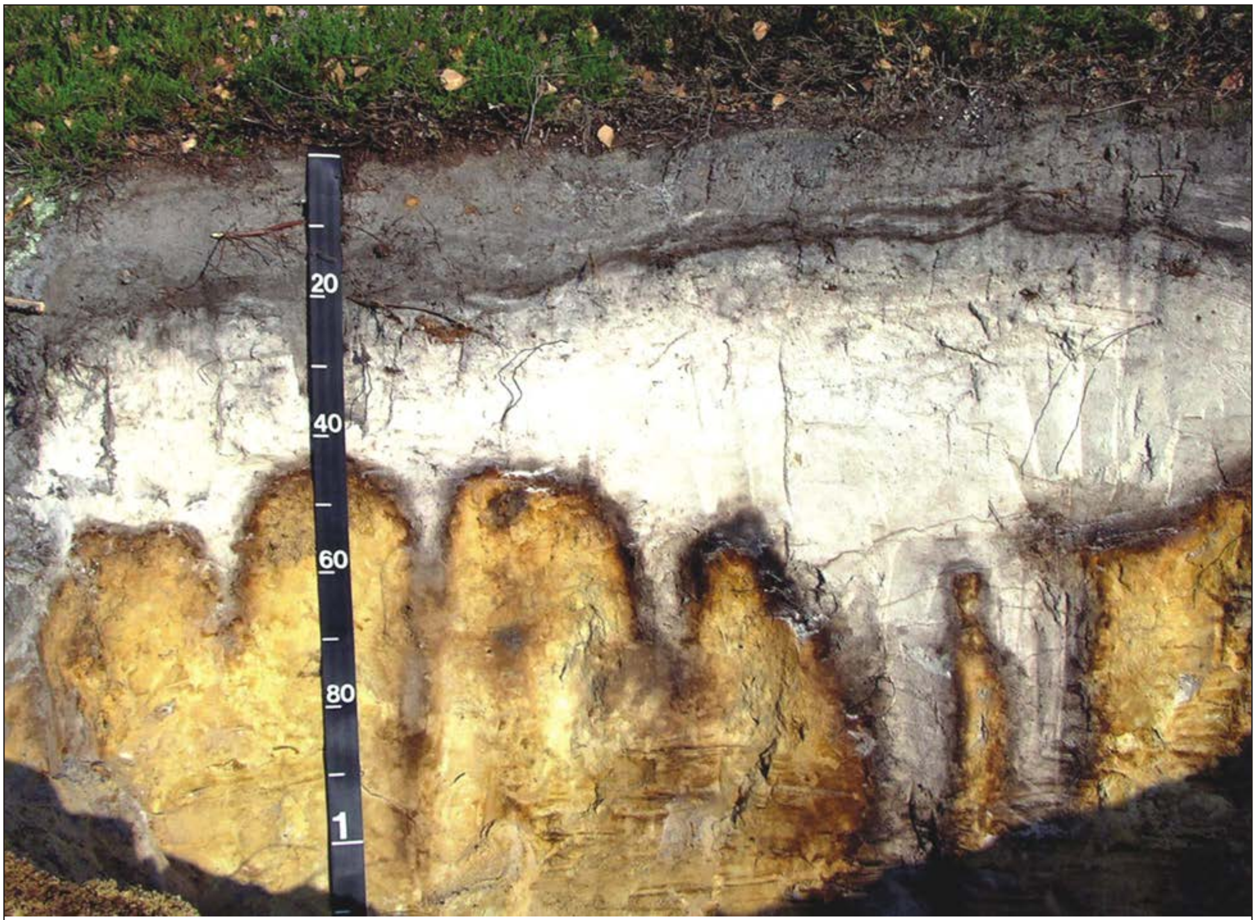

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# Research Article
# Phosphate Sorption Characteristics and External Phosphorus Requirements of Nitisols in Central Kenya Highlands

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## Abstract

**Background and Objective:** Availability of adequate phosphorus (P) for plant uptake is a major problem in acid soils worldwide. Characterization of soils in terms of phosphorus (P) sorption capacity is, therefore, fundamental for effective soil phosphorus fertility management and for efficient utilization of phosphorus fertilizers. A study was conducted to investigate the phosphorus sorption characteristics of selected acid soils from Meru, Embu, Kirinyanga, Nyeri, Kiambu and Kinangop and evaluate the external phosphorus requirements (EPR) for soil phosphorus fertility management. **Materials and Methods:** Sorption data was obtained by equilibrating the nine soil samples with 30 mL of $KH_2PO_4$ in 0.01 M $CaCl_2$, containing 0, 80, 100, 150, 180, 200, 250 and 300 μg $mL^{-1}$ for 48 h with shaking for 30 min at intervals of 8 h. Langmuir adsorption model was fitted to the test results and relationship between P Langmuir adsorption model was fitted to the test results and relationship between P adsorption Langmuir constants and soil properties determined by simple regression and correlations using Genstat statistical software. **Results:** The result of this study showed that the Nitisols were extremely acidic (pH 3.7-4.5), had low extractable P (<15 mg $kg^{-1}$ Bray 1) and the maximal phosphorous adsorption varied from 2986.73-2992.58 mg $kg^{-1}$ soil. The external phosphorus requirement (EPR) varied from 434.78-208.33 mg $kg^{-1}$ soil in the order: Nyeri = Embu>Kirinyanga>Meru = Kiambu>Kinangop. Correlation analysis revealed that Langmuir adsorption maxima (bL) and binding energy constant (kL) positively correlated with clay content and EPR and negatively correlation with organic carbon and soil pH. **Conclusion:** Due to differences in phosphorus fixation rates EPR within the study sites, different phosphate fertilization rates are required for optimum plant growth in such soils. Also management practices involving the use of organic matter and liming as basis for P adsorption reduction would be useful for improved crop production in the soils. There is, therefore, need for further research to determine optimal phosphorus requirements for soils in each research site under field conditions.

Key words: Phosphorus sorption, adsorption maxima, gibbsite, adsorption isotherms, nitisols

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Data Availability: All relevant data are within the paper and its supporting information files.

## INTRODUCTION

Phosphorus (P), after nitrogen, is the second most important macronutrient as an essential plant nutrient[1]. It is a key nutrient for higher and sustained agricultural productivity which is involved in an array of processes in plants such as photosynthesis, respiration, nitrogen fixation, flowering, fruiting and maturation[2-4]. However, phosphorus deficiency in soil is a common nutritional stress in many regions of the world, affecting 42% of the cultivated land in the world[5]. The P deficiency is caused either by low P content in the soils parent materials or by transformations of added P to forms not available or crop uptake. This deficiency results in poor root formation, slow development, poor seed set and fruit formation hence, poor crop yields[2, 6].

The predominant soils in most humid parts of Central Kenya highlands are "humic nitisols" that have moderate to high acidity with inherently high P fixing ability[7]. The soils are also dominated by gibbsite minerals which have larger surface area for P sorption[8]. The acidity prevalence in the soils is associated with phosphorus (P) deficiency in the soils, aluminium (Al) toxicity, high percent Al saturation, low extractable bases (Ca, Mg, K and Na) and reduced microbial activity resulting in low crop yield[9]. The aluminium saturation of the soils has been reported to be above 20% and P levels often as low as <5.0 mg kg$^{-1}$ P[10].

Adsorption isotherm is an important criterion used to estimate: Phosphorous concentration in aqueous phase of soil, energy of phosphorous adsorption, maximal value of its adsorption by soil, buffer strength of soil against phosphorous concentration variations in solution and equilibrium state between phosphorous in aqueous and solid phases and their[11,12]. The most widely used model to predict relationships between fixed and solution P is the Langmuir equation[13,14] which implies that P sorption takes place in a soil monolayer such that any increase in soil P above P sorption maximum does not increase its sorption. However, Freundlich equation has been documented by many authors to generate the best fit in many areas[15-19].

Phosphorus sorption relationships are commonly used in the determination of the external phosphorus requirement (EPR) of crops. According to Fox[20], EPR is the concentration of P in solution that is non-limiting to plant growth. This amount of P sorbed at the critical solution P concentrations of 0.2 ppm is an important statistic for comparing the phosphorus adsorption capacity of soils with varying buffering capacities[21] and forms the threshold over which no response to P is observed in most crops[22-24]. The determination of EPR aims at building up the status of soil phosphorus by a single application to a level which, thereafter, only requires maintenance application to replenish losses owing to plant uptake, removal by erosion or continuing slow reactions between phosphate and soil[25]. Limited information is available about EPR of soils in the Central highlands of Kenya. Such information is, however, necessary to guide P fertilizer recommendations to ensure that crop yields are not compromised due to under-fertilization and that ground water is not polluted with P transported from over-fertilized soils. The objectives of this study were, therefore: (i) To quantify the P sorption characteristics of Nitisols in Central Kenya Highlands and (ii) To determine the EPR of Nitisols in Central Kenya highlands.

## MATERIALS AND METHODS

**Location of the study sites:** The exploratory soil map of Kenya[26] was used to identify acid soils in Kenya highlands[7]. The study was carried out in October-November, 2013 and the study sites had been under continuous crop cultivation for years with minimal attention to the state of the art crop production practices. Descriptions of the selected sites are shown in Table 1.

**Soil sampling, preparation and characterization:** Soil samples were randomly taken from cultivated farmers' fields from the study sites. Nine point samples were taken with a soil auger at the 0-50 cm soil depth in a zigzag manner at each experimental site. The point soil samples were

Table 1: Description of the study areas

| County | Site | GPS of sites | | Elevation (m) | Soil type |
|---|---|---|---|---|---|
| Meru | Kaguru | 00 05 S | 037 39 E | 1460 | Humic nitisols |
| Embu | Kavutiri | 00 25 S | 037 30 E | 1700 | Ando-humic nitisols |
| Kerugoya | Inoi | 01 04 S | 036 47 E | 1539 | Ando-humic nitisols |
| Nyeri | Chehe | 00 25 S | 037 10 E | 1920 | Nitisols |
| Kiambu | Githunguri | 01 03 S | 036 45 E | 1720 | Nitisols |
| Kinangop | Magumu | 00 46 S | 036 35 E | 2691 | Eutric nitisols |

Soil type information sourced from FURP[27] thoroughly mixed and about 1.0 kg composite sample from each site was packed in polythene bags. The samples were air-dried, ground and passed through a 2 mm sieve and subsequently analyzed for various soil properties. Soil pH was measured in 1:2.5 soil 0.01 M $CaCl_2$ suspensions[28] and extractable P determined by the Bray 1 method[29]. Organic carbon (% C), total nitrogen (% N), CEC, particle size were analyzed according to the procedures described by Okalebo *et al*.[30].

**Phosphate sorption isotherms:** Three grams air-dried 2 mm sieved composite soil sample portions were equilibrated in 3 replicates with 30 mL of $KH_2PO_4$ in 0.01 M $CaCl_2$ containing 0, 80, 100, 150, 180, 200, 250 and 300 µg $mL^{-1}$ P for 48 h with shaking for 30 min at intervals of 8 h. Three drops of toluene were added to each of the soil-phosphate suspensions to inhibit microbial activity. Following equilibration, the soil suspensions were centrifuged at 3000 rpm for 10 min and filtered through Whatman No. 5 filter papers to obtain clear filtrates. Phosphorus in the filtrates was then determined colorimetrically based on the Murphy and Riley[31] method. The amounts of P sorbed were calculated as the differences between the amounts of P added and those remaining in the equilibrium solution[32] and the P-adsorption isotherms plotted as adsorbed against equilibrium concentration. The P adsorbed data for the soils used in this study were fitted into the linearized form of the Langmuir Eq:

$$\frac{C}{X} = \frac{1}{K_L b_L} + \frac{C}{b_L}$$ [33]

Where:

C = Equilibrium concentration of phosphorus in solution (mg $L^{-1}$) P

X = mg of P adsorbed (mg $kg^{-1}$)

$b_L$ = Adsorption maximum for the Langmuir model (mg $kg^{-1}$) P (inverse of the slope)

$K_L$ = Bonding energy constant of the Langmuir model (L $mg^{-1}$ P) (slope/intercept)

The Langmuir adsorption isotherms was plotted by taking C/X against C while the external P requirements (EPR) of each soil were determined by substituting the desired P content ration into the fitted Langmuir equations[34]. Linearized Langmuir equation X= CkLbL/1+CkL was used in the EPR calculations.

**Statistical analysis:** Relationships between P sorption parameters and P sorbed at equilibrium with 0.2 mg $L^{-1}$ P ($P_{0.2}$), with selected soil chemical properties were determined or calculated based on simple regression and correlation and tested for significance at $p \leq 0.05$ using the Genstat statistical software[35].

## RESULTS

**Chemical and physical properties of the soils from the study sites:** Chemical and physical properties of the composite soil samples from the six counties are as presented in Table 2. The pH, hence the soil reaction of the six composite soil samples ranged from 3.7-4.5 rated as extremely acidic (pH<4.5).The soil CEC was only low (<15 cmol $kg^{-1}$ soil) in Nyeri soils. All the soils had low amounts of Bray 1 P (<15mg $kg^{-1}$).

**Phosphate adsorption isotherms:** Comparing the highest amount of P adsorbed, in the P adsorption isotherms, it is evident that soils in each site had different capacities to adsorb P (Fig. 1). The graphic representation of the adsorption isotherms of the soils were in the order Nyeri>Embu≥Meru> Kirinyanga>Kiambu>Kinangop.

Maximal P adsorbed varied among the sites with Nyeri soils having the highest maximal P adsorbed while Kinangop soils had the lowest (Table 3). The regression coefficient ($R^2$) was significant ($p \leq 0.05$) in soils of all sites.

Table 2: Chemical and physical properties of the soils from the six study sites

| Site/property | Kerugoya | Meru | Embu | Kinangop | Kiambu | Nyeri |
|---|---|---|---|---|---|---|
| pH $CaCl_2$ | 4.5 | 4.1 | 3.9 | 4.0 | 3.8 | 3.7 |
| Total nitrogen (%) | 0.8 | 0.6 | 1.0 | 0.3 | 0.2 | 0.3 |
| Carbon (%) | 8.9 | 7.9 | 8.7 | 5.1 | 2.6 | 2.7 |
| P (mg $kg^{-1}$) | 10.2 | 8.9 | 9.3 | 9.7 | 5.7 | 9.8 |
| CEC (cmol $kg^{-1}$) | 15.3 | 16.0 | 17.9 | 15.5 | 15.0 | 13.1 |
| **PSD*** | | | | | | |
| Clay (%) | 14.3 | 51.7 | 49.0 | 22.3 | 50.3 | 28.3 |
| Silt (%) | 27.3 | 21.3 | 26.7 | 39.3 | 16.7 | 16.0 |
| Sand (%) | 58.3 | 27.0 | 24.3 | 38.3 | 33.0 | 55.7 |
| Textural class | SL | Clay | CL | Loam | SL | SL |

*Particle size distribution, SL: Sandy loam, CL: Clay loam

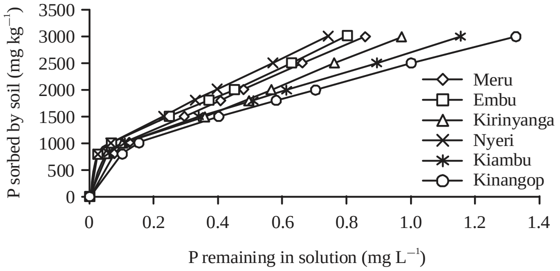

Fig. 1: Phosphate adsorption isotherm of soils from six sites

Table 3: Maximal adsorbed P of soils from the six sites

| Site | *Maximal P adsorbed (mg kg$^{-1}$ P soil) | $R^2$ |
|---|---|---|
| Meru | 2991.42 | 0.957 |
| Embu | 2991.97 | 0.935 |
| Kirinyanga | 2990.30 | 0.949 |
| Nyeri | 2992.58 | 0.934 |
| Kiambu | 2988.46 | 0.934 |
| Kinangop | 2986.73 | 0.941 |

All $R^2$ values were significant at $p \leq 0.05$ level, *Highest amount of P adsorbed at the highest level of P incubated

Table 4: Parameters of the fitted Langmuir adsorption equations

| Site | $R^2$ | bL (mg kg$^{-1}$) | kL | EPR (mg kg$^{-1}$ P) |
|---|---|---|---|---|
| Meru | 0.795 | 3333.333 | 0.429 | 263.158 |
| Embu | 0.841 | 3333.333 | 0.750 | 434.783 |
| Kirinyanga | 0.790 | 3333.333 | 0.500 | 303.030 |
| Nyeri | 0.888 | 3333.333 | 0.750 | 434.783 |
| Kiambu | 0.762 | 3333.333 | 0.429 | 263.158 |
| Kinangop | 0.687 | 3333.333 | 0.333 | 208.333 |

$R^2$: Regression coefficient, bL: Adsorption maxima, kL: Constant related to binding energy, EPR: External phosphate requirement

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

| Pairs | Correlation coefficient ($R^2$) | p-value |
|---|---|---|
| bL vs OC (%) | 0.895 | 0.001 |
| bL vs maximal adsorbed P | 0.974 | 0.000 |
| bL vs EPR | 0.873 | 0.002 |
| OC (%) vs maximal adsorbed P | -0.822 | 0.007 |
| OC (%) vs EPR | 0.670 | 0.048 |
| Phosphorus vs CEC | 0.689 | 0.040 |
| Maximal adsorbed P vs soil pH | -0.840 | 0.002 |
| Maximal adsorbed P vs Clay | 0.900 | 0.000 |

bL: Adsorption maxima (mg kg$^{-1}$), kL: Constant related to binding energy, EPR: External phosphate requirement (mg kg$^{-1}$ P). Correlation is significant at p = 0.05 level (two tailed)

**Fitting the adsorption data to the Langmuir models:** Regression coefficients ($R^2$) for the fitted Langmuir P adsorption isotherms were significant for soils from all sites (Table 4). The $R^2$ values were highest in Nyeri and lowest in Kinangop. The slopes of the plots (1/ bL) were found to be <0.01 for all the soils. The binding energy was highest in Nyeri and Embu soils and lowest in Eldoret soils. The external P requirement (EPR) of the soils varied from site to site with Nyeri and Embu soils having the highest EPR while Kinangop soils had the lowest EPR.

**Relationship between adsorption and soil properties:** A significant (p = 0.05) positive correlation was observed between maximal adsorbed P, Langmuir constants (bL, kL), EPR and clay content (Table 5). Organic carbon and soil pH negatively correlated with maximal P adsorbed.

## DISCUSSION

The soils sorption capacities varied widely as reflected by the ranges in maximal P sorption and Langmuir adsorption maxima (bL) (Table 2, 3). Soils collected from Nyeri and Embu had the highest P sorption and EPR values and thus could be categorized as high P sorbers whereas soils from Meru, Kirinyanga, Kiambu and Kinangop are moderate sorbers based on the scale of phosphate sorption of Buresh *et al.*[36]. Earlier studies have also reported similar magnitudes of P sorption capacities[10]. The differences observed in P sorption capacities between soils from the various sites could be attributed to differences in amorphous hydrous oxides of Al and clay minerals[8,10]. Acid soils from Embu, Meru, Kerugoya, Kiambu and Kinangop are highly weathered and consist predominantly of gibbsite minerals, with large surface area for P sorption[8,10,37,38]. This might have greatly influenced the P sorption reactions, hence the quantities of P adsorbed.

The significant positive correlation between maximal P adsorption, clay content and the total amount of phosphorous adsorbed by the soil, can be attributed to presence of sorptive sites on the active soil constituents. According to Jaetzold and Schmid[8], these soils are dominated by low-activity clays (clay fractions with a low CEC) often containing gibbsite [Al $(OH_3)$] besides kaolinite, generally as discrete clay size particles. Applied Phosphorus ions are, therefore, strongly attracted and fixed[2,39]. Similar correlations have also been reported by Tamungang *et al.*[40] in selected volcanic affected soils of Foumbout in the Western Region of Cameroon, Hadgu *et al*[18] in fluvisols, cambisols, vertisols and nitisols of Ethiopia and Muindi *et al.*[41] in acid soils of Western Kenya.

Negative correlation observed between adsorbed P with organic matter content can be attributed to the following: (i) Adherence of, large, humic molecules to sorbing surfaces that mask fixation sites and prevent them from interacting with phosphorus ions in solution, (ii) Organic acids produced by plant roots and microbial decay can also serve as organic anions, which compete with phosphorus ions or positively charged sites on the surface of clays and hydrous oxides or (iii) Certain organic compounds can entrap reactive Al and Fe in stable organic complexes called chelates and once chelated, the metals are unavailable for reaction with phosphorus ions in the soil solution. Additionally, microbial mineralization of many P-rich organic materials can also contribute to reduced P fixation[2,42]. Similar correlations have been reported in acid soils found in various countries by Hoseini and Taleshmikaiel[16], Mnthambala *et al.*[43] and Wolde *et al.*[44], who reported that presence of organic matter reduced P sorption capacities of soils due to occupation of adsorption spaces by organic anions.

Negative correlation between soil pH and maximal adsorbed P in the current study supports the hypothesis that P sorption decreases with increasing pH. This is consistent with reports by Mnthambala *et al.*[43] in acid soils of Malawi and Wolde *et al.*[44] in acid soils of Bulle and Wonago Woreda, Southern Ethiopia. According to Haynes[45], the sorption decrease can be ascribed to increased electrostatic repulsion caused by increased negative surface charge as pH increases. The decreased adsorbed P with increase in pH can also be attributed to either, competition of hydroxyl ($OH^-$) concentrations 1,000 times higher with phosphate ions for specific sorption sites on mineral surfaces as pH increases[46] or neutralization of sites where more reactive Al surfaces were once present by aluminium hydroxide polymers as pH increases[47]. According to Sims and Pierzynski[48], pH of both solid and liquid matrices of the soil can impact sorption of P by affecting protonation and deprotonation of functional groups and surface binding sites. These effects alter the electro negativity of the surfaces of soil particles; a relationship commonly referred to as the adsorption envelope[48]. Soils dominated by goethite and gibbsite, as are the soils used in this study, are particularly susceptible to each of the above-named phosphate adsorption mechanisms and relationships[8,38].

## CONCLUSION

The six soils varied widely in their capacity to fix P with Embu and Nyeri soils classified as high P fixers and Meru, Kerugoya, Kiambu and Kinangop soils classified as low fixers. The differences in the P adsorption maxima and EPR of the soils in the study sites indicate that application of blanket P fertilizer rates for all study sites is not viable. The recommended P fertilizer of 26 kg $ha^{-1}$ P for maize production by the Kenya Agricultural Research Institute, is, therefore, inadequate for optimal crop production at all the sites. This is because it can supply at most only 11.6 mg $kg^{-1}$ P, which is much below the soils EPR of between 208.33-434.78 mg $kg^{-1}$ P. Additionally, the study identified soil pH, clay and organic matter as some of the factors that influence P availability in the soils.

## SIGNIFICANCE STATEMENTS

This study discovered that external phosphorus requirement (EPR) of the nitisols varied from site to site in the study area. This means site specific fertilizer recommendations are important for optimal crop production. A positive correlation was found to exist between Langmuir adsorption maxima, clay content and EPR, this shows that clay content plays a positive role in phosphorus adsorption and increasing phosphorus requirements in such soils. The negative correlation between adsorbed phosphorus, organic carbon and soil pH, shows that management practices such as regulation of soil pH levels and addition of organic carbon can help in reducing phosphorus sorption hence increasing available P in the soils. The findings of the study will form a basis of soil fertility management trials and site specific fertilizer recommendation trails in the region.

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