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The effect of pH on phosphorus adsorption in acidic soils of Tsegede, Western Zone of Tigray, Ethiopia

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Abstract

Background: Although soils in the acidic soils of Tsegede (Skeletal Leptosols, Cambic Leptosols, Leptic Cambisols and Dystric Cambisols) are characterized by low available P contents, study on P adsorption characteristics is limited information. The purpose of this experiment was to evaluate P adsorption characteristics in different acidity ranges of soils.

Material and method: Potassium dihydrogen phosphate (KH_2PO_4) was used for the adsorption isotherm studies by duplicating 3 g soil from each soil types at different acidity ranges of ten soil samples with 50 ml of P in 0.01 M CaCl_2 solution having 0, 20, 40, 60, 80, 100 mg P L^{-1} . Langmuir and Freundlich adsorption isotherm models were used to describe adsorption processes and the relationships between P adsorption and soil properties were determined by correlation.

Results: Phosphorus adsorption increased significantly with increasing P levels and it increased as soil pH declines. The maximum and minimum P-adsorptions were obtained from very strongly acidic Skeletal Leptosols and from moderately acidic Dystric Cambisols, respectively. Comparing the two models, Langmuir linear model showed a better fit to the tested soils compared to Freundlich model. The regression coefficients (R^2) for the fitted Langmuir P adsorption isotherms were highly significant ranging from (0.955 to 0.999) and the adsorption maxima obtained from the Langmuir isotherm ranged from 357 mg P kg^{-1} soil in strongly acidic Dystric Cambisols to 2500 mg P kg^{-1} soil in very strongly acidic Skeletal Leptosols. The bonding energy (k) for Langmuir adsorption model varied from 0.012 to 2.8 L mg^{-1} and both the highest (2.8 L mg^{-1}) and lowest (0.012 L mg^{-1}) k values were obtained from strongly and moderately acidic Dystric Cambisols. The cation exchange capacity (CEC) and organic carbon (OC) were positively correlated with the Langmuir adsorption maxima (b) and negatively correlated with available P and soil pH.

Conclusion: Increments of soil pH using different amendments and their proper management in soils are important in making productive use and higher dose of P is required by soils with higher fixation.

Alternative P management strategies are also needed to reduce P adsorption and enhance P availability in such acidic soils in the study areas.

Keywords: Adsorption, isotherm, acidic soils and phosphorus

Introduction

Phosphorus is one of the vital elements which has significant role in plant growth and it is largely added to soil as a fertilizer and, thereby, increases the physiological productivity of crops (Xiang et al., 2012 and Plaxton and Lambers, 2015). Inorganic P in soil may be found (i) in soil solution, as free available for plant (ii) active forms of P bounded by Al, Fe, and Ca (iii) occluded in Al-Fe-P and reductant soluble Fe-P and (iv) entrapped in primary and secondary minerals (Walker and Syers, 1976). According to Sarker & Karmoker (2011), 92% soils of tropics are deficient in available P and the P deficiency occurs either low in the soil system or unavailable forms of applied fertilizer to plants (Sharif et al., 2013). Adsorption is one factor that limits P availability in soil solution by various physical and chemical soil properties and management practices (Tsado et al., 2012 Moazed, et al., 2010). Therefore, adsorption is the net accumulation of a chemical at the interface between the solid phase and aqueous solution phase, which determines availability of native soil nutrients and the rate of nutrients to be applied to soil as fertilizers (Khan et al., 2010).

The highlands of Tsegede soils, similar to other acidic soils of the tropics, are generally low in available P which is less than 10 mgkg^{-1} soil limits crop yield in cultivated lands (Kidanemariam et al., 2012; EthioSIS, 2014 and Gebremedhin, 2019); which is due to low pH leading to formation of more basic solid phase of aluminum/iron oxides and hydroxy phosphate can affect the fate of applied P and availability of P to plants (Wang et al., 2013) and hence P is one of the limiting elements in crop production. Phosphorus retention by soils is an important parameter for soil fertility as well as for determining the environmental fate of P. To solve this problem, adsorption isotherm equations can be used to predict fertilizer recommendation and devise suitable management system for adsorption of soils governed by physio-chemical

properties (Haile and Wolde, 2015). The adsorption curves provide an adequate basis for estimation of P requirements across a diversity of soils and environment at constant temperature and pressure (Islam, 2014 and Kruse et al., 2015). However, limited work has been carried out to evaluate the relationship between the P adsorption capacity and specific soil properties in the research areas and generally in Ethiopia (Chimdi et al., 2013; (Wogi et al., 2015; Haile and Wolde, 2015 and Ayenew et al., 2018). Thus, the objectives of this study were: (i) to quantify P adsorbed and compare the applicability of Langmuir and Freundlich equations in describing the adsorption of P in acidic soils of Tsegede highlands and (ii) to evaluate the relationships between P adsorption properties of the acidic soils across Tsegede highlands.

Materials and Methods

Description of the study Area

The study was conducted in acidic soils of Tsegede district in Western Zone of Tigray region, Ethiopia (Fig. 1). The specific study area lies between 37° 16'0" to 37°30'0" East longitude and 13° 18' 40"- 13°22' 0" North latitude and has an altitudinal range of 2319 to 2939 m a.s.l with highland agro-ecological zones. It is characterized by diverse physio geographic features with high and rugged mountains, flat topped plateau, deep gorges, incised river valleys and rolling plains (Kidānemariam et al., 2012). The dominant soils in highlands of Tsegede are Skeletic Leptosol (Chegarkudo site), Leptic Cambisol (Intabela) and Dystric Cambisol and Cambic Leptosol (Endassilassie). The acidity categories of Tsegede highlands were found to have 50%, 31%, 15%, and 4% of very strong acidic, strongly acidic, moderately acidic and slightly acidic coverage, respectively and about 20,000 ha soils are problematic with soil acidity (Kidānemariam et al., 2012 and Gebremedhin, 2019). The 10 years mean total annual rainfall is 2320 mm with the

high amount of rainfall in August. The mean annual maximum and minimum temperatures are 23.7 and 6 °C, respectively (Tigray Meteorological Service Center, 2019)

Crops grown in the district are mostly wheat (*Triticum spp.*), barley (*Hordeum vulgare*), teff (*Eragrostis tef*), finger millet (*Eleusine coracana*), faba bean (*Vicia faba*), field pea (*Pisum sativum*), noog (*Guizotia abyssinica*), linseed (*Linum usitatissimum*), sorghum (*Sorghum bicolor*) and sesame. The major indigenous forest trees found in the district include *Juniperus procera*, *Acacia abyssinica*, *Hagenia abyssinica*, *Boswellia papyrifera* and from the exotic species, Eucalyptus trees

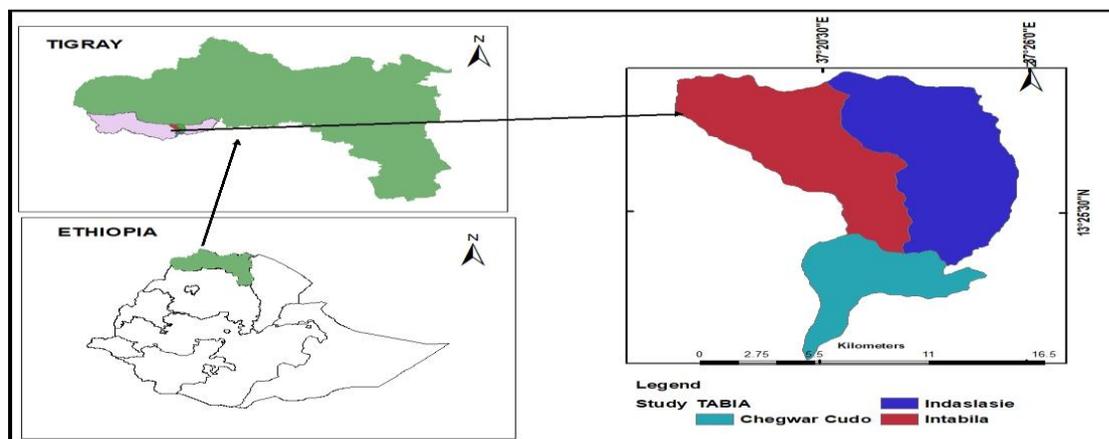


Figure 1: Map of the study area

Soil sampling and characterization

The study sites were selected in highland of Tsegede to represent different acidity levels and due to the presence of P deficiency (Kidanemariam et al., 2012; EthioSIS, 2014 and Gebremedhin, 2019). Then soil samples were purposely collected from cultivated lands with no application of lime practices in their farming system and had received no chemical and organic fertilizers. A total of 60 sub-soil samples were collected (0 - 20 cm depth) after harvest by auger sampler

containing 30, 15 and 15 sub samples from Endassilasie, Chegarkudo and Intabela, respectively from each soil type. Ten composite bulk soil samples were collected out of 60 sub-samples from each site and soil type composited according to their similarity in soil acidity ranges or rating (Jones, 2002), using portable pH meter.

The soil samples were put in plastic bag, tagged, and transported to laboratory in Mekelle Research Center in Tigray Agricultural Research Institute for analysis during the 2018/19. Consequently, adequate (about 1 kg) amount of composited soil samples were air dried and ground to pass through a 2 mm sieve for analysis of selected soil chemical and physical properties except for organic carbon in which case the samples were passed through a 0.5 mm sieve. Soil particle size distribution was analyzed by the Bouyoucus hydrometer method (Day, 1965). Soil bulk density was measured from three undisturbed soil samples collected using a core sampler following the procedure described by Density & Extensibility(2002). Soil pH was measured at 1:2.5 soil to water ratio in 0.01 M CaCl₂(Hendershot et al., 1993) and exchangeable bases were analyzed according to procedures described by Okalebo, (2002) and soil organic carbon was determined by the dichromate oxidation method as described by Walkley and Black (1934) Extractable P was determined by Bray II method(Bray and Kurtz, 1945). Cation exchange capacities of the soils were determined by making use of the method suggested by(Chapman, (1965). Exchangeable acidity was determined by saturating the soil samples with 1 M KCl solution and titrating with 0.02 M NaOH as described by(Mclean (1965).

Phosphorus adsorption

The P adsorption in laboratory was determined according to the method used by Graetz and Nair, (2000). Duplicate 3 g samples (<2 mm) from each of the 10 samples were mixed with 50 mL of 0.01 M CaCl₂, containing concentration of 0, 20, 40, 60, 80, and 100 mg P L⁻¹ KH₂PO₄. They

were shaken with end-to-end shaker at 150 revolutions per minute (rpm) for 24 hours at room temperature (25°C). After equilibrium reached, the soil suspensions were centrifuged at 3000 rpm for 10 minutes and filtered through Whatman number 42 filter papers to obtain clear solution. Two ml of the P filtrate was used for the color development with ammonium molybdate solution containing potassium antimony tartrate and ascorbic acid (Murphy and Riley, 1962). Phosphorus in equilibrium solution was determined by Bray II extraction method Bray and Kurtz(1945) and the P contents of the filtrates were read on a spectrophotometer (model T80+) at 880 nm after the development of the blue color. The amount of P adsorbed by the soils were calculated by subtracting P concentrations in the equilibrium solution from initial added P (Fox & Kamprath, 1970) and it was determined by $X = (C_o - C_e) \frac{V}{w}$ (1). Where, X is the amount of P adsorbed per unit mass of soil (mg kg⁻¹); C_o and C_e are the initial and final concentrations, respectively, in mg L⁻¹; and v is the volume of the solution added (ml), and w is the weight of soil in g.

Phosphorus adsorption isotherm

The P adsorption data for the soils used in this study were fitted into the linearized form of the Langmuir and Freundlich equations proposed by (Dubus & Becquer, 2001). The linearized forms of the equations are described as $\frac{C}{X} = \frac{1}{Kb} + \frac{C}{b}$ for Langmuir and $\text{Log } X = \text{Log } K_f + \frac{1}{n} \text{log } C$ for Freundlich ; where X=amount of P adsorbed per unit weight of soil (mg kg⁻¹); C = equilibrium p concentration (mg L⁻¹); K = constant related to the binding energy (L mg⁻¹) calculated using (Uzoho, B. U., & Oti, 2005); and b = maximum amount of P that can be adsorbed (mg kg⁻¹). Linear form of Langmuir regression was obtained by plotting C/X against C using a stepwise regression model which was constructed using SPSS software of Version 20 (Arbuckle, 2014) to know the most influential soil variables that govern the coefficients obtained from each isotherm.

From the regression equation, the reciprocal of the slope was taken as adsorption maxima (b) and by dividing the slope by intercept to put the value of bonding energy (k). K_f = Freundlich distribution coefficient ($L\ kg^{-1}$); and $1/n$ = an arbitrary constant (dimensionless) indicating the linearity of the equation. The linear regression was obtained by plotting $\log C$ vs $\log X$ from this $1/n$ represents to slope and $\log k_f$ was defined to intercept (Hussain et al., 2006).

Statistical analysis

The different graphs were plotted using Microsoft Excel and the numerical values of slope and intercept for both the isotherms were worked out. Correlation and Regression analysis were performed using the data analysis tool of excel and SPSS software of Version 20.

Results and discussion

Physico-chemical properties

Selected physico-chemical properties of soils are summarized in (Table.1). The textural classes of studied soils were predominantly silty clay. In this respect, the clay and silt contents of the studied soils ranged from 42 to 48% and from 30 to 52%, respectively.. Generally, the textural classes indicated similar relative proportions to all soils with different pH ranges that indicating similar source of parent materials and similar pedogenesis processes as reported by (Melese et al., 2015). According to the ratings by Tekalign (1991), the highest OC content was obtained at very strongly and strongly acidic Skeletic Leptosols in Chegarkudo sites and at very strongly acidic Cambic Leptosols in Intabela site while it was low at moderately acidic soils of Dystric Cambisols in Endassilassie site. The high levels of OC were in agreement with the observations made by (Haile, 2015) who reported that a large proportion of cultivated field's soils in acidic

soils had high OC. This may be due to high amount of rainfall that reduces the rate of OM decomposition in the study sites (Mandiringana et al., 2005 and Kidanemariam et al., 2012).

The pH (H₂O) value of the soils varied between 4.84 and 5.76. Based on (Jones (2002)); the soils of study area were rated as very strongly acidic, strongly acidic and moderately acidic soils (Table: 1). The CEC of the studied soils ranged from 12.8 to 28.6 cmolc kg⁻¹. According to Hazelton & Murphy (2007); the CEC of the soils were in the ranges of moderate to high values. The variation in CEC among the soils might be due to the differences in OM content, clay mineral content and pH ranges (Table 1). In agreement with the current study, Melese et al.(2015) reported that clay and organic matter are the main sources of CEC and the higher clay and organic matter soil contents, the higher were their CECs in acidic soils of South Gonder, Farta district. The exchangeable acidity and exchangeable Al of the studied soils were found to be in the range of 0.2-3.8 cmolc kg⁻¹ and 3.5-3.6 cmolc kg⁻¹, respectively. The variability in exchangeable Al in soils was probably due to the different soil types and other soil chemical properties, such as pH, OC content and CEC of the soils(Abdulaha-Al Baquy et al., 2017).

Exchangeable Ca was dominant in the exchange sites of the soil colloidal materials of the soils studied. This was followed by Mg, K and Na ions in that order. Similar results were reported from acidic soils of Chena and Hagere selam of Southern Ethiopia by (Haile and Wolde, 2015). As per the ratings of (FAO, 2006), the exchangeable Ca in all acidic ranges of the soils was very low; while the exchangeable Mg, K and Na were low to medium in different acidity range of various soil types in the study sites. These results were in agreement with the findings of Haile and Wolde (2015) who reported low in exchangeable bases, which may be due to the higher rainfall and intense leaching of bases and accumulation of exchangeable Al. The amount of P extracted with Bray-2 ranged from 1.89 to 6.845 mg kg⁻¹. Then, there was a considerable variation among

acidic soils of the study area in terms of the available P. This result of available P was rated as very low as also reported by [Kidanimariam et al. \(2012\)](#) and [Gebremedhin,\(2019\)](#).

Table: 1. Selected physicochemical properties of soils

Site	Soil type	pH	OC %	Exchangeable-bases					CEC	Particle size (%)			Tex. Class	Ex (Al)	EX-acidity	Av. P mgkg ⁻¹
				Cmolc kg ⁻¹				CEC		Sand	Silt	Clay				
				Ca	Mg	Na	K									
Chegarkudo	Skeletal	4.9	3.64	0.8	0.4	0.39	0.2	25.8	2	52	46	SC	3.6	3.4	2.64	
	Leptosols	5.3	3.28	2.2	2	0.39	0.4	28.6	10	46	44	SC	3.5	0.7	3.5	
		4.98	1.92	1.8	1.4	0.3	0.5	16.2	6	52	42	SC	3.6	3.8	3.6	
Intabela	Leptic Cambisol	5.3	2.22	2.2	1.4	0.29	0.3	12.4	4	52	44	SC	3.6	1.9	5.05	
		5.7	2.4	3	2.2	0.31	0.3	20	6	48	46	SC	3.5	0.6	6.84	
		4.9	1.98	1	0.8	0.4	0.4	12.2	4	50	46	SC	3.5	3.8	4.7	
E/slassie	Dystric Cambisol	5.3	2.36	1.6	1.2	0.3	0.4	12.8	14	42	44	SC	3.5	2.2	5.06	
		5.8	1	4.8	4.2	0.33	0.3	31	22	30	48	C	3.5	0.6	6.25	
	Cambic Leptosols	4.8	3.45	1	0.8	0.38	0.4	15.4	6	48	46	SC	3.6	1.5	1.89	

5.3 2.02 1.2 1 0.09 0.4 15 8 48 44 SC 3.6 0.2 3.8

Note: SC = Silty clay, C = Clay, Av P = Available phosphorus (mgKg^{-1}), Ex (Al) = Exchangeable aluminum (mgKg^{-1}), Ex-acidity = Exchangeable acidity (mgKg^{-1}) and CEC = Cation exchange capacity (mgKg^{-1})

Phosphorus adsorption characteristics of the soils

The effect of pH on adsorption of phosphorus

The phosphorus adsorption isotherms of highlands of Tsegede were described by plotting the equilibrium concentration of phosphate against the amount of phosphate adsorbed at 24 h equilibration period. The amount of P adsorbed and amount of P remaining in the equilibrium solution are presented in Figure 2 and Table 2. Adsorptions of P increased with increasing P concentrations in the equilibrium solution and/or with addition of P to all soil samples of the study sites with different acidity ranges. This result was in agreement with [Wogi et al.\(2015\)](#); [Muindi et al., \(2017\)](#) and [\(Ayenew et al. \(2018\)\)](#) reported the amount of phosphate adsorbed by soil increases with increases in the solution concentration of phosphate.

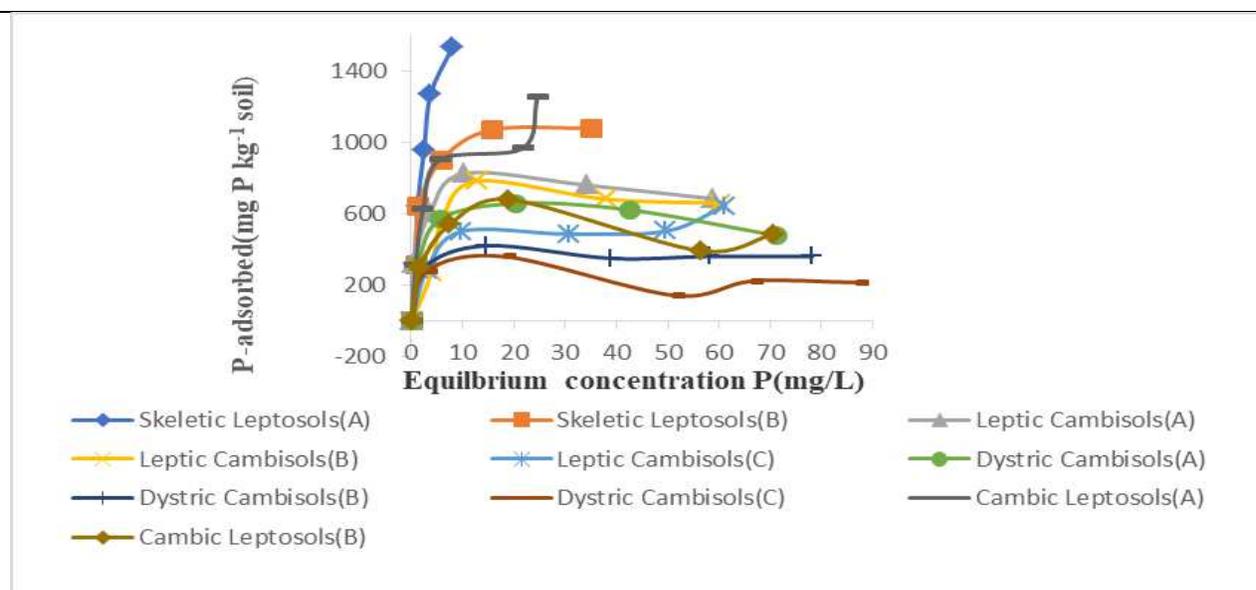
At very strongly acidic soil of Chegarkudo site (Skeletal Leptosols), Intabela (Leptic Cambisols) and E/sslasi (Dystric Cambisols and Cambic Leptosols), P-adsorption corresponded to 91 to 98% with the addition of the lowest P (20 mg P L⁻¹) whereas, addition of the highest P (100 mg P L⁻¹) corresponded to 29 to 42% . Therefore, percentage of adsorbed P increased with decreasing P concentrations added P. This might be due to low amounts of adsorption sites for P probably adsorbed as P increasing added to the soil. In agreement with the present study [Muindi et al., \(2017\)](#) and [Ayenew et al. \(2018\)](#) indicates that the P adsorption of P regularly showed a sharp increase at lower initial P levels and then approached a steady state at higher phosphorus levels. The highest adsorption of P was observed at very strong acidic Skeletal Leptosols and Cambic Leptosols in contact with the P solutions and lowest adsorption was observed at moderately acidic and strongly acidic in Dystric Cambisols. The graphic representation of the adsorption data hence the adsorption isotherms indicated that the quantities of P adsorbed by the soils were in the order Skeletal Leptosols > Cambic Leptosols> Leptic Cambisols > Dystric Cambisols (Figure 2). Soils

in each site had different capacities to adsorb P with respect to variations in acidity levels of soils and also could be due to differences in soil physical and chemical characteristics (Tables 2).

Phosphorus adsorption sharply increased as soil acidity increased or increment of soil pH in the soils of Skeletic Leptosols, Cambic Leptosols, Leptic Cambisols and Dystric Cambisols. The average value of P adsorption variations increased by up to 15% when pH was decreased from 5.3 to 4.9 in Skeletic Leptosols, increased by up to 48 and 54% when pH decreased from 5.26 to 4.92 and 5.74 to 4.84 in Dystric Cambisols and Leptic Leptosols, respectively and increased by up to 41% when pH was decreased from 5.26 to 4.84 in Cambic Leptosols in acidic soils of highlands of Tsegede (Table 2). The result also matched with [Muindi et al.\(2017\)](#) study who revealed that P- adsorption was highly significant with very low soil pH of Nitisols in central highlands of Kenya with increasing order of Nitisols (pH 3.7) > Ando-humic Nitisols (pH, 3.9) > Humic-Nitisols (pH, 4.17) and similar result was reported by [\(Lopez-Hernandez and Burnham, 2006\)](#) under different pH ranges of soils who showed that P adsorption clearly increased at low pH than pH 7. [Chimdi et al., 2013](#)) also showed that soils with lower pH had higher value in P adsorption in cultivated land than other land use system with higher pH values in Western Oromiya Ethiopia and adsorption of P was increased as soil pH decreased in Dinsho district in Bale zone and Cheha district in Gurage zone, Ethiopia [\(Ayenew et al. ,2018\)](#). Contrary to this, in consistence with study in acid soils of Western Kenya where [Muindi et al. \(2015\)](#) for Orphic-Acrisols P adsorbed were reported higher from the sites of Barondar (pH=4.83) and Yenga (pH=4.68) than the lower soil pH Sega (pH=4.08).

Table: 2. Influence of P addition on P adsorption (mg kg^{-1}) for acidic soils of Tsegede Tigray, Ethiopia

Site	Soil type	pH rating	P addition (mg L^{-1} of P)					Average
			20	40	60	80	100	
Chegarkudo	Skeletal Leptosols	very strong	321	647	959	1271	1534	946
		Strong	318	642	903	1073	1082	804
Intabela	Leptic Cambisol	very strong	325	606	828	762	687	642
		Strong	269	567	785	684	661	593
	Dystric Cambisol	Moderate	284	504	488	505	647	485
		very strong	312	572	660	624	480	530
E/slassie	Dystric Cambisol	Strong	294	423	352	363	363	359
		Moderate	283	362	144	225	217	246
	Cambic Leptosols	very strong	319	629	906	971	1257	816
		Strong	304	542	683	394	489	482



(Note: A = Very strong acidity, B = Strong acidity, C = Moderate acidity)

Figure: 2. Phosphorus adsorption isotherms for different acidity range in acidic soils of Tsegede

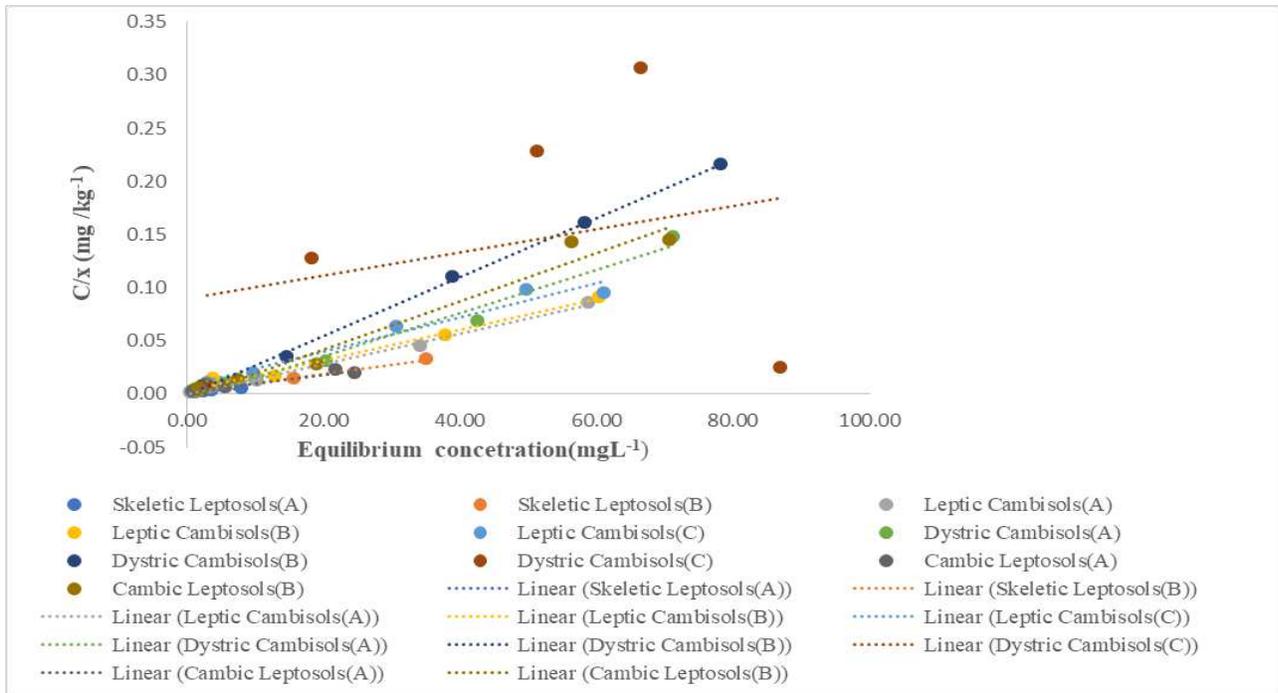
Adsorption isotherms, model validation and adsorption parameters

Adsorption data was fitted using adsorption equation by plotting the linear forms of Langmuir and Freundlich models. Application of both Langmuir and Freundlich isotherms for explaining P adsorption for different locations were also reported by other researchers (Melese et al., 2014; Muindi et al., 2017 and Ayenew et al., 2018). According to Idris & Ahmed, (2012); the goodness of fitted between two models were determined by looking at the coefficient of determination (R^2) from simple linear regression. Accordingly, Langmuir model showed a better fit to the data as compared to Freundlich model in all soil types with in the different acidity ranges except in moderate acidity in Dystric Cambisols (Table 3). The four soil types under different acidity ranges tested showed significant fit to Langmuir adsorption isotherm ranged from R^2 0.955 to 0.999. However, regression coefficients (R^2) for the fitted Freundlich P adsorption isotherm in study sites were only significant in some range of acidity of soils with low R^2 (0.161-0.974) as compared with Langmuir (Table 3).

These results agreed with the findings of (Hartono et al.(2005) who reported regression coefficients(R^2) ranging from 0.90 to 0.98 in acid soils of Indonesia that fitted more with Langmuir than Freundlich model. The findings by Hadgu et al.(2014) showed good fits to Langmuir adsorption isotherm in Cambisols of Agulae areas and Fluvisols of Brki sites from Tigray region and latest studies also indicated that Langmuir adsorption isotherm was better fitted for the soil characteristics to similar present study (Haile and Wolde, 2015 and Wang et al., 2017).

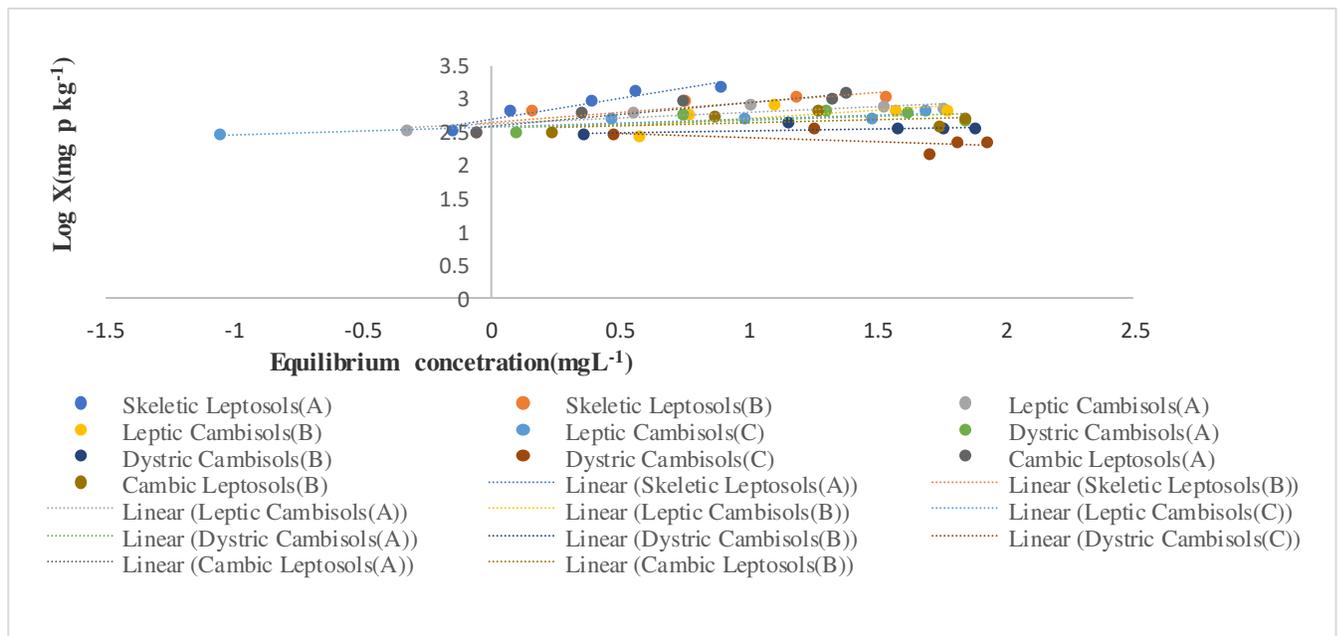
The adsorption maxima 'b' and binding energy 'k' were calculated from the slope and intercept of the Langmuir equation, respectively, both of which are presented in Table (4). The adsorption maxima (b) of the soils were ranged from 357 to 2500 mg kg⁻¹. The lowest (357mg P kg⁻¹) and highest (2500mg P kg⁻¹) b values were observed in strongly acidic Dystric Cambisols and very strong acid Skeletic Leptosols from the adsorption study, respectively. Many studies have also reported similar ranges of P adsorption maxima (Haile and Wolde, 2015; Melese et al , 2014 and Ayenew et al.,2018). Alternatively, soils under the present study appeared to have lower b as compared to acidic soils of Western Kenya (Muindi et al., 2017) and much wider than reported for non-acidic soils of Tigray region reported by Hadgu et al.(2014) in gray desert soil of Xinjiang, China. The higher values of P adsorption maxima clearly indicate that these soils would require higher rate of P fertilizer to increase crop production.

The Langmuir adsorption energy coefficient or binding energy constant of P on the adsorption sites (k) values ranged from 0.012 to 2.8 L mg⁻¹ in different acidity ranges of soils indicating that the studied soils had variable adsorption energy coefficient. Lin& Banin(2005)reported 0.25–0.26 and 0.02–0.05 L mg⁻¹ of the binding energy which were categorized as strong and weak sites. The highest and lowest adsorption energy coefficient were obtained both from strong acidic soils of Dystric Cambisols (2.8 Lmg⁻¹ P) and moderately acidic Dystric Cambisols (0.012Lmg⁻¹ P), respectively. Bonding energy is one of such factors that indicate adsorption energy and the higher its value, the higher determination of P adsorption(Munhoz et al., 2011).



Note: A=very strong acid B=Strong acid and C=moderately acidic

Figure 3: Langmuir adsorption isotherms for different acidity range in acidic soils of Tsegede



Note: A=very strong acid B=Strong acid and C=moderately acidic

Figure: 4. Freundlich adsorption isotherms for different acidity range in acidic soils of Tsegede

Table: 3. Regression equations with R² value for soils in highlands of Tsegede.

Site	Soil type	pH rating	Langmuir		Freundlich	
			R ²	Equation	R ²	Equation
Chegarkudo	Skeletal	very strong	0.959	$y = 0.0004x + 0.0015$	0.92	$y = 0.6311x + 2.6901$
	Leptosols	Strong	0.998	$y = 0.0009x + 0.0014$	0.79	$y = 0.295x + 2.6525$
Intabela	Leptic	very strong	0.976	$y = 0.002x + 0.0048$	0.72	$y = 0.1636x + 2.6375$
		Strong	0.998	$y = 0.0028x + 0.001$	0.46	$y = 0.2444x + 2.4617$
	Cambisol	Moderate	0.084	$y = 0.30011x + 0.0898$	0.89	$y = 0.1132x + 2.5901$
		very strong	0.995	$y = 0.0014x + 0.007$	0.43	$y = 0.1224x + 2.5715$
E/slassie	Dystric	Strong	0.995	$y = 0.0014x + 0.0007$	0.29	$y = 0.0485x + 2.4862$
		Moderate	0.955	$y = 0.0016x + 0.0076$	0.30	$y = -0.1362x + 2.5677$
	Cambic	very strong	0.961	$y = 0.0008x + 0.002$	0.87	$y = 0.3469x + 2.6063$
		Leptosols	Strong	0.966	$y = 0.0023x + 0.0032$	0.16

Table: 4. Parameters of the Langmuir and Freundlich adsorption equations for soils of Tsegede

Site	Soil	pH rating	Langmuir		Freundlich	
			B	K	Kf	1/n
Chegarkudo	Skeletal leptosols	very strong	2500	0.27	517.6	0.576
		Strong	1111	0.642	449.3	0.295
Intabela	Leptic Cambisol	very strong	714	2	434	0.164
		Strong	714.3	0.48	289.5	0.244

	Moderate	625	0.21	389.1	0.113
	very strong	500	0.42	547.6	0.127
Dystric Cambisol	Strong	357	2.8	306.3	0.049
E/slassie	Moderate	909	0.012	369.6	0.136
	very strong	1250	0.4	403.9	0.347
Cambic Leptosols	Strong	435	0.72	371.5	0.081

b- Adsorption maxima (mg kg^{-1}); **k**- constant related to binding energy (L mg^{-1}), **kf** = adsorption capacity $1/n$ =bonding energy

Relationship between adsorption parameters and soil properties

Organic matter and CEC of the soils were significantly and positively correlated with Langmuir adsorption maximum, while available P and pH were negatively correlated with adsorption maxima ($p < 0.05$) (Table 5). Positive correlation of OM with adsorption capacity has also been reported by Mehmood *et al.* (2010), that could be due to the role of negatively charged OM adsorbed with cations such as Fe, Al and Ca and hence in decreasing the ability of P in solution soils that is attributed to increased P adsorption. While, significant negative correlation between adsorbed P with OM content has also been reported by Muindi *et al.* (2016) and Zinabu *et al.* (2015) due to occupation of adsorption sites by organic anions which reduced P adsorption capacities of soils. Similar to the study of Asmare *et al.* (2015), the pH gave a significant and negative correlation with adsorption maxima that was observed indicating that P adsorption increases with decreasing pH. This decrease in adsorption may be attributed to enlarged electrostatic repulsion produced by increased negative surface charge as pH increases and pH can also affect P adsorption by affecting protonation and deprotonation of functional groups and surface binding sites (Muindi *et al.*, 2017).

Similarly, the CEC also positively and significantly correlated ($p < 0.05$) with adsorption capacity reported by Asmare *et al.* (2015). However, available P was negatively significantly correlated with adsorption capacity (b). The finding of this study was in agreement with those of Muindi *et al.* (2016) who observed extractable P negatively correlated with adsorption maxima in acidic soils of Kenya. In case of Freundlich isotherm, EC and CEC were negatively correlated with both Freundlich constants (K_f and $1/n$) and soil pH and clay were positively correlated with $1/n$. However, the result was contrary to Asmare *et al.* (2015) which reported positive relationship of CEC, with k_f . Tsadilas *et al.* (1996) reported that significant positive correlation of Freundlich $1/n$ with clay and pH and was in lined with the present study in highlands of Tsegede.

Table: 5. Correlation between soil properties and the Langmuir and Freundlich adsorption parameters

Soil-property	Langmuir		Freundlich	
	B	K	K_f	$1/n$
pH	-0.557*	0.349 ^{ns}	0.339 ^{ns}	0.642*
OM	0.656*	0.28 ^{ns}	0.023 ^{ns}	0.274 ^{ns}
CEC	0.531*	0.261 ^{ns}	-0.671*	-0.719*
Sand	0.292 ^{ns}	0.283 ^{ns}	0.231 ^{ns}	0.043 ^{ns}
Silt	0.184 ^{ns}	0.353 ^{ns}	-0.412 ^{ns}	-0.736*
Clay	0.296 ^{ns}	0.339 ^{ns}	0.315 ^{ns}	0.687*
P-availability	-0.539*	0.292 ^{ns}	0.519 ^{ns}	0.367 ^{ns}

* **Significant** at $P < 0.05$

Conclusions

Soils of the study areas had different P adsorption capacities from the different acidity ranges of Tsegede highlands. More P was adsorbed from Skeletic Leptosols and low in Dystric Cambisols. Phosphorus adsorptions of each soil were increased as the acidity level of soils increased. The relationship between adsorbed P and solution P to appraise the P adsorption properties of the soils by using two models and adsorption parameters and soil properties were evaluated by correlation. Therefore, Langmuir model could be considered as more precise than the Freundlich model in predicting P adsorption characteristics. The differences in the P adsorption maxima of the soils showed that application of low P fertilizer rates for all the study sites is not viable that was inadequate for optimal crop production. The Langmuir adsorption maxima play a prominent role in explaining P adsorption characteristics and important mechanism to develop increased availability of P by attenuating the P adsorption capacity of the soils in order to increase productivity especially for soils with relatively high P fixing capacity. A Langmuir adsorption maximum was influenced by pH, CEC and OM in the study area. At the end, intensive and proper management strategies of the soil constituents were important to increase P availability in the study areas.

Abbreviations

B: adsorption maximum; X: amount P adsorbed; CEC: cation exchange capacity; OC: organic carbon; pH: power of hydrogen; Co: initial P concentrations; Ce: equilibrium P concentrations; FAO: Food and Agriculture organization; Kf: Freundlich adsorption capacity; K: Langmuir energy of adsorption; SPSS: statistical package for social science; m a.s.l: meter above sea level; M: molarity; KH₂PO₄: potassium dihydrogen phosphate;

Authors' contributions

HA: collected, analyzed, interpreted the data and made the final write up on his Master thesis in Soil Science at Mekelle University, Ethiopia. GG and FH, as co-authors edited the final manuscript. All authors read and approved the final manuscript.

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Competing interests

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Consent for publication

Not applicable.

Ethics approval and consent to participate

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Figures

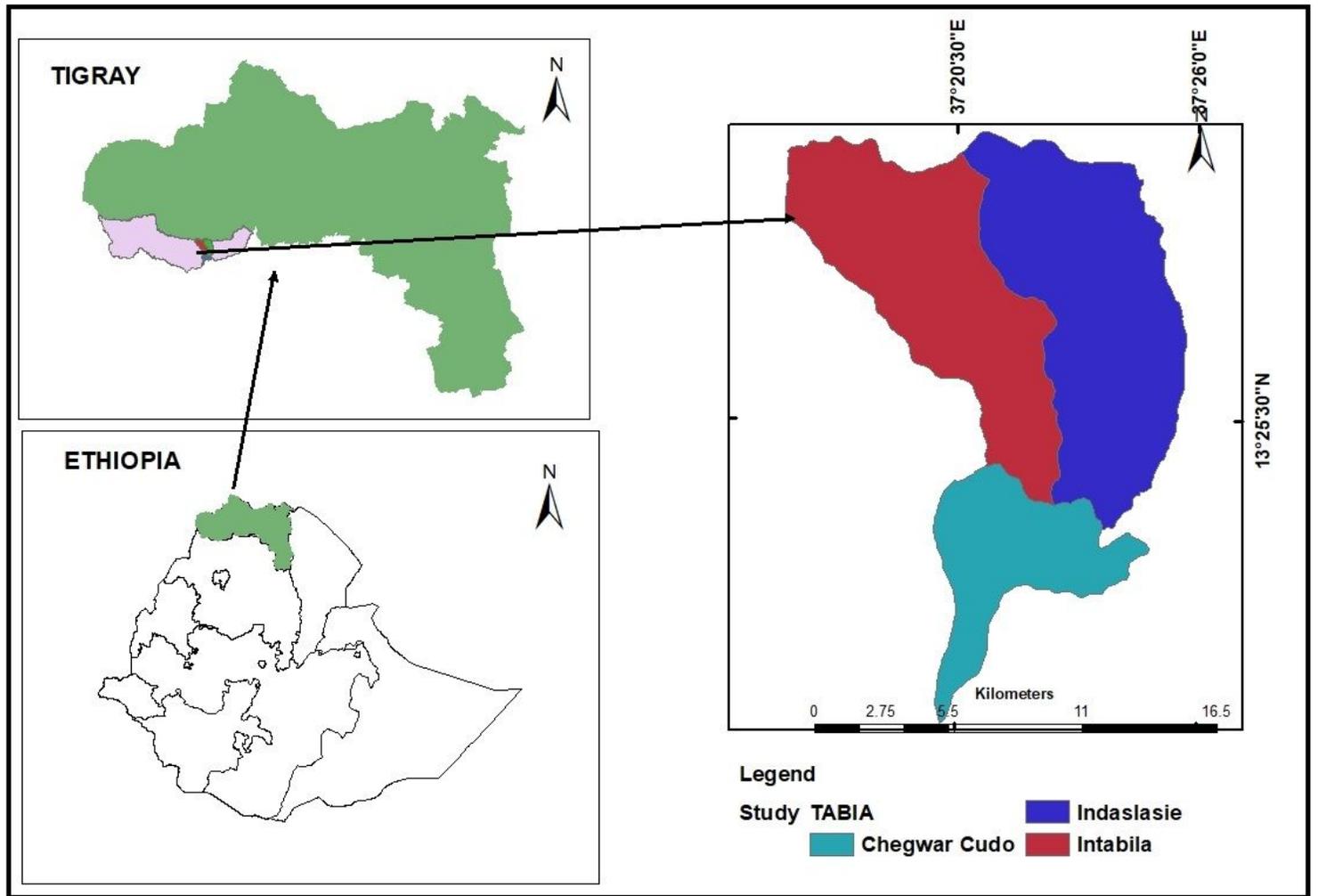
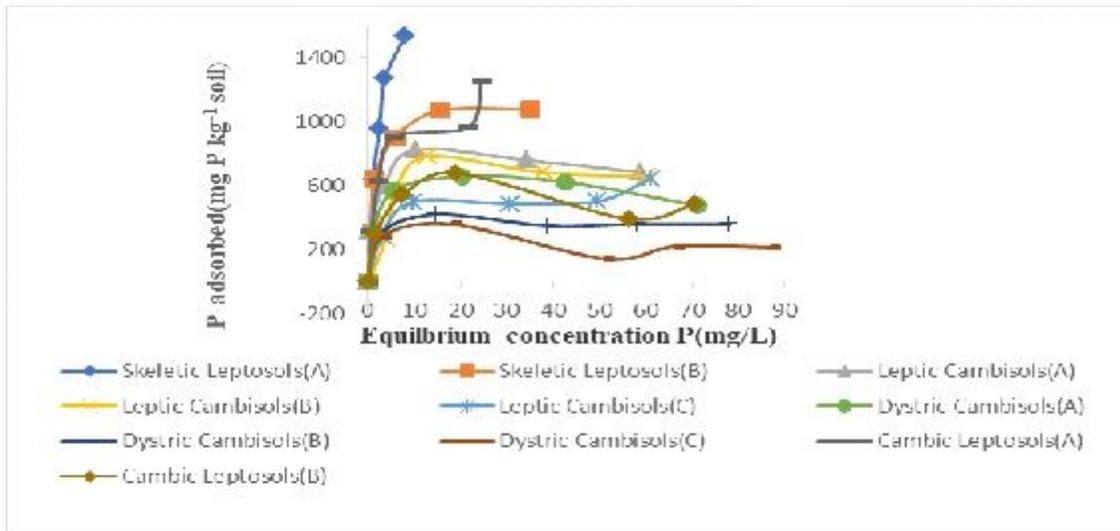


Figure 1

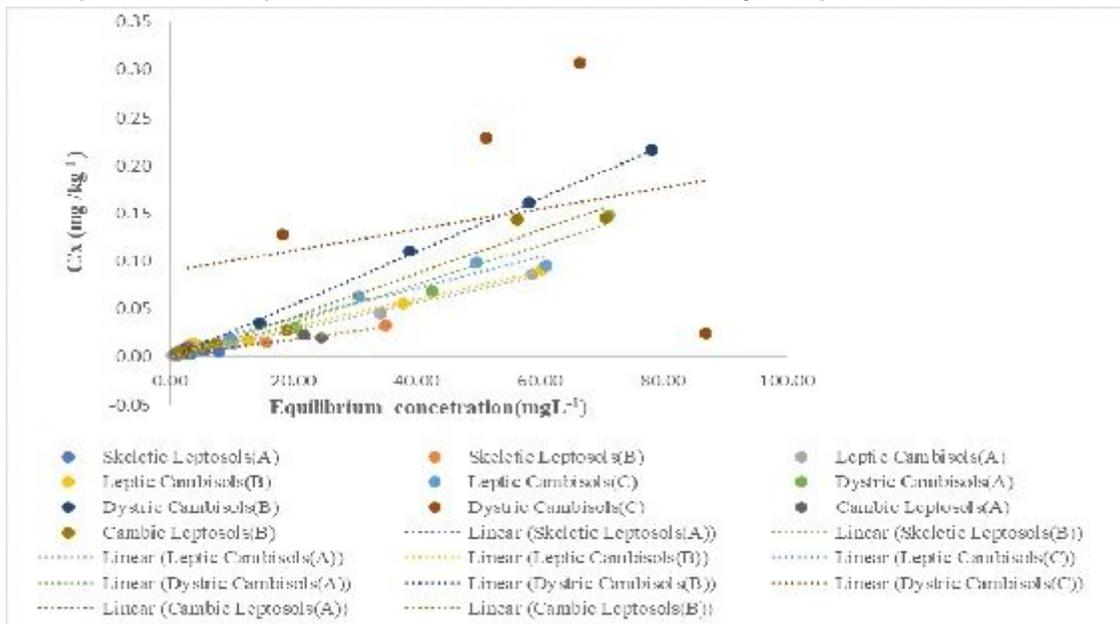
Map of the study area



(Note: A = Very strong acidity, B = Strong acidity, C = Moderate acidity)

Figure 2

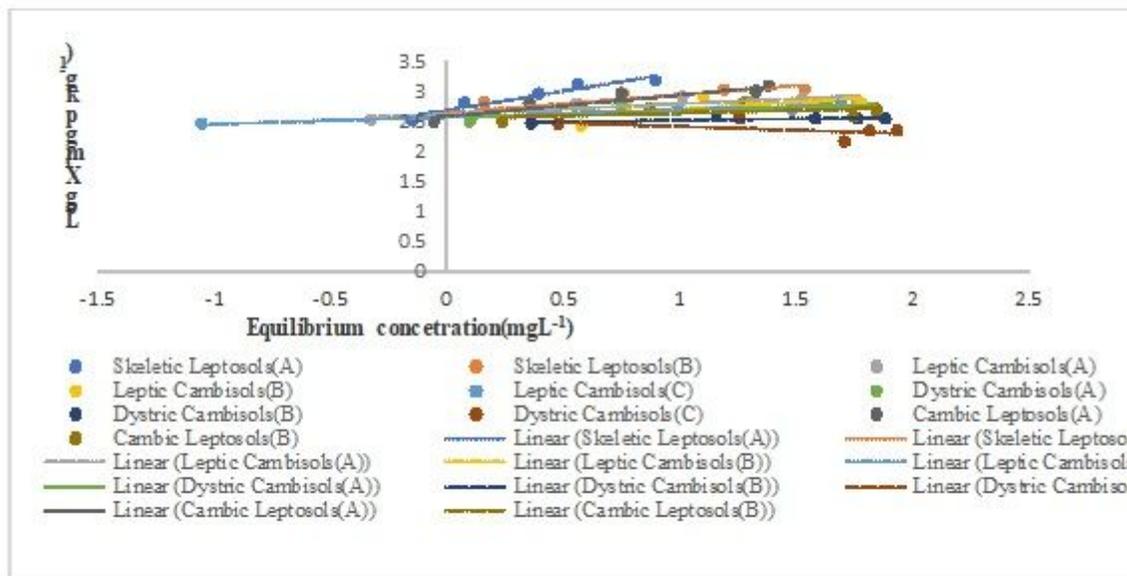
Phosphorus adsorption isotherms for different acidity range in acidic soils of Tsegede



Note: A=very strong acid B=Strong acid and C=moderately acidic

Figure 3

Langmuir adsorption isotherms for different acidity range in acidic soils of Tsegede



Note: A=very strong acid B=Strong acid and C=moderately acidic

Figure 4

Freundlich adsorption isotherms for different acidity range in acidic soils of Tsegede