

Research Article

Phosphorous Sorption Characteristics of Soils in Smallholding Land Use in Southern Ethiopia

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Purpose. This study evaluated the P sorption characteristics of soils under smallholding land use in Wolaita Zone, Southern Ethiopia. **Methods.** Soil samples (0–20 cm) were collected from each of the home garden, grazing land, cropland, and woodlot in three replications at two sites and analyzed for P sorption isotherm data and selected soil properties. **Results.** The P sorption data were generated by equilibration with P solutions and the data were fitted with the Freundlich model ($r^2 = 0.88–0.98$, $SE = 0.16–0.24$) and Langmuir model ($r^2 = 0.81–0.98$, $SE = 0.45–1.71$). The Langmuir P sorption maximum (Q_{max}) and Freundlich sorption coefficient (K_f) were the highest in the cropland soils while these parameters were the lowest in the home garden. Maximum buffering capacity (MBC) was in the order cropland > woodlot > home garden > grazing land, but Freundlich P buffering capacity (PBC) followed the order cropland > grazing land > home garden > woodlot. Langmuir bonding energy (b_L) and Freundlich phosphate sorption affinity ($1/n$) were in the order of home garden > woodlot > grazing land > cropland. The Q_{max} was positively correlated ($p < 0.05$) with clay, K_f , PBC, the oxalate and dithionates extractable Al, Fe, and Mn, but it negatively correlated ($p < 0.05$) with soil pH, SOC, AP and b_L . **Conclusion.** Generally, the effect of P sorption of the smallholding home garden was slightly different from eucalyptus woodlot and grazing lands but considerably different from cropland. The high P sorption capacity in cropland was attributed to the high amorphous and crystalline Fe/Al oxides/hydroxides, low SOC, and low soil pH. Hence, combinations of P managements are required for increasing P availability in the smallholding land uses.

1. Introduction

Phosphorous (P) has several functions in the plant, including photosynthesis, N-fixation, flowering, fruiting, seed formation, and crop quality. Information on the behavior of P and factors influencing P availability is very essential for plant production [1]. In degraded soils with lower pH and a higher proportion of sesquioxides in clay minerals, P fixation is very high which limits the availability of P to plant uptake [2]. Phosphorous can either be in available or unavailable form depending on the soil chemical and mineralogical properties, such as soil organic carbon (SOC), iron oxides, aluminum oxides, and soil pH [3]. Besides, low molecular weight organic acids, humic acids, and fulvic acids compete with phosphate on the surface of exchange sites, reduce P

fixation, and increase P phyto-availability [4]. Organic amendments including crop residues retention increase organic matter content of soil and improve P availability [5].

Phosphorus sorption properties of soils are mainly studied by sorption isotherm experiments. Phosphorous sorption isotherm is a tool to study the P sorption behavior of soils and describe the relationship between equilibrium solution concentration and P sorbed. Among the models that explain P sorption, the most commonly used sorption isotherms are Freundlich, Langmuir, and Temkin equations [6].

Phosphorous sorption isotherm was assessed on croplands in different parts of the world [7–9]. Besides, P sorption isotherm was studied on soils under different land-use systems [10–14]. The land uses considered in different P

sorption isotherm studied in different studies differ from the land uses in the agro ecosystems of southern Ethiopia. Shirvani et al. [10] assessed phosphate sorption characteristics of forest land and rangelands. Majumdar and Saha [11] evaluated the long-term effects of forestry, agriculture, agri-horti-silvi pastoral, and natural fallow on P sorption characteristics. Phosphorus sorption characteristics under orchard soil, cultivated land, forest soils, and tea garden are reported by Pal [12]. Chimdi et al. [13] reported P sorption characteristics in soils of the forest, communal grazing lands, and cultivated land. Roy and Pal [14] evaluated the phosphorus sorption characteristics under fallow, orchard soil, tea garden, and cultivated land. In the study area, farmers typically divide their land into different land-use types.

At present, the home garden, the cereal cultivation land, grazing land, and woodlots are evident in the agroecosystem of Wolaita as well as other densely populated areas of southern Ethiopia. Home gardens cover 31% of the cultivable land in the Southern Nations Nationalities and Peoples' Regional State [15]. The area beyond the home garden contains cropland which is used to grow cereals. Communal grazing lands are not common in the agroecosystem because of land fragmentation from population pressure. The grazing land is the land allotted by households where tethered animals graze. The woodlot is the land planted mostly with eucalyptus for household wood demand. Smallholders have a positive perception of eucalyptus woodlots due to its socio-economic benefits [16]. In southern Ethiopia, we came across a few published works who investigated the impact of smallholding land uses on P sorption characteristics. Thus, it is important to understand P sorption characteristics in the soils of smallholding land uses for the management of P, which is the most limiting nutrient. Therefore, the objective of this study was to evaluate the P sorption characteristics of the soils by comparing Langmuir and Freundlich models with soil properties under smallholding land uses of the home garden, grazing, cropland, and woodlot in Wolaita Zone, Southern Ethiopia.

2. Material and Methods

2.1. General Description of the Study Area. The study was conducted at Gununo Hamus and Waja Kero Kebeles (the smallest administrative units) in Wolaita Zone, Southern Nation Nationality People Regional State (SNNPRS), and Ethiopia (Figure 1). Gununo Hamus is situated in Damot Sore district and it is located 44 km southwest of Wolaita Sodo town, while Waja Kero is in Soddo Zuria district and 5 km west of Wolaita Sodo. Wolaita Soddo is located 329 km south of Addis Ababa. Wolaita Zone is one of the most densely populated areas in Southern Ethiopia with an average population density of 357 people per km². The geographical coordinates of Gununo Hamus is located at (37°39'0"–37°43'0"E, 6°55'0"–7°5'0"N) and Waja Kero (37°40'0"–37°45'0"E, 6°50'0"–6°55'0"N). Gununo Hamus is located 44 km southwest of Soddo town, while the Waja Kero is 5 km west of Soddo. The altitude at Gununo Hamus and Waja Kero ranges from 1900 to 2100 m above sea level. The topography of the study areas is level to sloping land.

The mean monthly average temperatures (°C) and mean monthly total rainfall (mm) over ten years are shown in Figure 2.

2.2. Analysis of the Soil Samples. Soil samples were collected from two sites with four smallholding land uses (home garden, grazing, cropland, and woodlot) with three replications. Twenty-four soil samples were collected and analyzed at the soil Laboratory of College of Agriculture, Hawassa University, and Chemistry Laboratory of Natural and Computational Science, Addis Ababa University. The sites were selected based on similar soil with similar geographical coordinates of altitude, slope, and topography. The soil sample was air-dried, ground with mortar and pestle, and passed through a 2 mm sieve. The soil parameters: pH, OC (organic carbon), clay, AP (available phosphorous), and CEC (cation exchange capacity) were determined as presented in Lulu et al. [17]. Dithionate-citrate-bicarbonate (DCB) extractable Fe, Al, and Mn oxides (Fe_d, Al_d, and Mn_d) were determined by the method described by Mehra and Jackson [18]. Acid ammonium oxalate-extractable Fe, Al, and Mn-oxides (Fe_{ox}, Al_{ox}, and Mn_{ox}) were determined according to the method described by Loeppert and Inskeep [19]. The extracts were filtered using Wattman filter paper (Grade 42, Amazon India) and concentrations measured by atomic absorption spectrophotometer (AAS novAA®350, Analytik Jena, Germany). The contents of crystalline aluminum oxides (c-Al), iron oxides (c-Fe), and manganese oxides (c-Mn) were calculated as the differences between dithionate extractable Al_d, Fe_d, and Mn_d oxides and oxalate-extractable Al_{ox}, Fe_{ox}, and Mn_{ox} oxides [20].

2.2.1. Phosphorous Sorption. Phosphorous sorption study was done according to the method described by Fox and Kamprath [21]. One g air-dried soil sample from each land use was added to a 50 ml glass with 30 ml aliquot of different KH₂PO₄ concentrations containing 0, 1, 2, 5, 10, 15, and 20 mg·P·L⁻¹, in duplicate and in 0.01 M CaCl₂. Separate plastic bottles without soil received 30 ml of each concentration of KH₂PO₄ in 0.01 M CaCl₂ to determine the concentration of added P. Plastic bottles were placed on a shaker at room temperature for 24 h at 85 oscillations per minute and equilibrated for 24 h at 25 ± 1°C to achieve equilibration [22]. After equilibration, the samples were centrifuged at 3600 revolutions per minute for 10 min, the suspensions were filtered using Wattman filter paper (Grade 42, Amazon India), and the filtrates P concentration were analyzed with ammonium molybdate ascorbic acid blue color method [23]. The amount of P sorbed was calculated as the difference between the initially applied P and the total amount of P concentration in soil solution at equilibrium reported as mg·kg⁻¹ dry weight of soil and computed as shown in the following equation.

$$Q = (C_e - C_e) \times \frac{V}{m}, \quad (1)$$

where Q is the amount sorbed by the solid phase of soil (mg kg⁻¹ soil); C_e and C_e are the initial and equilibrium P

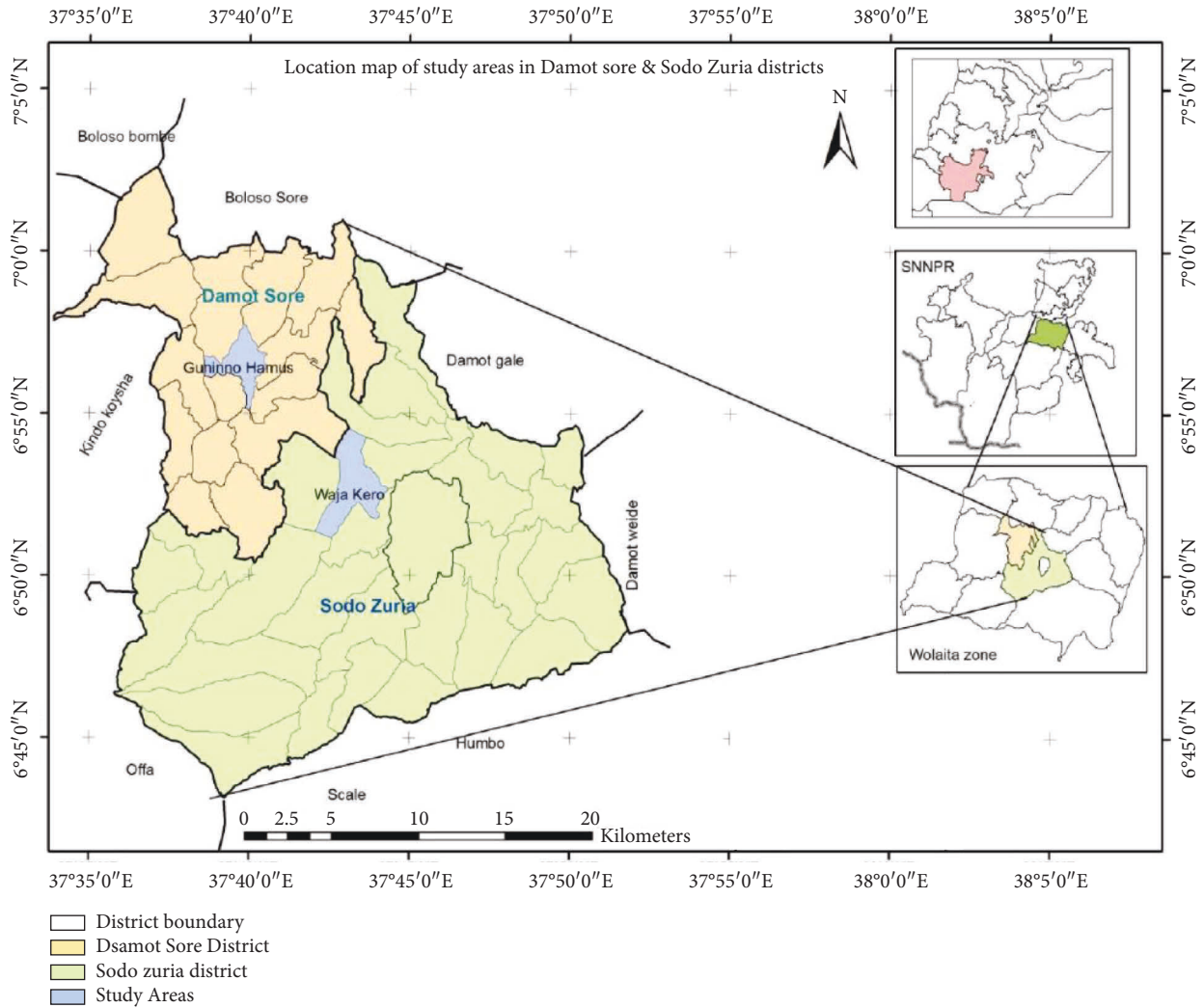


FIGURE 1: Location map of the study areas in Wolaita zone (Damote sore and Sodozuria districts).

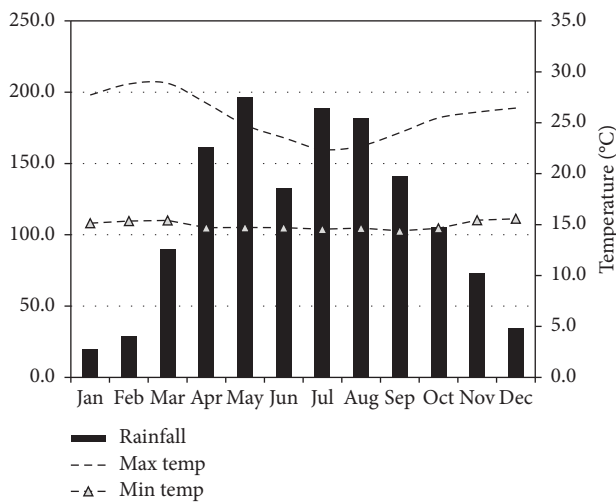


FIGURE 2: Mean monthly total rainfall (mm), maximum and minimum temperatures (°C) of the study areas from 2008 to 2017 (source: national meteorological agency, Hawassa branch).

concentrations in the solution (mg P L^{-1}), respectively; V is the solution volume (L) and m is mass of the soil (kg).

The P sorption data were fitted into linearized forms of the Langmuir and Freundlich sorption equations. The nonlinear form of Langmuir sorption isotherm is shown in the following equation.

$$Q = \frac{bL * Ce * Q_{\max}}{1 + bL * Ce} \tag{2}$$

The above equation is rearranged to the linearized form as described by Langmuir [24] and is shown in the following equation

$$\frac{Ce}{Q} = \frac{Ce}{Q_{\max}} + \frac{1}{bL Q_{\max}}, \tag{3}$$

where Ce is the equilibrium solution P concentration (mg P L^{-1}). A plot of Ce/Q versus Ce gives a straight line if the sorption process fits the Langmuir isotherm. The values of Q_{\max} and b_L were obtained from the slope ($1/Q_{\max}$) and the intercept ($1/b_L Q_{\max}$), respectively. The Q is the mass of P

TABLE 1: Significance levels from the ANOVA analyses of clay, pH, available P(AP), CEC, Al oxalate (Al_{ox}), Fe oxalate (Fe_{ox}), Mn oxalate (Mn_{ox}), Al dithionate (Al_d), Fe dithionate (Fe_d), Mn dithionate (Mn_d), crystalline of Al oxides (c-Al), crystalline of Fe oxides (c-Fe), crystalline of Mn oxides (c-Mn), and iron activity (Fe_{ox}/Fe_d) by site, land uses, and their interaction.

Source of variation	DF	Clay	pH	SOC	AP	CEC	Al_{ox}	Fe_{ox}	Mn_{ox}	Al_d	Fe_d	Mn_d	Fe_{ox}/Fe_d
Site	1	*	ns	ns	***	ns	**	ns	**	ns	ns		**
Land use	3	ns	**	*	***	**	**	*	**	*	*		**
Site * land use	3	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns		ns

Note: * = $p \leq 0.05$ is significant; ** = $p < 0.01$ is highly significant, ns = nonsignificant.

sorbed per unit mass of soil ($mg \cdot kg^{-1}$ soil), b_L is a constant related to bonding energy of P to the soil, and Q_{max} is the maximum P sorption capacity ($mg \cdot kg^{-1}$ soil).

The maximum buffering capacity (MBC; $L \cdot kg^{-1}$) which is the product of Q_{max} and b_L was determined following Karimian and Moafpourian [25] and Reyhanitabar et al. [26] using the following equation.

$$MBC = Q_{max} \times bL. \quad (4)$$

The Freundlich sorption equation in equation (5) is rearranged to the linearized form in equation (6).

$$(Q) = Kf ce^{1/n}, \quad (5)$$

$$Q = \log Kf + \frac{1}{n} \log Ce, \quad (6)$$

where Q is the mass of P sorbed per unit mass of soil ($mg \cdot kg^{-1}$ soil), and Ce is the equilibrium solution P concentration ($mg \cdot L^{-1}$).

A plot of $\log Q$ versus $\log Ce$ gives a straight line if the sorption process fits the Freundlich isotherm. The parameter K_f is the sorption capacity and $1/n$ is a phosphate sorption affinity to the soil surface [27]. The values of K_f and $1/n$ are obtained from the intercept ($\log K_f$) and the slope ($1/n$), respectively. The buffering capacity was derived from the nonlinear Q-Ce curve [28] of the Langmuir in equation (7) and Freundlich in equation (8). It was also derived from the linear equation by plotting P sorbed against P concentration at equilibrium is calculated as the slope of the line at $0.2 \text{ mg} \cdot P \cdot L^{-1}$ concentration of P [29].

$$PBC_L = \frac{Q_{max} \times bL}{(1 + Ce \times bL)^2}, \quad (7)$$

$$PBC_F = K_F \times \frac{1}{n} \times Ce \left(\frac{1}{n} \right)^{-1}. \quad (8)$$

2.2.2. Fitting to the Linear Equation. The sorption data obtained were fitted to the linear form of the Langmuir and Freundlich equation. The goodness-of-fit of the data to the equations was evaluated by the standard error (SE) and coefficient determination (R^2) for each land use. The lower value SE and higher R^2 indicate that the model fits the data.

2.3. Statistical Analysis. The data were subjected to analysis of variance (ANOVA) by SAS (Statistical Analysis System) version 9.4 software packages [30]. The significance of

differences in soil parameters with sites and land use types was tested using a two-way analysis of variance following the general linear model (GLM) procedure at $p < 0.05$. Mean separation for significant differences was made by using the least significant difference (LSD) test. Correlation analyses were used to estimate the relationships between P sorption parameters and the selected soil physicochemical properties.

3. Results

3.1. Soil Chemical Properties. The clay particle was significantly affected ($p < 0.05$) by site but not affected ($p > 0.05$) by land use and interaction effects of site and land use (Table 1). The soil pH value was significantly ($p < 0.05$) affected by land use, but it was not affected ($p > 0.05$) by site and the site and land use interaction effects. Soil pH was high in the home garden as compared to others; soil pH was not different among cropland, woodlot, and grazing lands (Table 2). The soil organic C (SOC) content was significantly affected ($p < 0.05$) by land use but not by site and their interactions (Table 1). The SOC in the home garden, the grazing land, and woodlot were significantly higher than in the cropland (Table 2). The AP was significantly ($p < 0.05$) affected by site and land uses ($p < 0.001$) (Table 1). In the home garden, a significantly higher amount of AP was observed as compared with other land uses (Table 2). The cation exchange capacity (CEC) was significantly affected by land uses ($p < 0.05$). In the home garden, a significantly higher amount of CEC was observed as compared with other land uses (Table 2). The concentrations of aluminum oxalate (Al_{ox}) and manganese oxalate (Mn_{ox}) were significantly ($p \leq 0.001$) influenced by site, land use, and interaction effects of site \times land use (Table 1). The concentration of iron oxalate (Fe_{ox}) was significantly ($p \leq 0.001$) influenced by land use (Table 1). The highest Al_{ox} and Fe_{ox} were found in the cropland and woodlot while the highest Mn_{ox} was found in the home garden and cropland (Table 3). The concentration of aluminum dithionate (Al_d) and iron dithionate (Fe_d) was significantly ($p \leq 0.05$) influenced only by land use while the concentration of manganese dithionate (Mn_d) was significantly ($p \leq 0.05$) influenced by the site and land use (Table 1). The Al_d in the cropland was significantly higher in cropland followed by home garden and grazing land and lowest in woodlot (Table 3). The highest Fe_d and Mn_d were obtained in the cropland and grazing land (Table 3). The iron activity (Fe_{ox}/Fe_d) ranged from 0.24 in the home garden to 0.48 in cropland (Table 3).

3.2. Phosphorous Sorption Isotherm. The P sorption parameters of sorption maximum capacity (Q_{max}), bonding energy (b_L), maximum buffering capacity (MBC), and P

TABLE 2: Mean value of clay, pH, SOC (%), AP (mg·kg⁻¹), and CEC (cmol(+)/kg).

Factor	Treatment	Clay (%)	pH (H ₂ O)	SOC (%)	AP (mg·kg ⁻¹)	CEC (cmol(+)/kg)
Land use	Home garden	34.20 ^a	6.43 ^a	2.72 ^a	19.19 ^a	28.38 ^a
	Grazing	31.80 ^a	5.73 ^b	2.56 ^{ba}	2.03 ^b	25.55 ^b
	Cropland	35.20 ^a	5.47 ^b	1.84 ^b	3.83 ^b	25.76 ^b
	Wood	37.80 ^a	5.57 ^b	2.52 ^{ba}	2.31 ^b	25.62 ^b

*mean values of treatments in each factor in a column with the same letter are not statistically different.

TABLE 3: Mean value of Al_{ox}, Fe_{ox}, Mn_{ox}, Al_d, Fe_d, Mn_d, c-Al, c-Fe, c-Mn_x and Fe_{ox}/Fe_d by land uses.

Factor	Treatment	Al _o	Fe _{ox}	Mn _{ox}	Al _d (mg·kg ⁻¹)	Fe _d	Mn _d	c-Al	c-Fe	c-Mn	Fe _{ox} /Fe _d
Land use	Home garden	0.16 ^b	0.54 ^{ba}	0.15 ^a	0.53 ^b	3.20 ^{ba}	0.18 ^b	0.37 ^a	2.70 ^b	0.13 ^b	0.24
	Grazing	0.25 ^b	0.39 ^b	0.11 ^b	0.63 ^{ba}	2.03 ^b	0.24 ^b	0.38 ^b	1.64 ^b	0.11 ^{ba}	0.40
	Cropland	0.41 ^a	0.67 ^a	0.16 ^a	0.86 ^a	4.64 ^a	0.30 ^a	0.45 ^b	3.97 ^a	0.14 ^a	0.48
	Wood	0.26 ^{ab}	0.61 ^a	0.13 ^b	0.54 ^b	1.32 ^b	0.14 ^b	0.28 ^{ba}	0.71 ^b	0.03 ^b	0.47

*mean values of treatments in each factor in a column with the same letter are not statistically different.

buffering capacity (PBC) were significantly ($p \leq 0.001$) influenced by land use, but not significantly influenced ($p > 0.05$) by site and its interaction effect with land use (Table 4).

The equilibrium P concentrations and P sorbed on four smallholding land use soils varied among each other at different P levels as shown in Figures 3 and 4. The coefficient of determination (R^2) of P sorption isotherms of the Freundlich and Langmuir models ranged from 0.88 to 0.98 and 0.81 to 0.98, respectively, while SE ranged from 0.16 to 0.24 in Freundlich and 0.45 to 1.71 in Langmuir P sorption isotherm, respectively, as shown in Figure 4 and Table 5.

The highest Q_{max} was obtained in cropland followed by grazing land and woodlot and the lowest in the home garden, whereas b_L followed the opposite trend (Table 6). The highest maximum buffering capacity (MBC) was obtained in the cropland followed in woodlot and home garden and, lowest in grazing land (Table 6). The highest P buffering capacity of Langmuir $PBC_{L(0.2)}$ was obtained in the cropland and woodlot.

The highest Freundlich sorption coefficient (K_f) was obtained in the cropland followed in grazing land and woodlot and lowest in the home garden (Table 6). The highest Freundlich phosphate sorption affinity ($1/n$) was obtained in the home garden followed in the woodlot ~ grazing land and the lowest in cropland (Table 6). The highest P buffering capacity of Freundlich $PBC_{F(0.2)}$ was obtained in cropland and grazing land (Table 6).

3.3. The Relation of Phosphorus Sorption Parameters to Soil Properties. Table 7 presents the significant correlations between soil P sorption parameters with soil physical and chemical properties. The Q_{max} was positively and significantly correlated with clay ($r = 0.98$), Al_{ox} ($r = 0.99$) and Al_d ($r = 0.97$), and K_f ($r = 0.97$) and PBC ($r = 0.80$), but it was significantly negatively correlated with pH ($r = -0.98$), SOC ($r = -0.94$), and b_L ($r = -0.89$). The b_L is positively and significantly correlated with soil pH ($r = -0.97$), but it was negatively and significantly correlated with AP ($r = -0.92$). The K_f was positively and significantly correlated with pH

($r = 0.91$), Al_{ox} ($r = 0.99$), and Fe_{ox} ($r = 0.96$), but it was negatively and significantly correlated with AP ($r = -0.97$). The PBC_f was positively and significantly correlated with Al_d ($r = 0.95$) and AP ($r = 0.97$), but PBC_f was negatively and significantly correlated with soil pH ($r = -0.57$).

4. Discussion

The amount of P sorbed and equilibrium P concentrations in the different land uses generally increased with increasing solution concentrations of phosphate added. This is consistent with Rashmi et al. [31], who showed that the P sorbed and equilibrium P concentrations increased with increasing P addition. The results indicate that both the Freundlich and Langmuir P sorption models were well fitted as evidenced by higher R^2 and lower SE values. In the same way, initially at low concentration, was linear but at high concentration it deviated from linearity. The linearity between equilibrium P concentrations versus P sorbed could be large intermolecular distance between P ions resulting in negligible mutual repulsion while deviation from linearity showed that the binding affinity of soil to P decreased with increase in surface saturation with P [32].

As the maximum P sorption capacity (Q_{max}) in the Langmuir isotherm of the soil represents the number of P sorption sites per unit mass of soil, it is widely used to evaluate the performance of P adsorption on the soil surface [33]. The Q_{max} in the current study followed the sequence cropland > grazing land = woodlot > home garden. The P sorption capacity of the soil as affected by soil properties such as clay content, and Al and Fe fractions [34]. A high amorphous aluminum oxide (Al_{ox}) or iron (Fe_{ox}) was found in cropland compared to the home garden, grazing land, and woodlot. This may indicate that greater sorption capacity could be due to their smaller dimensions and high specific surface areas in cropland soils [35]. The high crystalline (c-Al, c-Fe, and c-Mn) oxide in soils of cropland could also provide much of the P-sorption capacity [36]. The highest Q_{max} can be ascribed to the greater contents of Fe and Al oxide found in weathered soils because they provide the high sorption of P [37]. The Q_{max} is positively correlated and with

TABLE 4: Significance levels from the ANOVA analysis of sorption maximum capacity (Q_{max}), bonding energy (b_L), maximum buffering capacity (MBC), phosphorous buffering capacity (PBC) of Langmuir isotherm (L), and (F) Freundlich constant and by sites, land use, and their interaction.

Source of variation	df	Q_{max}	b_L	MBC	PBC L(0.2)	K_f	$1/n$	PBC F(0.2)
Site	1	ns	ns	ns	ns	ns	ns	ns
Land use	3	***	***	***	***	***	***	***
Site*land use	3	ns	ns	ns	ns	ns	ns	ns

Note: * = $p \leq 0.001$ is very highly significant; ns = nonsignificant.

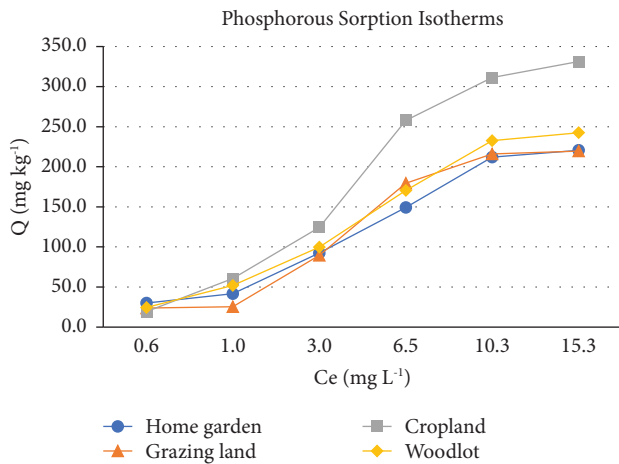


FIGURE 3: Phosphorous sorption isotherm curves of the amount of P sorbed versus equilibrium P concentration for different land use.

aluminum and iron oxides and it can be due to the increased surface area [38]. In addition to high Al and Fe oxides and hydroxides, the low level of SOC in the croplands contributes to the high Q_{max} [39]. The negative correlation of Q_{max} with SOC could imply the relatively lower P availability due to low SOC and its mineralization as well as the increased P sorption capacity of mineral surfaces with less competition from SOC [40]. Compared with other studies on croplands in Ethiopia, the Q_{max} values in the present study was in the middle of the range (5–2000 mg·P·kg⁻¹) determined for studies [7, 9, 41]. The Q_{max} is negatively correlated with soil pH representing the increase in Q_{max} with the decrease in soil pH and vice versa. This agrees with Siradz [42] who reported an inverse relationship between Q_{max} and pH values of three soils of Indonesia. The decreased Q_{max} with the increase in pH could be attributed to the higher competition of hydroxyl (OH⁻) concentrations with phosphate ions for specific sorption sites on mineral surfaces as pH increases [8].

On the other hand, the lowest Q_{max} in the home garden could be attributed to the low content of amorphous and crystalline Al, Fe, and Mn. Moreover, Q_{max} in the home garden was negatively correlated with SOC and soil pH. The SOC content is high in the home garden and the high SOC content in the home garden could reduce the Q_{max} as the organic acids derived from decomposition can form stable complexes with Fe and Al resulting in decrease in P sorption and increase in P availability [33]. In addition, low molecular weight acids, fulvic acids, and humic acids from SOC can compete with P for

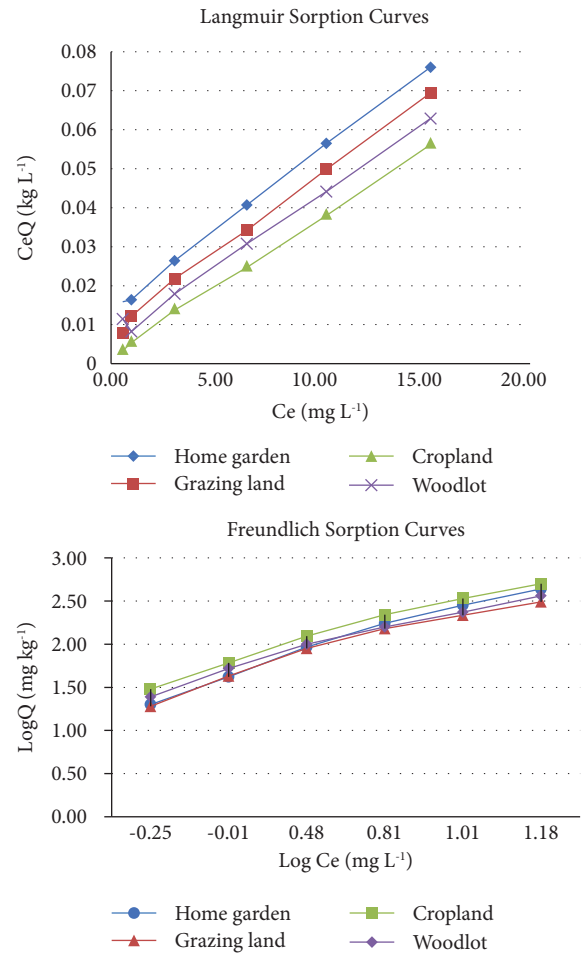


FIGURE 4: Langmuir P and Freundlich P sorption curve for different land use.

sorption sites [35]. At lower pH, SOC has low CEC, Fe and Al oxides develop more positive surfaces as well as greater Fe and Al ion concentrations are formed in the soil solution that contribute to higher P sorption [43]. The relatively high soil pH in the home garden has the opposite effect on Q_{max} . The Q_{max} followed the sequence cropland > grazing land ~ woodlot > home land. The order of P sorption of the smallholding land uses could be attributed to soil pH, SOC, amorphous and crystalline Fe/Al oxides and hydroxides.

The Freundlich constant (K_f) is a measure of absorbability. The K_f followed the sequence: cropland > grazing land > woodlot > home garden. The K_f value followed a

TABLE 5: The Langmuir and Freundlich P sorption linear line equations of the fitted P sorption data, r^2 and SE of the land use.

Factor	Treatment	Langmuir isotherm			Freundlich isotherm		
		Best equation fitting	r^2	SE	Best equation fitting	r^2	SE
Land use	Home garden	$y = 0.003xy + 0.020$	0.97	1.71	$y = 0.705x + 1.624$	0.97	0.16
	Grazing	$y = 0.002x + 0.02$	0.81	0.45	$y = 0.663x + 1.672$	0.88	0.18
	Cropland	$Y = 0.001x + 0.02$	0.96	1.58	$y = 0.594x + 1.806$	0.97	0.28
	Wood lot	$y = 0.002x + 0.01$	0.98	1.46	$y = 0.666x + 1.513$	0.98	0.24

TABLE 6: Mean value of Q_{max} , b_L , MBC, PBC, K_f and $1/n$ by land use.

Factor	Treatment	Langmuir isotherm parameters				Freundlich isotherm parameters			
		Q_{max} (mg·kg ⁻¹)	b_L (L mg ⁻¹)	MBC (L kg ⁻¹)	PBC _{0.2} (L·kg ⁻¹)	K_f (mg kg ⁻¹)	$1/n$	PBC _{0.2} (L kg ⁻¹)	
Land use	Home garden	333 ^c	0.15 ^a	50 ^c	47 ^c	42 ^d	0.71 ^a	48 ^c	
	Grazing	500 ^b	0.09 ^c	45 ^d	43 ^d	52 ^b	0.63 ^c	54 ^b	
	Cropland	1000 ^a	0.06 ^d	60 ^a	59 ^a	64 ^a	0.56 ^d	73 ^a	
	Wood lot	500 ^b	0.11 ^b	55 ^b	53 ^b	47 ^c	0.68 ^b	37 ^d	

*mean values of treatments in each factor in a column with the same letter are not statistically different.

TABLE 7: Correlation coefficients (r) among sorption parameters and related properties of soil parameters.

Sorption parameter	Q_{max}	b_L	K_f	PBC _f	Clay	pH	SOC	CEC	Al _{ox}	Fe _{ox}	Al _d	Fe _d	AP
Q_{max}	1	-0.89***	0.97***	0.80*	0.98*	-0.98**	-0.94*	-0.99*	0.99*	0.58*	0.97*	0.68*	-1.000*
b_L		1	-0.96**	-0.52*	0.88	0.97*	0.95	-0.94*	-0.23	-0.20	-0.34	-0.78	-0.92*
K_f			1	0.63*	0.80	0.91*	0.98	0.81	0.99*	0.46*	0.95*	0.53	-0.97*
PBC _f				1	-0.33	-0.54*	0.38	-0.14	0.76	0.26	0.95*	0.88	0.98*

Note: * $p \leq 0.05$ is significant; ** $p < 0.01$ is highly significant; *** $p < 0.001$ is very highly significant.

similar trend as the Q_{max} . The highest K_f value in cropland is due to P sorption on the surfaces of the Al/Fe oxides while the lowest K_f in the home garden is due to low retention of P [44]. From the K_f correlation with soil pH, Al_{ox}, Fe_{ox}, and Al_d, K_f value is more dependent on the Fe/Al oxides and hydroxides than SOC. The K_f values on croplands were much lower than other studies [7, 9].

The supply of phosphate is a function of buffering capacity [12]. The soil from the cropland had high PBC_{L,f} which could exhibit higher specific surface area attributed to less solution P concentration for plant utilization that it would maintain the P concentration for longer period of time as reported by Roy and Pal [14]. On the other hand, soils of the home garden, grazing land, and woodlot had low PBC_{L,f} and it would not maintain solution P concentration for longer period of time [14]. Variations in PBC among different land uses represent the variation in soil physical and chemical characteristics [12]. The negative correlation of soil pH with PBC_f may indicate the inverse relationship between the solution P concentration and buffering capacity (Pal 2009). The relatively low soil pH decreases the mineralization of organic matter incorporated resulting in low P release to soil solution [9].

The maximum P buffering capacity (MBC) from the Langmuir model evaluates the P supply and sorption capacity of soils [45]. Maximum P buffering capacity measures the partition of P between solution and solid phase [12]. The MBC followed the sequence: cropland > woodlot > home garden > grazing land. The high MBC found in cropland

could be due to the high sorption capacities of the soils. The high MBC in the cropland agrees with Rashmi et al. [31]. The high MBC in the cropland may also indicate the low rate of P fertilization in the study area. However, the lowest MBC in the grazing land and home garden suggests the lower P sorption capacity with increasing P concentrations in the soil. The organic matter input in the home garden and manure from grazing livestock in grazing land could contribute to the higher SOC [17]. Thus, less buffered soil can supply high P to soil solution due to higher SOC, of the mineralization as well as interference with sorption, supplies a relatively higher P to the soil solution [33]. In croplands of Ethiopia with low pH, the MBC ranged from 71 to 627.35 L·kg⁻¹ [9], but the MBC in our study is below this range.

The energy of sorption for P (b_L) of the Langmuir model was in the order home garden > woodlot > grazing land > cropland. The b_L showed similar trend of the difference with land use as the phosphate sorption affinity ($1/n$). The energy of sorption for P is related to the affinity of P to sorption sites of the soil [41]. The high b_L found in the home garden could be due to the high SOC which strengthens the binding energy of sorbed P [46]. In contrast, the lower b_L in the cropland could be due to the lower SOC in croplands which results in reduced interaction with sorbed P [13]. The b_L value in the present study was from 0.06 to 0.15 L·mg⁻¹, which is close to the values in Chimdi et al. [13] while it is low as compared to 0.30 to 0.31 L·mg⁻¹ in another study [12]. The b_L value of less than 0.4 indicates that phosphate sorbs rather than precipitates and thus the P sorption is

responsible for the removal of phosphate from the solution [13]. The soil pH is positively correlated with b_L and $1/n$. From the results of the present study, to increase the availability of P in the smallholding land uses, phosphorous fertilization can be essential management but due to the cost of fertilizers the smallholder farmers cannot afford to put fertilizer to in all land uses except the cropland and even in the cropland not to the required level. Thus, the most viable management should be managing the soil pH with lime and managing SOC with organic amendments such as crop residue retention, farmyard manure, and biochar.

5. Conclusions

Phosphorus sorption properties of soils mainly depend on sorption isotherm. The fitting of the Langmuir and Freundlich P sorption models showed the relationship between P in equilibrium solution and sorbed P. The result showed that the maximum sorption capacity and maximum buffering capacity of Langmuir model and the sorption coefficient and buffering capacity of the Freundlich model were high in croplands compared to the home garden, grazing land, and woodlot. This is explained by the high amount of Al and Fe oxides and hydroxides, and low level of SOC and soil pH in the cropland. The correlation coefficients obtained for the Langmuir and Freundlich sorption isotherm are the best estimate of the amount of P sorbed in soils of smallholding land uses. Therefore, phosphorous fertilizer management practices such as an organic matter and liming materials are necessary to maintain optimum P concentration in soil solution for decreasing P sorption capacity through real-time experiments in the studied land uses in Ethiopia. However, no information is available on the kinetics of studied soils. We recommend further studies to be carried out to investigate the Kinetic models, describing the possibility of P exchange in soils, provide more reliable information concerning the fate of applied P-fertilizer into the soil over time, and reveal the mechanism involved in the reaction.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

ML collected, analyzed, interpreted the data, and made the final write up. BL and AM edited the final manuscript. All authors read and approved the final manuscript.

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