive studies and proposed a number of techniques for evaluating P status in soil. Adsorption isotherm is an important criterion often used to estimate P content in aqueous phase of soil, energy of P sorption, maximum value of adsorbed P and buffer capacity (Muindi *et al.,* 2014 & 2017). Sorption isotherm is a functional relationship that quantifies the amount of P adsorbed as a function of solution concentration in a dynamic equilibrium (Saki *et al*., 2019). It is explained by fitting P adsorption data into Linear, Langmuir, Freundlich, Tempkin models, among others (Muindi *et al.*, 2014; Campos *et al*., 2016; Getie *et al*., 2021). These models are used to describe P sorption characteristics of soil as well as determination of external P requirement (EPR) for crops at equilibrium concentration of 0.2 mg L^{-1} soil solution (Muindi *et al.,* 2014; Getie *et al*., 2021).

Among the major challenges faced by farmers in Kiambu County are low crop yields due low available P content in soil attributed to fixation. It is therefore imperative to assess P adsorption behavior of such soil and establish P requirements for optimal crop yields. This study evaluated the influence of selected soil physico-chemical properties and land use type on P sorption characteristics. The data will help in the National and County government policy formulation, farmers and other stakeholders in the agricultural sector to make informed decisions as regards P management strategies for improved yields.

MATERIAL AND METHODS

Description of the study site

The study was carried out on 9 soil samples collected from Kenya Agricultural & Livestock Research Organization (KALRO) station at Tigoni, 40 km North-West of Nairobi city center, Kenya. The site is located on the latitude 1°9’0’’S and longitude 36° 41’0’’ E as shown in Figure 1, with an elevation of 2131m above sea level (Jaetzold *et al*., 2006). The rainfall distribution is bi-modal with long rains from March - May and short rains from October - December. The mean annual rainfall is about 1096 mm and average monthly temperature is 18.0 ºC with a minimum of 12°C and a maximum of 24 °C (Jaetzold *et al*., 2006). The soils are deep, well-drained, reddish-brown friable clays and are classified as humic Nitisol derived from quartz trachyte (Jaetzold *et al*., 2006; WRB, 2014). The soil pH range from 4.3 to 5.82 (Muthoni and Kabira, 2010). The crops grown in the area include tea, maize, potatoes, and horticultural crops.

Soil sampling and preparation for analysis

Soil sub-samples were collected from 9 sampling points in three diferent land use types including tea plantation, maize field and forest land (Fig. 1) at the depths of 0-25, 25-50 and 50-75 cm in a zigzag sampling scheme using a 600 cm^3 soil auger. Sub-samples from the same depth in each of the land use type were placed in the same plastic bucket then homogenously mixed to make a composite sample (3 land use types × 3 depths = 9 composite samples). 1 kg each of the composite samples were air-dried at room temperature and sieved to pass a 2 mm sieve. They were each divided into two portions; one portion was used in the determination of physico-chemical characteristics and the rest taken for adsorption experiments.

Determination of soil physico-chemical characteristics

The particle size distribution was determined by hydrometer method (Glendon and Doni, 2002) and soil pH measured in a 1:2.5 soil to water ratio using a pH meter (with glass electrodes). Organic carbon (%OC) was estimated by wet oxidation method (Nelson and Sommers, 1996). Cation exchange capacity (CEC) was determined by leaching the soil with 1 M NH_4OAc at pH 7 and the NH_4^+ ions quantified in the leachate by steam distillation using micro-Kjeldahl method (Bremner, 1996). Exchangeable cations were extracted using 1 M NH_4OAc and the extract analyzed for Na^+ by flame photometry, and Ca^{2+} and Mg^{2+} determined by atomic absorption spectrophotometer (AAS). Exchangeable Mn^{2+} and Fe^{2+} were extracted by Mehlich I method using a mixture of dilute acids that include 0.05 M HCl and 0.05 M H_2SO_4 (Mehlich, 1953) and analyzed by AAS. Exchangeable Al^{3+} was determined by extracting with KCl and titrating with NaOH (Yuan, 1959).

Phosphorous sorption experiment

The adsorption experiment was carried out according to Ayenew *et al*. (2018) and Saki *et al*. (2020) using KH_2PO_4 containing 0.1 M $CaCl_2$ solution. Specifically, 2 g of dry soil sample of particles size < 2mm was added 50 mL of KH_2PO_4 at rates of 50, 100, 150, 200 mg P L^{-1} in 0.01 M $CaCl_2$ background solution. Each of these concentrations was replicated three times for each soil sample. Three drops of toluene were added to each flask to inhibit microbial activity after which, the flasks were placed in a mechanical shaker rotating at a speed of 180 rpm for 24 h. The supernatant was filtered through a Whatman No. 42 filter paper and P content in the filtrate determined by molybdate blue method (Murphy and Riley, 1962) using a Uv-Vis spectrophotometer (UV-1700, Shimadzu Corporation, Japan). The procedure was carried out alongside a blank which contained the same amount soil and same volume of 50 mL 0.01 $CaCl_2$ solution (without P) to serve as background control for detection of any contamination or interfering compounds. The amount of adsorbed P was calculated from the difference between the initial and equilibrium concentration of P solution according to Equ 1 (Sun, *et al*., 2015).

$$Qe = \frac{V(C_o - C_e)}{W} \quad (1)$$

where, Qe is P adsorbed at equilibrium (mg kg^{-1}), Co and Ce are the initial and equilibrium concentrations of P solution (mg L^{-1}), respectively.

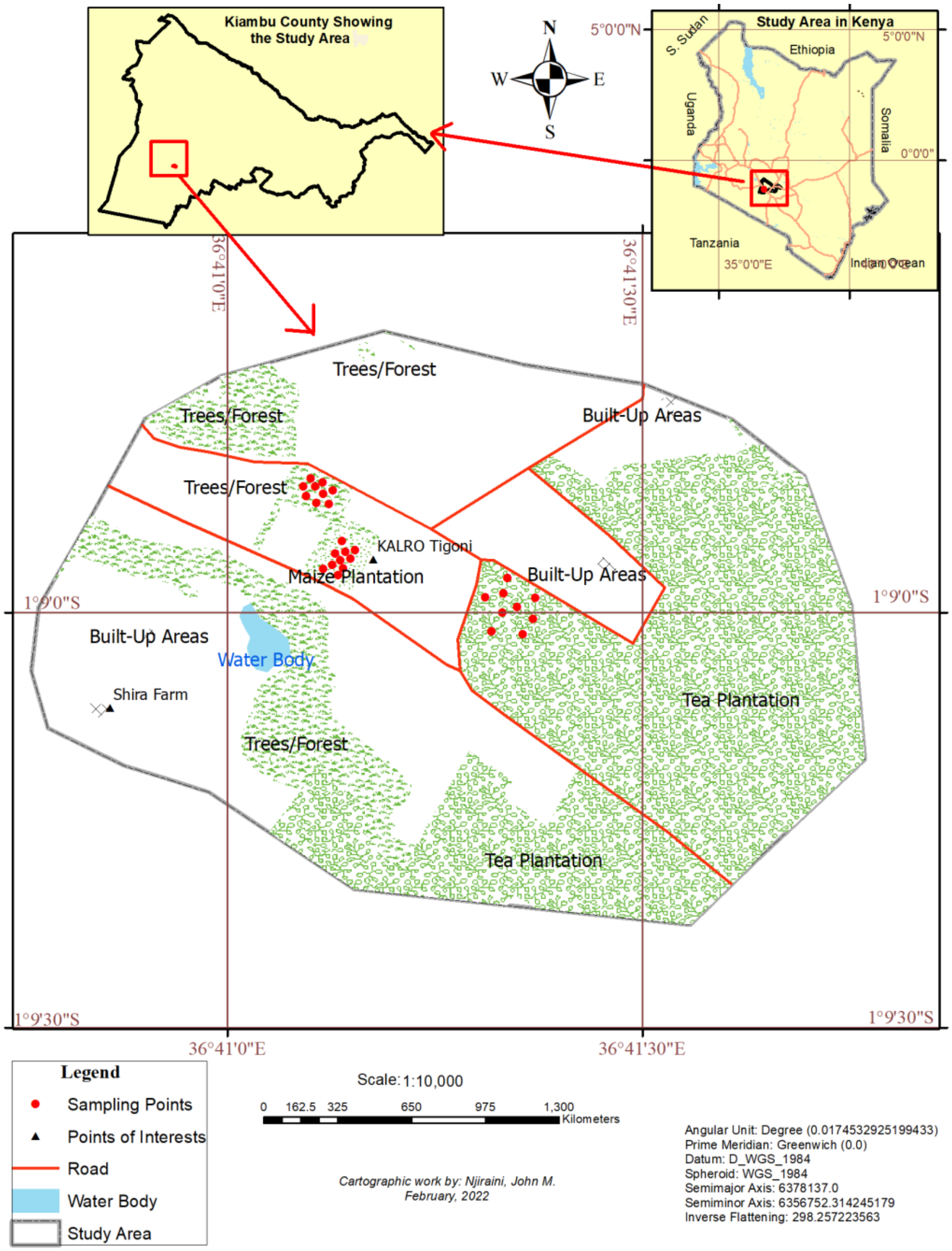

Figure 1. Geographical location of Tigoni, Kiambu county, central Kenya.

Determination of adsorption parameters

The data obtained from P adsorption experiment was fitted to linear forms of Langmuir and Freundlich models.

The linear form of Langmuir model is given by Equ (2).

$$\frac{Ce}{Qe} = \frac{1}{kQ_{max}} + \frac{Ce}{Q_{max}} \qquad (2)$$

where, Qe is the adsorbed P at equilibrium (mg kg^{-1}), Ce is the concentration of P solution at equilibrium (mg L^{-1}), k is the affinity constant related to bonding energy of soil (L mg^{-1}) (Moazed *et al.*, 2010; Campos *et al.*, 2016; Ayenew *et al.*, 2018). Q_{max} is the maximum adsorbed P (mg kg^{-1}) given by the reciprocal of the slope of the regression curve of Ce/Qe verses Ce. The product of Langmuir constants k and Q_{max} gives the buffering capacity of soil, a factor that measures the ability of soil to replenish P ions to the soil solution as they tend to get depleted

(Ayenew *et al*., 2018; Saki *et al*., 2020; Getie *et al*., 2021).

The Langmuir isotherm considers sorption onto homogeneous layers, whereas Fruendlich isotherm is an empirical model assuming sorption to be taking place on heterogeneous surfaces being predominantly chemisorption (Saki *et al*., 2020).

The Langmuir model was used to determine the separation factor R_L using Equ (3).

$$R_L = \frac{1}{1 + kC_o} \qquad (3)$$

where, C_o is the initial concentration of P in contact with soil, $R_L$is a representative for the shape of the isotherm; 0 <R_L<1 implies favorable sorption, R_L> 1 unfavorable, R_L= 0 irreversible, and $R_L = 1$ linear sorption (Saki *et al*., 2020).

The linear form of Freundlich model is given by Equ (4).

$$ln\ Qe = ln\ K_f + \frac{1}{n}\ ln\ Ce \qquad (4)$$

where, Qe is the amount of adsorbed P at equilibrium (mgkg^{-1}), Ce is the concentration of P solution at equilibrium (mg L^{-1}), K_f is the proportionality constant for Freundlich model representing the amount of P adsorbed (mg kg^{-1}) at a unit equilibrium concentration (Muindi *et al*., 2014; Saki *et al*., 2020) and n is the empirical constant related to binding energy of soil for P.

The external P requirements (EPR) were calculated using the Langmuir and Freundlich models. EPR is the amount of P that must be added to the soil to maintain a soil P solution concentration of 0.2 mg P L^{-1}, a critical level below which crops are P deficient (Getie *et al*., 2021; Muindi *et al*., 2017).

Statistical analysis

Statistical analysis was performed using IBM SPSS Statistics Version 20. P-sorption data was subjected to ANOVA, Tukey HSD post hoc test was used to compare and assess significance of the mean values at $P \leq 0.05$. Pearson correlation significance was computed between soil physico-chemical properties and P-sorption parameters at 0.05 and 0.01 confidence levels (P<0.05 and P< 0.01).

RESULTS AND DISCUSSION

The selected physico-chemical characteristics of studied soil are presented in Table 1. The percentage organic carbon (% OC), cation exchange capacity (CEC) and exchangeable Ca, Mg, Na, Mn and Al all generally decreased with depth except Fe which showed increased content in maize field soil (M1-M3). Exchangeable Al content was the highest in tea plantation soil (T1-T3; 1.28-1.86 cmol kg^{-1}) compared to forest (F1-F3) and maize field (M1-M3), an observation that could be related to the effect of other soil physico-chemical properties including the pH, OC content and CEC. According to Landon (1991), exchangeable Al content > 2 cmol kg $^{-1}$ is considered excess for many crops though there are no acceptable critical levels. CEC was < 15 cmol kg^{-1} hence considered low. The % OC content ranged from moderate to high with average and good structural conditions and stabilities, respectively (Landon 1991). The variation in the % OC content may be attributed to management practices such as soil pH, tillage practices, residue management, among others. Basic cations including Na^{+} were low, Ca^{2+} and Mg^{2+} ranged from low to moderate levels hence the varied soil reaction.

The pH values of soil ranged from strong to moderate acidity (Landon 1991), indicating presence of considerable quantities of H^{+}, Al^{3+}, Fe^{3+}, Mn^{4+} ions. The soil acidity was attributed to humid conditions in the studied site that causes leaching of basic cations such as Na^{+}, Ca^{2+}, Mg^{2+} and K^{+}. Soil pH showed a decrease with depth in the forest soil whereas an increase was observed in both tea plantation (T1-T3) and maize field (M1-M3) soil. Tea plantation soils recorded the lowest pH value in the surface horizon (0-25cm) probably due to higher Al content, low base saturation and relatively lower % OC content that create buffering capacity compared to those of forest and maize field. Soil organic matter plays a vital role in enhancing the buffering capacity of soil reducing the strength of P sorption (Yang *et al*., 2019). Li *et al*. (2016) assesing possible cause soil acidity in tea plantations using soil column experiments observed downward movement of H^{+}, NH$_4$-N and OC, and the organic matter enhanced top soil pH but not > 80 cm depth. These authors also noted excretion of more H^{+} to the rhizosphere by tea plants at higher planting density relative to those at lower planting density. Wan *et al* (2018) associates soil acidification in tea plantations with Al enhanced plasma membrane H^{+}-ATPase activity and excess cation uptake. The low pH values in tea plantation soil was also linked to lower Ca and Mg contents relative to those of forest and maize field. Ca^{2+} and Mg^{2+} ions are bases that have the effect of neutralizing the acidity of soil (Rop *et al*, 2018). The soil texture was predominantly clayey with some slight variation in clay content which may be attributed to the intensity of cultivation and land use history.

The amounts of P adsorbed at equilibrium (Q_e) with increased initial solution concentration (C_o) of KH_2PO_4 ranging from 50-200 mg L^{-1} are shown in Table 2. Q_e values of soil at similar depths were comparable at C_o of 50 mg L^{-1} which thereafter recorded significantly ($p \leq 0.05$) higher values at C_o of 100 mg L^{-1} and 150 mg L^{-1} in the soil samples from tea plantation (T1-T3) relative to those of forest and maize field. Statistically significant Q_e values were recorded down the profile in nearly all the sites at C_o of 100 and 150 mg L^{-1} which could probably be due to optimal activity of sorption sites of the studied soil type at these concentrations. The general increase in Q_e values with depth was attributed to the decrease in % OC, basic cations (Ca^{2+}, Mg^{2+}, K^+) content and the pH down the profile causing enhanced P sorption capacity (Table 1).

The values of Langmuir affinity constant (k), P sorption maxima (Q_{max}), buffering capacity and external phosphate requirement at 0.2 mg L^{-1} ($EPR_{(0.2)}$) are presented in Table 3. Adsorption data yielded high R^2 values ranging from 0.9100-0.9994 indicating good fit to the model. The Q_{max} values were higher in tea plantation soil (T1-T2), lower horizon of forest (F2 & F3) and maize field soil (M3) all recording 5,000 mg kg^{-1}relative to surface and sub-surface soil of F1, M1 & M2 which recorded 3,333 mg kg^{-1}. The high sorption values could be due

Table 1. Selected physico-chemical characteristics of studied soil.

Sample ID	Clay (%)	Silt (%)	Sand (%)	Textural class	OC (%)	pH (H_2O)	CEC (cmol kg^{-1})	Ca (cmol kg^{-1})	Mg (cmol kg^{-1})	Na (cmol kg^{-1})	$Al_{Ex.}$ (cmol kg^{-1})	Mn (mg kg^{-1})	Fe (mg kg-1)
F1	51	16	33	CL	2.11	5.9	8.4	1.32	4.40	0.15	1.12	195.4	120.1
F2	49	12	39	CL	2.00	5.4	8.2	1.12	2.89	0.14	0.87	137.0	70.0
F3	47	6	47	SCL	1.97	4.4	7.6	0.99	2.48	0.14	0.74	98.2	38.9
T1	47	14	39	SCL	1.93	4.6	12.4	0.75	1.99	0.18	1.86	197.9	101.4
T2	47	10	43	SCL	1.86	4.8	10.6	0.50	1.38	0.15	1.56	144.1	66.8
T3	47	8	45	SCL	1.58	4.9	10.4	0.36	1.28	0.14	1.28	89.7	40.8
M1	47	16	37	SCL	2.39	5.4	11.0	1.72	2.52	0.19	0.66	166.8	37.5
M2	47	14	39	CL	2.37	5.7	10.4	1.66	2.28	0.18	0.53	138.5	61.1
M3	49	12	39	CL	2.23	5.9	10.2	1.51	2.10	0.17	0.43	104.2	62.7

Note: The reported values are the averages (n=3)

Legend: *F1 forest 0-25 cm, F2 forest 25-50 cm, F3 forest 50-75 cm; T1 tea 0-25 cm, T2 tea 25-50 cm, T3 tea 50-75 cm; M1 maize 0-25 cm, M2 maize 25-50 cm, M3 maize 50-75 cm. OC-organic carbon, CEC-cation exchange capacity, CL-clay, SCL-sandy clay*

Table 2. Amount of P adsorbed at equilibrium (mg kg^{-1}) with increased initial solution concentration of P (mg L^{-1}).

Initial conc. of KH_2PO_4, Co (mg L^{-1})	50	100	150	200
Sample Id.	P adsorbed at equilibrium (Qe) mg kg^{-1}			
F1	1240 (±1.7)ab	2250 (±1.7)ab	2900 (±10)b	3765 (±106)abcd
F2	1243 (±2.0)b	2250 (±4.7)ab	3150 (±2.5)d	4157 (±206)cd
F3	1245 (±2.0)b	2375 (±4.2)d	3525 (±6.1)f	4289 (±83)cd
T1	1238 (±1.2)ab	2400 (±19.1)e	3325 (±9.0)e	3718 (±493)abc
T2	1238 (±3.0)ab	2450 (±7.0)f	3325 (±7.2)e	3947 (±62)bcd
T3	1245 (±3.8)b	2475 (±4.0)g	3550 (±6.0)f	4352 (±20)d
M1	1233 (±3.5)a	2225 (±5.6)a	2000 (±18.5)a	3302 (±139)a
M2	1240 (±3.6)ab	2275 (±5.7)c	3025 (±9.0)c	3560 (±185)ab
M3	1245 (±2.5)b	2375 (±5.3)d	3175 (±4.6)d	4118 (±146)bcd

Note: The values in parentheses are standard deviations (n=3). Diferent letters in the same column are significantly different (Tukey test; $p \leq 0.05$ level).

Legend: *F1 forest 0-25 cm, F2 forest 25-50 cm, F3 forest 50-75 cm; T1 tea 0-25 cm, T2 tea 25-50 cm, T3 tea 50-75 cm; M1 maize 0-25 cm, M2 maize 25-50 cm, M3 maize 50-75 cm.*

Table 3. Langmuir adsorption parameters. .

Sample Id	Regression Equ.	R^2	Q_{max} (mg kg^{-1})	k (Lmg^{-1})	Buffering capacity (L kg^{-1})	R_L	EPR$_{(0.2)}$ (mg kg^{-1})
F1	Y=0.0003x+0.0012	0.9565	3333	0.2500	833	0.020-0.074	158
F2	Y=0.0003x+0.0010	0.9590	5000	0.3000	1500	0.016-0.063	281
F3	Y=0.0002x+0.0006	0.9815	5000	0.3333	1667	0.015-0.057	312
T1	Y=0.0002x+0.0003	0.9904	5000	0.6666	3333	0.007-0.029	588
T2	Y=0.0002x+0.0002	0.9994	5000	1.0000	5000	0.005-0.019	833
T3	Y=0.0002x+0.0013	0.9506	5000	1.5385	7693	0.003-0.013	1176
M1	Y=0.0003x+0.0013	0.9100	3333	0.2308	769	0.021-0.080	147
M2	Y=0.0003x+0.0012	0.9807	3333	0.2500	833	0.020-0.074	158
M3	Y=0.0002x+0.0006	0.9665	5000	0.3333	1667	0.015-0.057	313

***Legend**: F1 forest 0-25 cm, F2 forest 25-50 cm, F3 forest 50-75 cm; T1 tea 0-25 cm, T2 tea 25-50 cm, T3 tea 50-75 cm; M1 maize 0-25 cm, M2 maize 25-50 cm, M3 maize 50-75 cm,* Q_{max} *is the maximum adsorbed P,* k *is the Langmuir constant,* R_L *is the separation factor,* $EPR_{(0.2)}$ *is the external P requirements at concentration of 0.2 mg P L*$^{-1}$.

to high clay content of soil which provides a large specific surface area for P sorption (Hartono, *et al*., 2005). In a similar study, Campos *et al*. (2016) evaluating P sorption index of humid tropical soils obtained high Q_{max} values up to 5,459.5 mg kg^{-1} in Mollic Fluvaquent attributing it high C and Al oxides contents. k values ranged from 0.2308 (M1) to 1.5385 L mg^{-1} (T3) and it generally increased with soil depth. This constant is a factor associated with bonding energy and it increases with tenacity of P sorption (Moazed *et al*., 2010; Wolde and Haile, 2015; Getie *et al*., 2021), implying more favorable P sorption conditions at the lower horizon than surface and sub-surface horizons of the studied soil. The tea plantation soil recorded the highest values of maximum buffering capacity ranging from 3,333-7,693 L kg^{-1} (T1-T3) compared with those from forest (833-1,667 L kg^{-1}) and maize field (769-1,667 L kg^{-1}) and this increased with soil depth. It can be observed that, soil with higher exchangeable Al content (T1-T3) appears to exhibit greater buffering capacity implying higher P sorption than less buffered ones (Table 1).

The separation factor (R_L) for all the samples were within the range of 0 to 1 suggesting favorable P sorption particularly at lower initial concentration of P solution than at higher initial concentration. For instance, at C_o = 50 mg L^{-1}; R_L= 0.074 (F1), 0.063 (F2), 0.057 (F3), 0.029 (T1), 0.019 (T2), 0.013 (T3), 0.080 (M1), 0.074 (M2), 0.057 (M3). This was ascribed to the decreased surface affinity with increased concentration of P, a phenomenon accredited to saturation of high affinity sites and increased electrostatic barriers as negatively charged P ions bind onto the surface of soil (Saki *et al*., 2020).

The EPR$_{(0.2)}$ values increased with depth and the highest values were obtained in tea plantation soil (T1-T3; 588-1176 mg kg^{-1}) compared to lowest values recorded in surface soil from maize field (M1; 147 mg kg^{-1}) and forest (F1; 158mg kg^{-1}). According to Fox and Kamprath (1970), soil sorbing < 150 mg kg^{-1} to meet an EPR value of 0.2 mg L^{-1} are considered low P sorbing soils while those with sorbing amounts greater than this value are high P sorbing ones (Getie *et al*., 2021). This therefore implies that, the EPR values recorded in M1 indicate low P sorbing soil while the rest are high P sorbing. Muindi *et al*. (2017) evaluating soils from central Kenya highlands using Langmuir model obtained comparable sorption maxima of 3,333 mg kg^{-1} and EPR $_{(0.2)}$ values ranging from 208-434 mg kg^{-1} at 0-50 cm depth. They attributed high P sorption capacity to highly weathered soil and predominant gibbsite [$Al(OH)_3$] minerals having large surface area for P sorption. The current study however obtained a relatively higher value of 5,000 mg kg^{-1} in tea plantation soil from 0-75 cm depth, lower horizons of forest soils at 25-75 cm depth and maize field at 50-75 cm depth. Similarly, Hartono *et al*. (2005) evaluating acidic soils of Indonesia observed increasing trend of EPR$_{(0.2)}$ with increased sorption maxima with soil depth. Kisinyo *et al*. (2013) studying soil at 0-20 cm depth using Langmuir model obtained higher P sorption capacity and lime requirements in the soils from East of Rift Valley (RV) compared to West of RV and attributed it to higher exchangeable Al and bonding energies between soil colloids and P ions.

Freundlich adsorption parameters including proportionality constant (K_f) and external phosphate requirement (EPR) are presented in Table 4. The R^2 values ranged from 0.6815 to 0.9971 indicating lesser fit of P adsorption data compared to Langmuir model. The extent at which P sorption data fit into these models has been linked to soil physico-chemical

Table 4. Freundlich adsorption parameters.

Sample Id	Regression Equ.	R^2	K_f (mg kg^{-1})	$EPR_{(0.2)}$(mg kg^{-1})
F1	Y=0.2051x+7.1778	0.6815	1310	942
F2	Y=0.2180x+7.3774	0.9463	1599	1126
F3	Y=0.2626x+7.4668	0.9552	1749	1146
T1	Y=0.2611x+7.3482	0.9813	1553	1020
T2	Y=0.2578x+7.4193	0.9335	1668	1101
T3	Y=0.2605x+7.4922	0.9775	1794	1179
M1	Y=0.1870x+7.1823	0.8599	1316	974
M2	Y=0.2128x+7.2974	0.9971	1476	1048
M3	Y=0.2105x+7.4767	0.9774	1766	1246

***Legend**: F1 forest 0-25 cm, F2 forest 25-50 cm, F3 forest 50-75 cm; T1 tea 0-25 cm, T2 tea 25-50 cm, T3 tea 50-75 cm; M1 maize 0-25 cm, M2 maize 25-50 cm, M3 maize 50-75 cm , K_f is the proportionality constant for Freundlich model, $EPR_{(0.2)}$ is the external P requirements at concentration of 0.2 mg P L^{-1}.*

properties and sorption sites. For example, sorption data of soil with homogeneous sites are better fitted to Langmuir than Freundlich model, while those having heterogeneous sites are best fitted to Freundlich model (Wolde and Haile, 2015). K_f values ranged from 1310 -1794 mg kg^{-1} and were generally higher in tea plantation soil compared to the rest at similar depths. High K_f values of soil are indicative of strong affinity of P towards the soil (Ayenew *et al.*, 2018). The variation in K_f values could be attributed to disparity in Al and Fe content as well as soil texture (Table 1). Based on Freundlich model, EPR at 0.2 mg L^{-1} ranged from 942 (F1) to 1246 (M3) mg kg^{-1} and generally increased with depth, and since these values are > 150 mg kg^{-1}, it is a clear indication of a high P sorbing soil.

The recommended P fertilizer application rates for small scale tea farmers is 600 kg NPK ha^{-1} 25:5:5 (30 kg P ha^{-1}) (Wachira, 2012; Kamunya *et al.*, 2019) equivalent to 15 mg P kg^{-1} soil, and that of maize in Kiambu County is 250 kg DAP ha^{-1} 23:23:0 (57.5 kg P ha^{-1}) (NAAIAP, 2014) equivalent to 28.75 mg P kg^{-1} soil. These rates are far much lower than the estimated EPR $_{(0.2)}$ values of 147-1176 mg kg^{-1} by Langmuir model (Table 3) and 942-1179 mg kg^{-1} by Freundlich model (Table 4). For that reason, application of P fertilizer based on the above blanket recommendation may result in poor yields due to P deficiency to the crops grown. The current P content in the fertilizer formula particularly for tea is generally low and hence, it ought to be increased to enhance the amount being supplied to the crop from soil. The availability of P could also be enhanced by devising ways in which high sorption capacity of soil can be reduced.

The relationship between soil physico-chemical characteristics and P sorption parameters are presented in Table 5. Phosphorous sorption maxima (Q_{max}) were negatively but significantly correlated with OC (r^2 = -0.700*) and Ca^{2+} (r^2 = -0.703*) contents. k and EPRL values were also negatively but significantly correlated with OC (r^2 = -0.852**, -0.880**), Ca^{2+} (r^2 = -0.864**,-0.902**) and Mg^{2+} (r^2 = -0.669*, -0.721*) contents. The negative correlation between adsorbed P and organic matter was attributed to direct interaction between them which occurs when they compete for soil adsorption sites leading to decreased P sorption (Janardhanan and Daroub, 2010). Muindi *et al.* (2017) made a similar observation attributing the negative correlation between maximum adsorbed P and organic matter to occupation of adsorptive sites by organic anions thus reducing P sorption capacity of soil. The pH of soil showed a negative but significant ($p \leq 0.05$) correlation with 1/n (r^2 = -0.868**) while, K_f and EPRF values were negatively but significantly correlated with Mn^{2+} contents (r^2 = -0.811**, -0.876**). The pH of soil and clay content were negatively correlated with adsorption parameters (Q_{max}, k, K_f, EPRL) while Al content was positively correlated though none of them was statistically significant. The observation could be due to the same type of soil with similar mineral composition and slight variation in physico-chemical characteristics.

The correlations between soil physico-chemical properties and P sorption parameters down the soil profile (0-75 cm) at each sampling site are presented in Table 6. Forest soil showed a negative but significant correlation between (i) Q_{max} and Na content, (ii) k and Ca, Al, Mn & Fe contents (iii) K_f and Ca, Al & Mn contents, (iv) $1/n$ and CEC, (v) $EPRL$ and % OC & Mg contents. A negative and significant correlation was observed in tea plantation soil between (i) K_f and Al & Mn contents, and (ii)

Table 5. Correlation between soil physico-chemical properties and P sorption characteristics.

Sorption parameter	% Clay	% OC	pH	CEC	Ca	Mg	Na	Al	Mn	Fe
Q_{max}	-0.229	-0.700*	-0.590	-0.011	-0.703*	-0.567	-0.500	0.363	-0.481	-0.167
k	-0.398	-0.852**	-0.489	0.343	-0.864**	-0.687*	-0.379	0.601	-0.335	-0.200
K_f	-0.318	-0.615	-0.455	-0.089	-0.583	-0.669*	-0.506	0.055	-0.811**	-0.431
$1/n$	-0.477	-0.831**	-0.868**	0.088	-0.891**	-0.569	-0.483	0.654	-0.290	-0.080
$EPRL$	-0.411	-0.880**	-0.546	0.341	-0.902**	-0.721*	-0.399	0.632	-0.347	-0.189
$EPRF$	-0.159	-0.368	-0.144	-0.157	-0.299	-0.563	-0.404	-0.248	-0.876**	-0.493

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

***Legend**: Q_{max} is the maximum adsorbed P, k is the Langmuir constant, K_f is the proportionality constant for Freundlich model, n is the empirical constant related to binding energy, $EPRL$ is the external P requirement determined by Langmuir model, $EPRF$ is the external P requirement determined by Freundlich model, OC-organic carbon, CEC-cation exchange capacity.*

Table 6. Correlation between soil physico-chemical properties and P sorption parameters down the soil profile (0-75 cm).

Land use	Sorption parameter	Clay content	% OC	pH	CEC	Ca	Mg	Na	Al	Mn	Fe
Forest land	Q_{max}	-0.866	-0.979	-0.756	-0.693	-0.92	-0.979	-1.000**	-0.942	-0.918	-0.925
	k	-0.993	-0.979	-0.954	-0.923	-1.000**	-0.979	-0.918	-0.998*	-1.000**	-1.000*
	K_f	-0.984	-0.991	-0.932	-0.895	-0.998*	-0.99	-0.942	-1.000**	-0.998*	-0.999*
	$1/n$	-0.953	-0.81	-0.993	-1.000*	-0.909	-0.809	-0.674	-0.883	-0.911	-0.904
	$EPRL$	-0.945	-1.000**	-0.867	-0.818	-0.978	-1.000**	-0.982	-0.989	-0.977	-0.98
Tea plantation	k	-	-0.98	0.948	-0.843	-0.956	-0.864	-0.915	-0.988	-0.991	-0.977
	K_f	-	-0.953	0.977	-0.896	-0.982	-0.913	-0.953	-0.999*	-1.000*	-0.994
	$1/n$	-	-0.161	-0.354	0.568	0.327	0.535	0.437	0.19	0.168	0.251
	$EPRL$	-	-0.972	0.959	-0.864	-0.967	-0.883	-0.93	-0.993	-0.996	-0.984
	$EPRF$	-	-0.941	0.984	-0.912	-0.989	-0.928	-0.964	-1.000**	-1.000**	-0.997*
Maize field	Q_{max}	1.000**	-0.993	0.803	-0.693	-0.961	-0.822	-0.866	-0.826	-0.892	0.548
	k	0.984	-0.998*	0.895	-0.809	-0.995	-0.909	-0.941	-0.912	-0.958	0.687
	K_f	0.936	-0.971	0.961	-0.902	-0.997*	-0.97	-0.986	-0.971	-0.994	0.807
	$1/n$	0.5	-0.596	0.918	-0.971	-0.721	-0.904	-0.866	-0.901	-0.837	.998*
	$EPRL$	0.998*	-0.998*	0.837	-0.735	-0.976	-0.854	-0.894	-0.858	-0.918	0.597
	$EPRF$	0.965	-0.989	0.931	-0.859	-1.000**	-0.943	-0.967	-0.945	-0.98	0.749

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

***Legend**: Q_{max} is the maximum adsorbed P, k is the Langmuir constant, K_f is the proportionality constant for Freundlich model, n is the empirical constant related to binding energy, $EPRL$ is the external P requirement determined by Langmuir model, $EPRF$ is the external P requirement determined by Freundlich model, OC-organic carbon, CEC-cation exchange capacity.*

$EPRF$ and Al, Mn & Fe contents. Q_{max}, EPRL positively and significantly correlated with clay content in the maize field soil, whereas a negative and significant correlation was observed between (i) k and % OC, (ii) K_f and Ca content, (iii) 1/n and Fe content (iv) EPRL and % OC, and (v) EPRF & Ca content. The negative correlation between sorption prameters and the % OC, Na, Ca, Mg, Al, Mn & Fe is due to decreased contents with depth (Table 1).

CONCLUSIONS

The sorption data better fitted to Langmuir model than Freundlich model. Soil samples from tea plantation had higher capacity to adsorb P compared to those of maize field and forest, suggesting that the type of land use influences P sorption capacity of soil. The EPR$_{(0.2)}$ values were generally > 150 mg kg^{-1} an indication of highly P sorbing soil and hence the need to carry out field experiments to validate the findings of this study. Sorption parameters (Q_{max}, k, K_f and EPRL values) were influenced by OC and cations contents including $Ca^{2+,}$ Mg^{2+} and Mn^{2+} while influence by soil pH, clay and Al contents were not statistically significant. The study recommends use of P management strategies such as application of lime and increasing soil organic matter content. The number of soil samples (n=9) and high specific surface area of soil used in the sorption experiments may however limit the findings of this study and therefore, field experiments covering most part of central Kenya highlands are recommended.

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