Phosphate Mobilization by Addition of Organic Acids in Two Soils of the Nigerian Guinea Savanna

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ABSTRACT--- *The application of organic acids has been suggested as a mechanism that can mobilize Phosphorus (P) especially in soils where phosphate levels are too low. The objective of this study was therefore, to evaluate the effectiveness of adding organic acids for mobilizing P in some selected soils of Southern Guinea Savanna of Nigeria by investigating changes in soil plant available P and inorganic P fractions following treatment with citric, tartaric and oxalic acids. Soil samples were incubated at $25\pm 1^{o}C$ and 40% moisture content for three weeks with citric, tartaric or oxalic acids at 1.0 mmol kg^{-1} of soil. Soil Olsen P and inorganic P fractions were analyzed.The result revealed that Olsen – P and NH_4Cl - Pwas significantly increased with the additions of these organic acids. While Aluminium phosphate (Al – P), Iron phosphate (Fe – P), Occluded phosphate (Occl – P) and Calcium phosphate) Ca – P were also mobilized and released to some degree as well. Their capacity for P mobilization appears to follows the order of citric acid >tartaric acid > oxalic acid. P mobilization by the addition of organic acids was also highly soil type dependent and was controlled by intrinsic P status such as amounts and distribution of P fraction in the soil. These result indicate that root released organic acids can increase the solubility of some of the more stable pools of soil P, which can be important for soil P availability and P losses from soil water bodies.*

Keywords--- mobilization, organic acids, olsen P, occl P, organic P, P.sorption

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1. INTRODUCTION

Phosphate deficiencies often limit crop production in tropical acid soils such as Oxisols, Ultisols and Alfisols. Native P contents of these soils are often low, and P added as soluble fertilizer is largely unavailable for plant use. When soil phosphate levels are too low, P deficiency in plant represents a major constraint to world agricultural production (Palomo *et al*., 2006). One problem is that fertilizer P can largely be fixed by the oxides, hydroxides and oxyhydroxides of Fe and Al and clay minerals in an acidic soil, which makes it less available or effectively unavailable to plants (Shen *et al.*, 2001; Agbenin, 2003). This is because the availability of both applied and native P is controlled largely by, the sorption and desorption characteristics of the soil.

Due to its low solubility and high sorption capacity of P in soil, the supply of phosphate can be a major constrain to plant growth. There is no overwhelming evidence, however, to suggest that some plants can directly modify the rhizosphere to gain access to previously unavailable soil P reserves. This can include the deregulation of P membrane transport systems, the manipulation of root hair length or density, the release of phosphates to replace organically bound soil P and the release of organic acid and H^+ to solubilize inorganic P ((Tsado, *et al.,* 2012)..

Soil contain complex, aromatic, relatively high molecular weight (i.e., > 2000) organic acids such as humic and fluvic acids. However, structurally simpler organic acids also exist in the soil such as low molecular weight C-, H-, and O-containing compounds. These organic acids are characterized by the possession of one or more carboxyl groups (Jones, 1998).Soil organic acids are derived from plant and animal residues, microbial metabolism, canopy drips and rhizosphere activities (Hue *et al*, 1994; Moradi *et al*., 2012).

In a review of organic acid in the rhizosphere, Jones (1998) indicated that typical concentrations of organic acids in the soil ranges from 0.1 – 100 µmol L^{-1}. Although the existence of organic acids in soils is short lived, organic acids may be produced and formed continuously. Hence, organic acids have a very important chemical significance (Jones, 1998) especially for the mobilization of various phosphates in soil (Marschner, 1995).In addition, Jones *et al* (2003) and Palomo *et al* (2006) reported that secretion of organic acids (such as citric, tartaric, oxalic acids e.t.c.) from plant root was the major mechanism for enhancing P availability in soils and hence improving crop yields. The supply of P to

plants is also strongly influenced in the rhizosphere by the presence of organic acids (Hue *et al*, 1994). This introduces the concept that it may be possible to mimic a plant's release of organic acids by artificially incorporating acids in to the soil which would increase P availability in soils with low P status.

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.

The objectives of this study were to evaluate the effectiveness of adding organic acids for mobilizing P in some selected soils of Southern Guinea Savanna of Nigeria by investigating changes in soil acidity, plant available P and inorganic P fractions following treatment with citric acids,tartaric acids and acids. For our study, we focused on low molecular weight organic acids.

2. MATERIALS AND METHODS

2.1 Soil sampling location

Soil samples were collected from two different locations of different pedogenic characteristics. These locations were Minna ($9^0$31'N, $6^0$30'E) and Mokwa ($9^0$18' N $5^0$05'E) in the Southern Guinea Savanna region of Nigeria. These soil types were classified as classified as Haplic Plinthosol (Typic Plinthustalfs) and Rhodic Nitosol (Rhodic Kandiustalfs) respectively (FAO, 2006; Lawal *et al.*, 2012).

2.2 Soil analysis

  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 titrations. Exchange acidity was determined by shaking the samples with 1.0 M KCl and titrating them with 0.1 M NaOH. Olsen P was determined by the Bray P 1 method (Murphy and Riley, 1962). Total P was determined after digestion with 70% $HCLO_4$. Phosphate in the digest was determined colorimetrically with the molybdate – ascorbic acid procedure. The content of ammonium oxalate soluble iron and aluminium oxides were determined by Mckeague and Day (1966) method. Selected properties of the soil samples are given in Table 1a and b.

2.3 Phosphorus sorption studies

Two grams of 2 mm sieved soil was placed into 50ml centrifuge tubes. Soil samples were equilibrated in 30 ml of 0.01M $CaCl_2$ containing various amounts 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 tolune were added to minimize microbial activity. Suspensions were shaken twice daily for 30 minutes and at the end of the sixth day, they were centrifuged at 10,000rpm and filtered through whatman No. 42 Filter paper. 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 against phosphorus concentration in the solution to obtain a P sorption isotherm.

The P sorption data for the soil samples used in this study were fitted into the following form of Langmuir equation: C/X = 1/kb+c/b. Where C = P concentration in equilibrium solution, X = P adsorbed by the soil (mg P kg^{-1}), b = adsorption maximum (mg P kg^{-1}) k = a constant related to the bonding energy of the soil for P or affinity constant.

2.4 Incubation experiments of Organic acids

Three organic acids were used for incubation studies in this experiment. These acids are; citric, oxalic and tartaric acids. These acids were obtained commercially (salts of these acids was used and not pure acids)

One hundred gram soil samples were weighed in triplicate into polyethelene plastic bottles with 10 ml of an organic acid (10 mmol L^{-1}) or dionised water to provide the following treatments: (i). Soil with dionised water (control), (ii).Soil with

citric acid, (iii). Soil with tartaric acid and (iv). Soil with oxalic acid .The bottles were covered with a plastic film with a small opening at a temperature of $25^{\circ}C$ and 40% soil moisture based on soil mass for an incubation period of 3 weeks. The bottles were weighed periodically and bring them back to their initial weight to maintain soil moisture at 40% during the experiment. During weighing, the soils were stirred to prevent them from becoming anoxic. At the end of the third week of experiment, the soils were air dried and sieved through 2mm sieve. The following analysis was carried out: Olsen P and inorganic P fractions

2.5 Fractionation of soil inorganic phosphorus

Various fractions of soil inorganic P was extracted sequentially from the treated soils and measured according to the procedure described by Chang and Jackson (1957). At first, 1.0 mol L^{-1} of NH_4Cl was used for the extraction of loosely bound P ($NH_4Cl – P$), then 0.5 mol L^{-1} of NH_4F for the Al phosphate (Al – P), 0.1 mol L^{-1} of NaOH for the Fe phosphate (Fe – P), 0.3 mol L^{-1} of $Na_3C_6H_5O_7.2H_2O$ and $Na_2S_2O_4$ for the Occluded phosphate (Oc – P) and Lastly, 0.25 mol L^{-1} of H_2SO_4 for the Ca – P. Phosphate in the supernatant were determined colorimetrically according to the procedure described by Murphy and Riley (1962) using spectrophotometer.

2.6 Statistical analysis

The data collected were subjected to analysis of variance (ANOVA) using a statistical package 'SAS' (2002) version 9.0. The Duncan Multiple Range Test (DMRT) was used to separate the means.

3   RESULTS AND DISCUSSION

3.1 Characteristics of the studied soils

Major physical and chemical characteristics of the studied soil are presented in table 1. The samples were slightly acidic with pH values Mokwa(4.6) and Minna(5.4). The particle size distribution showed that the texture of the soil was sandy clay loam (Minna and Mokwa). Although the organic carbon content of the soil was generally low, Minna soil had the highest value of $8.9g$ kg^{-1}. Jones and Wild (1975) reported that low to medium organic carbon rate for savanna soil was attributed to paucity of vegetation cover, rapid mineralization of organic matter, inadequate return of crop residue, bush burning and short fallow periods. Exchangeable bases were in the order of Ca>Mg>K>Na for both locations. The total P contents of the studied soils were 0.48 and 0.42 g kg^{-1}, while Olsen P was 4.21 and 3.30 mg kg^{-1} for Minna and Mokwa soils respectively. 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). The S_{max}were also 113. 96 and 144.53 mg kg^{-1}.The S_{max}represent the estimate of the soil's ability to adsorbed P and the sorption of P by the soils dictate the environmental fate of added P to soils in mineral fertilizer (Kleinman and Sharpley, 2002).

3.2 Inorganic phosphate mobilization

Generally the amount of $NH_4Cl – P$ was observed to be low. However, compared with control, the $NH_4Cl – P$ content of the studied soils was significantly increased after treatment with the three organic acids irrespective of the location of the samples (Figure 2). Citric, tartaric and oxalic acids increased $NH_4Cl – P$ by mg kg^{-1} respectively.Their capacity for P mobilization appears to follows the order of citric acid >tartaric acid > oxalic acid. Gang *et al* (2012) reported a similar findings that the effectiveness of organic acids to mobilize P occurred in order of tricarboxylic>dicarboxylic> monocarboxylic. Among the two soil types that were involved there was also a significant difference in the $NH_4Cl – P$ observed. Gang *et al* (2012) further concluded that the pattern of P mobilization by the addition of organic acids was highly soil type dependent and was controlled by intrinsic P status such as amounts and distribution of P fraction in the soil.

The amounts of the various form of inorganic P were obviously changed by organic acid addition (Figure 2). Al – P and Fe – P were observed to be significantly lower for those samples with organic acids addition compared to the control sample irrespective of the soil type. The mobilization of phosphate forms of Al and Fe will be released and hence reduce the P adsorption. Al and Fe oxides are the main phosphates adsorbents in many soils. Moradi*et al* (2012) reported that organic acids (citrate, tartrate etc) has a greater affinity for Fe^{3+} and Al^{3+} than P and may release the P predominantly held in Fe and Al – phosphate minerals. Phosphate adsorption capacity can be predicted by pedotransfer functions based on various Al and Fe oxides fraction such as oxalate extractible Al and Fe (Alo, Feo) and dithioniteextractible Fe (Fed) (Uzu*et al*, 1975; Borggard , 1990).

The effects of organic acid sources and soil types on Ca – P mobilization were also highly significant (Figure 3). Although generally lower than Al –P and Fe – P and compared to the control, significantly lower mobilization values are

obtained for treated samples. Wang, *et al* (2009) confirmed that on incubation, Ca – P get gradually solubilized and the larger contents of free Fe and Al may be responsible for the increase rate of conversion into other form. They further reported that phosphate predominantly precipitate as Fe –and Al – phosphate in acid soil while Ca – phosphate is the main inorganic P fraction in calcareous soils.

In our study, Occ- P was released by citric acid and tartaric acid possibly due to complexing dissolution. To mobilizing Oc – P,an organic acids must first remove its Al – Fe oxides coat which is generally achievable by complexing Al^{3+} and Fe^{3+} with organic ligands (John and Leoppart, 2006).

4   CONCLUSION

Soil samples incubated with low molecular weight organic acids were extracted sequentially according to the method of Chang and Jackson (1957). The results suggested that organic acids significantly increase P mobilization and the effectiveness of organic acids to release P occurred in the order of citric acids >tartaric acids > oxalic acids. The pattern of P mobilization by addition of organic acids is different from study to study. The comparison suggest that the mobilization was highly soil type dependent and the soil P status especially the amount and distribution of P fractions may be important for solubilization of P after addition of organic acids.

Table 1a.physico – chemical properties of the soils of the studied soils

Soil properties	Location	
	Minna	**Mokwa**
Particle size distribution (g kg^{-1})		
Sand	640	620
Silt	100	140
Clay	260	240
Textural class	Sandy Clay Loam	Sandy Clay Loam
pH: 0.01M CaCl$_2$	5.21	4.85
H$_2$0	6.07	5.92
Org. C. (g kg^{-1})	8.9	6.8
Total N. (g kg^{-1})	0.51	0.32
Available P. (mg kg^{-1})	4.21	3.30
Exchangeable bases (cmol kg^{-1})		
Ca	2.82	2.24
Mg	1.63	1.72
K	0.76	0.61
Na	0.26	0.16
Exch.acidity (cmol kg^{-1})	0.62	0.92
ECEC	6.09	5.65
BS (%)	89.82	83.72

Table 1b.Other chemical properties of the studied soils before incubation studies.

Properties	Location	
	Minna	**Mokwa**
Olsen P (mg kg^{-1})	4.21	3.30
Total P (g kg^{-1})	0.48	0.42
Fe$_{ox}$(g kg^{-1})	0.49	0.78
Al$_{ox}$(g kg^{-1})	0.39	0.64
Smax (mg kg^{-1})	113.96	144.53

Fe$_o$ = Oxalate extractable iron   Smax = P adsorption maxima
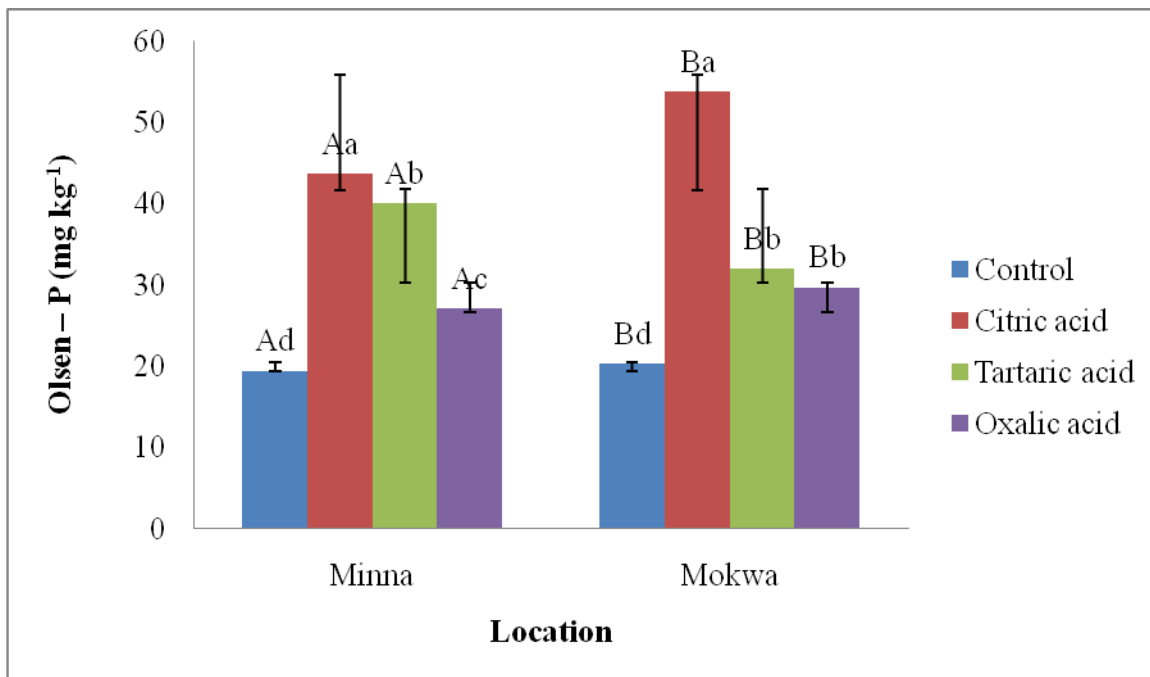Al$_o$ = Oxalate extractable aluminium

Figure 1: Olsen - P fraction of Soils Following Organic Acid Treatments.
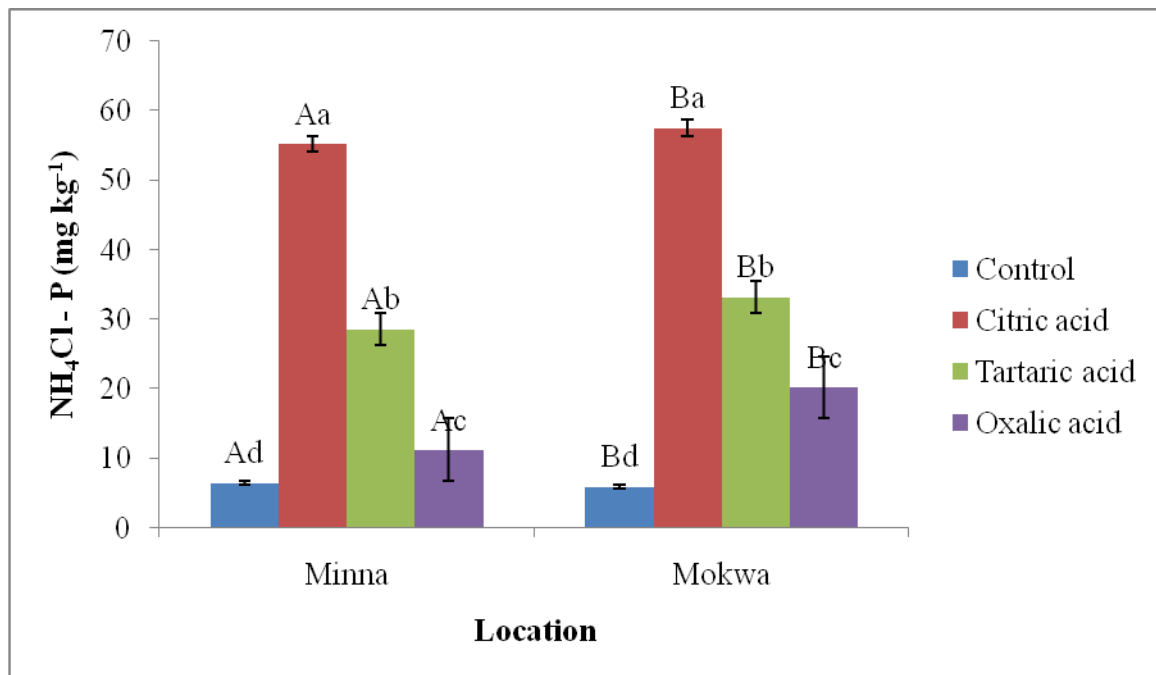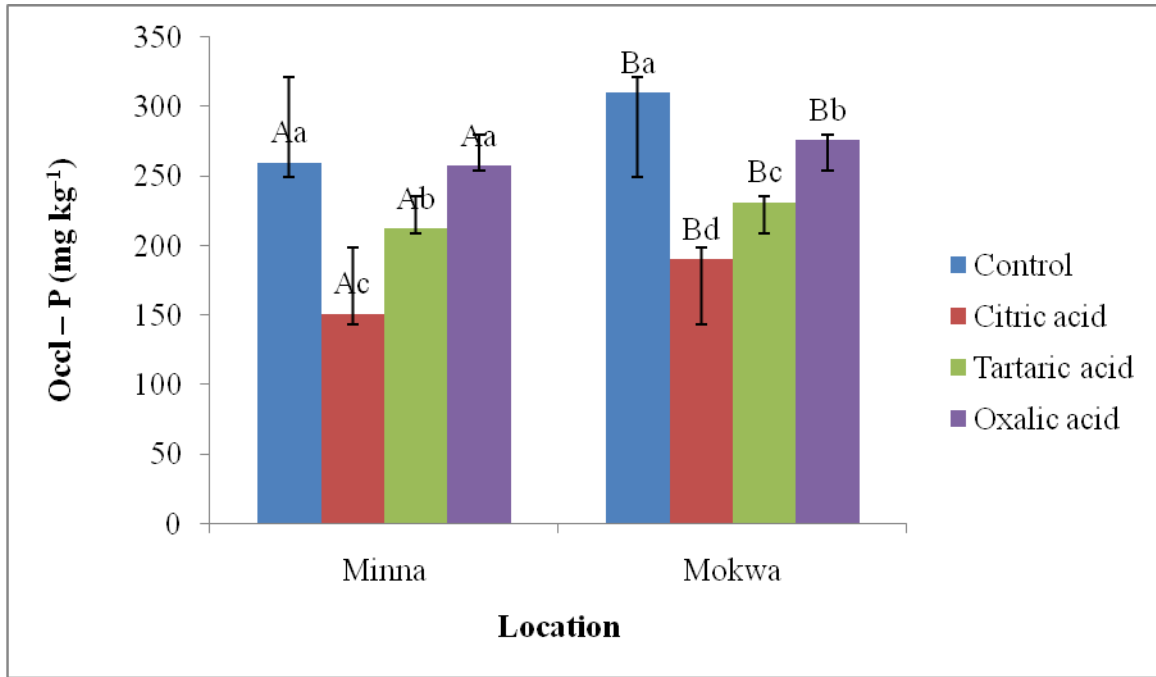

Figure 2: NH_4Cl - P Fraction of Soils Following Organic Acid Treatments.

Lowercase letters are used to indicate statistical differences within soils while uppercase letters are used to indicate statistical difference within the location. Mean values with the same lower case within each location are not statistically different and with the same upper case letter are not statistically different at $P < 0.05$. Error bars represent the standard deviations for the measurements.

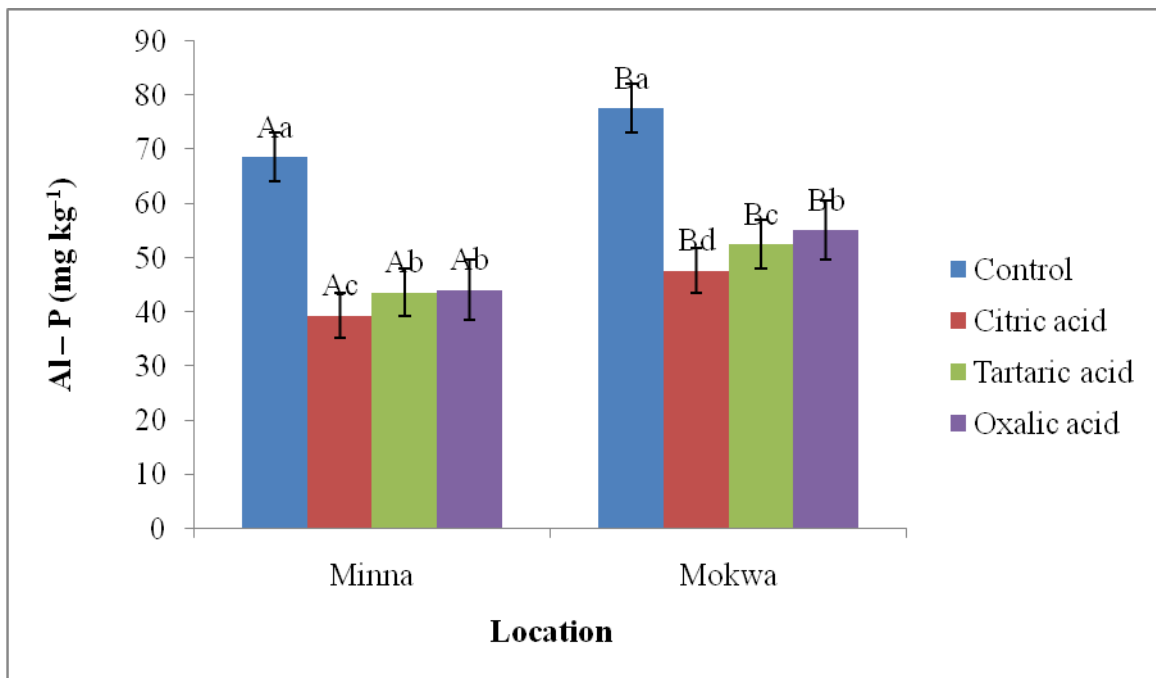**Figure 3**: Occl - P Fraction of Soils Following Organic Acid Treatments.

Figure 4: Al - P Fraction of Soils Following Organic Acid Treatments.

Lowercase letters are used to indicate statistical differences within soils while uppercase letters are used to indicate statistical difference within the location. Mean values with the same lower case within each location are not statistically different and with the same upper case letter are not statistically different at $P < 0.05$. Error bars represent the standard deviations for the measurements.
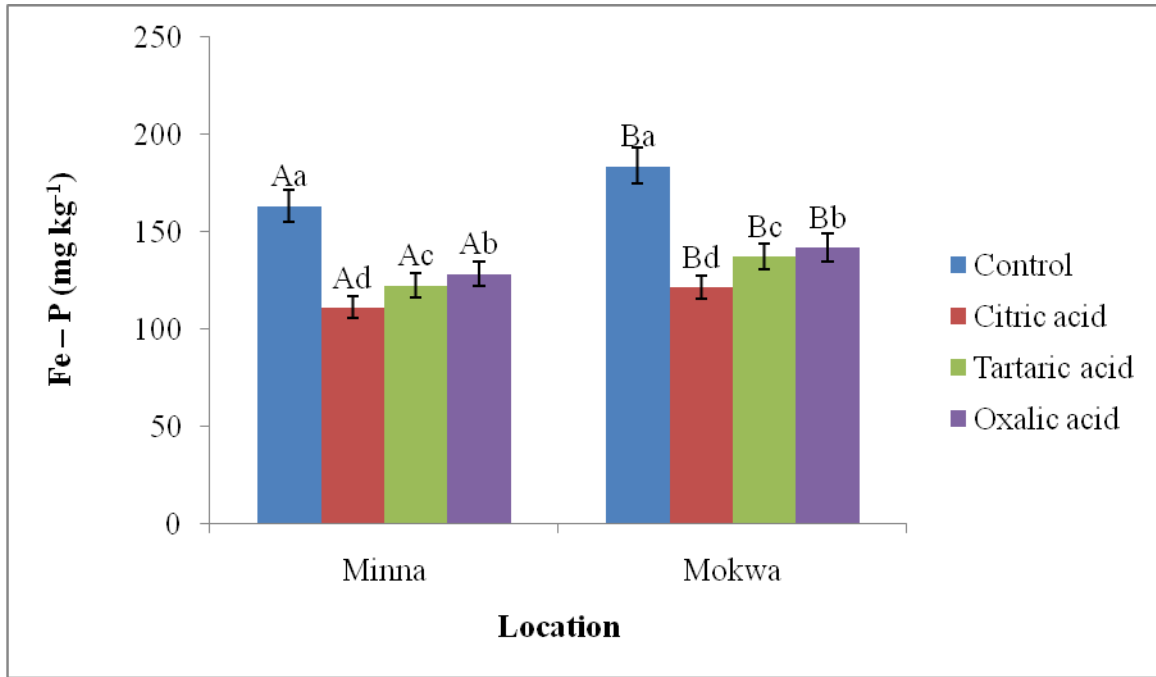
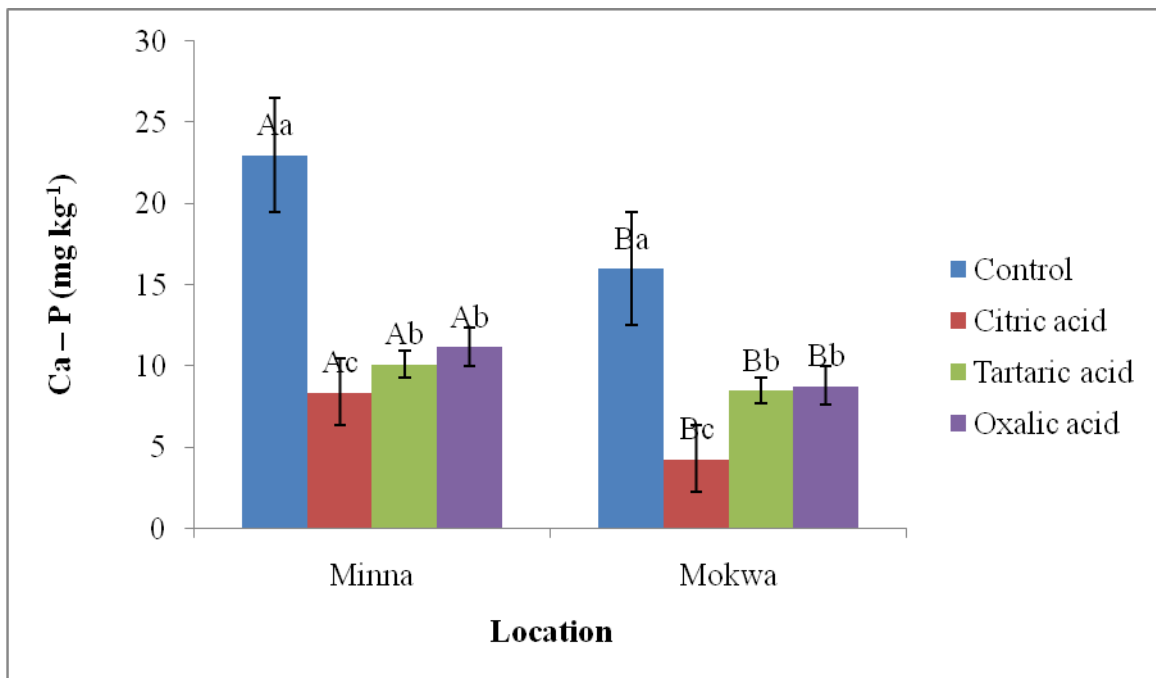**Figure 5:** Fe - P Fraction of Soils Following Organic Acid Treatments.

Figure 6: Ca - P Fraction of Soils Following Organic Acid Treatments.

Lowercase letters are used to indicate statistical differences within soils while uppercase letters are used to indicate statistical difference within the location. Mean values with the same lower case within each location are not statistically different and with the same upper case letter are not statistically different at $P < 0.05$. Error bars represent the standard deviations for the measurements.

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