

# phosphate Sorption in Three Cultivated Soils of the Nigerian Guinea Savanna as Influenced by the Addition of A Citric Acid

P.A. Tsado<sup>1</sup>, J.O. Agbenin<sup>2</sup>, A.O. Osunde<sup>1</sup> and A. Bala<sup>1</sup>

<sup>1</sup>Department of Soil Science, Federal University of Technology, PMB 65, Minna, Nigeria

<sup>2</sup>Department of Soil Science/IAR, Ahmadu Bello University, Zaria, Nigeria

## ABSTRACT

*Sorption of phosphate in the presence of low molecular mass organic ligands on tropical soils may be the rule and not the exception in rhizospheric soils. We studied the sorption of phosphate in the absence and presence of citric acids in three cultivated soils of the Nigerian Guinea Savanna. Soil samples were collected from three different locations of different pedogenic characteristic (Alfisol from Minna, Ultisol from Mokwa and Oxisol from Ankpa). Treatment consisted of three separate sorption experiment in which citric acids were added to the soil in sequence with phosphorus was conducted. These treatments included (1) addition of P before citric acid (2) addition of citric acid before P and (3) simultaneous addition of both P and citric acid. In the absence of citric acid (control), the concentration of phosphate sorbed was significantly higher than the concentration of phosphate sorbed when citric acid was added to all the soils. However, the amount of phosphate sorbed when citric acid was introduced to the soils was found to be dependent of the sequences of its additions. Adding citric acids before P to the soils significantly reduced phosphate sorption than either adding P before citric acid or adding citric acid and P simultaneously for all the soils studied. These findings suggest that citric acid was possibly sorbed to sites not only specific to ligands but also to sites common to both phosphate ions and organic ligands in soils. Therefore, adding organic residues before fertilizer-P in the same field can make for a better supply of P to crops.*

## INTRODUCTION

In many tropical acid soils, the oxides, hydroxide and oxyhydroxides of Al and Fe and low activity clays are the components that predominantly influenced phosphate sorption (Borggard, 1983). The fate and efficiency of native and applied P therefore, remains one of the biggest problems in arable crop production in the tropics. This is because, the availability of both applied and native P is controlled largely by the sorption and desorption characteristics of the soil. Already, the wide spread occurrence of P deficiency (usually, 10ppm or less) in Nigeria has lead to the intensive use of P fertilizers.

Several authors have 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 (Al, Fe, Cu, Zn and Mn). Violante and Huang (1989), also reported that Low Molecular Mass Organic Acids (LMMOA)

such as tartrate, citate, acetate, tannate e.t.c derived from degradation product of organic substances have greater affinity for Al oxides than phosphates. Thus these organic acids can compete strongly with phosphorus for adsorption sites on Al oxides systems. And in soils with appreciable amounts of these constituents, phosphate sorption will be severely curtailed in the presence of these ligands (Bhatti *et al*, 1998). The adsorption of these organic acids can also physically block phosphate sorption sites on soil colloids thereby reducing phosphate adsorption (Agbenin and Igbokwe, 2004).

Thus, the need therefore arises for specific studies aimed at understanding the effects of some selected organic acids on phosphate sorption in these soils and making specific recommendations for P availability to plants with a view to boosting agricultural productivity in the Guinea Savanna agroecology. Our objective was to investigate the effect of citric acids on the adsorption of phosphate in soils of Guinea Savanna Zone of Nigeria.



## MATERIALS AND METHODS

### Soil sampling and characterization

The soil samples were collected from three different locations of different pedogenic characteristics. These locations were: Minna (9°40'N, 6°30'E), Mokwa (9°18'N, 5°05'E) and Ankpa (6°32'N, 7°15'E) in the Guinea Savanna of Nigeria. Three sites were sampled as representative of each location. The soil samples were air dried and passed through a 2mm sieve.

The particle size distribution of the soil was determined by the hydrometer method after dispersion with sodium-hexametaphosphate. The soil pH was determined in duplicate, i.e. H<sub>2</sub>O and 0.01M CaCl<sub>2</sub> at the ratio of soil solution ratio of 1:2. Organic carbon was determined by Walkley-Black dichromate oxidation method as described by Walkley and Black (1934). Phosphorus was extracted with Bray 1 solution and measured by the method of Murphy and Riley (1962). Cation Exchange Capacity (CEC) was determined by Ammonium Acetate leaching. The Ammonium Oxalate extractable Fe and Al (Fed and Ald) were determined by the method described by Jackson *et al.*; (1986). While, the dithionite citrate-Bicarbonate (DCB) extractable Fe and Al (Fe<sub>o</sub> and Al<sub>o</sub>) were determined by the method of Mehra and Jackson (1960). The selected properties of the soil are presented in table 1.

### Sequences of citric acid and phosphate additions

The citric acid used in this experiment was obtained commercially. Concentrations of 0.05M of this acid were prepared. Three different sequences of citric acid and phosphate additions were evaluated to determine the effect of citric acid on P adsorption. The sequences were as follows:

#### Addition of P solution before citric acid.(P - CA)

2 g of sieved soils were weighed in to a polyethylene centrifuge tubes with tight screw caps. To the soils in the tubes were added five levels of phosphates (0, 50, 100, 200 and 400  $\mu\text{g g}^{-1}$ ) from a stock solution of KH<sub>2</sub>PO<sub>4</sub>. Some few minutes later, variable amounts of citric acid solution (0, 1.25, 2.50, 3.75, and 5.0 ml) were added to the soil and the tubes were made to 20ml mark with deionised water bringing the soil : solution ratio to 1 : 10. Two to three drops of chloroform was added and the centrifuge tubes were shaken in a reciprocal shaker for 16hrs. The soil suspension were centrifuged at 10,000rpm for 15mins and filtered through Whatman No 42(ashless) filtered paper.

Phosphate in the filtrate was determined colorimetrically. Phosphate sorbed was calculated as the difference between phosphate added and phosphate remaining in solution.

#### Addition of citric acid before P solution.(CA - P)

2g of sieved soil were weighed in to polyethylene centrifuge tubes. To the soils in the tubes were added variable amount of citric acid (0,1.25,2.50,3.75 and 5.0 ml). Five levels of P (0,50,100,200 and 400  $\mu\text{g g}^{-1}$ soil) were later added to the soil from stock P. solution. The tubes were made to 20ml mark with deionised water as described previously. Two to three drops of chloroform was added and the centrifuge tubes were shaken for 16hrs. The soil suspension was centrifuged at 10,000rpm for 15mins and filtered through Whatman No 42 (ashless) filter paper. Phosphate in the filtrate was determined colorimetrically, while the Phosphate sorbed was calculated as the difference between phosphate added and phosphate remaining in solution.

#### Simultaneous additions of P and citric acid.(P/CA)

2g of sieved soil were weighed in to polyethylene centrifuge tubes. Five levels of P(0,50,100,200 and 400  $\mu\text{g.g}^{-1}$ ) from a stock P solution along with various amounts of citric acids (0,1.25,2.50,3.75,and 5.0ml) were added to the soil in the tube. To achieve the simultaneous addition of P and citric acid at the same time, an aliquot containing the appropriate concentration of P was taken from the P stock solution and combined with appropriate concentration of citric acid in a 10ml glass cylinder. The mixed P and citric acid were transferred to the soil in the centrifuge tube. The tubes were made to 20ml mark with distilled water as described previously. Two to three drops of chloroform were added and the centrifuge tubes were shaken for 16hrs.The soil suspensions was centrifuge at 10,000rpm for 15minutes and filtered through Whatman No.42 (ashless) filter paper. Phosphorus in the filtrate was determined colorimetrically, while P sorbed was calculated as the difference between P added and P remaining in solution.

The statistical analysis of the data was done, separating the means using Duncan Multiple Range Test.

## RESULTS

### Citric acid and P sorption in Oxisol

The result obtained for the effect of citric acid on P sorption in Oxisol is shown in Figure 1. It was



observed that the concentration of P sorbed by the soil without citric acid addition (control) was greater than the concentration of P sorbed when citric acid was added to the soil. The amount of P sorbed when citric acid was added to the soil was found to be dependent of the sequence of its additions. In this result, the concentration of P sorbed when citric acid was introduced before P addition (CA – P) was significantly lower than the concentration of P sorbed when P was introduced before citric acid addition (P – CA) and when P and citric acid were combined and added to the soil (P/CA).

#### **Citric acid and P sorption in Ultisol.**

Similar to the result obtained above, the amount of P sorbed by the soil at control was also significantly higher than when citric acid was added irrespective of the sequence of the addition of P and citric acid. And the amount of P sorbed was observed to be lower at CA – P than at P – CA and P/CA (Figure 2).

#### **Citric acid and P sorption in Alfisol**

Similar trends of result were obtained for the Alfisol. Higher P concentration was sorbed under control treatment as compared to when acid were added. Also, CA – P had the least P sorption values as compared to P – CA and P/CA.

#### **DISCUSSION**

For all the soils used in this study, it was observed that the addition of citric acid (irrespective of the sequence of its addition with P) caused a significant reduction in P sorption. This confirmed the report of several authors that low molecular weight organic acids such as tartrate, citrate, malate, oxalate e.t.c are specifically adsorbed to Fe and Al hydroxides surface by ligand exchange reactions. And their additions can increase P availability to plants by

decreasing the P adsorption capacity of the soil (Violante and Gianfreda, 1993; Jones and Brassington, 1998; Haynes and Mokolobate, 2001).

The reduced P adsorption and increased P availability following the application of organic amendments is thought to be the cumulative results of several mechanisms (Iyamuremye and Dick, 1996). These include; release of inorganic P, blockage of P adsorption sites by organic molecules released from the residues, a rise in pH during decomposition and complexation of soluble Al and Fe by organic molecules.

Furthermore, it was also observed that out of the three sequences of additions of citric acid and P, concentration of P sorbed was least when citric acid was added before P as compared to adding P before citric acid or their simultaneous addition. One possible explanation for this could be that citric acid was probably interposed between phosphate ions and sorption sites in the soil thus shielding P from direct interaction or bonding with soil surface as suggested by Agbenin and Igbokwe (2005). Comparing the different soils involved, the differences in the P sorption values obtained could be attributed their differences in pedogenic characteristics.

#### **CONCLUSION**

The result of this study has demonstrated that citric acid can greatly reduced P sorption especially when added before P application. This practice whereby farmers apply organic residues (farmyard manure, poultry manure etc) and follow it with fertilizer-P in the same field can make a better supply of P to crops. Because, the use of these cheap and available organic residues by smallholder farmers will not only enhance the availability of added phosphorus fertilizers but also reduce the cost of their purchase.

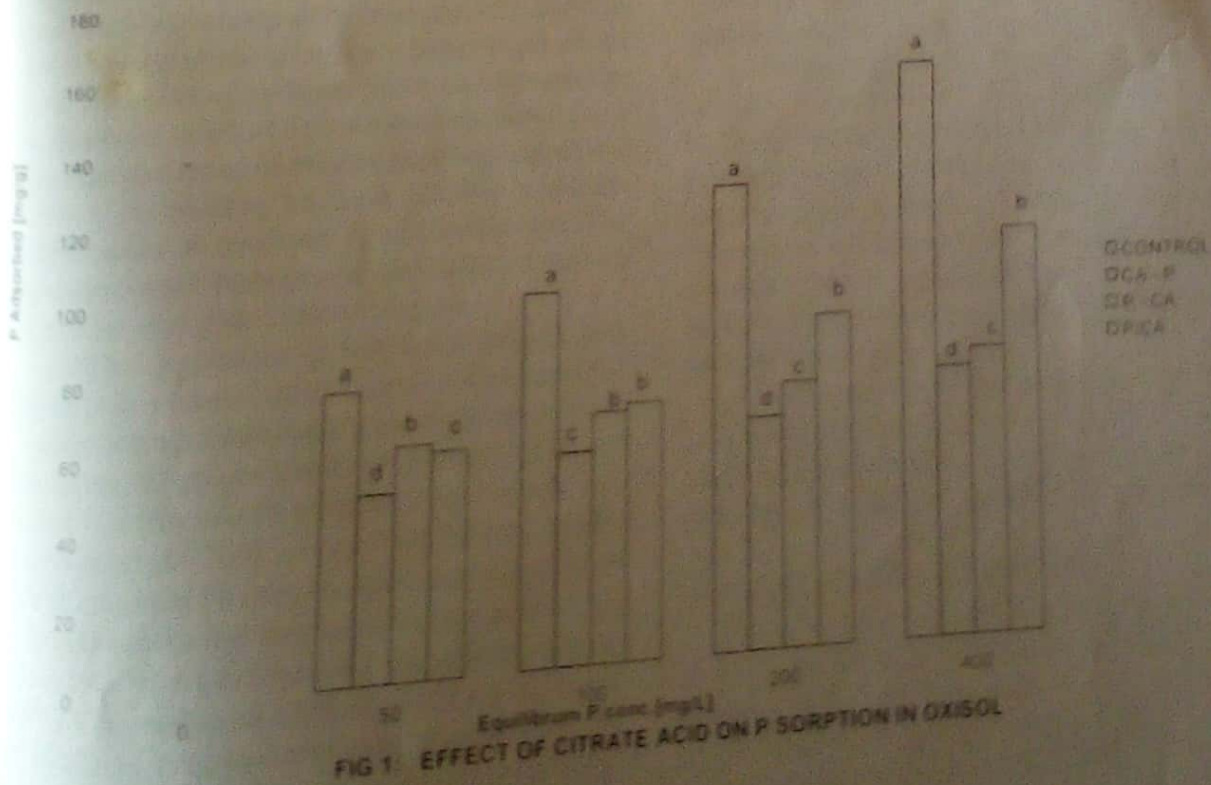


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**Table 1: Physical and Chemical properties of the Soils**

Soil Property	Ankpa (A)	Mokwa (B)	Minna (C)
Soil pH: 0.01M CaCl <sub>2</sub>	3.95	4.95	5.41
pH: H <sub>2</sub> O	4.72	5.93	6.32
Organic C	2.5	6.3	7.1
Available P ( $\mu\text{g g}^{-1}$ )	3.78	5.3	6.2
Exchangeable cations (cmole Kg <sup>-1</sup> )			
K	0.17	1.21	1.72
Ca	3.71	4.33	3.99
Mg	0.32	1.14	1.33
Na	1.03	1.83	1.42
Particle Size analysis (%)			
Sand	67.70	53.00	40.20
Silt	7.80	25.90	22.50
Clay	24.50	21.10	37.30
Fe <sub>d</sub>	6.20	5.50	4.82
Al <sub>d</sub>	0.192	0.045	0.153
Fe <sub>e</sub>	6.55	5.73	4.54
Al <sub>e</sub>	25	99	141



**FIG 1: EFFECT OF CITRATE ACID ON P SORPTION IN OXISOL**



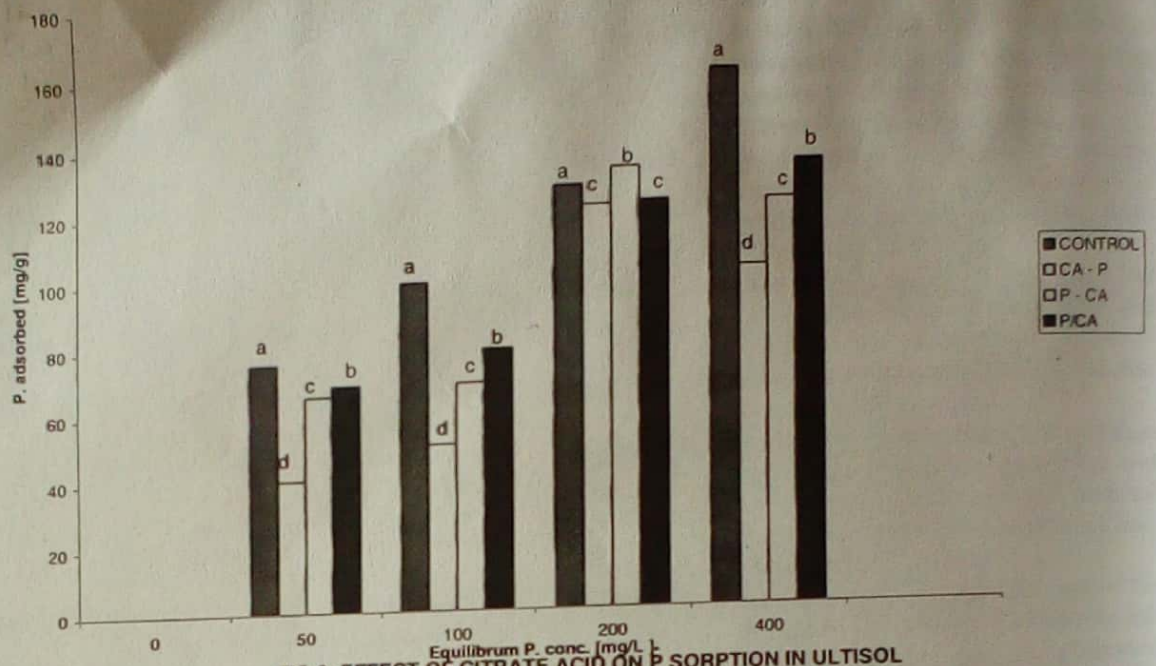


FIG 2: EFFECT OF CITRATE ACID ON P SORPTION IN ULTISOL