Research Article

Phosphorus Sorption Characteristics of Luvisols and Nitisols in North Ethiopian Soils

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Crop response to phosphorus (P) application is often erratic in most acidic soil types. The main processes for P losses from agricultural fields are fixation, crop removal, erosion, surface runoff, and subsurface leaching. The purpose of this experiment was to evaluate adsorption properties of selected soils, determine the external phosphorous requirements (EPRs) of the soils, and identify factors contributing to P sorption in two soils in North Ethiopia. In this experiment, separately weighed 1 g soil samples were equilibrated with KH2PO4 at rates of 0.5, 5, 10, 20, 30, 40, and 50 mg P L⁻¹. The P sorption data were fitted well with both Langmuir and Freundlich models with average r² values of 0.91 and 0.88, respectively. The adsorption maximum (Xm) of the Langmuir isotherm ranged from 588.20 mg P kg⁻¹ soil in Luvisol to 833.3 mg P kg⁻¹ soil in Nitisols. The EPR values ranged between 86.20 to 93.28 mg P kg⁻¹ for soils of the study area. Among the soil properties, clay content and Ex. Al were positively correlated with Xm. The path analysis revealed that clay, pH, and Av. P had a direct effect on P sorption parameters. The EPR, of the studied soils was 3.44 to 3.6 times greater than the blanket P fertilizer rate recommendation. It is concluded that P sorption models can effectively be used to discriminate soils based on P fixation ability. The result further indicates that the current P fertilizer application rate of 50 kg P ha⁻¹ being practiced across all soil types should be revised after validating the models and EPR values estimated in this study for each soil both under greenhouse and in-the-field conditions.

1. Introduction

Phosphorus (P) is an essential element both in natural and agricultural ecosystems [1], and it is required by plants for photosynthesis, respiration, seed production, root growth, and other critical plant functions [2]. Next to nitrogen, P deficiency in plants creates the second most important soil fertility problem throughout the world. Especially in tropical and subtropical acidic soils, low P availability is a major factor that limits plant growth [2, 3]. Similar to other agricultural soils of the tropics, Ethiopian soils are generally low in P [3] and, hence, P is one of the limiting elements in crop production in the highlands of the country. The reasons for low-P-containing parent material from which the soil was formed are low inherent P content, high weathering incidence and soil reaction, long-term anthropogenic mismanagement through imbalance between nutrient inputs, and P losses by erosion and surface runoff [4].

On the other hand, limited bioavailability of P could be due to conversion of soluble P into unavailable forms in the soil, a phenomenon commonly referred to as P sorption/fixation [5], leading to decreased availability of P for plant uptake [6]. Significant P fixation and its precipitation as iron and aluminum phosphates are widespread in acidic soils and as calcium phosphate in calcareous alkaline soils [7]. This situation is a very common in Luvisols and Nitisols. According to IUSS Working Group WRB [8], Nitisols and Luvisols are soils with deep, well-drained, red tropical soil having high clay content. In red soils with high clay content, there could be P fixation [9, 10] and there is a need to study sorption characteristics.

Soils greatly vary in P fixation capacities owing to their differences in physicochemical properties [9] and management [11]. The development of fertilizer recommendations based on crop response and soil test correlation methods is an expensive and time-consuming practice [12]. Thus, with...
2. Materials and Methods

2.1. Description of the Study Site. The study was conducted at the Tana Beles Sugar Development Project which is 576 km far from Addis Ababa. It is located between geographical coordinates of 11° 10' 44" to 11° 48' 57" N latitude and 36° 13' 39" to 36° 37' 12" E longitude with an elevation range of 806 to 1,242 m a.s.l. Totally, 72,944 ha of land was demarcated for the Tana Beles Sugar Development Project; among this, 37,207 ha and 35,737 ha were located at Upper Beles and Upper Ayma, respectively. The project area receives 1447 mm mean annual rainfall; and the mean maximum and minimum temperature are 32.5 (March) and 16.4°C (December), respectively. Overall, the project area is considered to be humid with the relative humidity ranging between 66 and 92%, reaching above 80% in more than 50% of the year [15]. In the upper catchment of the study area, the dominant soil types are Luvisols and Nitisols with an area coverage of 5120.6 and 684.2 ha, respectively, which began sugar can plantation since 2010 [15].

2.2. Soil Sampling and Preparation. A preliminary soil survey and field observation was made using a feasibility study map of the study area. Soil samples were collected from Luvisols and Nitisols, which were selected based on the soil mapping unit of the TBISDP [15]. Following the site selection, from each representative field, thirty-nine subsamples were collected to make one composite sample per soil type. The soil samples were collected from two depths, 0–30 cm and 30–60 cm, in a zigzag sampling scheme using an auger in each soil type. The two depths were taken due to the fact that most of the water and nutrients are extracted from the top 60 cm because approximately 85% of sugar cane root biomass occurs in the top 60 cm. Then, all the composite samples were transferred in to a clean plastic bucket and mixed thoroughly to make a composite sample. One kg from each composite sample was taken to the Ethiopian Sugar Corporation, Research and Development Center, soil laboratory, Wonji. In the laboratory, the samples were air-dried, ground to pass a 2 mm-sized sieve, 0.5 mm for OC, and preserved for analysis of physicochemical properties and P sorption isotherm experiments.

2.3. Analytical Procedures. The processed soil samples were analyzed for selected physicochemical properties: soil particle size distribution was analyzed by the Bouyoucos hydrometer method [16], pH was measured in a 1:2.5 soil water solution by using a pH meter, and organic carbon (OC) was measured by the wet digestion method [17]. The soil available P was determined by the Olsen method [18]. Exchangeable cations were extracted by 1 N NH₄OAc, and in the extract, Na and K were determined by using a flame emission spectrophotometer, whereas Ca and Mg were determined by using an atomic absorption spectrophotometer.

2.4. Phosphorus Adsorption Studies. Phosphorus sorption characteristics were determined by batch equilibrium methods in which soil samples were agitated with P solutions of known concentrations [19]. In view of the results of several studies on adsorption characteristics of acidic soils of Ethiopia [12, 20, 21], it was decided to use low initial P concentrations for adsorption experiments. A duplicate of one gram of soil sample was equilibrated with 25 mL of varying concentrations of P in a 0.01 M CaCl₂ solution in 100 mL centrifuge tubes. The CaCl₂ solution was used as an aqueous solvent phase to improve centrifugation and minimize cation exchange [22]. Following the procedure of Graft and Nair [19], separate air-dried grinded soils were equilibrated in 25 mL of 0.01 M CaCl₂ supporting electrolytes containing KH₂PO₄ at rates of 0.5, 5.0, 10.0, 20.0, 30.0, 40.0, and 50.0 mg P L⁻¹. The tubes were shaken for 24 h on an end-to-end shaker at 150 oscillations per min. The samples were then centrifuged for 10 min at 5211 revolutions per minute, and the supernatant was decanted. The decanted part was then filtered with filter paper (Whatman number 42), and the concentration of P in the clear extract was determined colorimetrically [23] at 882 μm wavelength. Phosphorus disappeared from the solution, was considered as sorbed P, and was plotted against P equilibrated concentration in the solution to obtain a P sorption isotherm. A blank was run for each soil type with the same amount of soil and total volume of 25 ml 0.01 CaCl₂ solution (without P) added and subjected to the same procedure. This served as a background control during the analysis to detect interfering compounds or contaminated soils.

The data obtained from the phosphate adsorption experiments were fitted to the linear forms of the Langmuir and Freundlich isotherms. The linear form of the Langmuir model could be written as follows:

Langmuir equations:

\[ C/X = 1/KXm + C/Xm \]

where \( C \) (mg L⁻¹) is the equilibrium concentration, \( X \) (mg kg⁻¹) is the amount of P adsorbed per unit mass of adsorbent, \( K \) (L mg⁻¹) is a constant related to the energy of sorption, and \( Xm \) (mg kg⁻¹) is P sorption maximum

Freundlich equation:

\[ X = KC^b \text{ or } \log X = \log K + b \log C \]

where \( K \) and \( b \) (\( b < 1 \)) are constants, \( X \) (mg kg⁻¹) is the amount of P adsorbed per unit mass of adsorbent, and
4. Phosphorous Adsorption Characteristics

4.1. Phosphorus Sorption Isotherms. A graphical illustration of the adsorption isotherms of the studied soils exhibited more or less similar trends (Figures 1(a) and 1(b)). This indicates that the affinity of P was higher to the soil than to the soil solution at lower equilibrium concentration of P. However, as the soil solution concentration increased, the situation is reversed and the affinity of P towards the soil solution became higher than to the soils [31]. But, the soils greatly varied in the steepness of the curve, whereby the isotherm of Nitrosols was steeper than those of Luvisols, for both surface and subsurface soils. The probable reason for this variation in adsorption capacity may be due to the disparity among the soils in terms of soil properties such as pH, clay content, OM, and oxides of Al or Fe, which control the availability of P [3, 32].

4.2. Phosphorus Adsorption Indices. Fitting adsorption data to the adsorption equations were carried out by plotting the data in the linearized forms of the adsorption equations. The soils greatly varied in P sorption capacity, and based on the Langmuir Equation, the P adsorption maxima (Xm) ranged between 588.2 and 769.23 mg P kg$^{-1}$, with a mean value of 674.18 mg kg$^{-1}$ (Table 2). It was the highest for subsurface Nitrosols and lowest for surface Luvisols. Although Xm is related to many factors, the higher value in Nitrosols could be due to the presence of high Ex. Al. The variation was much narrow than that reported for several acid soils of Indonesia from different parent materials, in which Xm values were in the range of 294 and 1,430 mg kg$^{-1}$ [33]. All the soils can be considered as having high sorption capacity, compared to values obtained for 16 soil samples from the Northwestern Highlands of Ethiopia which ranged from 5 to 108 mg Pkg$^{-1}$ [9] and for 3 different soils types in Fincha Sugar Estate soils which ranged from 227.3 to 333.7 mg P kg$^{-1}$ [34]. The values, however, are comparable with those obtained for some soils from Southern Ethiopia that ranged from 560 to 833.0 mg P kg$^{-1}$ [21].

The affinity constant ($k$) value of the Langmuir equation, which is related with bonding energy, varied from 0.69 to 0.86 L mg$^{-1}$, with a mean value of 0.77 L mg$^{-1}$ (Table 2). Asmare [20] reported that the bonding energy of P on the adsorption sites of clayey acidic soils of Farta district in the Northwestern Highlands of Ethiopia ranged from 0.21 to 0.96 L mg$^{-1}$. Therefore, the values measured in the present study are comparable with those for clayey acidic soils in Ethiopia. Affinity constant is a factor that indicates the energy of adsorption, and the higher its value, the higher will be the tenacity of P adsorption [35].

The maximum P buffering capacity is a product of Langmuir model Xm and $k$. This is a capacity factor that measures the ability of the soil to replenish phosphate ions in low concentrations in soil solution as they tend to be depleted [20]. The maximum P buffering capacity is potentially useful as a tool to characterize soil types, especially for the low-concentration range, because it describes both the nature and the capacity of P adsorption. The data revealed that the values of the MPBC ranged from 500.00 to 530.77 Lkg$^{-1}$,
Table 1: Selected physicochemical properties of the soils in the study area.

| Soil type | Particle size distribution (%) | Soil texture | pH (H₂O) | Av.P (mg/Kg) | OC (%) | Ex.Al (cmolc kg⁻¹) | EC (dSm⁻¹) | CEC (cmolc/Kg soil) | Exch. base (cmolc Kg⁻¹) | Ca²⁺ | Mg²⁺ | K¹⁺ | Na¹⁺ |
|-----------|--------------------------------|--------------|----------|--------------|--------|-------------------|------------|-------------------|------------------------|-------|-------|------|------|
| Luvisols  | 0–30 6.00 20.00 74.00 Clay     | 5.48 1.84 1.56 0.41 0.024 50.10 25.67 9.56 0.44 0.51 |
|           | 30–60 7.00 17.00 76.00 Clay    | 5.32 1.08 1.45 0.43 0.024 48.20 26.10 10.30 0.39 0.54 |
| Nitisols  | 0–30 4.00 12.00 84.00 Clay     | 5.04 1.46 1.32 1.01 0.020 55.30 16.20 17.60 0.77 0.52 |
|           | 30–60 6.00 14.00 80.00 Clay    | 5.03 1.17 1.22 0.92 0.026 52.10 22.00 6.60 0.45 0.55 |
| Mean value| 5.75 15.75 78.50 5.22 1.39 1.39 |

Table 2: P sorption indices of soils derived from the Langmuir and Freundlich equation.

| Soil type | Depth cm | Xm mg kg⁻¹ | k Lmg⁻¹ | MBC mg L⁻¹ | EPR(0.2) mg kg⁻¹ | R² | EPR(0.2) mg kg⁻¹ | R² |
|-----------|----------|------------|---------|------------|-----------------|----|-----------------|----|
| Luvisols  | 0–30     | 588.2      | 0.86    | 505.85     | 86.3            | 0.93| 0.38 105.8      | 0.9 |
|           | 30–60    | 625        | 0.8     | 500        | 86.2            | 0.92| 0.39 108.19     | 0.9 |
| Nitisols  | 0–30     | 714.28     | 0.71    | 505        | 88.48           | 0.9 | 0.38 115.85     | 0.87|
|           | 30–60    | 769.23     | 0.69    | 530.77     | 93.28           | 0.9 | 0.37 114.87     | 0.85|
|           |          | 674.18     | 0.77    | 510.41     | 88.57           | 0.91| 0.38 111.18     | 0.88|

with a mean value of 510.41 Lkg⁻¹ (Table 2). It can be seen that soils with higher clay percent and exchangeable Al appeared to have higher maximum buffering capacity. The soils with the highest MBC Nitisols have higher adsorption capacity, reflecting low P supply into the soil solution for a longer period as compared to the less buffered soils which can supply ample P to the soil solution. On the other hand, the lower values of MPBC in the present study indicate that a smaller P application rate is needed to the soils for maintaining desired P concentrations in the soil solution [36].

4.3. External Phosphorus Fertilizer Requirements (EPRs).

The Langmuir model was considered as the best model for the description of the P adsorption characteristics of the soils in this particular study area (Table 2). As a result, external P requirements (EPRs) were calculated from the Langmuir model. The EPRs of soils varied from 86.2 to 93.28 mg P kg⁻¹, with mean value of 88.57 mg kg⁻¹ (Table 2). The highest value of EPRs was recorded in Nitisols. The highest clay and Ex. Al recorded in soil samples collected from Nitisols compared to the other soils could have resulted in high P adsorption capacity and ultimately the highest amount of P fertilizer required, maintaining the P concentration in the soil solution for optimum crop production. Similar results were found by Ayenew et al. [3] who reported clay content and high Ex. Al had a strong impact on EPRs. According to Fox [24], soils that adsorb less than 150mg P kg⁻¹ soil to meet the EPR value of 0.2mg l⁻¹ in the soil solution are considered to be low sorbing soil and those adsorbing greater than this value are high P sorbing ones. As a result, all soils types under the study fall in the low P fixing range due
could also be related to the relatively large number of positive relationship of P adsorption with clay content and different soils in the Tigray Region, respectively. Fisseha et al. [37] reported that clay contents were major contributors to P adsorption at the Fincha sugar Estate. Fekadu et al. [34] and Moazed et al. [11]. On the other hand, other results showed that OM can have a significant and positive relationship with OM and negatively correlate with Xm (r = −0.64), indicating that P sorption increases with decreasing pH. In acidic soils (pH < 5.5), more sites on the soil matrix are protonated and Al is liberated, thus enhancing P sorption. The negative correlation between Xm and pH was expected in soils of the study area because the pH ranged from 5.02 to 5.48. The influence of the acidity in the soils is most likely overpowering on the correlations between Xm and pH that may result from the existence of Al and Fe in acidic soils. On the contrary, Dodor and Oya [42] did not get a significant relationship between the adsorption maxima of Okinawa Island soils and pH (with range 7.93–4.16) due to the very narrow pH range within the experimental soils.

Soil OC was significantly (p < 0.05) and negatively correlated with Xm (r = −0.66). This is in agreement with the observation by Burt et al. [43] and Moazed et al. [11]. On the other hand, other results showed that OM can have a significant and positive relationship with OM [3, 43]. Soil OM is able to complex Al, stabilizing the compound and possibly enhancing its ability to sorb P, which is in agreement with Darke and Walbridge [39]. Organic matter can also inhibit crystallization of both Fe and Al oxides, thus indirectly assisting P sorption. The effect of OM is often attributed to complexation with Al or both Al and Fe [39]. Organic matter has the potential to low P sorption, and limitation of P due to high P sorption is not a major problem at the soil of the study area.

The Tana Beles sugar development project has been practicing the application of P fertilizer at a rate of 250 kg P ha⁻¹ DAP (50 kg P ha⁻¹) across all soil types [35], which is equivalent to 25 mg P kg⁻¹ soil, and this rate was developed based on the result of soil analysis and experience of other estates, especially the Fincha Sugar Estate. However, compared to the EPRs estimated from the Langmuir equation for each soil type in this study, the rate of P being currently applied to the farms is very low for both soil types. The EPR values of Luvisols and Nitisols were 86.30 and 88.48 mg kg⁻¹ respectively, at 0.2 mg P L⁻¹ of equilibration, which is equivalent to 172.60 and 176.96 kg P ha⁻¹. Accordingly, these values are greater than the blanket recommendation by 122.60 and 126.96 kg P ha⁻¹ with respect to soil types mentioned above, respectively. The application of P fertilizers based on the blanket recommendation in the study area may result in a substantial yield reduction, i.e., yield remaining much below the maximum, owing to P deficiency.

4.4. Relationship between Soil Properties and P Adsorption Parameters. The soils in this experiment widely varied in P sorption capacity as estimated both by Langmuir and Freundlich equations, and these differences could be related to soil properties. The correlations of P adsorption parameters estimated at 24 h of equilibration period and selected soil chemical properties are given in Table 3. The P sorption index of Xm was found to significantly (p < 0.01) and negatively correlate (r = −0.84) with sand but significantly (p < 0.01) and positively correlate with clay (r = 0.79). In line with this, Fekadu et al. [34] and Fisseha et al. [37] reported that clay contents were major contributors to P adsorption at the Fincha sugar Estate and different soils in the Tigray Region, respectively. The positive relationship of P adsorption with clay content and negative correlation with sand content may be related with larger surface area of clay as compared to sand. It could also be related to the relatively large number of positive charges that can react and strongly bind the negatively charged phosphate ions in soil solution. Clayey soils also tend to have higher concentrations of Fe and Al oxides than coarser soils. Studies in the Southeastern US on acidic soils have also shown that fine-texture soils were able to sorb more P than coarser substrates [38, 39]. Soils with higher clay and silt contents had higher Xm than others (Table 2). This correlation may be partially explained by clay mineralogy [40], which is beyond the scope of this paper, as soils higher in clay and silt were positively correlated to both Fe and Al.

The sorption index (Xm) was significantly (p < 0.05) and positively correlated with exchangeable Al (r = 0.72). This is in agreement with the observation by Asmare [20] and Zhang et al. [41], which showed a positive correlation between Xm and Al. Similarly, Zinabu [13] found a strong and positive correlation between Al and Xm.

Soil pH was significantly (p < 0.05) and negatively correlated with Xm (r = −0.64), indicating that P sorption increases with decreasing pH. In acidic soils (pH < 5.5), more sites on the soil matrix are protonated and Al is liberated, thus enhancing P sorption. The negative correlation between Xm and pH was expected in soils of the study area because the pH ranged from 5.02 to 5.48. The influence of the acidity in the soils is most likely overpowering on the correlations between Xm and pH that may result from the existence of Al and Fe in acidic soils. On the contrary, Dodor and Oya [42] did not get a significant relationship between the adsorption maxima of Okinawa Island soils and pH (with rang 7.93–4.16) due to the very narrow pH range within the experimental soils.

| Table 3: Correlation coefficient (r) for the linear relationships between the P adsorption parameters and selected soil physicochemical properties. |
|--------------------------------------------------|
| Sand Clay pH Av. P OC Ex. Al CEC Xm Kf k b EPRf EPRf |  |
| Sand Clay pH Av. P OC Ex. Al CEC Xm Kf k b EPRf EPRf |  |
to impede or enhance P sorption. If it is of appropriate size, it may occlude sorption sites, either by filling them or by physically blocking them.

4.5. Path Analysis of P Sorption/Fixation. Simple correlation coefficients (r) between pH, clay content, OC, Av. P, Ex. Al, CEC, and Xm are presented for comparison with path analysis results (Table 4). The uncorrelated residual value (U) was low (0.31), while the coefficient of determination (R²) was high (0.90), indicating that the path analysis model explained the majority of variations in P adsorption by soil. Path analysis partitions each r value into one direct effect and five indirect effects. Partitioning by path analysis showed significant direct effects by clay (r = 0.74), pH (r = 0.65), and Av. P (r = −0.63) on Xm. The direct effect of Ex. Al on Xm was positive and not significant (p > 0.05).

The significant positive correlation between Ex. Al and Xm observed in the correlation analysis (Table 3) was due to the indirect effects of clay (r = 0.72; Table 4). Clay plays an important role in adsorption in soil because of its high specific surface area and reactivity [31]. Similarly, the indirect effects of both clay (r = −0.44) and Av. P (r = −0.42) contributed greatly to the correlation between OC and Xm.

5. Conclusions

The results revealed that P sorption data of all soils fitted well to both Langmuir and Freundlich models, but the Langmuir model was found to be best fitted in describing the P sorption data of the soils. Nitisols showed relatively higher P adsorption maxima compared to the Luvisols. The differences in the P adsorption capacities of the soils indicated that the use of blanket P fertilizer rate recommendations without studying optimum rate for sugar cane crop, used in the study area, may fail to increase yield as it may lead to underapplication of P. The results identified that soil properties such as clay, sand, pH, and OC contents influence P adsorption in the study area.

Data Availability

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.

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