American-Eurasian Journal of Scientific Research 8 (3): 109-116, 2013
ISSN 1818-6785

DOI: 10.5829/idosi.aejsr.2013.8.3.12056

Phosphorus Sorption Patterns of Soils from Different Land Use Systems of East Wollega, Ethiopia

[1]Achalu Chimdi, [2]Heluf Gebrekidan, [3]Abi Tadesse and [2]Kibebew Kibret

[1]Wollega University, College of Natural and Computational Sciences,
P.O. Box 395, Nekemte, Ethiopia
[2]Haramaya University, College of Agriculture and Environmental Sciences,
P.O. Box 138, Dire Dawa, Ethiopia
[3]Haramaya University, College of Natural and Computational Sciences,
P.O. Box 138, Dire Dawa, Ethiopia

Abstract: This study investigated P sorption patterns of surface soils of forest, grazing and cultivated lands in the Guto Gida District located in western Oromia, Ethiopia. Soil P sorption was measured in the laboratory by batch experiment in which the soils were equilibrated with solution varying in initial concentration of P (0, 5, 25, 50, 100, 150 and 250 mmol P/L) for 24 hours. From each land use type, extractable Al, Fe and Mn ions were evaluated using different extractants and P sorption isotherms were described by Langmuir equation and provided a good fit for the equilibrium P concentration. Values of the P sorption maximum of the soils ranged from 588-1280 mmol kg^{-1}. Soils of the cultivated land with high clay and extractable Al contents had high degree of P sorption than the remaing land use systems. Additionally, results of the study indicated that soils with high clay and containing oxides and hydroxide of Al and Fe had a high P-sorption capacity resulting in P-deficiency in the soils.

Key words: Acidic soil · Land uses · P sorption · Acid Extractability of Soil

INTRODUCTION

Phosphorus (P) is a fundamental macronutrient, known as the master key to agricultural soils. This is because low crop production in acidic soil is mainly due to lack of P than any other element [1]. Although P is ubiquitous in nature, its concentration and the amount of its plant available form in the soil is usually quite low and often inadequate to meet plant requirements. This is attributed to its sorption with cations such as aluminum (Al) and iron (Fe) oxides in acid soils and precipitation reaction of P with calcium (Ca) in calcareous soils of arid and semi arid regions [2]. The degree and strength to which P is bound in soils are determined by the presence of specific type of Fe, Al and Ca compounds and by other soil properties such as pH, organic matter (OM), clay mineralogy and the amount of P in the soil. These soils properties are mainly affected by land use changes [3, 4]. Study conducted by [5, 6] have shown that low soil pH and high Al, Fe, clay and OM contents are responsible for sorbing of P in the soil system. The ability of a soil to sorb P is important when considering the availability of P to plants, fertilizer and soil P use efficiency [7, 8]. Sorption isotherm is a key in differentiating soils into their sorbing characteristics and practicing appropriate remedies based on the intensity of P sorption-desorption of a particular soil. Quantitatively, the P sorption isotherms can be described by the Langmuir, Freundlich and Tempkin models [9]. However, the Langmuir isotherm, which can be determined by batch experiment, is the most commonly used to describe P sorption by the soils.

Many Ethiopian soils are supposed to have high P sorption properties, particularly those from high rainfall areas which tend to be acidic. Thus it is of a primary concern in the appraisal of the soil resources of Ethiopia because most of the soils including on the highland plateaus of the country are reported to show deficiency for inherent total available P, particularly in the central

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Corresponding Author: Achalu Chimdi, Wollega University, College of Natural and Computational Sciences,
P.O. Box 395, Nekemte, Ethiopia. E-mail: achaluchimdi@yahoo.com.

highlands which are low even under improved drainage conditions [5, 10,11]. According to [12] the low level of available soil P in Ethiopia is mainly due to its immobility and sorption.

Phosphorus deficiency becomes a rigorous challenge for subsequent P uptake in acidic soil areas where P sorption by Fe and Al oxides is significant [13]. The major problem may be due to the P fixation, low P status of the parent material, long term anthropogenic mismanagements through imbalance between nutrient inputs and export and P loss by erosion and surface runoff [14]. In line with this, the sorption of phosphate by the oxides and amorphous materials in soils is a major contributing factor to reduced effectiveness of added phosphates necessitating larger applications of fertilizer P to achieve good crop yields [15]. Although soil P status and its sorption have been studied in some Ethiopian soils [10, 16], the detailed study of soil P sorption in relation to different land use systems of these soils are not known. Therefore, the objectives of this study were to characterize the P sorption characteristics as affected by land use systems and to relate the sorption parameters to selected soil physicochemical properties.

MATERIALS AND METHODS

Description of the Study Site: The study was conducted in the Guto Gida District (East Wollega Zone) of Oromia Regional State, western highlands of Ethiopia (Figure 1).

The District is situated at a road distance of 320 km from the capital, Addis Ababa, within 08° 59’and 09° 06` north latitude and 37°09` and 37° 51`east longitude. According to the local and the Ethiopian agro-climatic zonation the study area belongs to the humid (Baddaa) and sub-humid (Badda Darree) climatic zones.

As per the climate data recorded at the nearby Meteorological Station, the ten years average annual rainfall of the study site is 1300 mm and the monthly mean minimum and maximum temperatures range between 11.25 and 14.50 and 25.00 and 29.00 °C respectively. The topography of the study site is mountainous and has a gentle sloping landscape. According to FAO classification, the soil class of most of the study area is Nitosols. The economic activities of the local society of the study area are primarily mixed farming system that involves animal husbandry and crop production. The major crops are coffee (*Coffee arabica* L.*)*, teff *(Eragrostis tef),* barley *(Hordeum vulgare* L*)*, maize (*Zea mays* L.) and potato *(Solanum tubersoum* L.). These major crops are produced usually once in a year.

Site Selection, Major Features of the Land Uses and Sampling Procedures: A preliminary survey and field observation were carried out using topographic map (1:50,000) in order to have general information about the land forms, land uses, topography and vegetation cover of the study site. Accordingly, three major representative land use systems (natural forest, grazing and cultivated

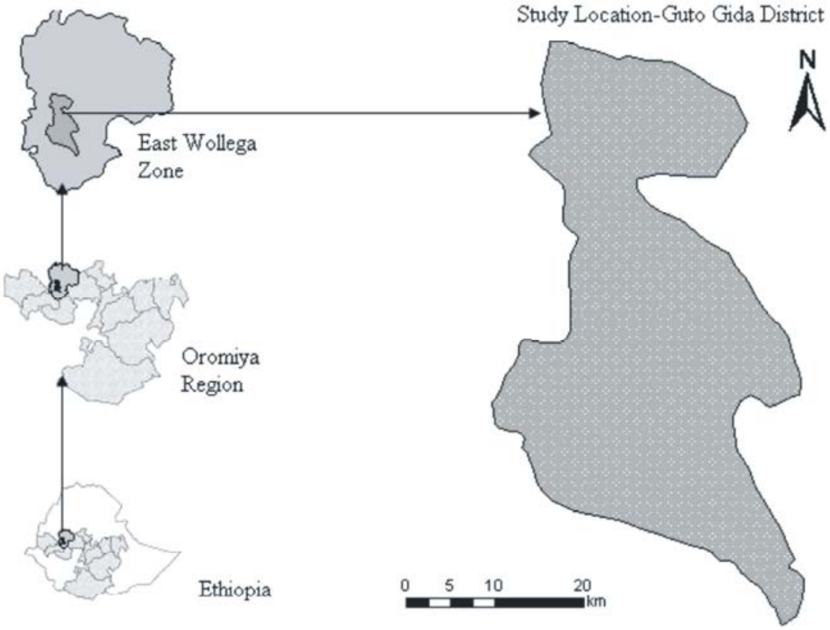

Fig. 1: General location map of the study area

lands) were identified from the Guto Gida district of East Wollega Zone, Western Oromia Region. The forest land is covered by indigenous natural forests with long and dense trees forming canopies, the grazing land comprises of communal and private grazing areas whereas the cultivated land is covered by rainfed annual crops and bounded by few scattered trees and settlements. Nine sub-samples from (0-20 cm depth) different sites of each of the representing land use systems of the Guto Gida District were collected and composited accordingly. The composited soil samples were air dried, ground, passed through a 2 mm sieve, packed and transported for laboratory analysis.

Analysis and Characterization of Soil Samples: Soil particle size distribution was analyzed by the Bouyoucos hydrometer method as described by [17]. Soil pH was measured using 1:2.5 soil to water ratio [18]. Organic carbon content was determined by the dichromate oxidation method as described by [19] and organic matter content was estimated from the organic carbon content by multiplying the latter by 1.724. The dithionite-citrate-bicarbonate-extractable forms of crystalline Al, Fe and Mn were determined by extraction method described by [20]. Acid ammonium oxalate-extractable forms of amorphous Al, Fe and Mn were determined by the extraction method described by [15]. Organically bound extractable Al, Fe and Mn were determined by extraction method described by [21]. The extracted Al, Fe and Mn were separated by centrifuging at 5000 rpm for 20 minutes and were filtered through a millipore filter with a 0.45 µm membrane filter. Finally, the concentrations of Fe, A1 and Mn extracted by various extracting solutions were then measured using AAS.

To measure the soil P sorption patterns, duplicates of one gram of air dried soil samples were equilibrated with 20 mL of 0.01M $CaCl_2$ solution containing 0, 5, 25, 100, 150 and 250 mg P L^{-1} as KH_2PO_4 for 24 hours using a mechanical shaker. Two drops of chloroform were added to suppress microbial growth [22]. At the end of the equilibration period, the soil suspensions were centrifuged at 5000 rpm for 20 minutes. After centrifugation, the soil solution was filtered with a 0.45 µm membrane filter. The filtered solution was taken for the measurement of the concentration of initial available P sorbed using a spectrophotometer at a wave length of 880 çm. The degree of the soil P saturation was calculated as the ratio of the oxalate extractable P as percentage of the soil P sorption capacity. Analysis of soils P sorption isotherms of the present study was made in parallel with the previously analyzed known data of the Finnish soil samples at the laboratory of the MTT Agrifood Research (Finland) to check the validity of the procedure followed.

Phosphate Sorption Characteristics: The sorption data obtained were fitted to the Langmuir equation isotherm (Equation.1). The amount of added P sorbed by the soil (S`) was calculated from the difference between the P concentration in the equilibrium solution and the initial P added to the soil. Since P sorption usually varies with pH, the experiment was conducted at the natural pH of the soils from different land use systems. Finally, P sorption data was fitted to the Langmuir sorption isotherm.

$$S' = \frac{[(C_o \times V) - (C \times V)]}{M} \qquad (1)$$

where S` is the amount of added P sorbed by the soil (mmol kg^{-1}), C_o is concentration of P in the input solution (mmol L^{-1}), V is the volume of liquid (L) and M is mass of the experimental soil (kg). The following linearized form of the Langmuir isotherms was used and the P sorption data of the soils of each land use system were satisfactorily described by the linearized form of the Langmuir equation given in Equation 2 to determine the P sorption maximum and binding energy as:

$$\frac{C}{S} = \frac{1}{KS_{\max}} + \frac{C}{S_{\max}} \qquad (2)$$

The P sorption maxima (S_{max}) and constant relating to binding energy (*K*) were calculated by regressing C/S versus C where C is the concentration of P in the final solution after 24 hours equilibration (mmol L^{-1}) and S is total amount of P sorbed in the soil (mmol kg^{-1}). The reciprocal of the slope of the regression is the S_{max}[2]. The sorption isotherm versus the equilibrium concentration was plotted as in (Figure 1) for each soil to obtain a straight line with slope $1/S_{max}$ and intercept $1/KS_{max}$.

Data Analysis: Data generated from analysis were subjected to statistical analysis using SAS software [23]. The phosphate sorption patterns of the soils were described by an exponential type relationship using the Sigma plot software version 8.0.

RESULT AND DISCUSSION

Relationships of Selected Soil Properties and P-Sorption Patterns: Soils with relatively high clay fraction like the cultivated land in the present study attained low pH and higher extractable Al using acid ammonium oxalate, dithionite-citrate-bicarbonate and sodium pyrophosphate (Table 1).

Table 1: Selected analytical properties of soils of the different land use systems

	Land use type		
Soil Parameters	Forest land	Grazing land	Cultivated land
Clay (%)	46.25	56.25	61.50
pH (H_2O)	5.25	5.15	4.65
OM (%)	8.01	4.02	3.64
Extractable Al_{AAO} (mg kg^{-1})	1.40	3.11	9.62
Extractable Fe_{AAO} (mg kg^{-1})	1.07	0.23	1.14
Extractable Mn_{AAO} (mg kg^{-1})	0.11	0.16	0.89
Extractable Al_{DCB} (mg kg^{-1})	0.30	0.34	8.50
Extractable Fe_{DCB} (mg kg^{-1})	4.41	5.10	0.45
Extractable Mn_{DCB} (mg kg^{-1})	0.09	0.10	0.30
Extractable Al_{SPP} (mg kg^{-1})	0.75	1.78	5.49
Extractable Fe_{SPP} (mg kg^{-1})	1.03	0.13	0.89
Extractable Mn_{SPP} (mg kg^{-1})	0.06	0.10	0.42

OM = Organic matter, AAO = Acid ammonium oxalate, DCB = Dithionite-citrate-bicarbonate, SPP = Sodium pyrophosphate

This may be attributed to the fact that, phosphate anion in acidic soils can form strong bond with the oxides and hydroxides of Al generating H ion through hydrolysis reaction that lowers the pH. The domination of extractable Al in the exchange sites of soils causes higher P sorption in the cultivated land than the remaining land use systems. Thus, the presence and domination of the oxide and hydroxide forms of Al and Fe tie-up plant nutrients like P in the soils. According to the research finding made by [24] the lower pH soils of cultivated land influences both the degree of ionization of orthophosphate ions and the oxide surface charge which is the main P-fixing component of the soils.

As the soil pH increases, the relative proportion of $H_2PO_4^-$ decreases and that of HPO_4^{2-} in the soil increases [25]. In fact, soil pH affected the P sorption by changing the cations that are capable of binding the phosphates. In this study, the value of K which indicates the strength of the soils P binding energy was higher in the cultivated land than in the remaining land use systems. The high K value recorded in cultivated land may be attributed to the tenacity of the higher degree of P-sorption properties of the soils with low P-equilibrium concentration (Table 3). This is supported with the finding of [26] who revealed the positive relationship of the constant K in the Langmuir equation with contents of extractable Al and Fe oxides. In the present study, soil OM combined with high extractable Al ion attained a higher degree of P sorption and lower sorption maximum than the OM combined with low Al and Fe oxides (Table 1). This may be logical in that the organic acid present in total soil organic matter may compete with the phosphate for binding sites and may accelerate the maximum P sorption to be achieved earlier in soil of the cultivated land than the remaining land use systems. Conversely, presence of higher soil OM in the forest land may inhibit Fe and Al oxides from formation of complex compounds and increase the sorption maximum for the phosphates. The slower turnover of OM in forest land favours the soils enhancing the P sorption maximum than grazing and cultivated lands. Studies conducted by [27, 28] and revealed that, as soil OM level in the soils increases, there are fewer sites (usually provided by Al and Fe) for P sorption. Generally, variations in the sorption parameters among the various land use systems might be attributed to the variations in their organic matter, hydrous oxides of Al and Fe in their corresponding soils.

Contents of the Extractable Al, Fe and Mn Ions in Soils: When comparisons are made among the three extractants, contents of extractable Al ion removed using acid ammonium oxalate (Al_{AAO}) in soils were higher than dithionate citrate bicarbonate extracted aluminum (Al_{DCB}) and sodium pyrophosphate (Al_{SPP}) extractable Al, but within the land use it was higher in soil of cultivated land than the remaining land use systems. This shows that, amorphous forms of Al ions accumulated in lower pH of the cultivated land than forest and grazing lands. The accumulation of Al ion in low pH soil of the cultivated land may accelerate the phosphate sorption of the soil to achieve earlier than the remaining land use systems [32]. Because of this fact, the domination of the amorphous forms of oxalate-extractable aluminum (Al_{AAO}) and organically bound aluminum contents (Al_{SPP}) decreased the decrease in soil OM content from forest, grazing and to cultivated land. The extractable Al and Mn in amorphous forms and crystalline forms of Fe in soils of the forest and grazing lands but amorphous forms of Al, Mn and Fe in the cultivated land are the dominant and principal metal ions (Table 1).

Among the three land use systems, the value of the contents of acid ammonium oxalate dithionite-citrate-bicarbonate and sodium pyrophosphate extractable Al increased from soils of natural forest and grazing to cultivated lands. The higher value of the contents of oxalate extractable Al in soil of cultivated land with low soil pH implies that, the content of the amorphous form of Al oxides played a leading role and is primarily responsible for P sorption and decreases P solubility in acidic soil systems. This finding is in agreement with the findings of [10, 30] who also observed that extractable Al had a greater influence on P sorption and played a more important role than Fe oxides in sorption of P in some acidic soils of the tropics.

Phosphorus Sorption Patterns and Selected Soil Properties: The simple correlation coefficients (Pearson r) of selected soil properties and sorption parameters are presented in (Table 2).

The output of the correlation coefficient demonstrated the negatively significant ($P < 0.05$) correlation of the soils pH and acid ammonium oxalate, dithionite-citrate-bicarbonate and sodium pyrophosphate extractable Al ion but these associations were insignificantly negative ($P > 0.05$) with the soils OM. These inverse relationships are most likely attributed to the domination of the concentration of Al ions in the soil exchange site which further acidify the soil by lowering the soil pH. Similarly, the clay fraction of the experimental soils showed negatively insignificant ($P > 0.05$) correlation with pH, OM and the sorption maxima (S_{max}).

The soil OM showed significant ($P < 0.05$) positive correlation with the P sorption maxima (S_{max}). This suggested an active participation of soil OM in P sorption processes of the experimental soils. Conversely, acid ammonium oxalate, dithionite-citrate-bicarbonate and sodium pyrophosphate extractable Al ions showed insignificantly positive ($P > 0.05$) relationship with each other. The Langmuir P sorption maxima (S_{max}) showed negatively significant ($P < 0.05$) correlation with the constant relating with the binding energy K and statistically insignificant negative association was recorded between OM and the acid ammonium oxalate, dithionite-citrate-bicarbonate and sodium pyrophosphate the extractable Al ions. The negative correlation of the S_{max} with binding energy K and extractable Al ion implies that the P binding energy may decrease with the decrease of the concentration of Al ions in the soil solution and an increase in OM content in the soil systems. For instance, soils of the cultivated land with relatively low OM content and high binding energy (K) attained high degree of sorption than the remaining land use systems.

The values of the Langmuir sorption parameters and selected soil properties of the different land use systems are indicated in (Table 3). The sorption curves of all the soils of the different land use systems were similar

Table 2: Correlation coefficients describing relationships of selected soil properties with P sorption parameters for soils studied

	Clay (%)	pH (H_2O)	OM(%)	Al $_{AAO}$(mg kg^{-1})	Al $_{DCB}$(mg kg^{-1})	Al $_{SPP}$(mg kg^{-1})	S_{max}mmol(+)kg^{-1}
Clay							
pH	-0.84						
OM	-0.96	0.67					
Al_{AAO}	0.87	-0.99*	-0.71				
Al_{DCB}	0.77	-0.97*	-0.57	0.98*			
Al_{SPP}	0.88	-0.99*	-0.72	0.99*	0.92		
Smax	-0.96	0.65	0.99*	-0.69	-0.54	-0.70	
K	0.99*	-0.87	-0.91	0.89	0.82	0.90	-0.98*

OM = Organic matter, AAO = Acid ammonium oxalate, DCB = Dithionite-citrate-bicarbonate, k = Constant related to binding strength, SPP = Sodium pyrophosphate, Smax = Sorption maxima, * = Significant at $P < 0.05$ probability level

Table 3: Langmuir sorption parameters and R^2 values of the regression analysis

	Soil sorption characteristics and R^2 value				
Land use system	S_o (mmol(+)kg^{-1}	K (Lmmol^{-1})	KS_{max}(Lkg^{-1})	DPS (%)	R^2
Forest land	2.47	0.142	177.50	0.002	0.99
Grazing land	3.34	0.160	100.00	0.005	1.00
Cultivated land	10.76	0.173	101.76	0.018	0.98

DPS = Degree of phosphorus sorption, K = Constant related to binding strength, S max = Sorption maxima, S_o= Originally sorbed P

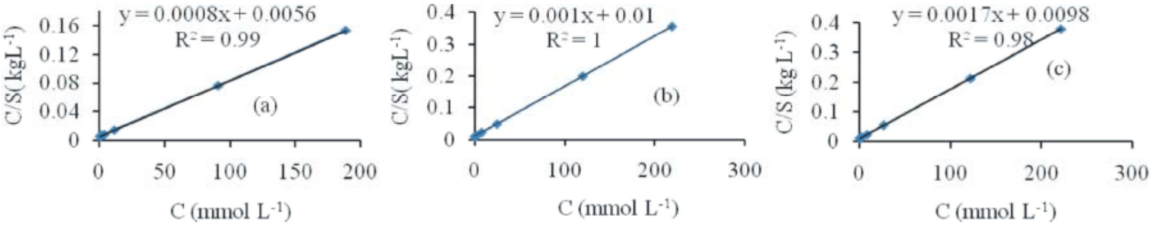

Fig. 2: Phosphorus sorption isotherms fitted to the Langmuir equation in soils of (a) forest land, (b) grazing land and (c) cultivated land

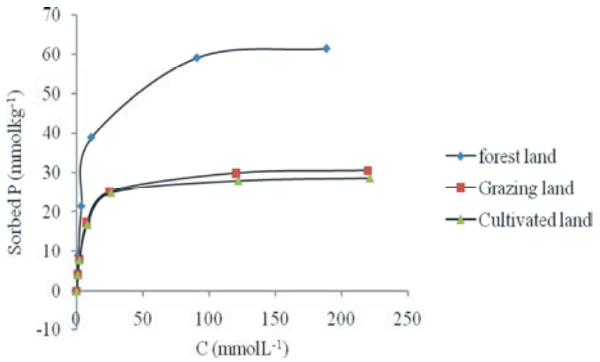

Fig. 3: Langmuir P sorption isotherms of soils of the different land use systems

indicating similarity in the nature of the soils` sorption reaction, but different in the intrinsic characteristics such as the slope of the isotherms and sorption capacity. Data obtained from the P sorption characteristics in soils of the different land use systems fitted well to the Langmuir sorption isotherm (Figure 2).

The mean values of the soil`s P sorption maximum (S_{max}) calculated from the Langmuir isotherm in the soils of all the land use systems ranged from 588 - 1280 mmol (+) kg^{-1}. The observed differences in sorption maxima among the soils of the different land use systems were most likely due to the variations in the amounts and nature of Al and Fe components present in the soils. However, the degree of P sorption calculated for the soils of each land use system was very low and ranged from 0.002 - 0.018. The lowest and highest values of the degree of P sorption were observed in soils of the forest and cultivated lands, respectively. The higher value of the degree of P sorption recorded in soils of the cultivated land is mainly attributed to its greater value of the originally sorbed P and lower S_{max} values as compared to the remaining land use systems. Results of the sorption curve (amount of soil P sorbed versus concentration) after 24 hours equilibration indicated that, P sorption and equilibrium P concentrations tend to increase with increasing levels of added P in soils of each land use system (Figure 3).

The variation in the phosphate sorption parameters among the different land use systems might be attributed to the accumulation of the relatively differential amount of organic matter in forest land and domination of cations like Al ion in soil exchange site as affected by land management of acidic soils. These variations were already evidenced and reported by [31]. In general, variations in soil physicochemical properties among the different land use systems of the present study most likely govern the P dynamics in soil and also responsible for the variations in soils P sorption maxima of different land use systems. Moreover, P sorption capacities of soils are generally influenced by soil properties such as free Al and Fe oxides, pH and the clay mineralogy of the soils [32, 33].

The rate of the concentration of P obtained after equilibration from soils of the different land use systems were increased with the increase of the rate of phosphate addition. The trends of the rate of increment of the P sorption for cultivated and grazing lands were almost similar and initially high however, the P sorption maxima attained differently under soils of the different land systems (Figure 3). In addition, the S_{max} and concentration of P obtained in final solution after equilibration at the highest phosphate addition (250 mmolL^{-1}) was respectively, 582.56 mmol/ kg and 221.41 mmol/L for soils of cultivated land. Similarly, the same phosphate addition gave a S_{max} and concentration of P in the final solution after equilibration of about 1233.27 mmol kg^{-1}and 188.45 mmol/L, in forest land and about 613.74 mmol kg^{-1}and 219.48 mmolL^{-1} in grazing land. Results of the sorption curve after equilibration tends to increase with increasing levels of added P and reach their corresponding sorption maximum at different rate for the soils of each land use system (Figures 2 and 3). In addition, the same rate of P was applied to the soils of each land use system, however, due to the differences in the severity of soil P sorption, the values of the sorption maximum calculated from the Langmuir isotherms also varies from soils of one land use system to the other.

The P sorption data showed that, the constant relating to binding energy (K) value determined from the Langmuir equation in soils varied from one land use system to the other. Accordingly, it was higher in soils of cultivated land than in soils of the forest and grazing lands.[33-36] The higher K value in soil of the cultivated land may be attributed to the presence of large amounts of clay fraction and strong sorption of soil P due to higher extractable Al ion causing the soil to attain more binding energy and degree of P saturation than forest and grazing lands. In addition, the variation in different phosphate sorption parameters among the land use systems could be due to the variation in the soils physicochemical properties, caused by differences in vegetation and crop rotation systems.

CONCLUSION

Phosphorus sorption patterns play a vital role in devising appropriate soil P management practices for its use efficiency in order to ensure better crop yields. The results of the study indicated that soils with high clay especially soils containing oxides and hydroxides of Al and Fe content like cultivated land in this study had a high degree of soil P-sorption than the remaining land use systems.

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