

PHOSPHORUS SORPTION ISOTHERMS AND EXTERNAL PHOSPHORUS REQUIREMENTS OF SOME SOILS OF SOUTHERN ETHIOPIA

ZINABU WOLDE and WASSIE HAILE¹

Ethiopian Sugar Corporation, Addis Ababa, Ethiopia

¹College of Agriculture, Hawassa University, P. O. Box 05, Hawassa, Ethiopia

Corresponding author: wassiehaile@yahoo.co.uk

(Received 22 January, 2015; accepted 16 May, 2015)

ABSTRACT

Information on P sorption characteristics of soils is important for making profitable P fertiliser recommendations and designing appropriate P management strategies for improving crop productivity. An experiment was conducted to determine the P sorption capacities and external P requirements (EPR) of some soils of southern Ethiopia. Sorption data were obtained by equilibrating 3.0 g of each sample with 30 ml of 0.01 M CaCl₂ containing various amounts of KH₂PO₄. The data were then fitted to the Langmuir and Freundlich Equations. Results revealed that both models fitted well with the P sorption data of the soils. The adsorption maxima (X_m) and bonding energy (b) values of the soils derived from Langmuir model were in the ranges of 560-833 mg P kg⁻¹ and 0.16-20 L kg⁻¹, respectively. The Freundlich capacity factor (Kf) ranged from 237 to 1200 mg kg⁻¹. The EPRs of the soils predicted by both models correlated well ($r = 0.99$) and ranged from 54 to 667 mg P kg⁻¹. Forty three percent of the soils had EPR values < 150 mg P kg⁻¹, and were thus classified as low P fixing soils; whereas 57% of the remaining soils had EPR > 150 mg P kg⁻¹ and were classified as high P sorbing soils. Exchangeable Al³⁺ and Fe²⁺ significantly and positively correlated with X_m , b and Kf. Aluminium and Fe²⁺ are major soil properties responsible for the variations in P sorption capacities of the soils.

Key Words: Freundlich, Langmuir Equation, P adsorption

RÉSUMÉ

Des informations sur le potentiel d'un sol à retenir le phosphore (P) sont essentiels afin de faire des recommandations sur l'utilisation adéquate des engrais phosphorés et de développer des stratégies de gestion appropriée du P en vue d'améliorer la production agricole. Une étude expérimentale a été réalisée afin de déterminer les capacités d'adsorption de P et les besoins externes en P de quelques sols au Sud de l'Ethiopie. Les données sur les capacités d'adsorption ont été obtenues en équilibrant 3.0 g de chaque échantillon avec 30 ml de CaCl₂ à 0.01 Molaire, ces échantillons contenaient des quantités variables de KH₂PO₄. Les données collectées ont été ensuite introduites dans les équations de Langmuir and Freundlich. Les résultats ont révélé que les deux modèles renseignent effectivement sur les capacités d'adsorption des sols. Les valeurs d'adsorption maximale (X_m) et d'énergie de liaison (b) des sols, déduites de l'équation de Langmuir étaient respectivement de 560 à 833 mg P kg⁻¹ et de 0.16-20 L kg⁻¹. Le facteur de capacité de Freundlich (Kf) variait de 237 à 1200 mg kg⁻¹. Les besoins externes en P prédits par les deux modèles étaient fortement corrélés ($r = 0.99$) et variaient de 54 à 667 mg P kg⁻¹. 43% des sols avaient des besoins en apport de P inférieurs à 150 mg P kg⁻¹, et pour cela, ces sols ont été classés sols à faible potentiel de fixation de P, tandis que les 57% de sols restants avaient des besoins en apport de P supérieur à 150 mg P kg⁻¹; ils étaient alors classés sols à haut potentiel d'adsorption de P. Les ions échangeables Al³⁺ et Fe²⁺ étaient positivement corrélés avec X_m , b and Kf. Aluminium et Fe²⁺ sont des éléments majeurs du sol responsables des variations en capacité d'adsorption des sols.

Mots Clés: Equation de Freundlich, Equation de Langmuir, adsorption de P

INTRODUCTION

Phosphorus is among the most important limiting nutrients in most soils of Sub-Saharan Africa (SSA). This could be due to low P content in the parent material from which the soils were derived, and/or due to depletion of soil reserve P through intensive cultivation, without adequate external replenishment (Stoorvogel and Smaling, 1990). Furthermore, limited bioavailability of P could result from conversion of soluble P into unavailable forms in the soil, a phenomenon commonly referred to as P sorption/fixation (Yitaferu, 1999), leading to decreased availability of P for plant uptake (Cox, 1994). In acidic soils, adsorption of P on surfaces of Al and Fe oxides is primarily responsible for P fixation; whereas in calcareous and volcanic soils, precipitation reaction and adsorption of P on surfaces of allophanes are responsible for P sorption, respectively. However, P retention in soils is a function of several mechanisms such as precipitation, adsorption and sorption by soil organic matter (Bohn *et al.*, 2001).

Soils greatly vary in P fixation capacities owing to their differences in physicochemical properties. For instance, Zhang *et al.* (2005) found 28 soils of Oklahoma to vary in P adsorption maxima in the order of 34-500 mg P kg⁻¹ of soil. These variations were related to the Al and Fe concentrations of the soils. In a similar study, Siradz (2008) reported the adsorption maxima (X_m) for three soils of central Java, Indonesia belonging to Oxisols, to be in the range of 719-2,747 mg kg⁻¹. Likewise, soils in SSA vary widely in the P sorption and P requirements. For instance Gichangi *et al.* (2008) studied the P sorption characteristics of South African soil, belonging to five soil types, and found that their P adsorption maxima ranged from 192.3 to 909.1 mg kg⁻¹. The adsorption maxima reported for south African soils were higher than those reported by Zhang *et al.* (2005) for Oklahoma soils, but lower than that for Indonesian soils.

The P requirements of 200 soil samples collected from West, east and Southern Africa were determined based sorption isotherms and were in decreasing order of Andisol>Oxisol>Ultisols >Alfisols>Entisols (Buresh and Smithson, 1997). It is thus important to know

about the P sorption capacities of soils to design P management strategies for higher crop yields. High P sorbing soils are characterised by clayey topsoil, and red colour as indicative of Fe and Al oxides. Such soils make the bulk of soils in smallholder farms of Africa (Sanchez *et al.*, 1997). This implies that P sorption is the major factor that limits P bioavailability in most African soils.

Information on P sorption characteristics of soils based on sorption models is important for designing appropriate P management strategies for high P fixing soils, and for making profitable fertiliser recommendations (Zhang *et al.*, 2005). For instance, in strongly acidic soils with pH<5.5 and high P sorbing soils, application of rock phosphate is more effective and cheaper than using TSP (Bationo *et al.*, 2011). Moreover, it enables determination of the external P requirement (EPR) of soils, also known as a standard P requirement (SPR), which is the amount of P that must be sorbed by a soil to maintain P concentration of 0.2 mg kg⁻¹ in soil solution (Fox, 1981). Soil solution concentration of P at 0.2 mg kg⁻¹ or above is thought to be non-limiting to crop growth (Fox, 1981). However, there is little information on P sorption characteristics of cultivated soils in the southern Ethiopia. Thus, this experiment was conducted in the laboratory. The objective of this study was to determine the P sorption/fixation capacities of some cultivated soils in southern Ethiopia as a basis for designing evidence based management strategies.

MATERIALS AND METHODS

Study area. Soil samples were collected from seven locations representing major agricultural soils of southern Ethiopia (Table 1). Chancha, Bullie and Hageselam are highland locations (> 2600 metres above sea level), with mean annual rainfall greater than 1250 mm. Halaba, Wolaita, Wongao and Hawassa are found in the rift valley and are mid-altitude (1650 - 2000 masl) areas with mean annual rainfall less than 1000 mm. The areas of the region vary widely in soil types and crops grown (Eyasu, 2002).

From each location, random soil samples were collected using Augur, from (0-20 cm), from 30 spots by walking in a zig-zag manner. Samples

TABLE 1. Geographic position, altitude, rainfall, soil type and major crops in each location in Ethiopia

| Location/Soil | Location | Altitude (masl) | Rainfall (mm) | Taxonomy FAO/ UNESCO | Dominant crops |
|------------------|------------------------|-----------------|---------------|----------------------|-------------------------------------|
| Chencha (Ch) | 6° 25' N and 37° 64' E | 2850 | 1350 | Allisol | Wheat, Enset and Potato |
| Halaba (HB) | 7° 12' N and 38° 26' E | 1650 | 909 | Andosols(Orthic) | Teff and maize, Sorghum and peppers |
| Bullie (Be) | 7° 07' N and 39° 3' E | 3100 | 1350 | Nitisol | Beans, Barely and Potato |
| Hagereselam (HM) | 7° 3' N and 39° 4' E | 2620 | 1250 | Nitisol | Beans, wheat and Enset |
| Damote-gale (Dg) | 6° 89' N and 38° 0' E | 2000 | 1090 | Nitisol | Teff and maize and Enset |
| Wonago (Wol) | 6° 13' N and 38° 24' E | 1670 | 1050 | Chromic luvisols | Sweet potato and Enset |
| Hawassa (HW) | 6° 58' N and 38° 19' E | 1740 | 951 | Dystric Cambisols | Maize and Vegetables |

masl = metres above sea level

collected from all spots were transferred into clean plastic buckets and thoroughly mixed, before subsamples were taken to the laboratory for analysis. The samples were initially air-dried and ground to pass 2 mm sized meshes.

Soil analysis. The analysis was done following standard laboratory procedures described in Jones (2001); and Anderson and Ingram (1996). Soil particle size distribution was determined by the Bouyoucous hydrometer method; the pH of the soil were measured in 1:2.5 soil water suspension using pH meter (Jones, 2001), organic carbon (OC) was by determined by Walkley and Black (1934) method; and available P was determined by Olsen's NaHCO_3 method (Olsen *et al.*, 1954).

Cation exchange capacity (CEC) and exchangeable bases were extracted using 1M ammonium acetate method. In the extract, exchangeable Na^+ and K^+ were determined by Flame photometry, and exchangeable Ca^{2+} and Mg^{2+} by atomic absorption spectrophotometry (AAS). Exchangeable Al^{3+} was determined by saturating soil samples with potassium chloride solution and titrating with sodium hydroxide as described by Jones (2001). Extractable micro-nutrients (Fe^{2+} , Cu^{2+} , Zn^{2+} and Mn^{2+}) in the soils were extracted with Diethylenetriamine-pentaacetic acid (DPTA) and determined by AAS. Some selected physicochemical properties of the experimental soils are summarised in Table 2.

Study procedure. This was conducted according to Graetz and Nair (2000) procedure, which involves 3.0 g of air-dried sample of each soil, transferred in to 50 ml centrifuge tube and equilibrated with 25 ml of 0.01 M CaCl_2 . To each tube, a solution containing 0, 1, 5, 10, 15, 20 and 30 mg P L^{-1} as KH_2PO_4 , was added and the final volume was adjusted at 30 ml by using 0.01 M CaCl_2 solution. The suspensions were shaken for 24 hr at a constant temperature of 25 °C on reciprocal shaker, at a speed of 380 rpm and at room temperature (approximately 25°C). Then, the suspension was filtered through Whatman filter paper No. 42, and the concentration of P in the clear extract was determined by the molybdenum blue method (Murphy and Riley, 1962). The

TABLE 2. Some of the physicochemical properties of soils used in the experiment

| Properties | Locations/soils | | | | | | |
|--|-----------------|--------|--------|--------------|---------|-------------|--------|
| | Chancha | Halaba | Bullie | Hagere-Selam | Hawassa | Damote-gale | Wonago |
| Texture | *Cl | L | SCL | CL | SL | CL | CL |
| pH (1:2.5 soil water ratio) | 4.7 | 6.4 | 5.4 | 4.4 | 7.6 | 5.7 | 6.0 |
| OC (%) | 1.7 | 2.7 | 2.0 | 2.1 | 1.7 | 2.1 | 2.7 |
| AvP (Olsen) (mg kg ⁻¹) | 3.7 | 6.3 | 4.2 | 3.1 | 28.2 | 4.5 | 6.9 |
| CEC (Cmol kg ⁻¹) | 11.0 | 22.1 | 11.5 | 14.8 | 21.7 | 13.0 | 21.0 |
| Ex. Al (cmol kg ⁻¹) | 9.0 | trace | 3.1 | 5.6 | trace | trace | trace |
| Exchangeable Cations (cmol kg⁻¹) | | | | | | | |
| Ca ²⁺ | 4.4 | 13.4 | 5.4 | 8.7 | 10.5 | 11.0 | 6.0 |
| Mg ²⁺ | 2.3 | 3.6 | 3.6 | 2.2 | 4.2 | 3.0 | 8.0 |
| K | 0.3 | 1.4 | 0.44 | 0.28 | 3.5 | 0.7 | 0.5 |
| Na | 0.2 | 1.0 | 0.9 | 0.4 | 1.5 | 0.4 | 0.7 |
| Micronutrients (mg kg⁻¹) | | | | | | | |
| Fe ²⁺ | 40.0 | 11.7 | 24.7 | 37.2 | 18.0 | 14.0 | 20.0 |
| Zn ²⁺ | 5.0 | 2.7 | 3.5 | 2.9 | 2.2 | 2.0 | 3.0 |
| Cu ²⁺ | 4.5 | 0.9 | 3.4 | 2.5 | 1.4 | 2.5 | 1.4 |
| Mn ²⁺ | 6.3 | 7.3 | 5.3 | 1.6 | 1.5 | 1.5 | 1.7 |

*CL = Clay loam, L = Loam, SCL = silt clay loam, and SL = silt loam

amount of adsorbed P by each soil was calculated using Equation 1.

$$\frac{(C_0 - C_f)XV}{\text{weight of soil (kg)}} \dots \dots \dots \text{Equation 1}$$

Where: C_0 = initial concentration of P (mg L⁻¹), C_f = final concentration of P (mg L⁻¹) and V = volume of solution (L).

The P sorption data of the soils were fitted to linearised forms of Langmuir and Freundlich Equations (Equations 2 and 3).

Langmuir Equations:

$$\frac{C}{x} = \frac{1}{bX_m} + \frac{C}{X_m} \dots \dots \dots \text{Equation 2}$$

Where: C is = equilibrium concentration P (mg L⁻¹), X = the amount of P adsorbed (mg kg⁻¹), b = a constant related to bonding energy of sorption (L mg⁻¹), and X_m = Langmuir's adsorption maxima (mg kg⁻¹).

Linear regressions for each soils were obtained by plotting C/X vs C . From the regression Equation, the reciprocal of the slope was taken as adsorption maxima and by dividing the slope by intercept the value of "b" was obtained.

Freundlich Equation:

$$\log X = \log kf + 1/n \log C \dots \dots \text{Equation 3}$$

Where: X (mg kg⁻¹) = the amount of P adsorbed per unit mass of soil, and C (mg l⁻¹) is the equilibrium concentration, Kf is a measure of sorption surface coverage (mg kg⁻¹) and n = a constant related to bonding energy (Siradz, 2008). Kf is also defined as capacity factor expressed in mg kg⁻¹ (Shayan and Davey, 1978) and a constant related related to sorption capacity (Idris and Ahmed, 2012). Thus, in this paper we use Kf as as capacity factor. The linear regression was obtained by plotting $\log C$ vs $\log X$. The slope represents 1/n and intercept represents $\log Kf$.

The external P requirement (EPR), also known as standard P requirement (SPR), is the amount of P that must be added in to the soil to maintain a soil concentration P at 0.2 mg P L^{-1} (Bolland *et al.*, 2006). A soil solution concentration of 0.2 mg P L^{-1} is the critical concentration of P below which crops/plants will suffer from P deficiency (Serstu and Ali, 1983). EPR of each soil was calculated from Langmuir and Freundlich equation developed for each soil. The EPRs of soils derived from Langmuir and Freundlich equations were represented as EPRL and EPRF, respectively.

Correlation analysis between soil properties and P sorption indices, derived from both Langmuir and Freundlich equations, was made using SAS software (SAS, 2000). Furthermore, multiple regression analysis was conducted to predict the relationship between soil properties and X_m and soil properties and Kf values using the same software.

RESULTS AND DISCUSSION

Phosphorus sorption isotherm. The P sorption isotherms of Hawassa (HW), Damote-gale (Dg) and Wonago (Wol) soils are shown in Figure 1. The vertical arrow indicates the amount of P that should be adsorbed by each soil to maintain known as external P requirement (EPR), the concentration of soil solution P (SPC) at 0.2 mg L^{-1} . Even if the values of EPR varied among the three soils, they were less than 150 mg P kg^{-1} for all of them. They were, thus classified as low P

sorbing soils. Moreover, the shapes of sorption isotherm graphs of these soils were more or less S-type (Fig. 1). In soils which exhibited S-type curve such as these ones, the affinity of P at lower soil solution concentrations up to 0.2 mg P L^{-1} is higher to the solution than to the soil. However, as the solution concentration of P increases above 0.2 mg kg^{-1} , the situation reverses and the affinity of P will be much higher (Sparks, 2003). This is due to the fact that as concentration of P in soil solution increases, new sorbing sites on the surface of such soils start to open (Sanchez *et al.*, 1997). In line with the current finding, Uzoho and Oti (2005) found that at lower concentration ($<0.2 \text{ mg P L}^{-1}$), the adsorption maxima for three Nigerian soils were 29.5, 33.1 and 34.5 mg kg^{-1} , but at concentrations beyond 0.2 mg L^{-1} , the X_m of these soils increased to 78.7, 66.7 and 38.6 mg kg^{-1} , respectively.

On the other hand, soils of Bullie (Be), Hagereselam (HM), Halaba (HB) and Chench (Ch) were in another group and their P sorption isotherms were represented by L-type curve (Fig. 2). The vertical arrow here too shows the amount of P adsorbed by each soil at standard P concentration or EPR at SPC of each soil. In soils which follow the L-type sorption curve, phosphorus has strong affinity to surfaces at lower equilibrium P concentrations $<0.2 \text{ mg L}^{-1}$ than to the soil solution. However, as the solution P concentration increased above 0.2 mg L^{-1} , the affinity of P to the soils decreased and eventually stabilised (Sparks, 2003). Even if all the soils in

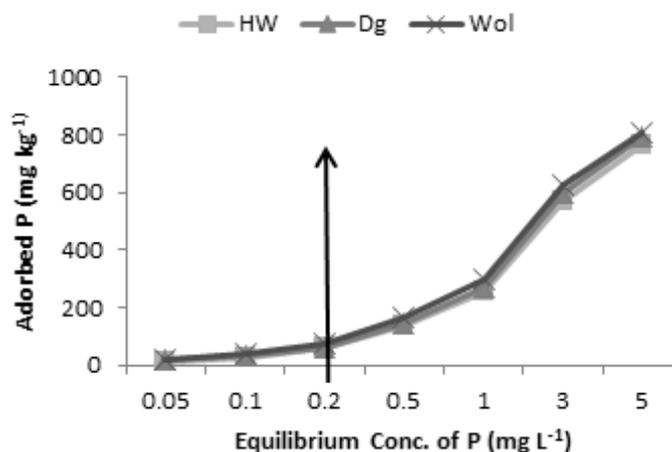


Figure 1. Phosphorus sorption isotherms of low P-sorbing soils of three soils of southern Ethiopia.

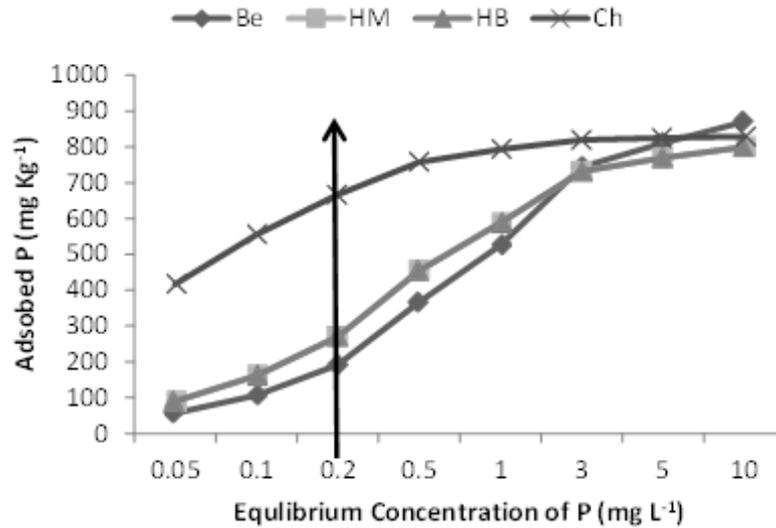


Figure 2. Phosphorus sorption isotherms of and high P-sorbing soils of four soils occurring in some areas of Southern Ethiopia.

Figure 2 showed a characteristic L-type sorption isotherm, there is a clear difference in the slopes and plateaus of each curve. Accordingly, the slope of the sorption curve by Chencha soils was steeper and reached a plateau earlier than the sorption curves of the remaining three soils. This implies that the soil of Chencha has stronger affinity for P than the rest of the soils. Furthermore, from the P isotherms of the soils in Figure 2, it can be seen that the EPR at SPC of all the soils is greater than 150 mg P kg⁻¹; thus they are classified as high P sorbing soils (Sanchez and Goro, 1980). However, the EPRS of Chencha soil is far higher than the EPRS of the rest of the soils.

P Sorption indices. Both models were able to sufficiently describe the P sorption data of the soils (Table 3). This was evidenced by the fact that the r^2 values derived from linearised equation of both models, were very high, indicating a significant relationship between P adsorbed by each soils and the corresponding P concentration in the equilibrium solution. However, the P sorption data of all soils was better fitted with Freundlich ($r^2=0.98$) than with Langmuir ($r^2=0.93$) equation (Table 3). For instance, in line with this finding, Khan *et al.* (2010) reported that Freundlich Equation fitted best with P sorption data of three soils in Pakistan compared to

Langmuir and Temkin Equations. On the contrary, Moazed *et al.* (2010) found that Langmuir equation model better fitted the P sorption data of five soils in Inran than Van Huay and Freundlich equations. On the contrary, Siradz (2008) reported that both Langmuir and Freundlich equations were equally fitted in describing the P sorption data of three Indonesian soils belonging to Oxisols. The differences in the degree to which P sorption data fitted with different equations are related to soil properties and sorption sites (Hussain *et al.*, 2003). For example, soil having homogenous sorption sites, their P sorption data are described with Langmuir than Freundlich equation. On the other hand, the P sorption characteristics of soils with heterogeneous sites are best fitted with Freundlich equations (Sparks, 2003).

The soils studied greatly varied in P sorption capacities, as was revealed by both equations. Based on the Langmuir Equation, the P adsorption maxima (X_m) ranged between 560 and 833 mg P kg⁻¹, with mean value of 703 mg kg⁻¹ (Table 3). The X_m values of the soils were in decreasing order of Chencha > HagereSelam > Bullie > Halaba > Wongao > Damotgale > Hawassa soil. The variation was much wider than reported for several acid soils of Indonesia origin, from different parent materials in which X_m values were

TABLE 3. Phosphorus sorption characteristics for seven soils samples collected from diverse locations of Southern Ethiopia

| Location | P-Sorption indices of Langmuir Equation | | | | P-Sorption indices of Freundlich Equation | | | |
|------------------|---|----------------------------|--------------------------------|----------------|---|------------------------------|----------------|--------------------------------|
| | *X _m (mg kg ⁻¹) | b (L mg ⁻¹) | EPRL (mg kg ⁻¹) | r ² | 1/n | Kf (mg kg ⁻¹) | r ² | EPRF (mg kg ⁻¹) |
| Chencha (Ch) | 833 | 20 | 667 | 0.97 | 0.41 | 1200 | 0.98 | 625 |
| Halaba (HB) | 732 | 2.4 | 270 | 0.93 | 0.43 | 538 | 0.99 | 269 |
| Bullie (Be) | 739 | 1.3 | 191 | 0.92 | 0.53 | 483 | 0.99 | 206 |
| HagereSelam (Hm) | 800 | 2.4 | 270 | 0.93 | 0.39 | 538 | 0.97 | 287 |
| Hawassa (HW) | 560 | 0.16 | 54 | 0.93 | 0.78 | 237 | 0.99 | 67 |
| Damote-gale (Dg) | 590 | 0.22 | 63 | 0.91 | 0.75 | 258 | 0.98 | 79 |
| Wonago (Wol) | 670 | 0.29 | 73 | 0.95 | 0.7 | 277 | 0.98 | 95 |
| Mean | 703.0 | 3.8 | 226.9 | 0.9 | 0.6 | 504.4 | 1.0 | 232.6 |
| Minimum | 560.0 | 0.16 | 54.0 | 0.91 | 0.39 | 237.0 | 0.97 | 67.0 |
| Maximum | 833.0 | 20.0 | 667.0 | 0.97 | 0.78 | 1200.0 | 0.99 | 625.0 |

*X_m = Adsorption maxima, b = bonding energy, EPRL = External P requirement estimated based on Langmuir model, 1/n and Kf = constant of Freundlich equation, EPRF = External P requirement estimated based on Freundlich model

in the range of 294 and 1,430 mg kg⁻¹ (Hartono *et al.*, 2005).

The present study soils and those from Indonesia can be rated as moderately high P fixing soils, compared with Brazilian Oxisols with mean X_m of 4482 mg kg⁻¹, which is rated as extremely high P fixing soils (Fontes, 1988). The affinity constant (b) value of Langmuir equation, which is related with bonding energy, varied from 0.16 to 20 L mg⁻¹. It was the highest for Chencha soils, followed by Halabab = HageSelam, Bullies and was the least for Hawassa, Wonago and Damote-gale soils in that order (Table 3).

Bonding energy (b) is one of such factors that indicate the energy of adsorption and the higher its value, the higher will be the tenacity of P adsorption (Munhoz *et al.*, 2011). In soils with binding strengths (b) less than 0.07 Lmg⁻¹, P is subject to loss in sub-surface flow (Mcdowell *et al.*, 2002). In this case, the soil of Chencha had very high values of b, five times greater than the means of all soils studied; moreover, it was significantly correlated with X_m and EPRL (Table 4). This implies that the soil of Chencha is extremely high P sorbing relative to the other soils.

On the other hand, the capacity factor (Kf) of experimental soils based on Freundlich model, ranged between 237 and 1,200 mg kg⁻¹, with a mean value of 504.4 mg kg⁻¹ (Table 3). Chencha

soils had the highest Kf value, followed by Halaba = HageSelam, and Bullie soil. The soils of Wonago, Damote-gale and Hawassa had the least Kf value in that order (Table 3). The sorption capacities factor (Kf) of the study soils were within the range of Kf values of five soils studied in Sudan (Kf 80-917 mg kg⁻¹) (Idris and Ahmed, 2012). Chencha soils had much higher Kf values than Sudanese soils. The constant (1/n) values of soils studied, based on Freundlich Equation ranged from 0.39 to 0.78. As the Kf increased, there was a corresponding decrease in the value of 1/n. The negative correlation between Kf and 1/n of Freundlich equation is in agreement with Bolland *et al.* (2006), who reported that as sorption of P increases, there is a slow decrease in the value of 1/n.

External P requirement. The external P requirement (EPR) varied between 54 and 667 mg kg⁻¹ based on Langmuir equation, but varied between 67 and 626 mg kg⁻¹ based on Freundlich model (Table 3). However, there was a significant and positive correlation (r²= 0.998) between EPRL estimated by Langmuir model and by Freundlich equation (Fig. 3). This indicates that EPR estimates for a single soil by Langmuir and Freundlich equations are similar. In line with this, Yitaferu (1999) studied the EPR of different highland plateau soils of Ethiopia and reported it

TABLE 4. Pearson correlation between soil properties and P-sorption indices of some soils of Southern Ethiopia

| Soil properties | pH | Al | Fe | Zn | Cu | Mn | X _m | b | EPRL | 1/n | Kf | EPRF |
|-----------------|--------------------|--------------------|---------------------|-------------------|---------------------|--------------------|----------------|---------------------|--------|--------|--------|------|
| pH | - | | | | | | | | | | | |
| Al | -0.75* | - | | | | | | | | | | |
| Fe | -0.8* | 0.97** | - | | | | | | | | | |
| Zn | 0.34 ^{ns} | 0.3 ^{ns} | 0.2 ^{ns} | - | | | | | | | | |
| Cu | 0.37 ^{ns} | 0.08 ^{ns} | -0.03 ^{ns} | 0.84* | - | | | | | | | |
| Mn | 0.86* | -0.5 ^{ns} | -0.5 ^{ns} | 0.5 ^{ns} | 0.4 ^{ns} | - | | | | | | |
| X _m | -0.8* | 0.84** | 0.9** | 0.2 ^{ns} | 0.5 ^{ns} | 0.4 ^{ns} | - | | | | | |
| b | -0.5 ^{ns} | 0.9** | 0.8* | 0.5 ^{ns} | 0.2 ^{ns} | -0.3 ^{ns} | 0.7* | - | | | | |
| EPRL | -0.6 ^{ns} | 0.9** | 0.9** | 0.3 ^{ns} | 0.05 ^{ns} | -0.4 ^{ns} | 0.83** | 0.95** | - | | | |
| 1/n | -0.7* | -0.7* | -0.8* | 0.1 ^{ns} | 0.5 ^{ns} | 0.5 ^{ns} | -0.9** | -0.53 ^{ns} | -0.76* | | | |
| Kf | -0.6 ^{ns} | 0.92** | 0.9** | 0.3 ^{ns} | -0.08 ^{ns} | -0.4 ^{ns} | -0.9** | -0.8* | 0.99** | -0.74* | - | |
| EPRF | -0.6 ^{ns} | 0.92** | 0.9** | 0.3 ^{ns} | -0.07 ^{ns} | -0.4 ^{ns} | 0.85** | 0.94** | 0.99** | -0.79* | 0.99** | - |

ns = non-significant, * and ** = Significant at 0.05 and 0.01 probability levels respectively

to be in the range of 50 - 201 mg P kg⁻¹. In line with this, four soils (Hawassa, Damote-gale and Wongao) studied had EPR values within this range. But the remaining four soils (Bullie, Hagereselam, Halaba and Chench) had EPR values > 260 mg P kg⁻¹ than reported by these authors. In any case, of all soils studied, Chench had extremely very high (>600 mg P kg⁻¹) EPR. However, the EPR estimated for Chench soil was less by half than that previously reported by Sertsu and Ali (1983), which was 1, 200 mg P kg⁻¹.

The observed difference in EPR estimated for Chench soil in the current study and that reported previously for the same soil could be attributed to difference in methods used to predict EPR. In this experiment, EPR of the soils were predicted using Langmuir and Freundlich equations, whereas in the previous experiment, the authors calculated the EPR from the data obtained from direct measurement of adsorbed P by Chench soil at standard soil solution P concentration of 0.2 mg L⁻¹. Differences in soil sampling spots within Chench location, time of sampling, handling and processing of the sample could also account for the observed wide gap in EPR of Chench soil estimated in this experiment and that reported by Sertsu and Ali (1983).

However, both results agree that the soil of Chench is extremely high P fixing soil among the soils investigated now. According to these authors, the P requirement of Chench soil was as high as 1,200 mg P kg⁻¹, which is twice as much as that estimated in this study. They have further stated that low pH and high amount of exchangeable Al and Fe in the soil of Chench is the major factors that account for its high P fixation or P requirement.

Determination of EPR based on sorption models is important to discriminate soils into high and low P sorbing categories. In this regard, Sanchez and Goro (1980) stated that soils that adsorb less than 150 mg P kg⁻¹ at a soil solution concentration of 0.2 mg P L⁻¹, known as standard P requirement, are classified as low P sorbing soils; and soil that require more than this 150 mg P kg⁻¹ are classified as high P sorbing soils. According to this guideline, soils of Hawassa, Damote-galea and Wonago which had EPR values of less than 150 mg P kg⁻¹, are classified as low P sorbing soils. On the contrary, soils of

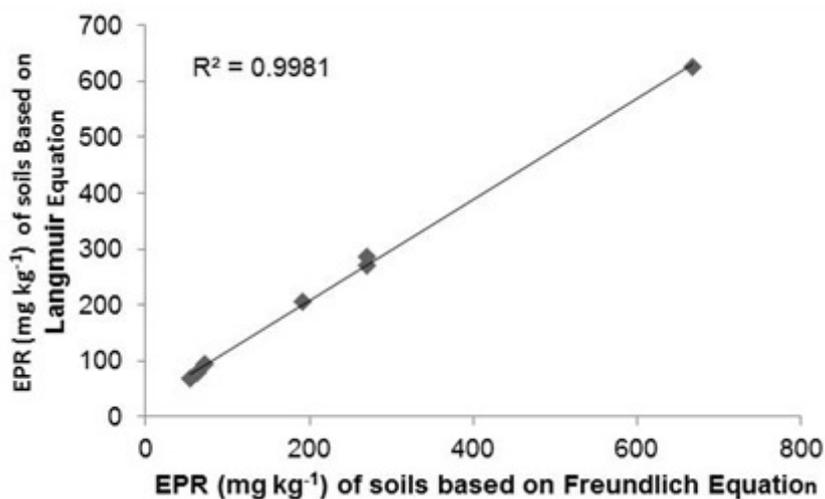


Figure 3. Relation between external P requirements of the study soils predicted by Langmuir and Freundlich equations.

Bullie, Halaba, HagreSelam and Chenchu require greater than 150 mg P kg⁻¹, and thus are classified as high P sorbing soils.

Soil properties affecting the P sorption indices.

The soils studied in this experiment widely varied in P sorption capacities as estimated both by Langmuir and Freundlich equations; and these differences could be related to soils properties. Table 4 presents the relationship between selected soil chemical properties (Table 2) and P sorption indices are presented. The P adsorption maxima (X_m) was significantly and positively correlated with exchangeable Al ($r = 0.84^{**}$) and extractable Fe ($r = 0.9$). This is in agreement with the observation by Zhang *et al.* (2005), who reported a positive correlation between X_m and Al and Fe. Similarly, Athanase *et al.* (2013) found a strong positive correlation between Fe and P sorption maxima; and negative correlation between CEC and P adsorption maxima in Andosols of great lake region of central Africa. Adsorption/sorption maxima (X_m) has significantly and negatively correlated with soil pH ($r = -0.8$). This is in agreement with Siradz (2008), who found an inverse relationship between P sorption maxima and pH values of three soils of Indonesia. On the contrary, Zhang *et al.* (2005) did not get a significant relationship between adsorption maxima of 28 Oklahoma soils and pH. This implies that the relationship

between soil pH and P sorption is inconsistent and hence soil pH is not a reliable indicator of P sorption characteristics of soils.

Langmuir's bonding energy (b) and Freundlich Kf were also significantly and positively correlated with Al and Fe (Table 4.). In low pH soils Fe and Al oxides and Al oxides are the major factors responsible for high P fixation ((Sanchez *et al.*, 1997); whereas in calcareous and volcanic soils precipitation reaction and adsorption of P surfaces of alloplanes are responsible for high P sorption (Bohn *et al.*, 2001). Thus, it is worth to have knowledge on soil properties directly linked to high P sorption by a particular soil so that it can be used as an entry point for designing appropriate P management strategies for improving P nutrition of crops (Athanase *et al.*, 2013). There were also a significant correlation between P sorption indices derived from Langmuir and Freundlich Equation (Table 4). X_m significantly and positively correlated with Kf ($r = 0.81$), EPRF ($r = 0.84$) and negatively correlated with $1/n$ ($r = -0.9$). The results suggest that here is a good agreement between the two equations in describing the P sorption characteristics of the experimental soils.

CONCLUSION

The P sorption data of the study soils fitted well with both Langmuir and Freundlich equations

suggesting that both equations can be used effectively to discriminate these soils according to their P sorption capacities. The EPRS' of the soils estimated by both equations correlated well with each other. Accordingly, Hawassa, Damotegale and wonago soils had $EPR < 150 \text{ mg kg}^{-1}$ and consequently classified as low P sorbing/fixing soils whereas the soils of Chench, HagereSelam, Bullie and Halaba require $EPR > 150 \text{ mg kg}^{-1}$ and hence classified as high P fixing soils. This suggests a need to determine P fertiliser rate specific to these soil for optimum crop production. Furthermore, the result implies that uses of methods that decrease P fixation such as lime and organic matter; and application of rock phosphate as alternative source of P are important in the later soils. Exchangeable Al and extractable Fe were identified as the two major soil properties responsible for high P fixation in these soils.

ACKNOWLEDGMENT

The authors thank the Norwegian Agency for Development Cooperation (NORAD) Project funded by Norwegian Government for sponsoring this study. Professor Lyford Conrad for his help in transferring publication fee.

REFERENCES

- Anderson, J.M. and Ingram, S.J. 1996. Tropical Soil Biology and Fertility: A Handbook of Methods, 2nd edition. CAB International, Oxford, UK. 215pp.
- Athanase, C.R., Tenywa, J.S., Ebanyat, P., Athanase, A. and Nduwumuremyi, A. 2013. Phosphate sorption characteristics of andosols of the volcanic highlands of Central African Great Lakes Region. *Journal of Environmental Science and Engineering* 2: 89-96.
- Bationo, A., Wasawa, B., Okeyo, J.M., Kihara, J. and Mokwunye, U. 2011. Fighting poverty in Africa: The multiple roles of legumes in integrated soil fertility management, Springer, New York, USA. 246pp.
- Bohn, H.L., McNeal, B.L. and O'Connor, G.A. 2001. Soil chemistry, 3rd Ed. John Wiley and Sons, Inc., New York. 322pp.
- Bolland, M.D.A., Allen, D.G. and Barrow, N.J. 2006. Sorption of phosphorus by soils. How it is measured in Australian soils. Bulletin 4591, Department of Agriculture, Chemistry Centre and GRDC, Perth, Australia.
- Buresh, R.J. and Smithson, P. 1997. Building soil phosphorus capital in Africa. In: Buresh, R.J., Sanchez, P.A. and Calhoun, F. (Eds.). Replenishing soil fertility in Africa, SSSA Special publication number 51, Soil Science Society of America, USA.
- Cox, F.R. 1994. Current phosphorus availability indices: Characteristics and short comings. In: Havlin, L.L. and Jacobson, J.S. (Eds.) Soil testing prospect for improving for nutrient recommendations. SSSA Special publication number 40, Soil science Society of America, Madison, USA.
- Duffera, M. and Robarage, W.P. 2009. Soil characteristics and management effect on phosphorus sorption by highland plateau soils of Ethiopia. *Soil Science Society of American Journal* 63: 1455-1462.
- Eyasu, E. 2002. Farmers perceptions of change and management of soil fertility. SOS Sahel-Sahel and Institute of Development studies. Addis Ababa, Ethiopia. 252pp.
- Fontes, M.P.F. 1988. Iron oxide mineralogy in some Brazilian Oxisols. PhD thesis. NCSU-Raleigh, North Carolina, USA.
- Fox, R.L. 1981. External phosphorus requirements of crops. In: Chemistry in the soil Environment. ASA Special Publication No. 40: 223-240.
- Graetz, D.A. and Nair, V.D. 2000. Phosphorus sorption isotherm determination. In: Pierzynski, G.M. (Ed.). Methods of Phosphorus Analysis for Soils, Sediments, Residuals, and Waters, Southern Cooperative Series Bulletin No. 396, Kansas State University, Manhattan, USA.
- Hussain, A.A., Ghafoor, M., Ul-haq, J. and Nawaz, M. 2003. Application of the Langmuir and Freundlich equations for P adsorption phenomenon in saline-sodic soils. *International Journal of Agriculture and Biology* 3: 349-356.
- Jones, B.J.J. 2001. Laboratory guides for conducting soil tests and plant analysis, CRC press, London, UK. 363 pp.

- Khan, Q.U., Khan, M.J., Saif-ur-Rehman and Ullah, S. 2010. Comparison of different models for phosphate adsorption in salt inherent soil series of Dera Ismail Khan. *Soil and Environment* 29 (1): 11 -14.
- Mcdowell, R., Sharpley, A. and Withers, P. 2002. Indicator to predict the movement of phosphorus from soil to subsurface flow. *Environmental Science and Technology* 36(7): 1505–1509.
- Moazed, H., Hoseini, Y., Naseri, A.A. and Abbasi, F. 2010. Determining phosphorus adsorption isotherm in soil and its relation to soil characteristics. *Journal of Food, Agriculture & Environment* 8 (2): 1153-1157.
- Munhoz, R.O., Berton, R.S. and Camargo, O.A. 2011. Phosphorus sorption and redistribution on soil solid phase in a Brazilian Haplorthox Amended with Biosolids. *Applied and Environmental Soil Science* 10:1-7.
- Murphy, J. and Riley, J.P. 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta* 27:31-36.
- Olsen, S. R., Cole. C. V., Watanabe, F. S. and Dean, L.A. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA circular 939. Washington DC, USA.
- Sanchez, P.A. and Goro, U. 1980. The role of phosphorus in agriculture. Symposium Proceedings. June 1-3, ASA, CSSA, SSSA, Madison, Wisconsin, USA.
- Sanchez, P.A., Shepherd, K.D., Soule, M. J., Place, F.M., Buresh, R.J., Izac, A., Mokwunye A.U., Kwesiga, F.R., Ndiritu, C.G. and Wooster, P.L. 1997. Soil fertility replenishment in Africa: An investment in natural resource capital. In: Buresh, R.J., Sanchez, P.A. and Calhoun, F. (Eds.). Replenishing soil fertility in Africa, SSSA Special publication number 51, Soil Science Society of America, USA. 251 pp.
- SAS. 2000. User's Guide, Statistics, Version 8.1 Edition. SAS Inst, Inc., Cary, North Carolina, USA.
- Sertsu, S. and Ali, A. 1983. Phosphorus sorption characteristics of some Ethiopia soils. *Ethiopia Journal of Agricultural Science* 5:1-12.
- Sertsu, S. and Bekele, T. 2000. Procedures for soil and plant analysis. National Soil Research Centre, Ethiopian Agricultural Research Organization, Addis Ababa, Ethiopia. 110p.
- Shayan, A. and Davey, B.G. 1978. A universal dimensional phosphate adsorption isotherm for soil. *Soil Science Society of American Journal* 42: 878-882.
- Siradz, S.A. 2008. Phosphorus sorption characteristics red soils from Lanjung, West and Central java. *Journal of Tanah Tropics* 14: 25-31.
- Sparks, D.L. 2003. Environmental Soil Chemistry, 2nd Edition, Academic Press, Amsterdam, the Netherlands. 352pp.
- Stoorvogel, J.J. and Smaling, E.M.A. 1990. Assessment of soil nutrient depletion in Sub-Saharan Africa: 1983-2000. Rep. No. 28, DLO Win and starring Centre for integrated land, soil and water research (CSC-DLO), Wageningen, the Netherlands.
- Uzoho, B.U. and Oti, N.N. 2005. Phosphorus adsorption Characteristics of selected South Eastern Nigerian soils. *Journal of Agriculture, Food, Environment and Extension* 4: 50-55.
- Walkley, A. and Black, I.A. 1934. An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Science* 37: 29-38.
- Yitaferu, B. 1999. Phosphorus status and sorption characteristics of the soils of northwestern highlands of Ethiopia. An MSc. Thesis Presented to Alemaya University of Agriculture, Alemaya, Ethiopia.
- Zhang, H., Schroder, J.L., Fuhrman, J.K., Basta, N.T., Storm, D.E. and Payton, M.E. 2005. Path and multiple regression analyses of phosphorus sorption capacity. *Soil Science Society of American Journal* 69: 96-106.