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Phosphorus sorption and external phosphorus requirement of soils: the Case of Metahara Sugar Estate, Ethiopia.

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Abstract

Low availability of P limits crop production in the Ethiopian soils. There are many reasons for low P availability to soil. One of them is sorption. Soil phosphorus sorption and supply characteristics of the Metahara Sugar Estate soils were investigated using soil samples collected from soil fertility Class I, Class II and Class III of the farms. In this sorption study, three grams of soil from each sample was equilibrated with 30 ml of 0.01 M $CaCl_2$ solution containing different amount of KH_2PO_4 and the concentration of P was determined by ascorbic acid-molybdate method. Eventually, the amount of adsorbed P by each soil was calculated and the data were fitted into the Langmuir and Freundlich equations. Results indicated that P sorption data of all soils fitted well with Freundlich equations but not with the Langmuir equation. Freundlich Kf and external P requirement (EPRF) of the soils ranged from 92.54-96.94 and 17.3-23.72 mg kg^{-1} respectively. There is no significant correlation in their Kf and EPR. The pH, OC, exchangeable K and Mg contents of soil had significant influences on the sorption capacities of Metahara sugar estate soils. Since all fertility class soils had EPR < 150 mg kg^{-1}, they were classified under the low P sorption category. The low P sorption nature of the soils permits the use of low P fertilizer dose in the range of 34.6–47.4 kg ha^{-1}. This implies that high P sorption is not P limiting factor in the estate. The result further indicates that current P fertilizer application rate of 30 kg P ha^{-1} being practiced across all soil classes of the farm needs to be revised after validating the EPR values estimated in this study for each soil both in the greenhouse and in the field at Metahara Sugar Estate.

Keywords: P Sorption, Langmuir equation, Freundlich equation

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Introduction

In Ethiopia, next to nitrogen, phosphorus (P) is the most important limiting nutrients for crop production. Continuous cropping, soil erosion, inadequate uses of organic and inorganic nutrients are some of the cause of declining soil P content (Wakene and Hiluf, 2003). According to Stoorvogel (1990), on the average 41, 6 and 26 kg ha^{-1} yr^{-1} of N, P and K, respectively, are removed from Ethiopian soils showing nutrient mining is alarmingly high. Deficiency of P in soils may also occur due to conversion of added soluble P fertilizer into unavailable form for plant uptake, a phenomenon called P sorption/fixation (Ravikovich, 1986). According to Gichangi (2007), P sorption is defined as a loss of orthophosphate from soils solution due to either adsorption or precipitation reaction. Soil P limitation due to sorption or fixation is a major problem in highly weathered tropical acid soils dominated by aluminum and iron oxides (Sanchez et al., 1997). The same authors compared the P requirements of 200 soil samples collected from West, East and Southern Africa based on their P sorption isotherm and found that Anidsols >Oxisols >Ultisols >Alfisols >Entisols. Most soils of the Metahara Sugar Estate are comparatively of recent alluvial origin and are classified as Cambisols with alkaline reaction (Booker, 2009).

Several scholars reported that the calcium bounded (Ca-P) is the major inorganic P fraction in saline and alkaline soils where its solubility increases with increased soil pH. According to studies of Piccolo and Huluka (1986) on phosphorus status of some Ethiopian soils, the most abundant form of phosphorus in soils is Ca bounded phosphorus. Phosphorous in saline and sodic soils is generally high and crops are not likely to respond to phosphorous fertilizer.

The availability of P in alkaline soils is determined principally by the solubility of the various Ca-phosphate compounds present. In alkaline soils, soluble H_2PO_4 quickly reacts with calcium to form a sequence of products of decreasing solubility (Samadi, 2006). For instance, highly soluble mono-calcium phosphate $(CaH_2PO4)_4$ added as concentrated superphosphate fertilizer rapidly reacts with Calcium carbonate $(CaCO_3)$ to form first dicalcium phosphate and then reacts again with $CaCO_3$ to form tri-calcium phosphate with decreasing solubility gradually. The tri-calcium phosphate may undergo further reactions to form even more insoluble compounds such as hydroxyl carbonates and hydroxyl apatite. These compounds are thousand times less soluble than freshly formed tri-calcium phosphates. The extreme insolubility of apatite in neutral or alkaline soils generally makes powdered phosphate rocks (which consists mainly of apatite minerals), not

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very effective source of P for plants unless grounded to very fine particles to increase weathering surface (Samadi, 2006). The extent of P sorption greatly varies from soil to soil owing to their differences in physicochemical properties and management (Moazed et al., 2010). Thus, understanding the P-sorption characteristics of soils is important for designing appropriate management strategies and predicting fertilizer requirements that need to be applied (Zhang et al., 2005). Langmuir and Freundlich equations are the most commonly used models employed to determine the P sorption capacities of soils. Sorption isotherms and indices derived from fitting in to these equations are very useful tools to differentiate soils according to their P sorption capacities. These indices help to develop soil specific fertilizer rate for a particular soil in short period of time and relatively at low cost against that obtained using cumbersome and expensive conventional P calibration method (Gichangi, 2007).

Though attempts were made by Zinabu et al. (2015), Birru et al. (2003), Meressa and Robarge (1999), and Sahlemedin and Ahmed (1983), little information is available on sorption capacities of Ethiopia's soil. Thus, it is important to determine the P sorption capacities of many arable soils of Ethiopia. The determination of P sorption capacities helps to identify properties affecting the sorption characteristics of soils. The identified information serves as a basis for improving the P nutrition of crops. Moreover, the P sorption capacities of soils are mostly determined by fitting sorption data of different soils into commonly known Langmuir and Freundlich equations (Stoorvogel, 1990). However, the degree to which the P sorption data of soil fit to these equations vary from soil to soil. Thus, it is necessary to test and identify best fitting equation that describes sorption characteristic of for a particular soil and external phosphorus to attain soil solution P at standard level.

In this regard, there is limited information on the sorption capacities of P in the soils of Metahara Sugar Estate in Ethiopia. Thus, an experiment was conducted to determine their P sorption capacities, external P requirements; and to evaluate the ability of Langmuir and Freundlich equations for describing the P sorption data of the Metahara Sugar Estate soils.

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Materials and methods

Study site description

The experimental soil was collected from Metahara Sugar Estate located at Ethiopia's Sugar Corporation. Geographically, Metahara Sugar Estate is located at 8°21' to 8o 53' N latitude and 39°12' to 39° 52' E longitude at an altitude of 950 m above sea level in the Eastern Shewa Administrative Zone, Oromia Regional State (Michael and Seleshi, 2007).

Most soils of the Metahara Sugar Estate are comparatively recent alluvial origin. Thus, most of them are classified as Cambisols. The Silt soils cover more than 90% of the estate. However, as classified by Booker Agricultural International, depending on the fertility of the soil, Metahara Sugar Estate's soils are grouped into three fertility classes: Fertility Class I, Class II and Class III (Booker, 2009).

Soil sampling and preparation

From each soil fertility class of Metahara Sugar Estate farm, five random soil samples were collected. It was made based on described standard procedure (Brook, 1983). In the description, surface soil (0-20cm) was taken using auger from thirty replicated points by waking in a zigzag manner. Then, all the thirty samples collected from each soil type were transferred in to clean plastic bucket and mixed thoroughly to make a composite sample. From the composite sample, 1 kg soil was taken from each subsample. The composited soil was brought to Fincha sugar estate soil laboratory. These samples were air dried, grounded to pass 2 mm sized sieve and preserved for analysis of physicochemical properties, P fractionation and P sorption isotherm experiments.

Analytical procedures

The processed sample's soil were analysed for selected physicochemical properties following procedures described in (Jones, 2001): soil texture was determined by Bouyoucous hydrometer method, pH measured in 1:2.5 soil water solution using pH meter, organic carbon (OC) by wet digestion method (Anderson and Inagram, 1996), soil available P determined by Olsen method (Olsen et al., 1954), exchangeable cations were extracted by 1N NH_4OAC and in the extract; Na and K were determined by flame emission spectrophotometer whereas Ca and Mg were determined by atomic absorption spectrophotometer.

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Phosphorus sorption experiment

From each sample, three grams of soil (Meressa and Robarge, 1999) were transferred in to 50 ml capacity plastic bottles and equilibrated with 30 ml of 0.01 M $CaCl_2$ solution containing 0, 1, 5, 10, 15 and 20 mg P L^{-1} in the form of KH_2PO_4. The bottles were shaken at 25^0C on reciprocal shaker for 24 hrs (Gratz and Nair, 2009). Then, the suspensions were filtered through Whatman filter paper No. 42 and the concentration of P in the clear extract was determined by ascorbic acid-molybdate method (Olsen and Sommers 1982). The amount of adsorbed P by each soil was calculated using equation 1.

$$\frac{(C0 - Cf)X V}{weight\ of\ soil(kg)} \tag{1}$$

Where: C_0 = initial concentration of P (mg L^{-1}), Cf = final concentration of P (mg L^{-1}) and V = volume of solution (L).

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

Langmuir Equations:

$$\frac{C}{X} = \frac{1}{bXm} + \frac{C}{Xm} \tag{2}$$

Where C is = equilibrium concentration P (mg L^{-1}), X = the amount of P adsorbed (mg kg^{-1}), b = constant related to bonding energy of sorption (L kg^{-1}), and X_m=Langmuir's adsorption maxima (mg kg^{-1}). Linear regressions for each soil were obtained by plotting C/X vs$C$. From the regression equation, the reciprocal of the slope was taken as adsorption maxima and the value of the b was obtained by dividing the slope by intercept.

Freundlich Equation:

$$logX = Logkf + 1/nLogC \tag{3}$$

Where: X (mg kg^{-1}) = Amount of P adsorbed per unit mass of soil, and C (mgL^{-1}) is the equilibrium concentration, Kf (mg kg^{-1}) = Capacity factor (Shayan and Davey, 1978). Besides, 1/n = a constant related to bonding energy (Siradiz, 2008). The linear graph and regression equation for each soil was obtained by plotting LogC against LogX. The slope and intercept were taken as 1/n and Kf, respectively.

The external P requirements (EPR) of the soils were determined by substituting the desired P concentration (0.2 mg P L^{-1}) in the soil solution into the fitted Langmuir and Freundlich equations (Dodor and Oya, 2000). The soil solution concentration of P at 0.2 mg L^{-1}(SPC)

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provides P adequately for many crops if it is maintained throughout the growing period and medium. This concentration P is known as standard soil solution concentration of P (Chaundhary et al., 2003). A soil with EPR < 150 mg kg^{-1} of soil at SPC are classified as low P and those soil with EPR values >150 mg kg^{-1} of soils are classified as high P sorbing soils (Fox, 1981).

Statistical analysis

Data on soil properties, soil P fractions and sorption indices were subjected to Pearson correlation analysis using SAS software (SAS, 2000), which was used to determine the relationship between soil properties, P fractions and P sorption indices.

Results and discussion

The textural classes of the soils under investigation are sandy loam for the Fluvisols, Cambisols and Arenosols, whereas it is clay for the Vertisols and Nitosols based on the soil textural triangle of the ISSS system (Rowell, 1994). The pH (in soil: water) of the soils of Metahara ranged between 8.5 –8.6 with mean value of 8.55 and as per the ratings for Ethiopian soils, which is classified as moderately alkaline according to Murphy (1982). The organic matter content varied between 1.5 - 1.6 % with mean value of 1.55 %. According to Jones (2001), soils with OC contents between 1-2 % are in low category and hence all soils of Metahara are classified as low in their OC contents. The available soil phosphorous in Metahara Estate soils is in medium to high range based on the critical limit description of Tekalign and Haque (1991). The exchangeable Ca and Mg contents of all samples were in high ranges. But the exchangeable K level of the soils was in medium range for sugar cane production (Table 1).

Table 1. The physicochemical properties of soil samples of Metahara Sugar States

Soil Class	Sand	Clay	Silt	Textural Class	pH (1:2.5)	OC (%)	Av P (mg kg^{-1})	Ca	Mg	K	Na	CEC
		%								Cmol kg^{-1}		
Class I	17.2	48.6	34.0	Clay	8.6	1.6	16.1	35.1	4.6	2.9	1.4	54.0
Class II	22.2	49.4	28.4	Clay	8.5	1.5	8.0	51.5	5.7	3.0	1.1	42.3
Class III	23.4	46.8	27.8	Clay	8.6	1.6	3.9	40.9	3.9	2.8	0.8	49.1
Mean	20.9	48.2	30.1	Clay	8.6	1.6	9.4	42.5	4.8	2.9	1.1	48.5

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According to Sahlemedin and Ahmed (1983), CEC value between 25 and 40 cmol (+) kg^{-1} are medium to high and satisfactory for agriculture with the use of fertilizer and CEC > 40 as high to very high.

Phosphorus sorption indices of metahara sugar estate soils

The P sorption data of all the three soil fertility class soils of Metahara Sugar Estate fitted well with Freundlich model with mean r^2 value of 0.94. However, the sorption data of these soils failed to conform well to Langmuir equation (Table 2).

Table 2. Phosphorus sorption indices of Metahara sugar estate soils derived from Langmuir and Freundlich equations

Soil type	P sorption Indices of Langmuir Equation				P sorption Indices of Freundlich Equation			
	X_m (mg kg^{-1})	B (Lmg^{-1})	EPRL (mg kg^{-1})	R^2	1/n	Kf (mg kg^{-1})	EPRF (mg kg^{-1})	R^2
Class I	219.88	0.92	40.36	0.80	0.97	96.94	19.88	0.93
Class II	219.64	1.42	36.50	0.68	1.01	92.54	17.30	0.95
Class III	177.22	1.14	37.14	0.77	0.93	93.38	23.72	0.95
Mean	205.58	1.16	38.00	0.75	0.97	94.3	20.30	0.94
Minimum	177.22	0.92	36.50	0.68	0.93	92.54	17.30	0.93
Maximum	219.88	1.42	40.36	0.80	1.01	96.94	23.72	0.95

It is natural that the P-sorption data of different soils fit with different equations to different degree and there are occasions where the P-sorption data of particular soils may not obey with one, two or none of such sorption equations (Chaundhary et al., 2003, Hussain et al., 2003). For instance, Moazed et al. (2010) studied the P sorption characteristics of five soils in Iran and they found that Langmuir equation was best fit than Freundlich equation. Contrary to these, Khan et al. (2010) reported that Freundlich equation was best in describing the P sorption data of three Pakistan soils. Such variations are related to P sorption mechanisms on the surfaces of different soils. Thus, it seems that the present soils had heterogeneous P sorption site on their surfaces. This is in agreement with Fisseha et al. (2014), where Agule cambisols best fitted Freundlich Equation. Even if the Freundlich parameters such as Kf and 1/n are derived empirically, they are

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considered to be meaningless. However, Shayan and Davey (1978) proposed that, Kf could be considered as capacity factor, meaning that soils having high values of Kf are high P-sorbing soils than soils having low values of Kf. The values of Freundlich Kf ranged between 93.9-113.8 mg kg^{-1} with mean value of 74 mg kg^{-1}. This shows that Freundlich Kf values are in low range.

The external phosphorus requirements (EPR)

The external P requirements (EPR) derived from Freundlich equation shows that the values varied from 17.30 – 23.72 mg kg^{-1} with mean value of 20.3 mg kg^{-1}. The amounts of added P required to maintain a concentration of 0.2 mg P L-1 (P0.2) in solution (EPR) were generally lower than ranges reported in other studies (Dodor and Oya, 2000; Iyamuremye et al., 1996; Warren, 1994; Mehadi and Taylor, 1988). For example, Meressa and Robarge (1999) reported values ranging from 50 to 201 mg P kg-1 for surface samples from non-cultivated and non-fertilized areas in Ethiopia. EPR has no significant correlation with Kf of the soils (Table 3),. This implies that as Kf values of the soils increase, there is no increases in values of EPR. According to (Fox, 1981), all soils of the Metahara Sugar Estate have EPR < 150 mg kg^{-1} and classified as low P-fixing soils. As all these soils are low P sorbing and at the same time account for more than 100 % of the farm, limitation of P due to high P sorption is not a major problem in Metahara Sugar Estate soils.

Relation between soil properties and sorption indices

The Pearson correlation coefficients between some soil properties and P sorption indices of Metahara Sugar Estate soils are presented in (Table 3).

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Table 3. Pearson correlation coefficients between soil properties and P sorption indices of

Metahara sugar estate soils

Properties	PH	P	OC	Ca	K	Mg	Na	Po	Kf	1/n	Eprf	CEC
pH	1											
P	0.01**	1										
OC	-0.53	-0.07*	1									
Ca	-0.71	-0.25	0.23	1								
K	-0.51	-0.14*	0.4	0.42	1							
Mg	-0.33	-0.12*	-0.2	0.55	0.19	1						
Na	0.10*	-0.28	0.04*	0.01**	0.03**	0.33	1					
Po	0.13*	0.01**	0..03*	-0.18*	0.17*	-0.79	0.39	1				
Kf	0.04*	-0.24	-0.06*	-0.21	0.14*	0.08*	-0.33	0.19	1			
1/n	-0.53	-0.28	0.03**	0.63	0.41	0.68	0.03**	-0.5	0.06*	1		
Eprf	0.11*	0.22	0.06*	-0.35	-0.21	-0.65	-0.3	0.64	0.35	-0.61	1	
CEC	0.04**	0.42	0.39	-0.43	0.12*	-0.32	-0.17*	0.21	0.37	0.16*	0.14*	1

* = Significant at 0.05 probability level. All figures without star (*) symbol are statistically non-significant.

As soil P sorption indices are affected by soil properties, it was found out that the EPR correlated significantly with pH of the soils. The Kf was found to significantly and negatively correlate with OC but positively correlated with pH; Mg and K content (Table 3).

Phosphorus sorption isotherms

The isotherms of Metahara sugar estate soils are similar and took more or less L-shaped curve. 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 (Fekadu et al., 2017).
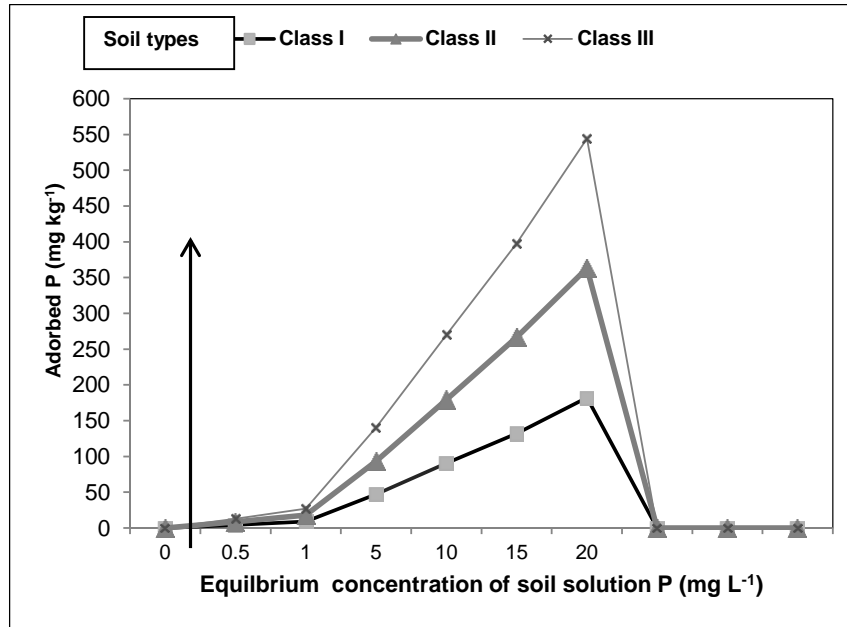

Figure 2. Phosphorus sorption isotherms of three soils of Metahara sugar estate

But, the soils greatly varied in the steepness of the curve where by the isotherm of Class III was stepper than those of Class I and Class II. This is evidenced by the fact that amount of adsorbed P by all classes at standard soil solution concentration of P (0.2 mg L-1) was < 150 mgkg-1 (vertical arrow in Figure 2).

Conclusion

The results of the sorption experiment revealed that the P-sorption data of all the three soils fitted best with Freundlich equation but not with the Langmuir equation. There is no significant correlation between their Kf and external P requirements (EPR). The Ph and OC are soil properties that significantly influence the sorption capacities of Metahara sugar estate soils. Since all the soils had EPR < 150 mg kg^{-1} suggesting that P limitation due to high P sorption is not a problem in the farm. The low P sorption natures of soils lead us to use low P fertilizer dose, which could be 34.6–47.4 kg ha^{1} in the area.

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Conflict of interests

The authors have not declared any conflict of interests.

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