

# THE EFFECT OF SOME SELECTED ORGANIC ACIDS ON PHOSPHATE SORPTION IN AN ALFISOL IN MINNA, NORTH CENTRAL, NIGERIA

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## ABSTRACT

*Phosphorus (P) is an important plant nutrient and of concern from an environmental point of view. We studied the effect of some selected organic acids (citrate, acetate and tartrate) on phosphate ( $P_i$ ) sorption in an Alfisol collected from Minna in North Central Nigeria. Soil samples were collected from the Teaching and Research Farm of the Federal University of Technology, Minna. Treatment comprised of four (4) separate sorption experiments consisting of (i) Addition of P to the soil without organic acid (OA) (control) (ii) addition of OA before P, (iii) addition of P before OA and (iv) simultaneous addition of OA and P. The quantity of  $PO_4$  sorbed when OA was added irrespective of the sequence of their additions. Adding OA before P to the soil significantly reduced  $PO_4$  sorption or adding OA and P simultaneously. The effect of the type of OA on the magnitude of P sorption reduction was in the order citrate > tartrate > acetate.*

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## INTRODUCTION

The reaction of  $PO_4$  with soil components have been extensively studied from the point of view of soil fertility, soil chemistry and environmental concerns (Sanyal and de Datta, 1999). For highly weathered soils of various parts of the tropics, sorption of  $PO_4$  has been variously attributed to different forms of Al and Fe oxides and other soil

properties (Yuan and Laukulic, 1994).

Research into management practices to increase P availability in a weathered soil and at the same time curtail its leaching to contaminate lakes, streams and ground water remain high imperative. The application of combined organic - inorganic inputs has been one of the



management practices suggested by Igbokwe and Igbokwe (2005) to increase  $PO_4$  sorption and thereby increase P availability in these soils. The incorporation of organic materials in soils along with P fertilizer application has also been reported to increase P availability (Guppy et al., 2005). This effect has commonly been ascribed to the competition effect between the decomposition product of organic matter and P for sorption sites, resulting in increased soil solution concentration. Huang (2004) reported that organic substances can be sorbed to the external and internal surfaces of the mineral colloids. Citric, citrate, tartarate and humic acids were found to be bound to structural cation edges of goethite, Al and Fe coatings on mineral colloids.

However, until now, little work has been carried out on the interaction of nutrients and OA on goethite-Al organic precipitates as a function of chemical composition and surface properties on the possible displacement of the ligands present in the precipitates (De Cristofaro et al., 2005). Furthermore, competition for sorption sites between P and OA in an Alfisol has not received much attention in the Southern Guinea part of Nigerian Savanna. The objective of this work was to

study the (i) competitive effects of some selected OAS on the adsorption of  $PO_4$  and (ii) the effect of sequences of P and OA additions on  $PO_4$  sorption in an Alfisol collected from Minna in North Central Nigeria.

### MATERIALS AND METHODS

The soil used for the experiment was collected from the Teaching and Research Farm of Federal University of Technology, Minna  $9^{\circ} 40' N$ ,  $6^{\circ} 30' E$ , in the Southern Guinea Savanna Zone of Nigeria. The soil in this area is classified as Typic Ustalfs in US soil taxonomy. Twenty core soil samples, 0-20cm depth, were collected from three locations within the field (upper, middle and lower portion), bulked, sub sampled and pass through a 2mm sieve. Particle size analysis was determined by hydrometer after dispersion with sodium Hexametaphosphate. The soil pH was determined in duplicate, i.e in water and 0.01M  $CaCl_2$  at a soil solution ratio of 1:2. Organic carbon was determined by Walkley-Black procedures as described by Walkley and Black (1934). Available P was extracted with Bray-1 method as described by Murphy and Riley (1962). Cation Exchange Capacity (CEC) was determined by 1N  $NH_4$  OAC leaching. The ammonium oxalate extractable Fe and Al ( $Fe_d$  and  $Al_d$ ) were determined by the method



described by Jackson et al (1986). While the dithionite - citrate - bicarbonate extractable Fe and Al ( $Fe_0$  and  $Al_0$ ) were determined by the method of Mehra and Jackson (1960). The properties of the soils are presented in Table 1.

The organic acids used in this study were obtained commercially. Concentration of 0.05 M of these acids were prepared. Three different sequences of OA and P additions were evaluated to determine the effect of OA on  $PO_4$  adsorption. The sequences were as follows:

#### **Addition of phosphate solution before organic acids (P - OA)**

Two gram of sieved soil was weighed into five polyethylene centrifuge tubes with tight screw caps. Into each of the five tube was added five levels of P (0, 50, 100, 200 and 400  $\mu g g^{-1}$  soil) respectively from a stock solution of  $KH_2PO_4$ . Few minutes later, variable amounts of each of OA solution (0, 1.25, 2.50, 3.75 and 5.00ml) were similarly added to the soil and the tubes were made to 20ml mark with distilled water bringing the soil: solution ratio to 1:10. Two the three drops of chloroform was added and the centrifuge tubes were shaken in a reciprocal shaker for 16hours. The soil suspension was centrifuged at 10,000rpm for 15 minutes and filtered through whatman N. 42 (ashless) filter paper.  $PO_4$  in the

filtrate was determined calorimetrically.  $PO_4$  sorbed was calculated as the difference between  $PO_4$  added and  $PO_4$  remaining in solution.

#### **Addition of organic acids before phosphate solution (OA-P)**

Two gram of sieved soil was weighed into five polyethylene centrifuge tubes with tight screw caps. Into each of the five tube was added variable amounts of each of OA solution (0, 1.25, 2.50, 3.75 and 5.00ml) five levels of P (0, 50, 100, 200 and 400  $\mu g g^{-1}$  soil) from a stock solution of  $KH_2PO_4$  were later added to the soil and the tubes were made to 20ml mark with distilled water bringing the soil: solution ratio to 1:10. Two three drops of chloroform was added and the centrifuge tubes were shaken in a reciprocal shaker for 16hours. The soil suspension was centrifuged at 10,000rpm for 15minutes filtered through Whatman N. 42 (ashless) filter paper.  $PO_4$  in the filtrate was determined calorimetrically.  $P$  sorbed was calculated as the difference between  $PO_4$  added and  $PO_4$  remaining in solution.

#### **Simultaneous addition of phosphate solution and organic acids (P/OA)**

Two gram of sieved soil was weighed into five polyethylene centrifuge tubes with tight screw caps. To the soil in the tubes was added five levels of P (0, 50, 100,



and 4000  $\mu\text{g g}^{-1}$  soil) from a solution of  $\text{KH}_2\text{PO}_4$  along variable amounts of each of solution (0, 1.25, 2.50, 3.75, 5.00ml) that were added simultaneously. To achieve this, an aliquot containing the appropriate concentration of P was taken from stock solution and combined with appropriate amount of OA in 20ml glass cylinder. The mixed P and OA were transferred quantitatively to the soil in the centrifuge tube. The tubes were filled to 20ml mark with distilled water bringing the soil solution to 1:10 two to three drops of formalin was added and the centrifuge tubes were shaken in a orbital shaker for 16 hours. The suspension was centrifuged at 4000 rpm for 15 minutes and passed through Whatman No. 42 (fast flow) filter paper.  $\text{PO}_4$  sorbed was calculated as the difference between  $\text{PO}_4$  added and  $\text{PO}_4$  remaining in solution.

#### Phosphate sorption data and statistical analysis

The  $\text{PO}_4$  sorption data were fitted into a two-parameter Langmuir model:  $q = \frac{kbc}{1 + kc}$ , where  $q$  was the quantity of  $\text{PO}_4$  sorbed,  $c$  is the equilibrium  $\text{PO}_4$  concentration in solution,  $b$  is the maximum and  $k$  is the affinity term reflecting the strength of binding of  $\text{PO}_4$  to sorption sites in soils. The two adjustable parameters were estimated by

fitting the sorption data into a linear Langmuir equation:  $c/q = 1/kb + c/b$

#### Statistical analysis

The statistical analysis of the data was done using the analysis of variance (ANOVA) and mean separation was achieved by using Duncan Multiple Range Test.

### RESULTS AND DISCUSSION

The  $\text{PO}_4$  sorption isotherms did not differ considerably among the organic acids used (fig 1-3). The result shows that the concentration of  $\text{PO}_4$  sorbed by the soil without the organic acid additions (control) was considerably greater than the concentration of  $\text{PO}_4$  sorbed when organic acids were added to the soil irrespective of the type of organic acid added. In a similar study on P and OA interaction by Huang (2004), he observed that OA such as oxalate, malate, citrate and tartrate can compete strongly with P for adsorption sites on Al oxide system. In a similar study on P and OA interaction by Huang (2004), he observed that OA such as oxalate, malate, citrate and tartrate can compete strongly with P for adsorption sites on Al oxide system. In soils with appreciable quantities of these constituents (Al oxides),  $\text{PO}_4$  sorption will be severely curtailed in the presence of these ligands (Bhatti et al., 1998).



In figure 1 and 2, the quantity of  $PO_4$  sorbed when organic acids were added before P addition were less than quantity of  $PO_4$  sorbed when either the P was introduced before the organic acids or their simultaneous additions. The adsorption of these OA can also physically block  $PO_4$  sorption sites on soil colloids thereby reducing  $PO_4$  adsorption as also suggested by Barlett and Riego (1972) especially when they are introduced to the soil before P.

However, the quantity of sorbed  $PO_4$  (Fig. 3) when acetate was added before P and when they were combined and added simultaneously were observed to be lower than when P was added before the acetate. This observation is consistent with earlier studies by Agbenin and Igbokwe (2005) who reported that there could be more sites specific to organic ligands to which if orthophosphate were sorbed to before organic acid addition, the organic ligands released from the acid would displace  $PO_4$  ion on sites common to both (Violante and Gianfreda, 1993; Huang, 2004).

The  $PO_4$  sorption isotherm with or without OA were modeled by Langmuir equation. Table 2 shows the Langmuir sorption parameters as affected by OA in the soil. There was significant higher sorption maxima under the control

treatment than when organic was added before P, addition before organic acids and simultaneous additions.

For all the OA added,  $PO_4$  sorption maxima was least in OA - sequence. This suggest that introduced to the soil before P be sorbed to sites not only specific to the organic ligands but also the sites common to both  $PO_4$  and organic in the soil. Consequently introducing the P later may readily displace sorbed organic from those common sites. Agbenin and Igbokwe (2005) further suggested that sorption of organic ligands would further repel P sorption due to the negative charge conveyed to the surface.

Comparing the effect of various organic acids used (Table 2), it was observed that citrate caused larger reduction of P adsorption (b and K), while acetate showed the least effect. This could probably be attributed to the large molecular size of citrate (which could cover enormous surface compared to tartrate and acetate). Barlett and Riego (1972) reported that the OAs that were most effective in P adsorption were in the order: citrate>oxalate>tartrate>acetate. Also, Stevenson and Vance (1989) concluded that hydroxyl acids as citrate, form stronger complexes than those containing a single COOH groups.

### CONCLUSION



The application of organic matter to acid soils in order to reduce the need for lime and that P would be considerably fit to resource-poor and subsistence farmers in terms of P availability to the crops. And, organic residues such as animal manures, composted wastes and grass and crop residues such as animal manures, composted grass and crop residues are usually readily available to a farmer in large quantities. Applications of these organic materials should be done prior to P fertilization and sufficient time allowed for the sorption of the fixed organic material before the application of P fertilizer. These would allow more time for fixation of the organic molecules to Al and Fe oxides.

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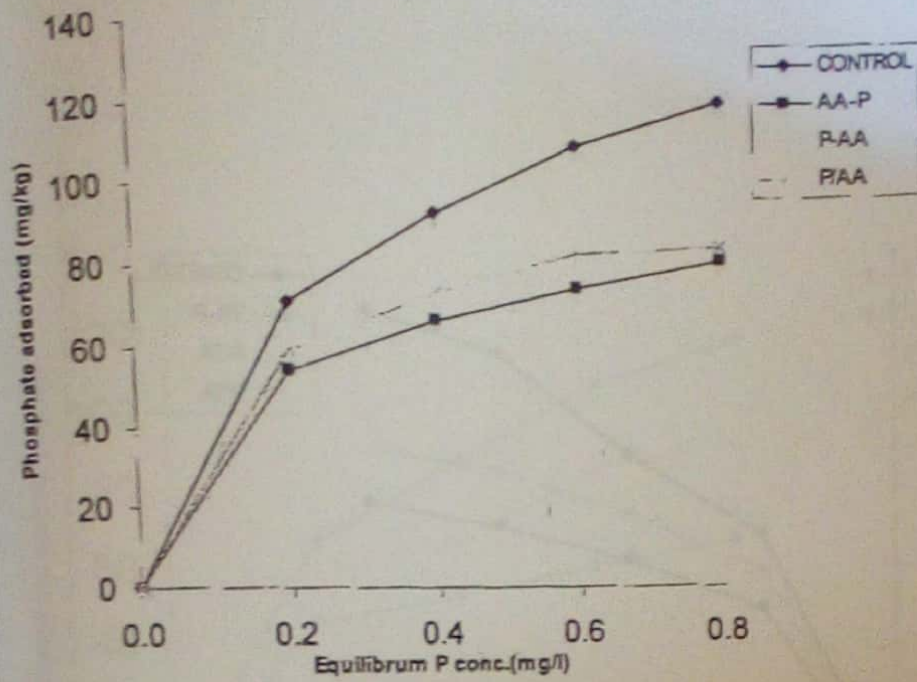
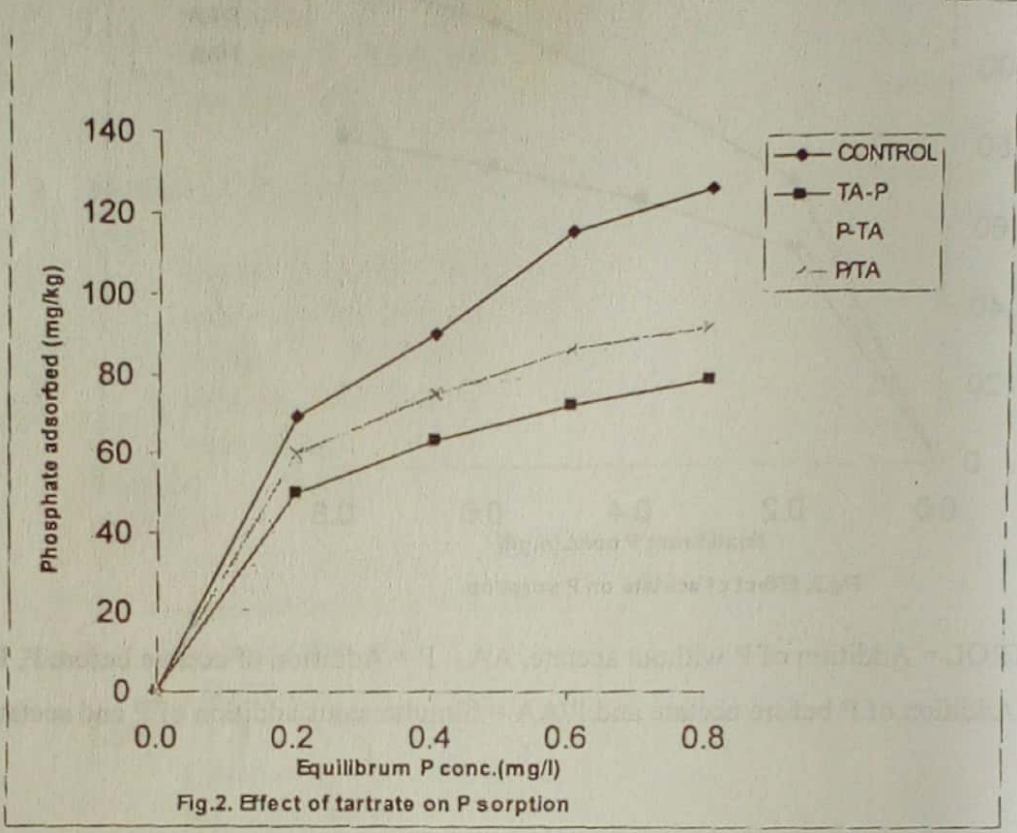


Fig.3. Effect of acetate on P sorption

CONTROL = Addition of P without acetate, AA - P = Addition of acetate before P, P - AA = Addition of P before acetate and P/AA = Simultaneous addition of P and acetate.





CONTROL = Addition of P without tartrate, TA - P = Addition of tartrate before P, P - TA = Addition of P before tartrate and P/TA = Simultaneous addition of P and tartrate.



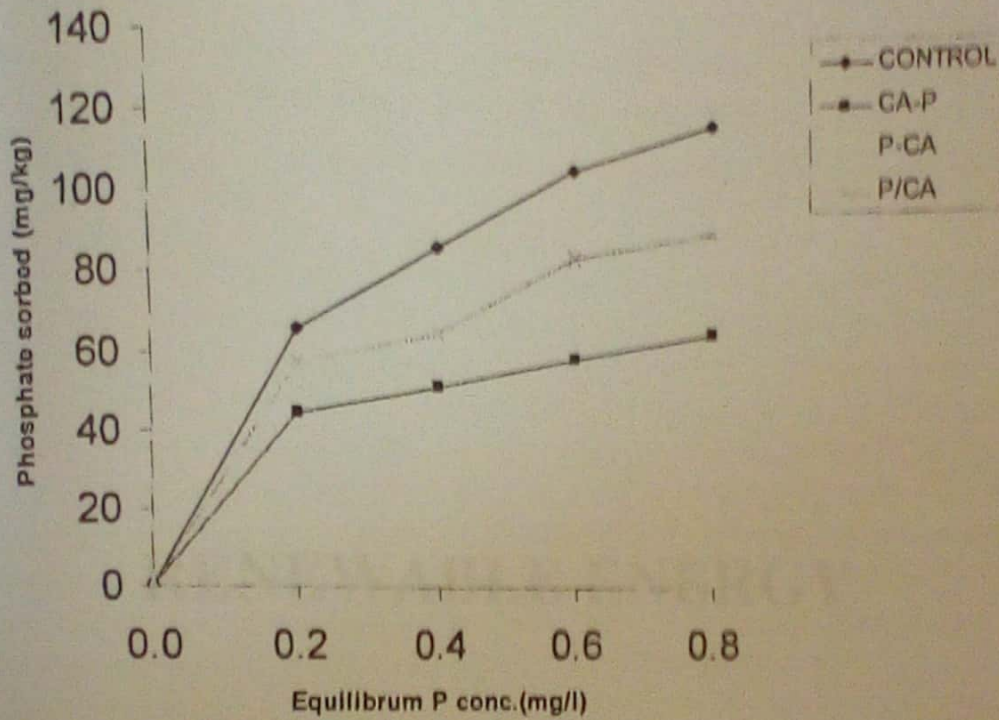


Fig.1. Effect of citrate on P sorption

CONTROL = Addition of P without citrate, CA - P = Addition of citrate before P, P - CA = Addition of P before citrate and P/CA = Simultaneous addition of P and citrate.