

EFFECT OF SEQUENTIAL ADDITION OF SELECTED ORGANIC ACIDS ON PHOSPHATE SORPTION IN AN ALFISOL IN NIGER STATE, NIGERIA.

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Abstract

Sorption of phosphate (PO_4) in the presence of low molecular weight organic ligands on tropical soils may be the rule and not the exception in rhizospheric soils. We studied the sorption of phosphate as influenced by sequential additions of selected organic acids (acetate, citrate and tartrate) in an Alfisol in Minna in Southern Guinea Savanna of Nigeria. Five levels of phosphorus (P) (0, 50, 100, 200 and 400 $\mu\text{g g}^{-1}$ soil) with or without addition of 0.05 M concentration of acetate, citrate and tartrate were introduced into the soil in sequential order. The P was either introduced before organic acids or organic acids were introduced before P and/or were added simultaneously in a completely randomized design at three replicates. The concentration of PO_4 sorbed by the treatment without the introduction of organic acid (control) was significantly ($P < 0.05$) higher than the concentration of the PO_4 sorbed when organic acids were added to the soils. The reduction in the amount of phosphate sorbed when organic acids were introduced to the soil was found to be dependent on the sequence of the additions and the type of organic acids used. Adding organic acids before P to the soil significantly ($P < 0.05$) reduced PO_4 sorption much more than either adding P before organic acid or adding both organic acid and P simultaneously. These findings suggest that the organic acids were probably interposed between PO_4 ions and sorption sites in the soils thus shielding PO_4 ions from direct interaction or bonding with soil surface. Organic acids were possibly sorbed to sites not only specific to ligands but also to sites common to both PO_4 ions and ligands in the soil. Reduction on P adsorption and increase in P availability appears to have followed the order of citrate > tartrate > acetate. In practice, application of these organic inputs should be done prior to planting and P fertilization and it is suggested that sufficient time be allowed for the sorption of the applied organic materials before the application of the P fertilizer.

Keywords: low molecular organic ligands; sorption; phosphate; Alfisol.

Introduction

The availability of applied and native phosphorus (P) is largely controlled by retention (sorption) and release (desorption) characteristics of the soil. Tropical soils particularly highly weathered ones like Nigerian soils (Oxisols, Ultisols and Alfisols) often have a high P retention capacity and the widespread occurrence of P deficiency in most arable lands in Nigeria has led to the intensive use

of P fertilizers (Tsado, *et al.*, 2012). Due to the apparent removal of P from the soil solution, plant – available P content is often very low (below 5 μm) compared to the total amount of P bound to the soil minerals and charged sites or fixed into organic forms which is not available to plants (Randall *et al.*, 2001). Therefore, the availability of P to plants is limited, to a large extent, by the rate of reactions that replenish soluble P pools. Phosphates are predominantly precipitated as Fe-phosphate and Al-phosphate in acid soils and as Ca-phosphate in calcareous soils. P sorption capacities of soils are dependent on exchangeable Ca and Mg, soil texture, porosity, pH, ionic strength and hydraulic conductivity (Bubba *et al.*, 2003). Generally, those clay minerals that possess greater anion exchange capacity due to a positive surface charge have a greater affinity for phosphate ion (Sarafzet *et al.*, 2009).

Understanding the role of organic acids in phosphorus sorption in soils is very important for economic and environmentally friendly management of soil P. Soil organic acids are derived from the decomposition of plant and animal residues, microbial metabolism, canopy drips and rhizosphere activity (Stevenson, 1967; Li *et al.*, 2000). Thus, these organic acids can compete strongly with P for adsorption sites on Al and Fe oxide systems. Jones (2000) and Palomo *et al.* (2006) also reported that citrate, tannate and tartrate derived from degradation of humic substances have greater affinity for Al and Fe oxides than phosphates. In soils with appreciable amounts of these oxides, phosphate sorption will be severely curtailed (Bar-Yosef, 1996). Organic acids/substances can be sorbed to both the external and internal surfaces of the mineral colloids. Fulvic, humic, citric and tartaric acids were reported to be bound to the structural cations of edges and hydroxyl Al and Fe coatings on mineral colloids (Huang, 2004). Violante and Gianfreda (1995) studied the competitive sorption of phosphate and oxalate. They reported that the order of addition of phosphate and oxalate strongly influenced the sorption of these ligands, and the maximum reduction in phosphate sorption occurred in acidic systems when oxalate was introduced before phosphate. Although the competitive adsorption of P and organic ligands by synthetic clay minerals and oxides have been studied (Sibanda and Young, 1986; Kafkafi, *et al.*, 1988; Violante *et al.*, 1991), there is a limited information on the fate of P in the presence of organic acids in natural soils (Hu *et al.*,

2001), competitive sorption behavior of phosphate and organic ligands on clay minerals (He *et al.*, 1999). Therefore, the exact mechanism among inorganic soil colloids, organic acids and P has not been well established in this agro ecology.

For this reason, we investigated the effect of sequential additions of selected organic acids on phosphate sorption in an alfisol of Minna in Southern Savannah Guinea Zone of Nigeria so as to provide scientific information on P sorption mechanisms in the presence of organic acids when they are introduced to the soil sequentially.

Materials and methods

Soil sampling and characterization

The experimental soils were from Minna (9°40'N, 6°30'E) in the Guinea Savanna Zone of Nigeria. These soil types were classified as Alfisol according to USDA Soil Survey Staff (1976) and as Haplic Plinthosol (Typic Plinthustalfs) (USDA, 2003; FAO, 2006).

Soil samples were collected from a depth of 0 – 20cm, they were air dried, sieved and then passed through 2mm sieve. 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). pH values of the samples were 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 atomic adsorption spectrophotometer. Exchange acidity was determined by shaking the samples with 1.0 M KCl and titrating them with 0.1 M NaOH. Available P was determined by the Bray P 1 method (Murphy and Riley, 1962). Selected properties of the soil samples are shown in Table 2.

Sequential addition of organic acids and phosphorus

The organic acids (Table 1) used in this experiment were obtained commercially. 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. Three separate (sequence) experiments were carried out to determine the effect of organic acids on phosphate adsorption. The sequences were as follows:

Table 1. Properties of Low Molecular Weight Organic Acids (LMWOAs) used during laboratory studies.

Organic Acids	Formula	Molecular weight
Tartaric acid	HO ₂ CCH(OH)CH(OH)CO ₂ H	150
Citric acid	HOOCCH ₂ (COOH)(OH)CH ₂ COOH	192
Acetic acid	CH ₃ COOH	90

(Source: Gang *et al.*, 2012)

Addition of orthophosphate solution before organic acid

Two grams of 2 mm sieved soils was weighed into polyethylene centrifuge tubes with tight screw caps. To the soils in the tubes, were added five levels of P (0, 50, 100, 200 and 400 µg g⁻¹) from a stock PO₄ solution of KH₂PO₄. Thirty minutes after PO₄ addition, variable amounts (0, 1.25, 2.50, 3.75 and 5.00 ml) of acetate, citrate and tartrate were added. 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 was added and the centrifuge tubes were shaken in a reciprocal shaker for 16 hr. the soil suspension was centrifuged at 10,000 rpm for 15 mins and filter through whatman No. 42.(ashless) filter paper and PO₄ in the filtrate was determined colourimetrically. Phosphatesorbed was calculated as the differences between PO₄ added and Po₄ remaining in solution.

Addition of organic acid before orthophosphate solution

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amounts (0, 1.25, 2.50, 3.75 and 5.00 ml) of acetate , citrate and tartrate. Thirty minutes later, were added five levels of P (0, 50, 100, 200 and 400 µg g⁻¹) from a stock PO₄ solution of KH₂PO₄. 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 was added and the centrifuge tubes were shaken in a reciprocal shaker for 16 hr. the soil suspension was centrifuged at 10,000 rpm for 15 mins and filter through whatman No. 42.(ashless) filter paper and PO₄ in the filtrate was determined colourimetrically. Phosphatesorbed was calculated as the differences between PO₄ added and PO₄ remaining in solution.

Simultaneous additions of orthophosphate solution and organic acid

Two grams of 2 mm sieved soils was weighed into polyethylene centrifuge tubes with tight screw caps. Five levels of P (0, 50, 100, 200 and 400 µg g⁻¹) from a stock PO₄ solution of KH₂PO₄ along with variable amounts (0, 1.25, 2.50, 3.75 and 5.00 ml) of acetate , citrate and tartrate were added. To achieve the simultaneous addition of PO₄ and organic acid at the same time, an aliquot containing appropriate

concentration of P was taken from the stock PO_4 solution and combined with appropriate concentration of organic acid in a 10 ml glass cylinder. The mixed PO_4 and organic acid solution was transferred to the soil in the centrifuge tube. 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 was added and the centrifuge tubes were shaken in a reciprocal shaker for 16 hr. the soil suspension was centrifuged at 10,000 rpm for 15 mins and filter through whatman No. 42.(ashless) filter paper and PO_4 in the filtrate was determined colourimetrically. Phosphatesorbed was calculated as the differences between PO_4 added and PO_4 remaining in solution.

Phosphorus content in the supernatant solution was determined colorimetrically according to the procedure described by Murphy and Riley (1962). Phosphorus that disappeared from a solution was considered as sorbed and the sorbed phosphorus was plotted againstequilibrium phosphorus concentration in the solution to obtain a P sorption isotherm.

Data collected were subjected to analysis of variance (ANOVA) using the Statistical Analysis System (SAS,2002) and means were compared using Least Significant Difference (LSD) at $P = 0.05$

Results and Discussion

Soil properties

Selected physical and chemical properties of the studied soils are presented in Table 2. The particle size distribution showed that the texture of the soil was sandy clay loam and classified as slightly acidic. Organic carbon and available P contents of this soil was also low. Adeboye, *et al*(2009) reported that low organic carbon is characteristic of the savanna due to rapid decomposition and mineralization of organic matter and annual burning of the sparse vegetation commonly carried out by the farmers. In the highly weathered and low activity clay soils of the tropics, organic matter is regarded as the major reservoir of P (Haynes and Mokolobate, 2001)). Exchangeable bases and acidity were also low, and the exchangeable baseswas in the decreasing order $\text{Ca} > \text{Mg} > \text{K} > \text{Na}$.

Table 2. Physico – chemical properties of the studied soil

Soil properties	Values
Particle size distribution (g kg⁻¹)	
Sand	640
Silt	100
Clay	260
Textural class	Sandy Clay Loam
pH (0.01M CaCl_2)	5.40
pH (H_2O)	6.11
Organic C. (g kg ⁻¹)	8.90
Available P. (mg kg ⁻¹)	4.21
Exchangeable bases (cmol kg⁻¹)	
Ca	2.20
Mg	0.63
K	0.26
Na	0.14
Exchangeable acidity (cmol kg⁻¹)	
Al + H	0.92

Effects of organic acids on phosphate sorption

Phosphate adsorption isotherms of the Alfisols in the absence and presence of sequential additions of various organic acids are shown in Figs 1, 2 and 3. Generally, the adsorption of PO_4 by the soils increases with increasing equilibrium concentration of P but the amount adsorbed was observed to be higher at a lower P equilibrium concentration than at a higher concentration for each sequence of additions and organic acid type. Bala (1992) and Fortin and

Karam (2001) reported similar findings and observed that PO_4 sorption was found to be concentration dependent, which is due to concentration gradient and change in the range of diffusion coefficient, which increased with increasing amount of P added. This also suggested that reaction between PO_4 and soil was rapid on initial contact, perhaps due to low available P content of this soil resulting in the high adsorption potential of the soil (Tsado, 2008).

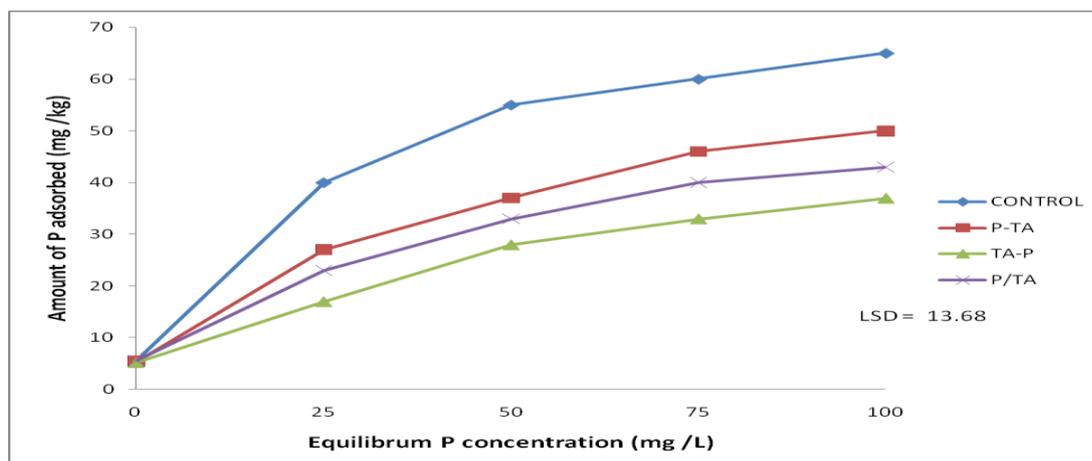


Fig. 1. Phosphate adsorption isotherm of the Alfisols in the absence and presence of tartarate. Control (no tartarate), P-TA = phosphorus addition before tartarate, TA-P = tartarate addition before phosphorus and P/TA = simultaneous addition of phosphorus and tartarate.

The concentration of PO_4 sorbed by the soils without acetate, citrate and tartrate additions (control) was significantly ($P < 0.05$) greater than the concentration PO_4 sorbed when these acids were added to the soil. Our results indicate that LMWOA's have the potentials to decrease P sorption in the studied soil, and the magnitude of reduction on P sorption also decreased at higher levels of added organic acids. It implies that there was competition between organic

acids and P for surface soils. These organic acids may have greater affinity for Fe and Al oxides than PO_4 and can compete strongly with P for adsorption sites on Fe and Al oxide system (Tsadoet *et al.*, 2012). The degree of reduction in P adsorption in the presence of acetate, citrate, tartrate, and oxalate depends on their concentrations and the greater the concentration of organic acid added, the higher the reduction in P adsorption (Hu *et al.*, 2001).

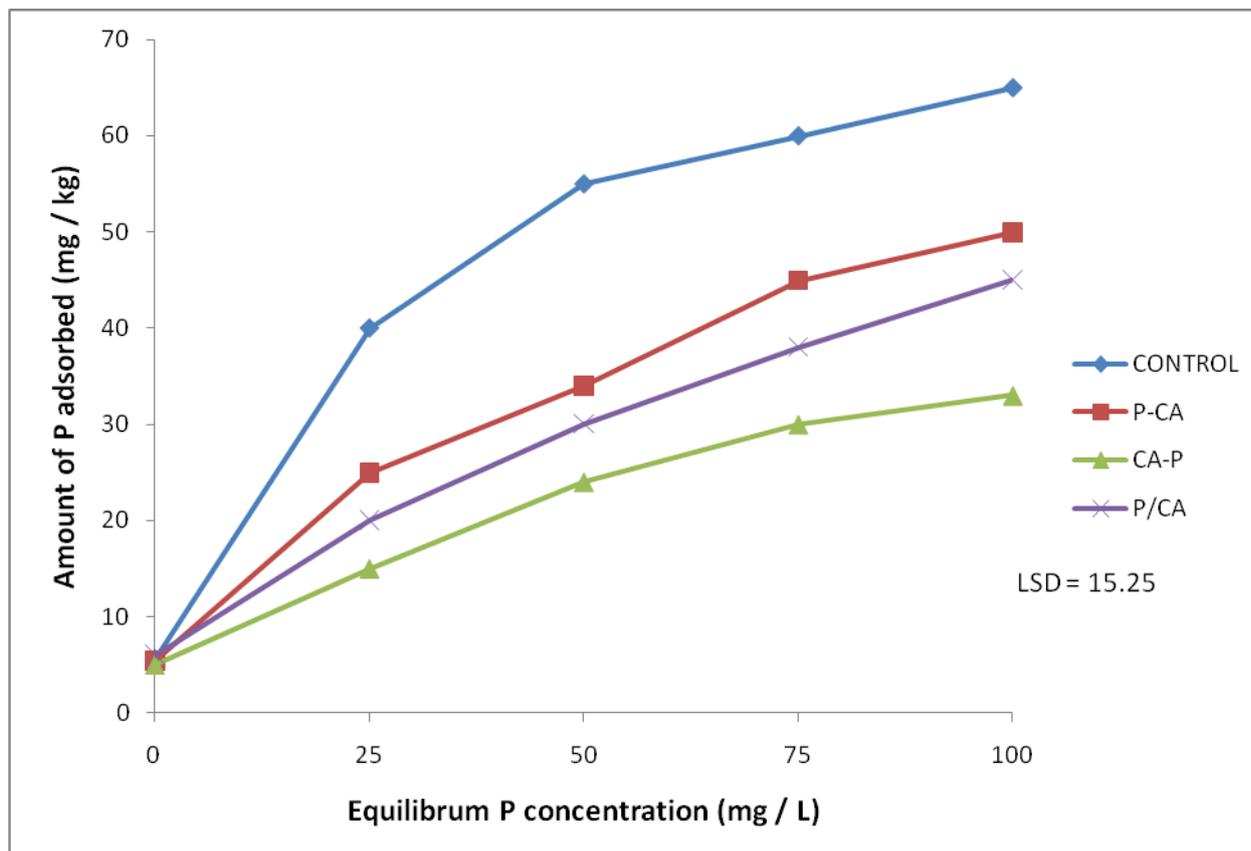


Fig. 2. Phosphate adsorption isotherm of the Alfisols in the absence and presence of citrate. Control (no citrate), P-CA = phosphorus addition before citrate, CA-P = citrate addition before phosphorus and P/CA = simultaneous addition of phosphorus and citrate.

The amounts of PO₄ sorbed when they were treated with organic acids was found to be dependent on the sequences of their additions. Different trends of PO₄ sorption isotherms were noticed for the sequences of additions. The results showed that the concentration of PO₄ sorbed when organic acids (acetate, citrate and tartrate) were introduced before P additions were significantly ($P < 0.05$) lower than the concentration of PO₄ sorbed when P was either introduced before the additions of these organic acids or when P and the organic acids were combined and added simultaneously to the soil. Hu *et al* (2001) reported that the way (sequences) of additions of organic acids influences P adsorption as a result of competition for sorption site between organic acids and PO₄. They further explained that in the addition of organic acids before P, the organic acids will occupy the surface site first, and P will only be adsorb through the desorption of some weakly held organic acids so that a maximum reduction of P adsorption occurs. Organic acids as an organic amendment could also be interposed between PO₄

and reactive sites, protecting PO₄ from direct interaction or bonding with soil surface – reactive sites and reducing PO₄ adsorption (Agbenin and Tiessen 1995; Antelo *et al.*, 2007). The addition of P before the organic acids will result to P occupying the surface sites more easily. In this case, the addition of organic acids will only result in the desorption or displacement of P which are adsorbed weakly to the surface, so that maximum adsorption of P occurs. Agbenin and Igbokwe (2006) also reported that most ligands capable of competing strongly and displacing PO₄ in sites specific to organic ligands would include oxalate, malonate, citrate and tartrate. In soils with appreciable amount of these organic ligands, PO₄ sorption will be severely curtailed. When P and organic acids are added to the soil simultaneously, either of them could arrive at the adsorption sites at different speed. The binding sites could also trap these ligand ions at a different or similar way. Therefore, the amount of P adsorption depended on the concentration ratio of organic anion to P and relative affinity.

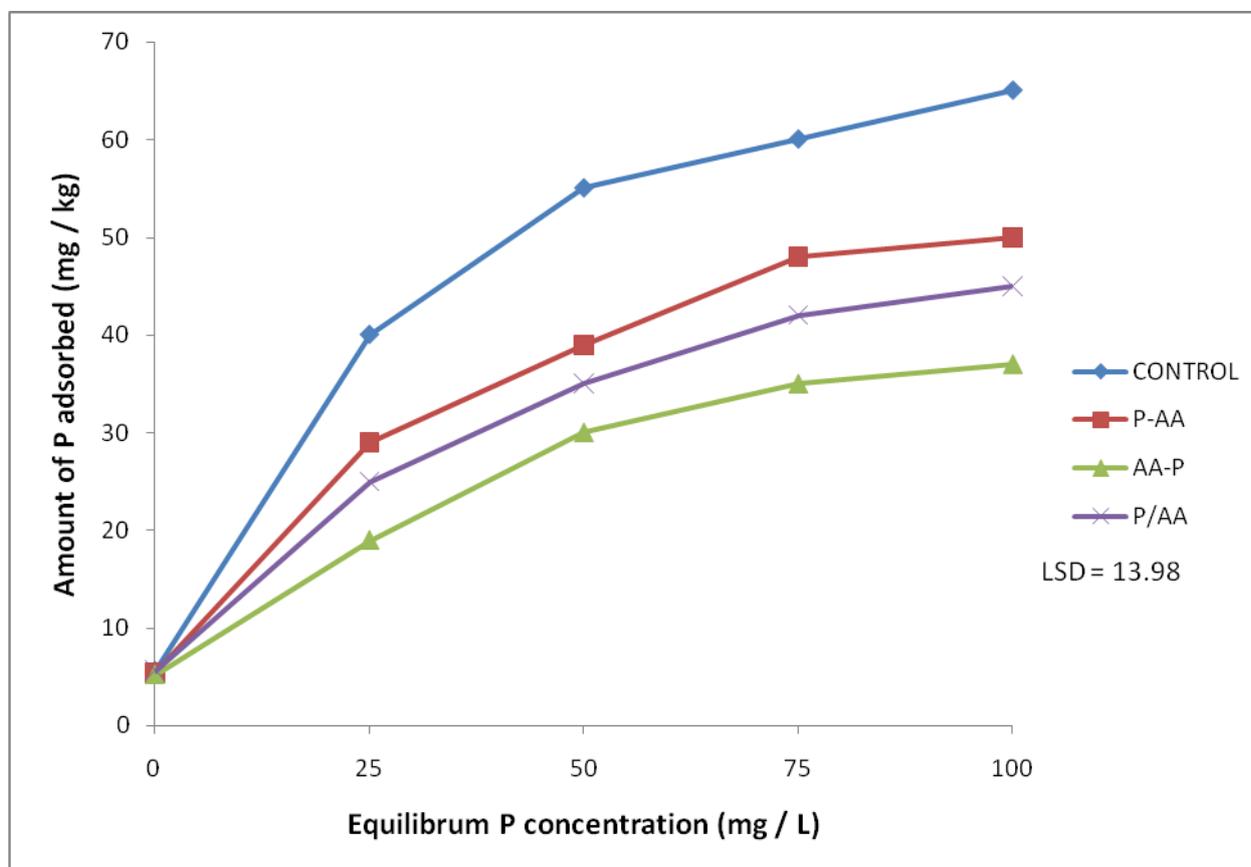


Fig. 3. Phosphate adsorption isotherm of the Alfisols in the absence and presence of acetate. Control (no acetate), P-AA = phosphorus addition before acetate, AA-P = acetate addition before phosphorus and P/AA = simultaneous addition of phosphorus and acetate.

The capacity for reduction on P adsorption and increase in P availability appears to follow the order of citrate > tartrate > acetate. This could probably be

attributed to larger molecular size of citrate (which could cover enormous surface) compared to tartrate and acetate (Tsado, 2008). Earl *et al* (1979) reported

that hydroxyl acids such as citrate, form stronger complexes than those containing single COOH groups. Generally, Gang *et al* (2012) concluded that the effectiveness of organic acids to mobilize P occurred in the order of tricarboxylic > dicarboxylic > monocarboxylic acids.

Conclusion

Present results of this study have demonstrated that LMWOA's (acetate, citrate and tartrate) addition may cause changes in PO₄ sorption characteristics. Addition of organic acids before P significantly reduced PO₄ adsorption and hence, increased its availability in the soil. Organic acid type, timing (sequences) and quantities of addition of organic amendment are among other factors controlling the soil PO₄ adsorption characteristics. Phosphate availability and efficiency could be improved by combination of inorganic PO₄ fertilizer and organic manure, probably due to the effects of organic – ligand to reduce PO₄ adsorption and increase PO₄ desorption in Alfisols.

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