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Phosphorus sorption and external phosphorus requirements of ultisols and oxisols in Malawi

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Oxisols and ultisols are the major soils of Malawi but the P sorption of these soils has not been studied intensively. As of now, in terms of P fertilizer application these soils are treated the same. This research was conducted to determine the phosphate sorption properties and external P requirements (EPR) of these soils and to derive sorption values from selected soil properties. Physical and chemical analysis showed difference in these soils. Soil exchangeable aluminium, soil pH and soil organic matter is some of the soil properties that affect P sorption and these were different in these two soils. The sorption maxima were 315.5 and 413.0 mg P kg⁻¹ for ultisols and oxisols respectively and EPR values were 37.8 and 52.2 mg P kg⁻¹ of soil for ultisols and oxisols respectively. Exchangeable aluminium, soil pH (H2O), and organic matter found to be highly correlating with sorption maxima. The results from this study showed that, blanket application of phosphate fertilizer may not be a good strategy because ultisols and oxisols demand different amounts of P fertilizer and this blanket application may lead to under-application or over-application of P in some areas. The results also show that farming practices which improve soil organic matter and soil pH should be encouraged.

Key words: External P requirement, P-sorption, Langmuir equation, sorption affinity, Malawi, oxisols, ultisols.

INTRODUCTION

Although a dynamic equilibrium exists between the solid and solution phases, P retention in the solid phase is favoured by several-folds, resulting in insufficient soil solution P to meet plant needs (Gartley and Sims, 1994). Availability of P to plants has been shown to be related to its concentration in the soil solution (intensity) and the soils' ability to replenish or buffer it as the nutrient is removed by plants (Magdoff et al., 1999). When solid or liquid phosphorus fertilizers are applied to the soil, some of the orthophosphate ions ($H_2PO_4^-$, HPO_4^{2-}) react with various soil components that remove phosphorus from the solution phase and convert it to less soluble phosphates. The phenomena by which phosphorus fertilizers in soils are converted from a soluble state to a less soluble state is referred to as phosphorus retention and has been reviewed by several authors including Parfitt (1978), White and Thomas (1981), Sample et al. (1980), Ayed (1984), and Matar et al. (1992).

Retention of phosphate by soils is an intensively studied subject worldwide. This is not surprising since the phosphorus deficiency in plants is believed to be the second most important soil fertility problem throughout

*Corresponding author. E-mail:fmnthambala@gmail.com Author(s) agree that this article remain permanently open access under the terms of the <u>Creative Commons Attribution</u> <u>License 4.0 International License</u> the world (Parfitt, 1978). Prediction of response to phosphorus application is generally based on available P status as well as on the magnitude and rate at which the added P is converted into insoluble forms in the soil (Parfitt, 1978). The relationship between plant P uptake and retention parameters should be an important factor to understand the P supplying characteristics of the soil and in making fertilizer recommendations.

There are many factors which affect the soils' capacities to adsorb phosphorus. These include the soil organic matter, clay contents, oxides of Fe and Al, exchangeable Fe and Al and pH (Hakim, 2002; Udo, 1985). Physiochemical properties of soils such as exchangeable Ca and Mg, texture, porosity, bulk density, hydraulic conductivity, pH and ionic strength of competing ions also affect soil adsorption capacity (Bubba et al., 2003). Some authors reported that factors relating to soil, climate, crop and management also influence soil P adsorption capacity (Amapu et al., 2000). There is inconsistence on the effects of organic matter (OM) and pH as P adsorption could be increased, decreased or not affected at all by their presence while the relationship content, sesquioxides, physiochemical with clay properties is constantly positively correlated (Bubba et al., 2003).

Knowledge of phosphorus retention processes is essential for the effective use of phosphorus fertilizers with respect to the amount, kind, frequency and most effective placement of the fertilizer. The two chief mechanisms that are used to describe phosphorus retention processes are surface sorption and precipitation and precipitation. Discrete surface precipitation occur when concentrated phosphate solutions react with soils or soil minerals, whereas surface phosphorus sorption by soil minerals may be responsible for the removal of phosphate from more dilute phosphate solutions. Surface sorption includes physical sorption, chemisorption and anion exchange (ligand exchange) (Sample et al., 1980). Physical sorption is the process whereby the adsorbed P accumulates on the surface and then diffuses into the soil constituents. Chemisorption occurs with an inner sphere exchange reaction between phosphate ions and hydroxyl ions associated with metal while anion exchange is when P adsorbed to surfaces and edges of hydrous oxides, clay minerals and carbonates by replacing H₂O or OH (Bramley et al., 1992).

The relation between the amounts of phosphorus that a soil will adsorb from a phosphate solution and the concentration of the phosphorus left in the solution is known as the sorption isotherm. A wide range of phosphate concentrations have been used to generate phosphorus sorption data. Most studies are made at equilibrium P concentrations up to about 3 mg P dm⁻³ (Fox and Kamprath, 1970; Fernandes and Warren, 1994) while a few studies are made at equilibrium phosphorus concentration up to 3.5 mg P dm⁻³ (Agbenin and Tiessen, 1994; Sharma et al., 1995).

The P adsorption reaction affects phosphorus fertilizer use efficiency. The estimation of P, demands that allowance always be made for portion of soil P adsorbed by the soil constituents. This is necessary since adsorbed P is directly related to soil solution P (Agbede 1988). Phosphorus adsorption isotherm technique that uses the relationship between adsorbed P (capacity factor) and soil solution P (intensity factor) has been successfully used in predicting P requirement of crops in different soil systems (Agbede 1988; Bilal et al, 2007; Yasin et al, 2007). It is based on the principle that crop P requirement is directly related to the amount of P sorbed at a critical supernatant solution P known to be non-limiting to plants.

This critical solution P concentration has been arbitrarily suggested to be 0.2 ppm and when continuously maintained in solution can provide adequately for crop production (Nnadi and Haque 1985). The amount of P sorbed at the critical solution P concentration of 0.2 ppm or the standard equilibrium solution P concentration is an important statistic for comparing the phosphorus adsorption capacity of soils with varying buffering capacities (Nnadi and Haque, 1985).

The data obtained from the phosphate adsorption experiments are fitted to the linear forms of Freundlich and Langmuir isotherms. A linear form of the Freundlich equation can be written as:

$$\log x = \log aF + \frac{1}{nF \log c}$$

Where: c = is the concentration of P in the equilibrium solution (mg dm⁻³), x = the amount of P sorbed per unit weight of soil (mg P kg⁻¹ soil), aF and nF = are empirical constants that relate to sorption surface (distribution coefficient) and sorption energy, respectively (Barrow, 1978).

The linear form of the Langmuir equation can be written as:

$$\frac{x}{c} = \frac{bXm}{1 + Xm c}$$
or

$$\frac{c}{x} = \frac{1}{Xm \ x \ b} + \frac{c}{1+Xm}$$

Where: b = is a constant related to bonding energy; Xm = is the Langmuir sorption maximum (mg P kg⁻¹ soil). The other terms are as defined previously in Freundlich equation.

If sorption data fit the Langmuir equation, a plot of c/x against c produces a straight line with a slope 1/Xm and intercepts 1/bXm. The Langmuir constant b is obtained

by dividing the slope (1/Xm) by the intercept (1/bXm). The coefficients of the equations which best describe the sorption data are used for correlation studies.

The values of Langmuir (Xm) and Freundlich parameters (aF) and P adsorption indices (P buffering capacity and P adsorbed at 0.2 mg P dm⁻³) are related to soil properties. Phosphate buffer capacity (PBC) is obtained by derivating x with respect to c in the fitted equations. The properties that best describe P sorption are selected using a stepwise multiple regression analysis (Abacus Concepts, 1996).

The mechanisms proposed for P retention in soil by crystalline clay minerals is through a ligand exchange reaction with (OH) H groups coordinated with Al ion on the edge of crystals (Muljadi et al., 1966; White, 1981). Thus the sorption capacity depends, among other factors, on the proportion of the surface area occupied by edge faces and the number of reactive Al-OH (H) groups per unit area of the edge face. At quite low solution concentrations (<3 mg dm⁻³), P will be adsorbed to the edge face of kaolinite through replacement of surface hydroxy groups by phosphate (Kuo and Lotse, 1974). At high solution concentrations of P (>300 mg kg⁻¹ P) it has been reported (Gillman et al., 1989), that there is a slow dissolution of kaolinite to release Si and Al, with the subsequent precipitation of Al-P compounds.

Highly weathered soils of the tropics and subtropics are products of harsh climate to which they have been subjected and are typically dominated by clay fractions consisting of low activity minerals such as kaolinite, Al and Fe oxides (Gillman et al., 1989). These minerals possess surface charge that is partly variable (pH dependent) so that anion exchange capacity increases as pH decreases, and have a greater affinity for phosphate ions, and therefore a high P sorption capacity. The location of Malawi shows that the country has tropical and sub-tropical environments. These are aggressive soil-forming environments. As a result soils formed have low inherent fertility because their clay components are predominantly 1:1 (kaolinite) and oxides, both of which are inactive materials

Most of the upland soils (oxisols and ultisols) in Malawi are, however, dominated by the poorly buffered 1:1 kaolinite and halloysite and oxides of iron and aluminium, reflecting that the soils are highly weathered and leached (Maida, 1973; Mwandemere and Robertson, 1975; Ntokotha, 1974). The poorly buffered soils account for over 40% of soils in Malawi. Mughogho in (1975), conducted P sorption studies on soils from Mulanje, Bvumbwe, Dedza and Bunda. The soils were Oxisols for Mulanje and Bvumbwe, Ultisols for Dedza and Bunda. Since then no sorption studies have been conducted

Phosphorus sorption relationships are commonly used in the determination of the external phosphorus requirement (EPR) of crops. EPR is the concentration of P in solution that is non-limiting to plant growth (Fox, 1981). For most crops, the amount of P in equilibrium with 0.2 mg P dm⁻³ (P_{0.2}) has been shown to be the threshold over which no response to P is observed (Beckwith, 1965; Iyamuremye et al., 1996; Nziguheba et al., 1998). The P requirements, estimated in this manner:, aim at building up the status of soil phosphorus by a single application to a level which, thereafter, only requires maintenance application to replenish losses due to plant uptake, removal by erosion or continuing slow reactions between phosphate and soil (Henry and Smith, 2003).

There is no information on the EPR of any of the soils in Malawi and yet such information is necessary to guide P fertilizer recommendations to ensure that crop yields are not compromised due to under-fertilization, that the soils are not mined with respect to their P contents, and that ground water is not polluted with P transported from over-fertilized soils. Currently, there is a blanket recommendation of 42 kg P_2O_5 ha⁻¹ (MoAFS, 2005).

This research was conducted to obtain information regarding P-sorption and external P requirements of the two major Malawi soils

MATERIALS AND METHODS

Soil preparation

Twelve top soil samples (0- 20 cm) were collected from each soil group (ultisols and oxisols) to represent each of the soil group under different management practices (24 soil samples in total). The soils were air-dried, ground and passed through a 2 mm sieve.

Soil characterization

Soil pH was measured in water (soil: solution ratio of 1:2.5) using a pH meter with a glass and reference calomel electrode after shaking the soil suspensions for 30 min and leaving them to stand for 1 h. Particle-size distribution was determined using the Bouyoucos hydrometer method (Bouyoucos 1962) as outlined in soil and plant analysis manual used by the Department of Crop and Soil Sciences. Total N was determined by the Kjeldhal digestion/distillation method as outlined in soil and plant analysis manual used by the Department of Crop and Soil Sciences. Organic carbon determined by the Walkley and Black wet oxidation method as outlined by Allison (1965) was value converted to organic matter by multiplication using a factor of 1.72

Total P was estimated following wet digestion with H_2O_2/H_2SO_4 (Okalebo et al., 2002). Exchangeable Ca²⁺, Mg²⁺, and K⁺ were extracted using Mehlich-3 and determined by atomic absorption spectrophotometer. Exchangeable acidity (Al³⁺ + H⁺) was extracted with 1.0 M KCl and titrated with 0.05 M NaOH (Okalebo et al., 2002) (Table 1).

Phosphate sorption isotherms

2 g of air-dried (<2 mm), soil samples were weighed in triplicates into 50 ml centrifuge tubes and suspended in 30 ml of 0.01 M CaCl₂ of supporting electrolyte containing various concentration of P as KH₂PO₄ to give 0, 100, 200, 300, 400 and 500 P mg/kg of soil for six days at a room temperature. Three drops of toluene were added to minimize microbial activity. Suspensions were shaken twice daily for 30 min and at the end of the sixth day, they were centrifuged at 10,000 rev min⁻¹ and filtered through Whatman No. 42 filter paper. Phosphorus content in the supernatant solution was determined

	Treatment			
Soil properties -	Ultisols	Oxisols		
OM (%)	0.726	0.343		
pH (water)	4.650	4.650		
Al _{ex} cmol _c /kg	4.310	7.900		
Total N (%)	0.179	0.149		
K(cmol _c /kg)	0.734	0.165		
Mg (cmol _c /kg)	0.734	0.418		
Ca(cmol _c /kg)	7.607	10.56		
P (mg/kg)	63.270	23.75		
Sand %	88.750	88.00		
Silt %	2.750	3.50		
Clay %	8.500	8.50		

colorimetrically by the molybdate-ascorbic acid method (Murphy and Riley, 1962).

The amount of P remaining in solution was taken as the equilibrium concentration (c) and expressed as mg P dm⁻³. The difference between the initial concentration and the equilibrium concentration will be taken as the adsorbed P per unit of soil (x/m) and expressed in mg P kg⁻¹ soil. The adsorption isotherm of x/m against c will be plotted for the three treatments to obtain a straight line with slope of 1/b and intercept of 1/kb. In order to obtain adsorption capacities and the constants related to the bonding energy, the following form of Langmuir equation will be used thus:

 $C/(x/m) = 1/S_{max}b + c/b$

Where: c = P concentration in equilibrium solution; x/m = P adsorbed by soil (ug/g); $S_{max} =$ adsorption maximum (ug/g); b = a constant related to the bonding energy of the soil for P or affinity constant (Uzoho and Oti, 2005).

Soil external P requirements were determined by substituting the desired P (0.2 ppm) concentration into the fitted Langmuir equations (S = SmaxbC/(1 + bC)) (Dodor and Oya, 2000).

Statistical analysis

The relationship between P sorption parameters, and P sorbed at equilibrium with 0.2 mg P dm⁻³, with selected soil chemical properties was determined with simple regression and correlations and tested for significance at 0.01 and 0.05 probability levels using the GenStat statistical software. The contribution of soil properties to sorption parameters was examined using the maximum R^2 improvement stepwise model-building procedure. The differences in P sorption among the treatments within site and across sites was analysed using ANOVA and tested at significant level 0.05.

RESULTS AND DISCUSSION

Sorption and external phosphate requirement

The study first evaluated the differences in P sorption between these two soil types. This was done by conducting sorption studies on soil samples from conventional farming plots only. The results from sorption studies fitted well Langmuir equation, with both soil types produce $r^2 > 98\%$ as shown in Figure 1.

Ultisols gave low sorption maxima, and low EPR as compared to oxisols and these were significant at 5% probability level as shown in Table 2.

As reported by many researchers; Mughogho (1975), Uzoho and Oti (2005) and Tsado et al. (2012) oxisols had higher P sorption maxima, affinity and external P requirement as shown in (Table 2). The differences in organic matter, exchangeable acidity, sorption maxima were all significant at 5 per cent probability level. The ultisols had more organic matter and lower exchangeable acidity and sorption maxima. It is the higher content of organic matter and lower exchangeable aluminium that make the ultisols to have low sorption maxima making ultisols to have lower EPR compared to oxisols. Low organic matter and higher exchangeable aluminium in oxisols increases aluminium ions in the soil solution which readily complex P in solution. Soil organic matter helps to complex aluminium ions from solution.

With high sorption maxima in Oxisols it means most of the fertilizer P applied will be sorbed leaving the soil solution with low P concentration. Therefore high amounts of P will need to be applied in order to raise soil solution P to meet crop requirement. Similar results were reported by Mughogho (1975), where the oxisols from Mulanje district gave high sorption maxima compared to ultisols from Bunda. Gichangi et al. (2008), Uzoho and Oti (2005), Tsado et al. (2012) and Moazed et al. (2010) also found lower sorption maxima and EPR in soils with higher organic matter.

These results revealed that the P requirements for these soils are not similar. Using blanket recommendation means in other areas the P requirement of the soil is not satisfied. This may cause low productivity of crops because most of the P applied is not available for crop uptake. This also means, in some areas soils are over supplied with P which is expensive to the farmer and harmful to the environment.

Table 3 shows correlations of soil chemical/physical parameters measured in this study. Organic matter and exchangeable acidity showed a very strong negative correlation (-0.753) at 0.001 probability level. This means, soils with low organic matter will have high exchangeable aluminium. The presence of organic matter provides surfaces on which AI, Fe and Mn ions get complexed there-by reducing the concentration of these ions in soil solution. Organic matter also raises the pH of the soil; this also makes AI ions concentration in the soil to decrease. As pH raises solubility of aluminium reduces.

EPR showed strong correlation with exchangeable aluminium (0.822) and organic matter (-0.781). EPR is higher on soils that adsorb a lot of P applied to the soil and a lot of P is adsorbed in soils with high exchangeable aluminium. This makes the correlation of EPR and exchangeable aluminium to be positive (Table 3). On the other hand, as explained earlier, increase in organic

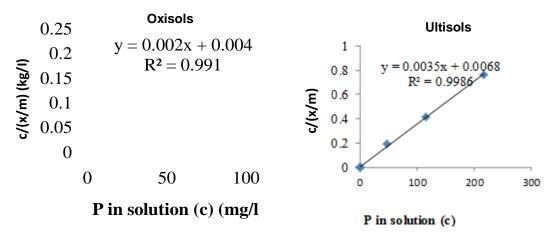


Figure 1. Graphs showing fitted Langmuir equations for oxisols and ultisols.

Table 2. Means of phosphate sorption parameters, organic matter, exchangeable aluminium and EPR (P0.2) for ultisols and oxisols.

T	Variables						
Treatment	OM (%)	Al _{exc} (cmol/kg)	S _{max} (mg/kg)	b (dm³/kg)	EPR (P _{0.2})		
Ultisols	0.726	4.310	315.5	0.730	37.800		
Oxisols	0.343	7.900	413.0	0.720	52.200		
Grand mean	0.535	6.100	364.2	0.725	45.000		
LSD(0.05)	0.173	1.979	47.94	0.206	13.500		
CV%	18.700	18.700	7.600	16.400	17.300		

Table 3. Matrix of correlation coefficients for soil parameters analysed.

	Al _(ex)	ОМ	EPR	b	рН	Ν
OM	-0.753**					
EPR	0.822**	-0.781**				
В	0.654**	-0.699**	0.939**			
рН	-0.483*	0.5078*	-0.532**	-0.523**		
Ν	-0.275	-0.012	-0.254	-0.055	0.261	
S _{max}	0.803**	-0.657**	0.814**	0.578**	-0.364	-0.484*

** Significant at 0.001% and * significant at 0.05% probability level.

matter reduces the concentration of exchangeable aluminium and raise the soil pH. Which means increase in organic matter counteract the factors that promote P sorption thereby influencing EPR. This is evidenced by negative relationship of EPR and organic matter.

Sorption affinity's correlations with exchangeable aluminium, organic matter and EPR were 0.654, -0.699 and 0.939. This means that soils having high exchangeable aluminium hold P ions strongly as compared to soil having low exchangeable aluminium. Therefore the soil requires high amount of P to be added as evidenced by the strong and positive correlation of

sorption affinity and EPR. Soil pH showed negative correction (-0.438, -0.532 and -0.523) to exchangeable aluminium, EPR and sorption affinity respectively. The soil pH is affected by the solubility of aluminium. When more aluminium ions is soil solution pH goes down, hence the negative relationship. On the other hand pH and organic matter should positive correlation. Organic matter, after decomposition and mineralisation cations are released into the soil thereby raising the soil pH. Smax showed that when aluminium ions are increasing more P is sorbed. This is because the aluminium ions are the ones responsible for P sorption. When soil has high organic matter content less P is removed from the solution by the metal ions and vice versa.

The results showed that the blanket application of P fertilizer in Malawi is not a good strategy and also showed that in both soils if organic matter is increased the sorption maxima and EPR can be reduced. So it is important to continue promoting farming practices that increase the organic matter content in the soil, for example conservation agriculture and agroforestry.

Conflict of Interest

The authors have not declared any conflict of interest.

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