INFLUENCE OF ORGANIC ACIDS ON PHOSPHATE SORPTION AND AVAILABILITY IN AN ALFISOL OF NIGERIAN GUINEA SAVANNA

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ABSTRACT

The combined application of organic acids and inorganic phosphate fertilizer has been suggested as a means of reducing phosphate adsorption and increasing the availability and solubility of applied phosphate in weathered tropical soils. We studied the effect of some selected organic acids on phosphate sorption and availability in an alfisol of Nigerian Guinea Savanna soil under laboratory conditions. Five levels of phosphorus (0, 50, 100, 200 and 400 $\mu g\ g^{-1}$) with or without the addition of 0.05 M concentration of acetic, citric and tartaric acids were introduced into the soil in a completely random design at three replicate. The concentration of phosphate sorbed by the soil in the treatment without the introduction of organic acid (control) was significantly ($P \leq 0.05$) greater than the concentration of phosphate sorbed when organic acid was added irrespective of the organic acids used. The capacity for reduction on P adsorption and increased in P availability appears to followed the order of citrate > tartrate > acetate (31, 43 and 70mg kg^{-1} respectively). These three organic acids have the potentials to increase the availability of P in soil but need to be evaluated at the field scale.

INTRODUCTION

Phosphate deficiency often limits crop production in acid tropical soils such as oxisols, ultisols and alfisols. These soils contain appreciably amount of oxides, hydroxides of Iron and Aluminium and low activity clays that predominantly influence phosphate sorption (Palomo et. al, 2006). When phosphate levels are too low, phosphorus deficiency in plant represents a major constraint to world agricultural production (Wang et. al, 2008). The widespread occurrence of phosphorus deficiency in most arable lands in Nigeria has led to the intensive use of phosphorus fertilizer.

Research into management practices to increase phosphate availability in a weathered soil and at the same time curtailed its leaching to contaminate lakes, streams and ground water remains highly imperative. The application of combined organic - inorganic inputs has been one management practices suggested to increase phosphorus availability in weathered soils (Agbenin and Igbokwe, 2005).

Several authors (Earl et. al, 1979., Bhatti et al,1998., Agbenin and Igbokwe, 2005 and Palomo et. al, 2006.) reported that many naturally occurring soil organic acids released during the decomposition process of plant and animal residues, root exudates and some intermediate product of plant and microbial metabolisms are capable of complexing and chelating metal ions like Al, Fe, Cu, Zn and Mn. In addition, Jones (2000) and Palomo et. al, (2006) reported that citrate, tartrate, and tannate derived from degradation of humic substances have greater affinity for Al and Fe oxides than phosphate (Violante and Huang, 1989). Thus, these organic acids can compete strongly with P for adsorption sites on Al and Fe oxide systems. In soils with appreciable amounts of these oxides, phosphate sorption will be severely curtailed in the presence of these ligands (Bhatti et al., 1998). The adsorption of these organic acids can physically block phosphate sorption sites on soil colloids thereby reducing phosphate adsorption.

There is little information on the effect of organic acids on phosphate sorption in the guinea savanna soils. Therefore, the objective of this study was to evaluate the influence of three organic acids on phosphate sorption and availability in upland sandy clay loam alfisol of Nigerian Southern Guinea Savanna.

MATERIALS AND METHODS

Soil sampling and characterization.

The site for soil sample collection was Teaching and Research Farm of the Federal University of Technology, Gidan Kwano, Minna (Latitude $9^{\circ}40'N$ and Longitude $6^{\circ}30'E$)within the Southern Guinea Savanna region of Nigeria with a sub-humid tropical climate. The geology of the area is made up of basement complex rock. This soil was classified as an alfisol according to USDA Soil Survey Staff (1975). Soil samples were collected from 0 - 20cm depth and air dried, sieved and passed through 2-mm sieved. Particle size distribution was determined by the hydrometer method after dispersion with sodium hexametaphosphate according to the procedure described by I.I.T.A (1976). The soil pH was determined in distilled water and 1.0N KCl solution using a soil - solution ratio of 1:2 (McLean, 1982). Organic carbon was determined by the Walkley – Black wet oxidation method (Allison, 1965). Exchangeable basic cations were extracted with neutral normal ammonium acetate with potassium (K) and sodium (Na) determined by flame photometry and calcium (Ca) and magnesium (Mg) by EDTA titrations. Available P was determined by the Bray P 1 method (Bray and Kurtz, 1945). Selected properties of the soils are given in Table 1.

Phosphorus sorption studies

Two gram of 2 mm sieved soil was placed into 50ml centrifuge tubes. The soils were equilibrated in 30 ml of 0.01M $CaCl_2$ containing various amount of P as KH_2PO_4 to give 0, 25, 50, 100, 200, 400, 800 and 1000μg L^{-1} P for six days at a room temperature. Two - three drops of toluene were added to minimize the microbial activities. The suspension was shaken twice daily for 30 minutes and at the end of the sixth day, the soil suspension was centrifuged at 10,000rpm and filtered through whatman No. 42 Filter paper. Phosphorus in the supernatant solution was determined colorimetrically according to the procedure described by Murphy and Riley (1962). Phosphorus that disappeared from the solution was considered to be sorbed and phosphorus sorbed was plotted against phosphorus concentration in solution to obtain P sorption isotherm.

Effect of organic acids on phosphate sorption

The organic acids used in this experiment were obtained commercially. These acids are salts of acetate ($CH_3COOONa$), citrate ($C_3H_4(OH)COOH_3.H_2O$) and tartrate ($CHOHCOOH)_2$. Concentrations of 0.05 M of these acids were prepared and the pH was adjusted to 6.5 using appropriate amount of 0.1 M NaOH.

Two grams 2 mm sieved soils were weighed into polyethylene centrifuge tubes with tight screw caps. To the soils in the tubes were added variable amounts (0, 1.25, 2.50, 3.75 and 5.00 ml) of acetic, citric and tartaric acids. Fifteen minutes later, five levels of PO_4 concentration (0, 50, 100, 200 and 400 μg g^{-1}) were added to the soil from a stock PO_4 solution of KH_2PO_4. The tubes were made to 20 ml mark with deionized water bringing the soil solution ratio to 1:10. Two to three drops of chloroform were added to the suspensions and the centrifuge tubes were shaken in a reciprocal shaker for 16 hours. The soil suspensions were centrifuged at 10,000 rpm for 15minutes and filtered through Whatman no. 42 Filter paper, and PO_4 in the filtrate was determined colorimetrically. Phosphate sorbed was calculated as the difference between PO_4 added and PO_4 remaining in solution.

RESULTS AND DISCUSSION

Physico – chemical properties of the soils studied.

Selected physico - chemical properties of the soils studied are shown in Table 1. The soil was slightly acidic with pH value of 5.41. The particle size distribution showed that the texture of the soil was sandy clay loam. Although the organic carbon content of the soil was low, Jones and Wild,(1975) reported low to medium organic carbon rate for savanna soils which was attributed to paucity vegetation cover, rapid mineralization of organic matter, inadequate return of crop residues, bush burning and short fallow periods, Exchangeable bases was in the decreasing order of Ca>Mg>K>Na.

**Table 1. Physico – chemical properties of the experimental soil used in the study.**

Soil properties	Series A
Sand (g kg^{-1})	640
Silt (g kg^{-1})	100
Clay (g kg^{-1})	260
Textural class	Sandy Clay Loam
pH (CaCl$_2$)	5.41
Org. C. (g kg^{-1})	8.9
Exch.Ca (cmol kg^{-1})	2.20
Exch.Mg (cmol kg^{-1})	0.63
Exch.K (cmol kg^{-1})	0.26
Exch.Na (cmol kg^{-1})	0.14
Exch.acidity (mmol kg^{-1})	0.02
Available P. (mg kg^{-1})	4.21

Phosphate adsorption isotherm

The phosphate adsorption isotherm of the soil used in the study was determined by plotting the equilibrium concentration of phosphate against the amount of phosphate adsorbed. The graphical representation of the adsorption isotherm of the soil is shown in Figure 1. The curve followed a smooth plateau pattern. It is evident from the curve that the rate of P adsorption increased with the increase in the concentration of P, but at a certain point of higher concentration, the level of P becomes almost constant with no more capacity to adsorbed P. Similar adsorption isotherms have already been reported by Li et .al, (2000), Agbenin, (2003) and Sarfaraz et. al, (2009).These authors reported that the main soil components influencing phosphate sorption includes: soil pH, nature of clay content, organic matter and amorphous Fe and Al oxides.

The relative amount of P adsorbed was dramatically higher at low concentration than at higher concentration. This suggests that reaction between phosphate and the soil was rapid on initial contact. This perhaps could have been due to the low available P content (Table 1) resulting in the high adsorption potential at the surface. Similar observations have already been reported by Bala, (1992).
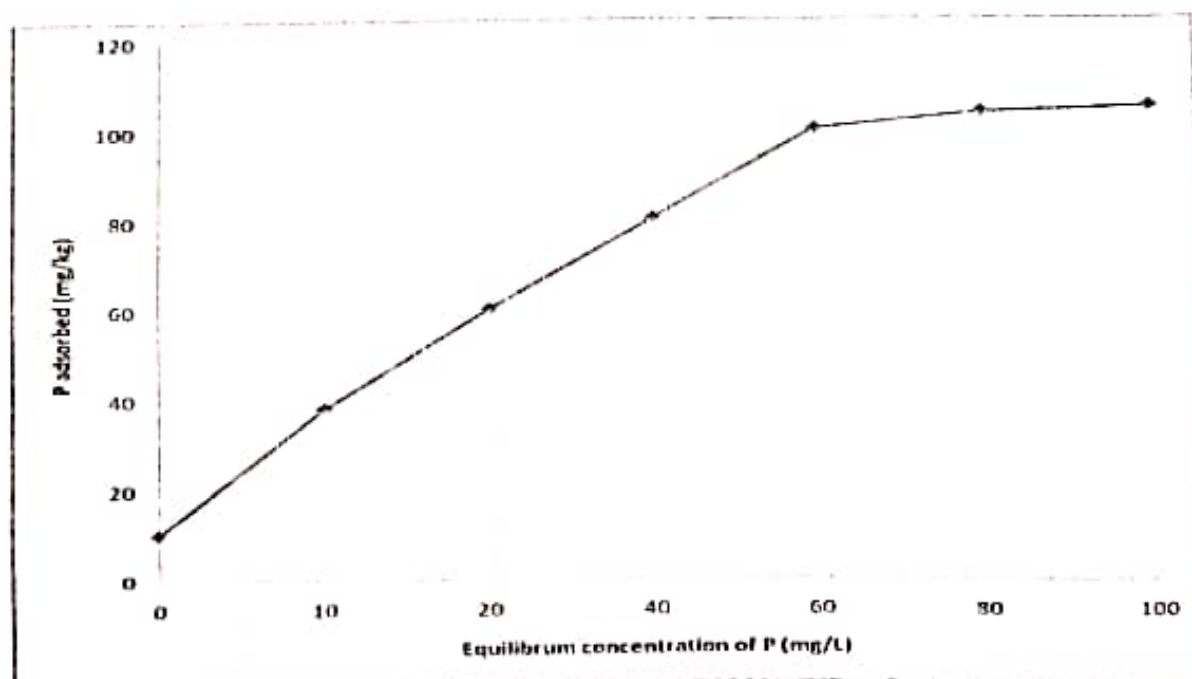
Figure 1. Phosphate sorption isotherm of the experimental soil used in the study.

Effect of organic acids on P sorption

The influence of organic acids addition on PO_4 adsorption is presented in Figure 2. It was observed that the concentration of P sorbed by the soil when no any organic acid was added (control) was significantly greater than the concentration of P sorbed when organic acids were added to the soil. This appears to confirm the observations of Jones and Brassington (1998), Johnson and Loeppert (2006) and Wang et al. (2008) that low molecular weight organic acids such as citric, tartaric oxalic acids etc are specifically adsorbed to Fe and Al hydroxide surface by ligand exchange reactions. And their additions can increase P availability to plants by decreasing the P adsorption capacity of the soil. These organic acids may have greater affinity for Fe and Al oxides than PO_4 and therefore can compete strongly with P for adsorption sites on Fe and Al oxides system. Agbenin and Igbokwe (2005) also reported that most ligands capable of competing strongly and displacing PO_4 in sites specific to organic ligands would include oxalate, citrate, malonate and tartarate. In soils with appreciable amount of these constituents, PO_4 sorption will be severely curtailed.
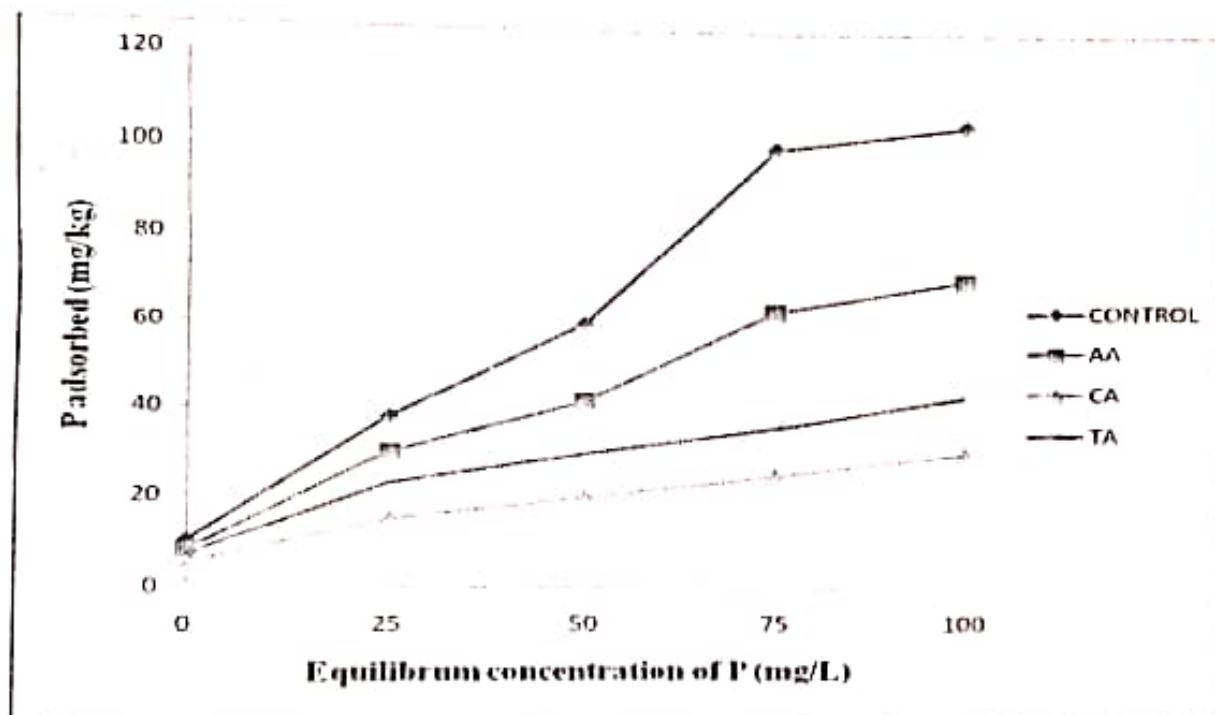

Figure 2. Effect of organic acids on orthophosphatesorption isotherm of the soil. Control = soil with P addition only, AA = acetic acid with P, CA = citric acid with P and TA = tartaric acid with P.

The capacity for reduction on P adsorption and increased in P availability appears to followed the order of citrate > tartrate > acetate (Figure 2). This could probably be attributed to the larger molecular size of citrate (which could cover enormous surface) compared to tartrate and acetate. Also hydroxyl acids such as citrate may form stronger complexes than those containing a single COOH group. Similar observation has been reported by Nagarajah et. al. (1970) on the effect of wide range of organic acid anion on P adsorption by oxide surfaces. They reported that the reduced P adsorption by organic acids was in the order: citrate = oxalate > malonate = tartarate > acetate =

succinate. This also confirmed the findings of Earl et. al. (1979) and Wang et. al. (2008) that in both soils and synthetic Al and Fe oxides, citrate caused larger reduction in P adsorption than did tartrate, whereas acetate and succinate had little or no effect.

In conclusion, this study has clearly demonstrated that the three organic acids greatly reduced PO_4 adsorption, thus increasing the availability of P in the soil. Citric acid displayed the greatest capability to reduce PO_4 adsorption followed by tartaric and acetic acids. Thus low molecular weight organic acids have the potentials to increase the availability of P in soil but need to be evaluated at the field scale.

REFERENCES

Agbenin, J. O. 2003. Extractible iron and aluminium effect on phosphate sorption in a

savanna Alfisol. *Soil Sci. Soc. Am. J.*, 67: 587 – 595.

Agbenin, J. O and Igbokwe, S. O. 2005. Effect of soil-dung manure incubation on the solubility and retention of applied phosphate by a weathered tropical semi-arid soil. *Geoderma.* 133: 191 –203.

Allison, I. E., 1965. Organic carbon : In C. A. Black (ed). Methods of Soil Analysis. *Agron. 9 Amer. Soc. Agron.* Madison Wis pp 374 – 390.

Bala, A. 1992. The effect of phosphate on zinc and copper sorption by a tropical soil. M.Sc. Dessertation. Department of Soil Science, University of Reading, UK. Pp 33

Bhatti, J. S., Comerford, N. B., Johnson, C. T. 1998. Influence of oxalate and soil organic matter on sorption and desorption of phosphate on to a spodic horizon. *Soil Sci. Soc. Am. J.* 62: 1089 – 1095.

Bray, R.H. and L.T. Kurtz. 1945. Determination of total, organic and available forms of phosphorus in soils. *Soil Sci.* 59: 39 – 45.

Earl, K. D., J. K. Syers and J. R. Launglin. 1979. Origin and effect of citrate, tartrate and acetate on phosphorus sorption by soils and synthetic gels. *Soil Sci. Soc. Am. J.* 43: 674 – 678.

IITA. 1976. Selected methods for soil and plant analysis. IITA, Ibadan – Nigeria. Manual series No 1. Pp 70.

Johnson, S. E. and R. H. Loeppert. 2006. Role of organic acids in phosphate mobilization from iron oxide. *Soil Sci. Soc. Am. J.* 70: 222 – 234.

Jones, D. L. 2000. Organic acids in the rhizosphere: A critical review. *Plant Soil.* 205: 25 – 44.

Jones, D. L. and D. S. Brassington. 1998. Sorption of organic acids in acid soils and its

implications in the rhizosphere. *Eur. J. Soil Sci.* 49: 447 – 455.

Jones, M.J. and A.Wild, 1975. Soil of West Africa Savanna. Commonwealth Agricultural Bureaux, Harpenden.U.K. pp.24.

McLean, E. O. 1982. Soil pH and lime requirement. In: A. L. Page et. al. (eds), Methods of soil analyses (No. 9, part 2), 199 – 224. Amer. Soc. of Agron.; Soil Sci. Soc. Am; Inc. Madison, Wisconsin, U.S.A.

Murphy, J and J. P. Riley. 1962. A modified single solution for the determination of phosphorus in natural waters. *Anal.Chem. Acta* : 31 - 36

Nagarajah, S., A. M. Posner and J. P. Quirk. 1970. Competitive adsorption of phosphate and polyacturonic and other organic anions on kaolinite and oxide surface. *Nature.* 228: 83 – 84.

Palomo, L., N.Claassen and D. L. Jones. 2006. Differential mobilization of P in the maize rhizosphere by citric acid and potassium citrate. *Soil Biol. Biochem.*, 38: 683 – 692.

Sarafaz, M., M. Abid and S. M. Mehdi. 2009. External and internal phosphorus requirement of wheat in Rasulpur soil series of Pakistan. *Soil and Environ.*, 28: 38 – 44.

USDA Soil Survey Staff. 1976. Soil Taxonomy, a basic system of soil classification for making and interpreting soil surveys. Handbook No. 436. US Govt. Printing Office, Washington D. C., USA.

Violante, A and Huang, P. M. 1989. Influence of oxidation treatment on surface properties and reactivities of short – range ordered precipitates of aluminium. *Soil Sci. Soc. Am. J.* 53:1402 – 1407.

Wang, Y., Y. He, H. Zhang, J. Schroder, C. Li and D. Zhou. 2008. Phosphate mobilization by citric, tartaric and oxalic acids in a clay loam ultisol. *Soil Sci. Soc. Am. J.* 72: 1263 – 1268.

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