PHOSPHATE MOBILIZATION BY ADDITION OF ORGANIC ACIDS IN TWO SOILS OF THE SOUTHERN GUINEA SAVANNA OF NIGRIA

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DEPARTMENT OF SOIL SCIENCE
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NSUKKA

NOVEMBER, 2014

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A Thesis submitted to the Department of Soil Science, University of Nigeria, Nsukka, in partial fulfillment of the requirements for the award of the Degree of Doctor of Philosophy in Soil Science (Soil Chemistry)

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CERTIFICATION

This is to certify that as a Postgraduate student in the Department of Soil Science, University of Nigeria, Nsukka, TSADO, Philips Alkali with Registration Number PG/Ph.D/09/50707 has satisfactorily completed the research work for the Degree of Ph,D of Soil Science (Soil Chemistry). The work embodied in this thesis is original and has not been submitted in part or full for any other degree or diploma of this or any other University.

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Professor C. A. Igwe	Dr. P. I. Ezeaku
(Project Supervisor)	(Head of Department)
Date _____________	Date _____________

DEDICATION

To my Lord and Saviour, Jesus Christ who bestowed upon me wisdom, knowledge and understanding.

To my beloved wife, all my Teachers, family members, friends and colleagues who over the years have made it possible for me to be what I am today.

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TABLE OF CONTENTS

CHAPTER ONE

CHAPTER TWO

CHAPTER THREE

CHAPTER FOUR

CHAPTER FIVE

CHAPTER SIX

LIST OF FIGURES

LIST OF TABLES

TABLE TITLE PAGE

ABSTRACT

One mechanism by which plants can mobilize organic and inorganic forms of phosphorus (P) in soils is by exudation of low molecular weight organic acids. Laboratory and field trial were carried out during 2011 and 2012 cropping seasons to study the effects of additions of organic acids (citric, oxalic and tartaric acids) on the mobilization of phosphate of soils from Minna and Mokwa, both in Southern Guinea Savanna of Nigeria. For initial laboratory studies and prior to field cultivation, soil samples were collected from these locations and incubated at 25± 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 experimental design used during the field trial was split plot design with organic material sources (orange waste, amaranthus and tamarind pulp) assigned to the main plot while the rates (0, 2.0, 4.0, 6.0 and 8.0 tons ha^{-1}) of application occupied the sub-plots. Each treatment received three replications in each of the locations. Maize was planted during the two cropping seasons as test crop. Both agronomic, Olsen – P and soil inorganic P data were determined. The results indicated that Olsen – P and NH_4Cl – P were significantly increased by treating with the three organic acids. Al phosphate (Al – P), Fe phosphate (Fe –P), occluded phosphate (Occl – P) and Ca phosphate (Ca – P) were also mobilized and released in various degrees in each of the locations irrespective of the cropping season. The relative fractions of inorganic P was in the order Occl - P > Fe - P > Al - P > Ca – P. The effect of organic acid sources on maize plant height at 4 and 7 weeks after planting in the two locations were not significant during 2011 cropping season, but significant during 2012 cropping season. However, the effect of sources of organic acid and their rates of application on maize grain yield was significant in each location and the season. It was also observed that the results of soil inorganic P after the field trial followed similar trend with what was obtained from the initial laboratory studies (Occl - P > Fe - P > Al - P > Ca – P), but the effect was much lower. The order of increased mobilization of phosphate by these organic acids was citric acid > tartaric acid > oxalic acid and orange waste > tamarind pulp > amaranthus leaves respectively for both initial laboratory studies and field trial. Also, it could be concluded that hydroxyl acids i.e tricarboxylic acids such as citrate form stronger complexes than those containing single COOH groups. The pattern of P mobilization by addition of organic acids differed from one location to another. The comparison suggested that the mobilization of P was highly soil dependent, and the soil P status such as amount and distributions of P fractions may be important for solubilization of P after the addition of organic acids. These three organic acids therefore have the potentials to increase the availability of available P. The practical implication of these processes is that organic residues could be used as a strategic tool to reduce the rates of fertilizer P required for optimum crop growth on acidic and P-fixing soils of Nigeria.

CHAPTER ONE

INTRODUCTION

Phosphorus (P) is an important plant nutrient and the reactions of phosphate with soil components have been extensively studied from the point of view of soil fertility, soil chemistry and environmental concerns (Parfit, 1978; Sanyal and De Datta, 1991; Hue *et al*., 1994; Wang *et al*., 2007). In tropical and subtropical acidic soils, low P availability becomes one of the limiting factors for plant growth; at the other extreme, accumulation of soil available P has negatively affected water quality (Sharpley, 1995). The misapplication of phosphate fertilizers usually causes eutrophication of water bodies, unbalanced plant nutrition and low P utilization efficiency. When soil phosphate levels are too low, P deficiency in plant represents a major constraint to agricultural production (Palomo *et al*., 2006). One problem is that P fertilizer can largely be fixed by the oxides, hydroxides and oxyhydroxides of Iron (Fe) and Aluminium (Al) and clay minerals in an acidic soils, which makes it less available or effectively unavailable to plants (Fankem *et al.*, 2006). This is because the availability of both applied and native P is controlled largely by, the sorption and desorption characteristics of the soil.

Variable charge minerals are also the major components of most soils of the tropics that affect P unavailability to plants. Such is the case with soils of Nigeria which is dominated by sesquioxides and low activity clays (Bala, 1992). The most likely areas appear to be those dominated by Oxisols, Ultisols and Alfisols. The low amount of total and available P in these soils make investigation into problems associated with phosphorus availability imperative. Already, the widespread occurrence of P deficiency in most arable land in Nigeria has led to the intensive use of P fertilizer. It has been reported that land utilization also influences P sorption capacity (Odunze, 2009).

Due to the low solubility and high sorption capacity of P in soil, the supply of phosphate can be a major constrain to plant growth. There is 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 (Tinker and Nye, 2000).

Researches into management practices to increase phosphate availability in a weathered soil, and at the same time curtail its leaching to contaminate lakes, streams and ground water remains highly imperative. Efficient use and alternative management of phosphate fertilizers are critical to ensure global food production and security (Cordell *et al*., 2009).The application of combined organic – inorganic inputs has been one management practices suggested to increase P availability in weathered soils (Agbenin and Igbokwe, 2006).

Soils contain complex, aromatic, relatively high molecular weight (i.e., > 2000) organic acids such as humic and fulvic acids (Hue *et al*., 1994). However, structurally simpler organic acids also exist in the soil such as low molecular weight (citric, oxalic, succinic, malic, tartaric acids) 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; Wang *et al*., 2007).

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 (2000) 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 rhzosphere 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 into the soil which would increase P availability in soils with low P status.

Citric, tartaric, and tannic acids 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 (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 and acids were reported to be bound to the structural cations of edges and hydroxyl Al and Fe coatings on mineral colloids (Huang, 2004)

The uptake of P from soil through root exudation is mostly from various inorganic phosphate. Although the mobilization is very complex, some understanding of the mechanism have been gained. Hinsinger (2001) reported that the solubility of Ca increases with a decreasing pH of the environment due to H^+ released of organic acids from plant roots. The cheletion of Fe^{3+}, Al^{3+} and Ca^{2+} by organic anions lead to the release of inorganic P bound by these cations (Jones *et al*., 2003), and organic anions that compete with P adsorption on the surface of soil particles further stimulate the desorption of adsorbed anions (He *et al*., 1998)

Although the competitive adsorption of P and organic ligands by synthetic clay minerals and oxides have been extensively studied (Sibanda and Young, 1986; Kafkafi *et al.*,1988; Violante and Gianfreda, 1995; Violante *et al.*,1996), there is a limited information on the fate of P in the presence of organic acids in natural soils (Yuan, 1980; .He *et al.*, 1997). Therefore the exact mechanism among soil inorganic colloids, organic acids and P has not been well- understood. While some detailed studies have been carried out on some soils of the derived savannas of Nigeria especially in terms of P sorption and desorption characteristics, very little attention has been given to the soils of the Southern Guinea part of the Nigeria Savanna (Tsado, 2008). Thus, the need arises for specific studies aimed at understanding the effect of some selected organic acids on phosphate mobilization in these soils. This will facilitate making specific recommendations for P availability to plants with a view to boosting agricultural productivity in the Southern Guinea agro ecology.

This study investigated the effect of some selected organic acids on the availability of phosphate in some of the soils of the Nigerian Southern Guinea Savanna. Thus, the specific objectives were to:

1. investigate the effect of different organic compounds on the adsorption of phosphate in some major soil types of Southern Guinea Savanna Zone of Nigeria,
2. study the influence / regular application of different rates of the organic material applications to the preceding year cropping and
3. evaluate phosphate sorption characteristics of these soils with a view to efficient management of P fertilization.

CHAPTER TWO

LITERATURE REVIEW

2.1. Phosphorus (P) dynamics in soil

2.1.1. Soil P transformation

Soil P exists in various chemical forms including inorganic P (Pi) and organic P (Po). These forms differ in their behavior and fate in soils (Hansen *et al*., 2004; Turner *et al*., 2007). Pi usually account for 35 to 70 5 of total in soils (Harrison, 1987). Primary P minerals including apatites, strengites and varisites are very stable and the release of available P from these minerals through weathering is generally too slow to meet crop demand through applications of phosphate rocks (i.e. apatites) and has only proved relatively efficient for crop growth in acidic soils. In contrast, secondary P minerals including calcium (Ca), aluminium (Al) and iron (Fe) phosphates vary in their dissolution rates depending on their size of mineral particles and soil pH (Pierzynski *et al*., 2005; Oelkers and Valsami-Jones, 2008). With increasing soil pH, solubility of Fe and Al phosphates increases but the solubility of Ca phosphates decreases, except for pH values above 8 (Hinsinger, 2001). The P adsorbed on various clays and Al/Fe oxides can be released by desorption reactions. All these P forms exist in complex equilibra with each other ranging from very stable, sparingly available to plant-available P pools such as labile and solution P.

In acidic soils, P can be dominantly adsorbed by Al/ Fe oxides and hydroxides such as gibbsite, hematite and goethite (Parfitt, 1989). P can be first adsorbed on the surface of clay minerals and Al/Fe oxides forming various complexes. The nonprotonated and protonated bidentate surface complexes may co-exist at pH 4 – 9, while the protonated bidentate innersphere complex is predominant under soil acidic conditions (Luengo *et al*., 2006; Arai and Sparks, 2007). Clay minerals and Al/Fe oxides have large specific surface areas, which provide large number of adsorption sites. The adsorption of soil P can be enhanced by increasing ionic strength. With further reactions, P may be occluded in nanopores that frequently occur in Fe/Al oxides, thereby becoming unavailable to the plants (Arai and Sparks, 2007).

In neutral- to- calcareous soils, P retention is dominated by precipitation reactions (Lindsay *et al*., 1989), although P can also be adsorbed on the surface of Ca carbonate (Larsen, 1967) and clay minerals (Condron *et al*., 2005). Phosphates can precipitate with Ca, generating dicalcium phosphates (DCP) that are available to plants. Ultimately, DCP can be transformed into more stable forms such as octocalcium phosphates and hydroxyapatites (HAP), which are less available to plants at alkaline pH (Arai and Sparks, 2007). HAP accounts for more than 50% of total Pi in calcareous soils from long – term fertilizer experiments and dissolution increases in soil pH (Wang and Nancollas, 2008) suggesting that rhizosphere acidification may be an efficient strategy to mobilize P in calcareous soils.

Po generally may account for 30 to 65% of the total P in the soils (Harrison, 1987). Soil Po may exists in stabilized forms as inositol phosphates and phosphonates and active forms as orthophosphate diesters, labile orthophosphate monoesters and organic polyphosphates (Turner *et al*., 2002; Condron *et al*., 2005). The Po can be released through mineralization processes mediated by soil organisms and plant roots in association with phosphatase secretions. These processes are highly influenced by soil moisture, temperature, surface physical and chemical properties and soil pH and Eh (for redox potential). Po transformation has a great influence on the overall bioavailability of P to plant (Turner *et al*., 2007).

2.1.2. Chemical fertilizer P in soil

The modern terrestrial P cycle is dominated by agriculture and human activities (Oaklers and Valsami-Jones, 2008). The concentration of available soil Pi seldom exceeds 10 µM

(Bieleski, 1973), which is much lower than that in plant tissues where the concentration is approximately 5 to 20 Mm Pi (Raghothama, 1999). Because of the low concentration and poor mobility of plant available P in soils, applications of chemical P fertilizers are needed to improve crop growth and yield. The major forms od phosphate fertilizers include Mono Calcium Phosphate (MCP) and Mono Potasium Phosphate (MPP). Application of MCP can significantly affect soil physical properties. After application to soil, MCP undergoes a wetting process, generates large amounts of protons, phosphates and DCP and eventually form a P-saturated patch (Benbi and Gilkes, 1987). This P-saturated patch forms three different reaction zones including direct reaction, precipitation reaction and adsorption reaction zones. The direct reaction zone is very acidic (pH = 1.0 – 1.6), resulting in an enhanced mobilization of soil metal ions. These metal ions can also react with high concentrations of Pi in the zone thus causing further precipitation of Pi. The amorphous Fe –P and Al – P that thereby form can be partly available to plants. In calcareous soil, new complexes of DCP and MCP can be formed and with time DCP is gradually transformed into stable forms of Ca – P (othocalcium phosphate or apatite). Because the Pi concentration is relatively low, P adsorption by soil minerals is dominat in the outer zone (Moody, *et al,* 1995).In contrast, the application of monopotassium phosphorus has little influence on soil physical and chemical properties (Lindsay, *et al*., 1989). Therefore, the matching P fertilizer types with soil physical and chemical properties may be efficient strategies for rational use of chemical fertilizer P.

2.1.3. Manure P in soil

The application of manure is widely practiced to increase the productivity of soils that contain inadequate levels of organic carbon. The effects of manure on P availability in various soils has been widely studied, and the general conclusion has been that it is a source of P; interact with soil components in a manner that increases P recovery by crops; and enhances the effectiveness of inorganic P fertilizer. P added from manure and other sources, however, tends to become less available to plant with the passing of time.(Sample *et al.*, 1990). Whalen and Chang (2001) also observed that manure application guidelines are frequently based on N requirements of the crops, and P is therefore over supplied and liable to either accumulate or be removed by surface or subsurface transport. As regards the eventual status of fertilizer P in the soil, it is interesting to note that the manure and mineral (KH_2PO_4) fertilizer appear to contribute to different P pools (Griffin *et al.*, 2003). The later is efficient at increasing $CaCl_2$ extractible P and Mehlich – 3 P while manure has a greater effect on modified Morgan P as well as other types of P.

Manure can be applied to increase P fertility, the total P content in manure is very variable and nearly 70% of total P in manure is labile. In manure, Pi account for 50 – 90% (Dou *et, al*., 2000). Manure also contains large amount of Po, such as phospholipids and nucleic acids (Turner and Leytem, 2004), which can be released to increase soil Pi concentrations by mineralization. Furthermore, small molecular organic acids from mineralization of humic substances in manure can dissolve Ca – P, and especially from citrate. It can efficiently weaken the nanoparticle stability of HAP, by controlling the free Ca availability and thereby the nucleation rate (Martins *et al*., 2008). P adsorption to soil particles can be greatly reduced through applying organic substances. The humic acids contain large numbers of negative charges, carboxyl and hydroxyl groups which strongly compete for adsorption sites for Pi. Manure can also change soil pH and thus alter available P.

2.2. Phosphorus dynamics in the rhizosphere

The rhizosphere is the critical zone of interactions among plants, soils and microorganisms. Plant roots can greatly modify the rhizosphere environment through their various physical activities, particularly the exudation organic compounds mucilage, organic acids, phosphatases and some specific signaling substances, which are key drivers of various rhizosphere processes. The chemical and biological processes in the rhizosphere not only determine the mobilization and acquisitions of soil nutrients as well as microbial dynamics, but also control the nutrient – use efficiency of crops and, thus profoundly influence crop productivity (Hinsinger *et al*., 2009; Richardson *et al*., 2009; Wissuwa *et al*., 2009; Zhang *et al*., 2010).

Due to its low solubility and mobility in the soil, P can be rapidly depleted in the rhizosphere by plant uptake, resulting in a P gradient concentration in a radial direction away from the root side (Wissuwa *et al*., 2009; Zhang *et al*., 2010). In spite of total soil P content usually exceeding plant requirements, the low mobility of soil P can restrict its availability to plants. Soluble P in the rhizosphere soil solution should be replaced 20 to 50 times per day by P delivery from bulk soil to the rhizosphere to meet plant demand (Marschner, 1995). Therefore P dynamics in the rhizosphere are mainly controlled by plant root growth and function and also highly related to physical and chemical properties of the soil (Neumann and Romheld, 2002). Because of unique properties of P in soils low solubility, low mobility and high fixation by soil matrix as well as the availability of P to plant are dominantly controlled by two key processes; (1) Spatial availability and acquisition of P in terms of plant roots architecture as well as mychorizal association, and (2) bioavailabilty and acquisition of P based on rhizosphere chemical and biological processes (Zhang *et al*., 2010).

2.3. Mechanisms of phosphate solubilization

The potential mechanism for phosphate solubilization might be acidification either by protone extrusion associated with ammonium assimilation (De Freitas *et al*., 1997; Reyes *et al*., 1999) or by organic acids production and proton extrusion (Dutton and Evans, 1996; Nahas, 1996; Jones, 1998). Acid phosphatases and phytases secreted by these microorganisms also have an important role on phosphate solubilization (Richardson *et al*., 2000; Tarafdar *et al*., 2003; Aseri *et al*., 2009).

P solubilization is carried out by large number of saprophytic bacteria and fungi acting on sparingly soluble soil phosphates, mainly by chelating-mediated mechanism (Moghimi *et al*., 1978; Whithelaw, 2000). Inorganic P is solubilized by the action of organic and inorganic acids secreted by PSMs in which hydroxyl and carboxyl groups of acids chalate cations (Ca, Al and Fe) and decrease the pH in basic soils (Kpomblekou and Tabatabai, 1994). The PSMs also dissolve the P through production of organic acids such as (acetate, lactase, oxalate, tartrate, succinate, citrate, gluconate, ketogluconate and glycolate (Goldstein, 1995; Gyaneshwar *et al*., 1998; Kim *et al*., 1997,1998; Deubel *et al*., 2000) and lowering the pH of the rhizosphere. The pH of the rhizosphere is lowered through biotical production of proton/ biocarbonate release (anion / cation balance) and gaseous (O_2 / CO_2) exchanges.

Release of root exudates such as organic ligands can also alter the concentration of P in the soil solution (Hinsinger, 2001). The organic acids produced by PSMs solubilize insoluble phosphates by lowering the pH, chelation of cations and competing with phosphate adsorption sites in the soil (Nahas, 1996). Inorganic acids such as hydrochloric acids can also solubilize phosphates but are less effective compared to organic acids at the same pH (Kim *et al*., 1997). In certain cases, phosphate solubilization is induced by phosphate starvation (Gyaneshwar *et al*., 1999). Organic phosphate is catalysed through hydrolysis of C-O-P ester bond by phosphatase and phytase released by PSMs (Tarafdar and Rao, 1996; Tarafdar *et al*.,2001; Yadav and Tarafdar 2007; Yadav and Tarafdar 2010; Yadav and Tarafdar, 2011)

2.4. Solubilization of calcium phosphate (Ca-P)

Soil phosphates mainly the apatites and metabolites of phosphatic fertilizers are fixed in the form of calcium phosphates in alkaline conditions under arid and semi arid regions. Many of the calcium phosphates, including rock phosphate ore (fluorapatite, francolite), are insoluble in soil with respect to the release of inorganic P (Pi) at rate necessary to support agronomic levels of plant growth (Goldstein, 2000). Phosphate solubilizing microorganisms could increase P nutrition of plant through increased solubility of Ca-phosphates (Sujatha *et al*., 2004; Vassilev *et al*., 2006) and their solubility increases with a decrease of soil pH. phosphate solubilization is the result of combined effect of pH decrease and organic acid production (Fankem *et al*., 2006). Microorganisms through secretion of different types of organic acids (Deubel *et al*., 2000;) and rhizopheric pH lowering mechanisms (He and Zhu, 1988; Hinsinger, 2001) dissociate the bound forms of phosphates like $Ca_3(PO_4)^2$. Nevertheless, buffering capacity of the medium reduce the effectiveness of PSMs in releasing P from tricalcium phosphates (Stephen and Jisha, 2009). Acidification of the microbial cell sorroundings releases P from apatite by proton substitution / excretion of H+ (accompanying greater absorption of cations than anions) or release of Ca^{2+} (Villegas and Fortin, 2002). While the reverse when uptake of anions exceeds that of H^+ (Tang and Rengel, 2003). Carboxylic anions produced by PSMs, have high affinity to calcium, solubilize more P than acidification alone (Staunton and Leprince, 1996). Complexing of cations is an important mechanism in P solubilization if the organic acid structure favours complexation (Fox *et al*., 1990). lt is controlled by nutritional, physiological, and growth of microbial culture (Reyes *et al.*, 2007), but it is mostly due to the lowering of pH alone by organic acids (Moghimi *et al*., 1978) or production of microbial metabolites (Abda Alla, 1994). Organic anions and associated protons are effective in solubilizing forms of P, chaleting metal ions that may be associated with complexed forms of P or may facilitate the release of adsorbed P through ligand exchange reactions (Jones, 1998). Ca-P release results from the combined effects of pH decrease and carboxylic acids synthesis, but proton release cannot be the single mechanism (Deubel *et al*., 2000)

2.5. Solubilization of iron phosphate / aluminium phosphate (Fe- P / Al- P)

Solubilization of Fe and Al occurs via proton release by PSMs by decreasing the negative charge of adsorbing surfaces to facilitate the sorption of negatively charged P ions. Proton release can also decrease P sorption upon acidification which increases $H_2PO_4^-$ in relation to HPO_4^{2-} having higher affinity to reactive soil surfaces (Whitelaw, 2000). Carboxylic acids mainly solubilized Al-P and Fe – P (Khan *et al.*, 2007; Henri *et al.*, 2008) through direct dissolution of mineral phosphate as a result of anion exchange of PO_4^{3-} by acid anion, or by chelation of both Fe and Al ions associated with phosphates (Omar,1998). It is through root colonizing pseudomonads with high affinity Fe uptake system based on the release of Fe^{3+} chaleting molecules i.e. siderophores (Altomare *et al.*, 1999). Moreover, carboxylic anions replace phosphate from sorption complexes by ligand exchange (Otani *et al.*, 1996; Whitelaw, 2000) and chelate both Fe and Al ions associated with phosphate, releasing phosphate available for plant uptake after transformation. Ability of organic acids to chelate metal cations is greatly influenced by its molecular structure, particularly by the number of carboxylic and hydroxyl groups. Type and position of the ligand in addition to acid strength determine its effectiveness in the solubilization process (Kpomblekou and Tabatabai, 1994).

2.6. Soil P fixation

P. fixation is a serious problem in agricultural soils, particularly in highly weathered soils and those form from volcanic ash (Sanchez, 1976; Sanchez and Uehara,1980; Trolove *et al.*, 2003). Sanchez and Logan (1992) estimated that the soils exhibited high P fixation capacity of 1018 million ha / year in the tropics. And in tropical America, there are about 659 million ha affected, 210 million ha in Africa and 199 million ha in Asia. The term P fixation is used to describe reactions that remove bioavailable P from the soil solution into the soil solid phase (Barber, 1995). There are two type of reaction: (i) P sorption on the surface minerals and (ii) P precipitation by cations such as Al^{3+}, Fe^{3+} and Ca^{2+} in the soil solution (Trolove *et al.*, 2003).

P sorption is particularly strong on iron and aluminium hydrous oxides (crystalline or non-crystalline) that predominate in highly weathered soils of humid regions and acid savannas (Mattlingly, 1975). Trolove *et al.* (2003) characterized the P sorption by 11 Puerto Rican soils and found that the surface area of goethite was a primary factor accounting for P sorption , with gibbsite and hematite contributing little to P sorption. Jackman *et al.* (1997) observed similar results for Hawailian soils. Thus, P sorption was satisfactorily predicted by soil mineralogical composition.

In soils derived from volcanic ash parent materials, humus- Al / Fe complexes, allophones, ferrihydrite and goethite are the soil minerals responsible for strong P fixation observed (Parfitt, 1989; Schwertman and Herbillion 1992; Shoji *et al.*, 1993; Jackman *et al.*, 1997). On the other hand, in calcareous soils, P is sorbed on the surface of calcium carbonate (Mattlingly, 1975).

In acid soils, P precipitation occurs with active forms of aluminium (Al^{3+}, $Al(OH)_2^+$, $Al(OH_{)2}^+$ and Fe^{3+}), while in neutral and alkaline soils, it occur mostly with calcium (Ca^{2+}) (Bohn *et al.*, 1985). The extent of dominance of these cations depends mainly on the degree of weathering and soil pH. Phosphate ions precipitate to form initially amorphous (non – crystalline) compounds, becoming much more stable as crystalline forms are formed over time (Brady and Weil, 1999). Amorphous minerals are slightly more soluble than their crystalline forms because they have smaller particle size and consequently larger surface area. For instance, the crystalline mineral variscite ($AlPO_4.2H_20$) has a surface area of 1.54 m^2 / g ((Mattlingly, 1975) and its solubility product (K_{SP}) is $10^{-30.5}$ (Bohn *et al.*, 1985). On the other hand, its amorphous aluminium- phosphate counterpart has a surface area of 10.5 m^2 / g

(Sanchez and Uehara, 1980) and its K_{SP} is $10^{-28.1}$ (Veith and Sposito, 1977). In alkali soils, P compounds are similarly transformed to more insoluble forms. Initially P ions precipitate to calcium-monohydrogen-phosphate ($K_{SP} = 10^{-6.6}$) (Boul *et al.*, 1997), which is then converted to calcium- orthophosphate ($K_{SP} = 10^{-24}$), and finally to apatite ($K_{SP} = 10^{-55.9}$) (Snoeyink and Jenkins, 1980).

Fox and Kamprath (1970) showed that the degree of P fixation varies among soils with Andisols, Oxisols and Ultisols (USDA Taxonomy) having a high P fixation capacity (Boul *et al.*, 1997). These soils are usually acidic and generally have high amounts of exchangeable Al and clay minerals that can sorb high amounts of P (Sanchez and Uehara, 1980).

2.7. Organic matter and P interaction in the soil

In highly weathered soils, the phytoavailability of P can be greatly reduced through sorption to sesqiuoxides (Pushparajah,1998). Organic matter (OM) interacts with P in soils in a variety of ways that potentially influence these P sorption reactions (Saunders, 1965). As applied OM decomposes in the soil, carbon compounds are produced through microbial action that may react directly with P sorption sites in soil, potentially increasing the solution P concentration and, hence, P phytoavailability (Easterwood and Sartain, 1990; Bar-Yosef, 1996).

The direct effect of dissolved organic carbon compounds on P phytoavailability potentially includes several important processes. Competitive sorption between humic and fulvic acids (HA and FA) (Sibanda and Young, 1986) or low molecular weight organic acids (LMWOAs) and P for soil sorption sites result in increased concentration of P in the soil solution (Nagarajah *et al.*, 1970; Earl *et al.*, 1979; Traina *et al.*, 1987; Hue ,1991; Bolan *et al.*, 1996; Hue *et al.*, 1994). Similar LMWOAs are also produced by plant roots and can persist in the soil for varying period of time. Although competitive inhabitation has been considered the primary mechanism through which P and OM interactions increases solution P concentrations (Stauton and Leprince, 1996), metal complexation and desolution reactions (affecting Fe and Al soil oxides) (Lopez – Hermandez *et al.*, 1979; Traina *et al.*, 1987; Fox and Comerford, 1990, 1992; Bolan *et al.*, 1996) could potentially reduce the number of sorption sites, releasing P for plant uptake (Maurice *et al.*, 1995). Other direct effects of OM on P phytoavailability include increased formation of metal bridges leading to increased sorption of P (Levesque and Schnitzer, 1967; Lopez – Hermandez and Burnham, 1974; Wada and Higashi, 1976; Dalai, 1979; Owusu-Benoah and Acquaye, 1989). Several authors reported that sorption of OM compounds may increase the negative charge on the soil surface or decrease the point of zero charge (PZC) thus making it more difficult for P sorption to occur (Bowden *et al.*, 1980b; Lopez – Hermandez *et al.*, 1986; Easterwood and Sartain, 1990; Erich *et al.*, 2002). Finally, increased P phytoavailability may arise simply due to the P contained in the added OM (Dalai,1979).

Indirectly, addition of OM to the soil surface may improve the soil moisture regime, promoting root growth and hence the plants' exploitation of soil P reserves (Othieno, 1973; Parmar and Sharma, 1996 ; Erich *et al.*, 2002). Addition of OM may also cause structural changes in micro-aggregates, reducing the soil surface area, and consequently decreasing the number of potential P sorption sites (Agbenin and Tiessen, 1995; Linquist *et al.*, 1997; Wang *et al.*, 2001). Also indirectly, (Mokolobalate and Haynes (2003) OM addition can result in short-term increases in soil pH, thereby decreasing the likelihood of P sorption and increasing P phytoavailability. Similarly, decreases in soil pH following OM addition may have the opposite effect on P phytoavailability. However, caution is warranted in drawing firm conclusions regarding the effect of soil pH changes on P phytoavailability (Sumner and Farina, 1986).

2.8. Phosphorus mobilization

Richardson *et al.*(2009) defined mobilization as the initiation of P movement; solubilization and detachment are the two primary processes by which plant P may be mobilized. Solubilization indicates the transfer of P from a solid phase to a water phase and the driving is chemical non-equilibrium. Physical detachment brings in to suspension soil particles and colloids with attached P due to mechanical forces exerted by moving water. The reactions responsible for solubilization are dissolution/precipitation, sorption/ desorption and mineralization/organication that control the amount of P in the soil water both in inorganic and organic forms. To predict the risk of P mobility of solid soil particles, both the amount of P associated to the different size fractions and the dispersibility of soil particles as a function of soil properties and management practices must be evaluated

Due to the heterogeneity of the soil both the entity and the direction of the processes regulating P solubilization and detachment, vary substantially from one particle to the others, and both in vertical and horizontal directions determining the overall fate of the mobilized P. So researches aimed to develop a basis for understanding the mobilization processes regulating P export from soils to waters need to use a range of scale issues and of methods of investigation. Laboratory experiments have been designed to assess the relationships between soil properties, including P surplus, and potential P mobility. Profile or plot-scale experimental studies provide accurate data on P losses related to specific soil type, agronomic practices and climatic conditions; field scale research provides information P losses induced by particular land use and allows the assessment of heterogeneity within the systems. Laboratory, profile, plot and field studies cannot provide information on the fate of exported P beyond their individual boundaries but they do provide a means of determining the relative significance of individual processes and identifying the controlling factors. These two information are essential when considering system behavior at large scale (Zhang *et al*., 2010).

2.8.1. Phosphorus mobilization by soil micro organisms

Micro organisms directly affect the ability of plants to acquired P from soil through a number of structural or process-mediated Mechanisms. These include (i) an increase in the surface area of roots by either an extension of existing root systems (e.g mycorrhizae association) or by enhancement of root branching and root hair development (i.e growth stimulation through phythohormone), (ii) through stimulation of metallic processes that are effective in directly solubilizing and mineralizing P from poorly available forms of inorganic and organic P. These processes include excretion of hydrogen ion, the release of organic acids, the production of siderophores and the production of phosphate enzymes that are able to hydrolyse organic P. in particular, organic acids and associated protons are effective in mobilizing and solubilizing precipitated forms of soil P, chelating metal ions that may be associated with complex forms of P or may facilitate the release of adsorbed P through ligand exchange reactions (Jones, 1998).

Raghothama, (1999) established that plant roots effectively increase soil P acquisition through modified root growth and architecture and similarly produce metabolites that directly influence P availability. However, Isherwood, (2001) suggested that processes such as rhizosphere acidification, exudation of organic acids and secretion of phosphatase from plant roots occur in responds to P deficiency, and are established mechanisms by which plant acquired P. Furthermore, it has been suggested that microbial-mediated processes on their own may be insignificant in soil environments and are unlikely to mobilized sufficient P for plant requirements (Tinker, 1980).

2.9. Phosphorus and OM incubation

Incubating OM in soil, and subsequently determinining P sorption, reveals the net effect of fertilizer P and OM interactions. A number of studies have shown reductions in P sorption following incorporation of OM (Singh and Jones, 1976 ; Bumaya and Naylor, 1988 ; Iyamuremye, *et al*., 1996a ; Nziguheba, *et al.*, 1998). Yhe underlying mechanism for reduced P sorption has been attributed to a combination of increased Ph, decreased exchangeable Al and the amount of mineralized P released by the various OM sources (Iyamuremye, *et al.*, 1996a). Increased P availability has also been attributed to a combination of increased Ph and decreased exchangeable Al resulting in reduced P sorption. Easterwood and Sartain (1990) observed decreases in the PZC associated with the additions of white clover residue and P. A reduction in PZC would result in both greater CEC and inhibition of anion sorption, resulting in increased P availability to Plants. The authors concluded that the amount of P supplied in the white clover residue was unlikely to result in the doubling in dry matter yield and was observed where OM was applied, and hence the effect of the white clover residue on sorption had a dominant effect on P uptake and availability.

There are persistent claims attributing the improved P phytoavailability resulting from OM application to competition between DOC breakdown products from the OM and fertilizer P (Iyamuremye and Dick, 1996 ; Ngachie, 1996 ; Erich, *et al.,* 2002). In evaluating the results of these studies, it appeared that most of the decrease in P sorption due to organic matter addition can be accounted for by considering the amount of P mineralised from the added OM and not through competitive inhibition of P sorption by DOC compounds. Guppy *et al.*(2005) suggested that, rather than any change in the fundamental P response of the soil due to DOC production, the release of P from OM residues satisfies, at least to some extent, P sorbing sites, resulting in an apparent reduction in P sorption. A similar suggestion was proposed in a review by Haynes and Mokolobate (2001) of the role of OM additions in ameliorating Al toxicity and P deficiency in soil. This proposition is also supported by the conclusions of Iyamuremye, *et al.* (1996a), who observed that the P sorption response of soils amended with OM residues reflected the increase in soil extractible P concentration. Iyamuremye *et al.* (1996b) further suggested that the release of P from OM, and to a lesser extent (through mineralization), modified P sorption characteristics through reaction with potentially available sorption sites.

In many incubation experiments examining the influence of OM addition on P sorption, the OMis air – dried and ground prior to application (Singh and Jones, 1976 ; Iyamuremye *et al.*, 1996a ; Nziguheba *et al.*, 1998). The release of soluble P is usually greater from air-dried OM than from fresh material (Grierson et al., 1998). The early (up to 30 days incubation) P sorption reduction response to OM application observed by Singh and Jones (1976) could be attributed to the finely ground nature of the OM. Use of OM with P concentrations (>0.4%) increases the amount of rapidly released P (Hue, *et al.*, 1994 ; Bahl *et al.*, 1998). Of the many demonstrations of P sorption reduction due to OM incubation, the results of Nziguheba *et al.* (1998) deserve attention. These authors compared the influence of OM of high (tithonia 0.27% R 3.8%N) and low (maize stover 0.07%R 0.64%N) nutrient status on P sorption. After taking into account differences in P addition and rapidly soluble P release, P sorption was still significantly reduced by addition of tithonia, with the beneficial effects extended over four months. However, maize stover with only 25% of the P content of tithonia and added at 4 times the rate to maintain equal P additions, had no effect on P sorption capacity. Thus, high quality (and hence rapidly mineralisable) OM residues can in some instances decrease P sorption in highly weathered soils.

2.10. Phosphate Solubilizing Microorganisms (PSMs)

Evidence of the involvement of microorganisms in mobilization and solubilization of inorganic phosphates was reported as early as 1903 (Kucey *et al.*, 1989; Khan *et al.*, 2007). Since then, extensive studies on the solubilization of the mineral phosphates by microorganisms have been review (Tarafdar *et al.*, 2003; Archal *et al.*, 2007; Aseri *et al.*, 2009). Phosphate solubilizing microorganisms (PSMs) are ubiquitous, and their numbers varies from soil to soil. In general among the whole microbial population in soil P solubilizing bacteria constitute 1-50% and P solubilizing fungi 0.1-0.5 % of the total respective population (Chen *et al.*, 2006). Phosphate solubilizing bacteria generally out-number P solubilizing fungi by 2-150 folds (Kucey, 1983; Kucey *et al.*, 1989; Alam *et al.*, 2002). Most of the PSMs solubilize Ca-P complexes and only a few can able to solubilze Fe-P and Al-P (Kucey *et al.*, 1989). Hence, these PSMs could be effective in calcareous soils in which Ca-P complexes are present, but not in other soils such as Oxisols, Alfisols and Ultisols in which phosphates are comlexed with Fe and Aluminium ions (Tarafdar *et al.*, 2003; Aseri *et al.*, 2009). Most P solubilizing bacteria (Venkateswarul *et al.*, 1984) and fungi (Venkateswarul *et al.*, 1984; Tarafdar *et al.*, 2003; Yadav and Tarafdar 2010; Yadav and Tarafdar, 2011) were isolated from rhizosphere of various plant and are known to be metabolically more active than those isolated from sources other than rhizosphere. The phosphate solubilizing ability in bacteria was lost upon repeated sub culturing but no such loss has been observed in the case of phosphate solubilizing fungi (Kucey, 1983). In general, fungal isolates exhibit greater P solubilizing ability than bacteria in both liquid and solid culture (Venkateswarul *et al.*, 1984; Kapoor *et al.*, 1989)

2.10.1. Soil microbial biomass phosphorus and contribution to plant nutrition

Oberson, *et al*. (2001) reported that the microbial biomass in soil contain a significant amount of P (as high as 100 kg P ha^{-1}) and generally account for 2 to 5% of the total P and around 10 to 15% of the soil organic P . But they further observed that microbial P is a dynamic component of a soil P cycle and is responsive to soil fertility, seasonal conditions and management practices.

A number of studies have highlighted the potential importance of microbial P in providing available P to plants. Seasonal dynamics indicates that significant amount of P are released from the biomass in response to moisture deficiency, and it is estimated that soil microbial P is completely turned over at least annually (He, *et al*., 1997). The actual P-turnover through microorganisms makes to the mobilization of soil P therefore remain to be fully determined. Nevertheless, it is well known that soil P is significantly depleted in close proximity to roots, that roots release significant quantities of C that is available to soil micro organisms and that microbial populations in the rhizosphere are enhanced by many orders of magnitude (Bowen and Rovira,1999)

2.11. Organic acids in soils.

Important factors that determine the competitive efficacy of LMWOAs with P in soils include composition, concentration and sorption of organic acids and their persistence in soils (Mokolobalate and Haynes, 2003).

2.11.1. Composition and concentration

Dissolved organic carbon (DOC) consists of HA, FA, tannic acid, LMWOAs and aromatic acids, amines, polysaccharides and numerous other carbon compounds (Stevenson, 1994). Extracted concentration ranges up to 75 mmol kg^{-1} soil, although the median (≥ 4mmol/kg) is markedly lower (Zsolney 1986). Soil solution DOC concentration ranges from 0.2 TO 2.5 mM (Drever, 1994), although higher concentrations (16-60 mM) have been observed under temperate forests (Mokolobalate and Haynes, 2003), mostly as high molecular weight organic acids (HMWOAs) compounds. Solubility, and hence concentration of HMWOAs DOC compounds is reduced at low pH (Bolan *et al*., 1996) due to strengthened of self assembling, heterogenous, and smaller humic molecules (Piccolo, 2002).

Jones (1998), observed that the major sources of LMWOAs in the soils are plant exudation, OM decomposition and microbial synthesis. Also in his findings, he reported that the concentration of LMWOAs in plant materials is 10-100 times higher than that found in soil due to their role in cell metabolic processes (Jones, 1998). Therefore, addition of OM to the soil results in a rapid, short-term increase in LMWOA concentration (Baziriamakenga., *et al*, 1995). Approximately 2-10% of the total DOC in soils consists of LMWOAs (Fox and Comerford,1990; Stevenson, 1994). The prevalence of common LMWOAs varies between soils, but monocarboxylic LMWOAs (i.e acetate, formate, lactate) are present in greater concentrations than dicarboxylic acids (i.e oxalate, malate) or tricarboxylic acids (i.e. citrate). Most of these data, with the exception of those reported by Hue *et al*, (1986) and Baziriamakenga *et al*, (1995), are from the temperate soils with high total organic carbon (>5%). These conditions are unlikely to occur in high P-sorbing tropical soils in which competitive inhibition of P sorption following OM addition has been proposed. For example, George *et al*., (2002) dictated no LMWOAs in the bulk soil or rhizosphere of maize (Zea mays) or tithonia (Tithonia diversifolia) grown in Kenyan Oxisol.

Another factor affecting the magnitude of LMWOA concentrations in soil solution is the method of extraction. Higher concentrations of LMWOAs were extracted from recently re-wet air dried soils (Elkhatib 1990; Baziriamakenga *et al*., 1995), values are likely to decrease along with decrease in DOC as reported by Menzies and Bell (1988). A recent review (Jones *et al*., 2003) highlighted these low and relatively constant concentrations of organic acids in solution and hypothesized that sampling procedures may be inadequate, that LMWOA concentration may be extremely localized in soil microsites (and hence underestimated), and that extremely high solid phase buffering of LMWOA solution concentration may be widespread.

Soil LMWOA have been derived predominantly from work on forest soils; LMWOA concentration may be substantially lower in arable soils. strobel *et al*.,(1999) reported that LMWOA concentration were approximately one-third lower in adjacent cultivated land than in forest soil. Some plant species exude LMWOAs in response to P and iron (Fe) deficiency (Imas *et al*., 1997; Geelhoed *et al*., 1999) and to toxic monomeric aluminium (Al) (Hocking, 2001). This increases the phytoavailability of Fe and react with and detoxified Al. the amount of LMWOAs produced sometimes constitutes 30-40% of the total carbon released from roots, depending on both plant species and soil pH (Bar – Yosef, 1996; Hocking, 2001). Consequently, the concentration of LMWOAs in the rhizospheres is often considerably higher than that in bulk soil (Jones, 1998), but elevated rhizosphere LMWOA concentration is not universal, being soil – and plant – specific. Recently, many instances have been reported where there are no differences, or only minimal differences, between bulk and rhizosphere soil LMWOA concentrations (George *et al*., 2002)

2.11.2. Sorption and persistence of organic acids

Processes governing the persistence of LMWOAs in soils are important in determining the potential of DOC to successfully compete with sorption sites. Three important processes affect DOC persistence; microbial activity, metabolic availability of the cation substrate, and sorption to soil colloids. For example, 10-40% of DOC in soil was rapidly mineralized by native soil biota (Kalbiltz *et al*., 2003), and Jones (1998) reported that LMWOAs were degraded in as little as 2-3 hours to soil at realistic (10-100 mM) concentrations. Factors affecting microbial activity (i.e. aeration, moisture, temperature and pH) greatly influence the rate at which DOC mineralized in soil (Paul and Clark, 1989; Kusel and Drake, 1998).

Paul and Clark (1989) concluded that soil heterotrophs utilize a wide range of C substrates to gain metabolic energy. Compounds vary in resistance to microbial attack, affecting their persistence in the soil (Hue, 1991). The more humified the OM from which DOC is derived, the greater the resistance to microbial attack (Kalbiltz *et al*., 2003). Bioavailability of the C substrates is also affected by physical accessibility to soil biota for mineralization. The interaction of cations with DOC compounds can increase DOC structural stability by linking negatively charged functional groups of DOC together. These stable metals – DOC complexes can then adsorb to soil colloids (through cation bridging) further decreasing the physical accessibility of the DOC to microbial attack (Swift, 1999; Piccolo, 2001). Thus, sorption of DOC compounds to soil colloids protects them from microbial degradation (Kalbitz *et al.*, 2003) and increases the potential efficacy of competitive reaction between P and OM (Jones and Edwards, 1998; Geelhoed *et al*., 1999)

Sorption of simple LMWOAs to soils and synthetic oxides conforms to principles of inorganic anion sorption (Barrow, 1987) and occurs primarily through ligand exchange (Appelt *et al*., 1975a; Fox and Comerford, 1990). Similar to P sorption, the reactions of LMWOAs in the soils are closely linked to soil sesquioxides and the relative affinity for mineral surfaces is similar to that of P (amorphous Al compounds > ferrhydrite > goethite) (Jones and Brassigton, 1998; Kaiser and Zech, 1998). Jones and Brassigton (1998) demonstrated that the ligand exchange reaction of LMWOAs are weak, rapidly saturating the anion sorption capacity of the soils examined. The amount sorbed followed the series phosphate>>> oxalate> citrate> malate>> acetate. Shen *et al*., (1996) found that <25% of 10 mM addition of malate, oxalate or citrate were recoverable from a Spodosol under beech forest, reflecting the soil's sorption preference for di- and tri- carboxylic acids. The preference for di- carboxylic and tri-carboxylic acid groups reflect the greater stability constant for complexes with Fe or Al in solution or on colloid surfaces and their increased capacity to form bidentate ligand exchange bonds. In comparison, complete recovery of some monocarboxylic acids (e.g. acetate) was observed. The recent review of Jones *et al*., (2003) questioned many of the techniques used to determine LMWOA sorption, highlighting the confounding of sorption estimation with mineralization of the added C substrate.

2.11.3. Competitive sorption of Decomposable Organic Carbon (DOC) and P

Competition sorption, in this context is the process whereby organic anions and P compete for the same sorption sites in soils. Many studies have been undertaken to assess the competitive effect of LMWOAs on P sorptions in soils and synthetic surfaces. The direct effects of DOC compound on P phytoavailability include several important processes. Competitive sorption between humic and fluvic acids (Sibanda and Young, 1986; Agbenin and Igbokwe, 2006) or LMWOAs aliphatic acids and P for sorption sites result in increased concentrations in the soil solution (Hue *et al*., 1994). Sorptions of OM compound may also increased the negative charge in the soil surface or decrease the point of zero charge (PZC) thus making it more difficult for Psorption to occur (Easterwood and Sartain, 1990; Erich *et al*., 2002).There are few studies, however, using DOC compounds. Furthermore, most research has been undertaken on materials with high P sorption capacity, such as allophone-rich inceptisols, oxide –rich Oxisols and Ultisols, and synthetic Al compounds. Concentrations of the LMWOA or DOC compounds used in many competition studies have ranged up to 300 mM. This is substantially greater than native soil LMWOA concentrations, which rarely exceed 10 mM in soil solution.

He *et al*.,(1998) reported that many of the experiments may have been affected by methodological inadequacies. They further explained that high LMWOAs concentrations (1.5 mM for oxalate and 3.0 mM for citrate) inhibit measurement of P in methods using phosphomolybdate blue. Consequently, incorrectly high P sorption may have been reported in some competition studies, because LMWOA interference resulted in the underestimation of P remaining in solution P concentrations used in many DOC or LMWOA, and P competition studies were also higher than those observed in soils outside of fertilizer application bands. However, despite these limitations, useful conclusions can be drawn regarding competition between P and DOC compounds in soils and synthetic oxides

2.11.4. Competition between P and Low Molecular Weight Organic Acids (LMWOAs)

Sorption of P in the presence of LMWOAs is dependent on the concentration and type of the LMWOAs present, pH, the nature of the adsorbent, and the background electrolyte used (Barrow *et al*., 1980; Violante and Gianfreda, 1995). Although low concentrations of LMWOAs have been reportedly reduce P sorption, even at high P concentration (Nagarajah *et al*., 1970; Hue, 1991), the efficacy of LMWOAs in reducing P sorption is greatest at high adsorbent concentrations (Earl *et al*.,. 1979; Lopez-Hermandez *et al*., 1986). Competitive efficacy decreases in the order tricarboxylic> dicarboxylic > monocarboxylic LMWOAs (Bolan *et al*., 1996; Violante and Gianfreda 1995; Wang *et al*., 2008; Gang *et al*., 2012). These authors observed low dissociation constants of LMWOA. They concluded that sorption of these ligands as the pH decreases and thus, competitive inhibition of P sorption should increase with a decrease in soil pH. the stability of LMWOA – metal (Fe and Al) complexes also affect P sorption (Earl *et al*., 1978; Cajuste *et al*., 1996), the more stable complexes being more effective in preventing P sorption (Bar- Yosef, 1996). Generally, materials high in oxides (e.g. gibbsite, goethite) show the greatest response to competitive inhibition on P sorption because of the capacity of these materials to form stable Fe and Al complexes and ligand exchange bonds (Nagarajah *et al*., 1970; Earl *et al*., 1979). Some LMWOAs (particularly oxalate) demonstrate greater competitive efficacy on specific adsorbents (e.g. Al hydroxides) (Cajuste *et al*., 1996; Violante *et al*., 1996).

The competitive sorption reactions between P and LMWOA anions conform to a behavior predicted by the mechanistic model of Bowden *et al*. (1980a). Both P and most LMWOAs are multiprotic anions, indicating that the species and charge of the anion in solution is affected by pH. When two anions are present in solution, competition is expressed either through direct physical competition for sorption sites (Hingston *et al*., 1971) or through electrostatic competition arising in the 'plane of adsorption' following adsorption of the respective anions (Bowdenn *et al*., 1980b). this second effect, a consequence of increased negative surface charging following adsorption, can occur where concentrations are not high enough for physical competition for sites to become significant and will be higher where anions sorbed to the surfaces in the 'plane of adsorption' (Bowden et al., 1980b). When considering the competition between LMWOAs and P for sorption sites, both negative surface charging and physical competition are involved and need to be considered.

Table1. Phosphorus and organic acid content of some LMWOAs

Residues	Phosphorus content (mg/100g dry weight)	TA	CA (%)	OA
Tamarind pulp	138	13.2		
Orange waste	82		18.3	
Amaranthus leaves	67			10.5

TA = Tartaric acid, CA = Citric acid and OA = Oxalic acid

Sources: Ishola *et al*.,(1990); O'brien and Price (2008) and Olubukola *et al.*,(2010)

Afift *et al*. (1994) examined the ability of P to competitively displace adsorbed LMWOAs from Brazilian Oxisol over time. They reported that addition of P released 1-9 (micro) mol LMWOA/g (predominantly oxalate and malate), increasing both with the amount of P applied and with time. Slow P displaced approximately 2 moles of LMWOA for each mole of P adsorbed and was correlated with the ratio of OM, to specific surface area. The greater the proportion of 'active' (sorbing) surface covered by OM, the slower the subsequent P sorption. Importantly, sorption of P was only delayed, not prevented, by the presence of OM. The authors concluded, however, that even a small delay in P sorption may be useful in optimizing the timing of P fertilizer application to highly weathered soils, increasing the uptake of P by plants.

Both decreased microbial activity and substrate bioavailability are important in prolonging the persistence of LMWOAs in soils. Hue (1991) examined the competitive sorption processes between LMWOAs and P in laboratory batch studies and in field experiments.

Laboratory experiments indicate malate to be the most efficient competitor of P for soil sorption sites. In the field, however, the greatest beneficial effect of LMWOA addition (i.e. increased P phytoavailability and plant growth) was observed with protocatechuate, a compound that is more resistant to microbial breakdown. There is generally a rapid increase in microbial biomass and activity, and hence, in LMWOA production, following the OM addition to soil. The increase is transient and related to the amount of the easily utilizable C substrate (Chantigny, 2003). The most common explanation for increased P phytoavailability following incorporation of OM in soil is that DOC, particularly LMWOAs, produced during the decomposition of the OM competitively inhibits P sorption. The concentration of the LMWOAs in soil solution, however, is critical in determining whether any inhibition of P sorption will occur. Inhibition of P sorption is often justified on the basis of batch competition studies demonstrating that at concentrations of 1-10 mM, significant inhibition of P sorption occurs (Strom *et al*., 2002). Baziramakenga *et al*. (1995) reported that increased monocarboxylic acids (e.g. acetate and formate) concentrations occurred in soil following incorporation of OM.

2.11.5. Competition between P and High Molecular Weight Organic Acids (HMWOAs)

The possible role of HMWOA compounds in reducing P sorption needs careful examination, given their high concentration in the soil solution. Both Humic and Fluvic acid complexes are soluble under agronomically suitable pH conditions. As with LMWOAs, competition between these compounds and P for sorption on soil colloids may result in higher solution P concentration. Leaver and Russell (1957) pre-treated a Tanzanian Oxisol with FA and measured a 27 – 63% reduction in P sorption. However, after 10 days, the efficacy of FA additions in reducing P sorption decreased up to 25%. Sibanda and Young (1989) also observed a significant reduction in the sorption of P on gibbsite, goethite and 2 highly weathered soils after the addition of HA or FA. FA was more effective than HA in reducing P sorption, with the greatest effects observed on gibbsite (Sibanda and Young, 1986 and 1989). The competitive ability of both HA and FA increases at lower pH (Sibanda and Young, 1986; Heng, 1989), corresponding with the sorption maximum identified for HA compounds by Nambu and Yonebayashi (1999). A diffuse peak around pH 4-5 strongly related to the number of carboxylic (-COOH) groups. Additions of HA and FA, also reduced P sorption (< 10%) in 5 highly weathered soils of Malaysia (Heng, 1989).

Humic acid and FA do not only compete with P for sorption sites, but in many instances, act as a P sorbing surfaces also (Appelt *et al*.,1975b). The propensity of HA to sorb P is closely correlated with Fe and Al content, particularly Al (Wada and Higashi 1976; Heng 1989; Owusu-Bennoah and Acquaye 1989). In some soils, reaction of metals with HA and FA greatly increase P sorption, and are critical to P cycling processes (Turner *et al*., 2007). Pushparajah (1998) suggested that in highly weathered soils, sorption of P to HA or FA may help alleviate problems associated with high P fixation through the slow mineralization of these complexes. That HA may have detrimental effect on P availability was demonstrated by Othieno (1973), who repeatedly observed yield decreases and lower tissue P concentrations when P and HA were added to highly weathered soils. Further elucidation of the relationships between HA or FA and P in competitive sorption processes is necessary, specifically because both increase and decreased P phytoavailability may result.

2.12. Mineralization of organic phosphate

Mineralization of soil organic P plays an imperative role in P cycling of a farming system. Organic P may constitute 4- 90% of the total soil P. Almost half of the microorganisms in soil and root possess P mineralization potential under the action of phosphatases (Tarafdar *et al*., 2003). Mineralization of organic to inorganic phosphate involved processes catalyzed by phosphatase enzymes. Which are specifically involved in this conversion? Acid and alkaline phosphatases use organic phosphate as a substrate to convert it into inorganic form (Beech *et al*., 2001). Principal mechanism for mineralization of soil organic P is the production of acid phosphatases (Hilda and Fraga, 1999). Release of organic anions and production of siderophores and acid phosphatase by plant roots / microbes (Yadav and Tarafdar, 2001) or alkaline phosphatase (Tarafdar and Clasen, 1988) enzymes hydrolyze the soiln organic P or split P from organic residues. Many PSMs produce these enzymes (Tarafdar *et al*., 1988; Tarafdar *et al*., 2003; Aseri *et al*., 2009). In addition, some fungi produce phytase, an enzyme which releases soluble inorganic (PO_4^{3-}) phosphate from organic P compound (inositol hexaphosphate) (Tarafdar and Gharu. 2005; Yadav and Tarafdar, 2007; Yadav and Tarafdar, 2011).

Some heterotrophic microorganisms are also capable of solubilizing phosphates combined with calcium or magnesium (Atlas and Bartha, 1988). Thease soluble forms can now be readily take up by plants, algae, cyanobacteria and autotrophic bacteria and assimilated into organic cellular components such as DNA, RNA and ATP. Phosphatase enzymes are present in all organisms but only bacteria, fungi and some algae are able to secrete them outside of their cells. As exoenzymes, they participate in the dissolution and mineralization of organic phosphate compounds in the environment (Yadav and Tarafdar, 2007).

CHAPTER THREE

3.0 MATERIALS AND METHOD

3.1.1 Study location

The studies were conducted at two different locations with different pedogenic characteristics during 2011 and 2012 cropping seasons. The locations are Minna (9^{o}31’N, 6^{o}30’E) and Mokwa (9^{o}18’N, 5^{o}05’E) classified as Haplic Plinthosol (Typic Plinthustalfs) and Rhodic Nitosol (Rhodic Kandiustalfs) respectively (FAO, 2006; USDA, 2003).The rationale behind the field trials at different locations for this study is to obtain soil groups/types with a wide range of physico – chemical characteristics that will profoundly affect phosphate adsorption and organic acid interaction. Minna is located in Chanchaga Local Government Area, while Mokwa is located in Mokwa Area of Niger State. The two locations are in the Southern Guinea Savanna (SGS) agro-ecology zone of Nigeria.

The field trials were conducted at the Teaching and Research farm of Federal University of Technology, Gidan Kwano – Minna and College Experimental field of Niger State College of Agriculture, Mokwa.

3.1.2 Climate

Both Minna and Mokwa are located in in the sub – humid climatic zone of the tropics and are influenced by two air masses, the South Westerly Monsoon and North Easterly dry harmattan. These are responsible for the distinct wet and dry seasons in the area. The locations experiences a mean annual precipitation of 1200mm (90% of which falls between the months of June and August).

Fig. 1: Map of Niger State showing the location of the experimental sites

Temperatures rarely fall below 22^{o}C, while wet season temperature averages about 28^{o}C. The peaks are 38^{o}C (February – March) and 34^{o}C (November – December) (Ojanuga, 2006).

3.1.3 Geology

The soils of Minna and Mokwa are derived from basement complex rocks and Nupe sand stone respectively. They ranged from shallow to very deep soils overlying deeply weathered geises, granites, quartzites, schist and magmatites which gave rise to a wide variety of soil (Bennett,*et al*., 1979). Some are underlain by iron pan at varying depth. Alhassan, *et al*. (2012) and Lawal, *et al*. (2012) observed quartz to be prominent mineral constituents of the soils around the study locations. They are strong brown to red sandy clay especially soils of Mokwa area.

3.1.4 Vegetation

These locations are belt of complex vegetation zones, being and fired and a continuous attempt by the plants to adapt themselves to the climatic changes. The trees therefore developed long tap roots and truck barks to enable them survive the long dry season and resist bush fire (Okoye *et al*., 1995). These locations are characterized by the following vegetations: *Andropogon spp, imperata cylindrical, Doniella spp, Isoberlina doka, Parkia biglobosa, Vitellarias spp, Tamarindus indica, Hyparrhenia spp.e.t.c*

3.2 Soil sampling and preparations

Prior to the ploughing of the field, soil samples were collected randomly at 0 – 20cm from each location of the experimental plots using auger and sample bags. The samples were bulked, mixed together, air dried and sieved to pass through 0.5 and 2mm sieves. The resultant sub samples of soil collected were subjected to three different laboratory studies. These included; physico-chemical analysis, sorption and incubation studies. Post harvest soil samples were also taken at the end of each cropping season at the same depth for same routine analysis to observe the changes in such properties.

3.3 Laboratory studies I: 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 was 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.

Phosphorus adsorption isotherms for these soils were obtained using the methods described by Fox and Kamprath (1970). In order to obtain adsorption capacities and the constants related to the bonding energy, the following form of Langmuir equation was employed: $C/(x/m) = 1/kb+c/b$. Where C = P concentration in equilibrium solution, x/m = P adsorbed by the soil (µg g^{-1}), b = adsorption maximum (µg g^{-1}) k = a constant related to the bonding energy of the soil for P or affinity constant.

3.4 Laboratory studies II : 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 were 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

(iv) Soil with oxalic acid

The bottles were covered with a plastic film with a small opening at a temperature of $25^{o}C$ and 40% soil moisture based on soil mass for an incubation period of 3 weeks. The bottles were weighed periodically and brought 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 soil was then air dried and pass through 2mm sieve. The following determinations were made: soil organic and inorganic P fractions.

Table 2. Properties of Low Molecular Weight Organic Acids (LMWOAs) used during laboratory studies.

Organic Acids	Formula	Molecular weight
Tartaric acid	$HO_2CCH(OH)CH(OH)CO_2H$	150
Citric acid	$HOOCCH_2 (COOH)(OH)CH_2COOH$	192
Oxalic acid	HOOCCOOH	90

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

3.5 Field studies

3.5.1 Experimental Design

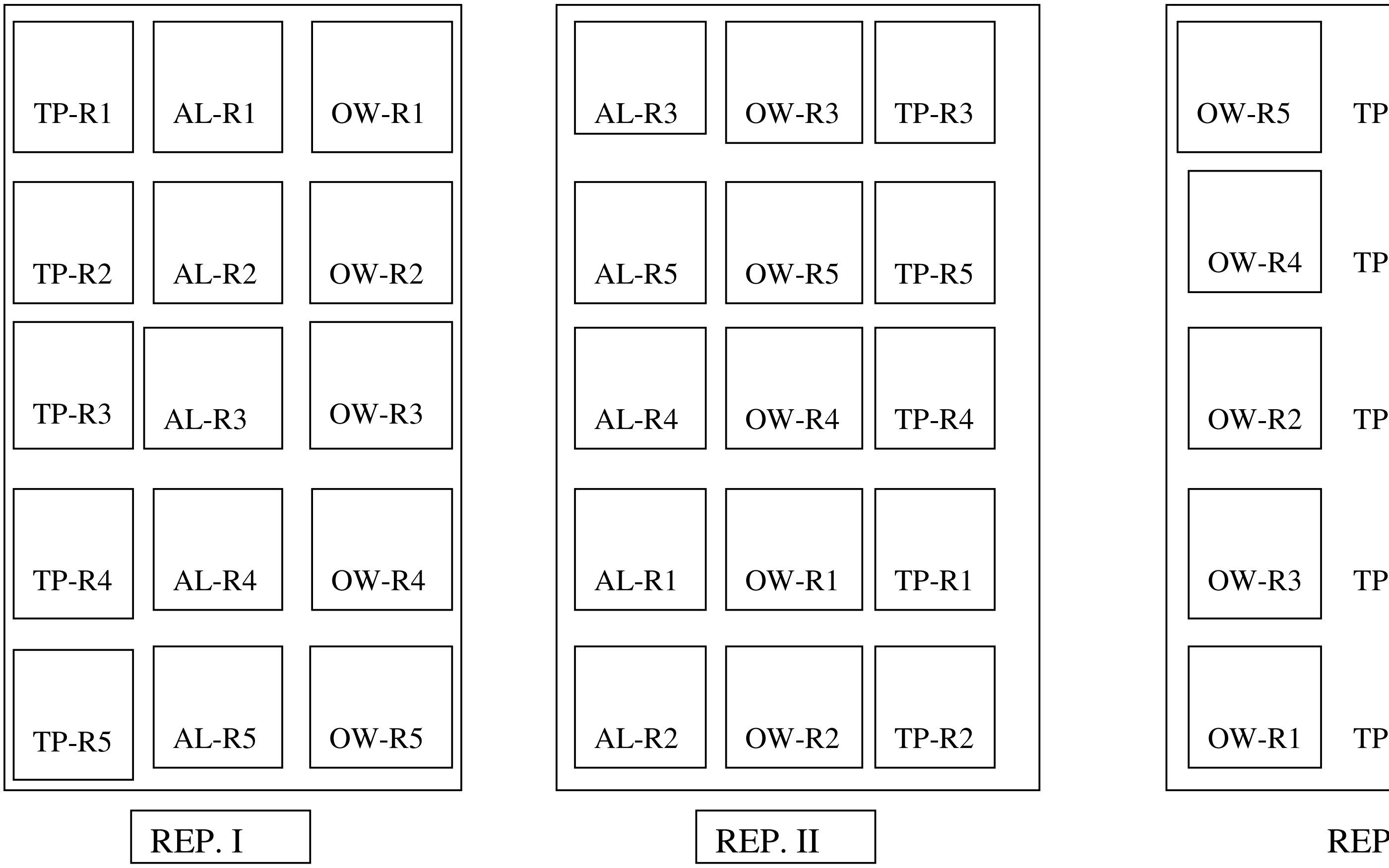
The experimental design used was split plot with organic acid source occupying the main plot while the rates of application was assigned to the sub-plot at three replications in each of the locations.

3.5.2 Treatments

1. Three organic acid source
    - i. Tamarind pulp (tartaric acid)
    - ii. Orange waste (citric acid)
    - iii. Amaranthus leaves (oxalic acid)
2. Five rates of application
    - i. 0 tons ha^{-1}
    - ii. 2.0 tons ha^{-1}
    - iii. 4.0 tons ha^{-1}
    - iv. 6.0 tons ha^{-1}
    - v. 8.0 tons ha^{-1}

3.5.3 Field management

Maize was the test crop used for the purpose of this experiment (maize is one of the major common crop grown by the farmers in both locations). The field was cultivated manually using hoe. Prior to the cultivation, these organic materials were crushed, grounded and applied by broadcasting on the field two weeks before sowing for both 2011 and 2012 cropping season. Three seeds/stand (at intra-row spacing of 50cm and inter-row spacing of 75cm) was planted and later thin to two, 2 weeks after planting (WAP). Each plot size measured 6m x 5.4m and 1m distance between two plots. At 2 and 6 WAP, 120kg N, 60kg P_2O_5 & 60kg K_2O ha^{-1} was applied as basal application.



NB: TP = Tamarind pulp, AL = Amaranthus leaves, OW = Orange waste and R1, R2, R3, R4, R5 = Rates

Fig. 2: Layout of the treatments at both Minna and Mokwa experimental sites.

Three seeds/stand (at intra-row spacing of 50cm and inter-row spacing of 75cm) was planted and later thin to two, 2 weeks after planting (WAP). Each plot size measured 6m x 5.4m and 1m distance between two plots. At 2 and 6 WAP, 120kg N, 60kg P_2O_5 & 60kg K_2O ha^{-1} was applied as basal application.

Weeding was carried out at 4 and 7 WAP. During the growing period of maize, parameters such as: plant height at 4 and 8 WAP was observed. On maturity, the maize was harvested, threshed and the grain yield weight was determined for each treatment.

NB. The same field experiment of 2011 was repeated during 2012 cropping season. All the sampling was confined within the four inner ridges.

3.6 Post harvest soil analysis

The soil samples at 0 – 20cm depth from each treatment plot were taken after each year's harvest for various forms of soil inorganic P analysis at the laboratory of Department of Soil Science, Federal University of Technology , Minna.

3.7 Laboratory Analysis

3.7.1 Soil Characterization

Some selected physico – chemical analysis carried out on these soils are described as described below:

3.7.1.1 Particle size: Determination of soil textural class was carried out using hydrometer method after dispersion with 5% sodium hexametaphosphate according to the procedure described by I.I.T.A (1976).

3.7.1.2 pH: The soil pH was determined in duplicate. i.e. in distilled water and 1.0 N KCl solution using a soil - solution ratio of 1:2 (McLean, 1982).

3.7.1.3 Organic Carbon: Organic carbon was determined using finely ground soil samples by Walkley and Black dichromate oxidation method as described by I.I.T.A (1979).

3.7.1.4 Available P: The available P was determined by the Bray P 1 method (Bray and Kurtz, 1945).

3.7.1.5 Total N: This was determined using the Kjeldahl method as described by I.I.T.A (1979).

3.7.1.6 Cation Exchange Capacity (CEC): This was determined using the neutral ammonium acetate (1.0 N. NH_4 OAC) method in which 0.1N KCl solution was also used to counter leached and from the leachate, CEC was determined according to the procedure described by Thomas (1982).

3.7.1.7 Exchangeable Bases: Na and K were determined from ammonium leachate using flame photometer. While, Ca and Mg was determined by titration method as described by Thomas (1982).

3.7.1.8 Exchangeable Acidity (EA): This was determined titrimetrically using 1.0N KCl extract (McLean, 1982).

3.7.2 Fractionation of soil organic phosphorus

Various fractions of soil organic P were extracted sequentially from the treated soils and measured according to the procedure described by Chang and Jackson (1957).

3.7.2.1 NH_4Cl – P

One gram of soil was taken in a 50 ml polyethylene centrifuge tube, 25 ml of 1 M NH_4Cl solution was added and shaken for 30 minutes. Supernatant solution after centrifugation was taken for NH_4 – P determination which was estimated by molybdate sulphuric reagent using stannous chloride as reductant after taken the extractant in a 10 ml isobutyl alcohol. The blue colour was measured in a spectrophotometer at 660 nm.

3.7.2.2 Aluminium Phosphate (Al – P)

The soil residue left in the centrifuge tube after the extraction of NH_4 – Cl was shaken for one hour with 25 ml of 0.5 ml of NH_4F (pH 8.2). The suspension was centrifuged to get a clear solution. Phosphorus in the solution was determined by chloromolybdic – boric acid method using stannous chloride as a reductant. The intensity of the blue colour developed was read in a spectrophotometer at 660 nm.

3.7.2.3 Iron Phosphate (Fe – P)

The soil sediment that remains after Al-P determination was washed with 25 ml of saturated NaCl shaking and centrifuging. The soil sediment was then treated with 0.1 M NaOH, shaken and centrifuged after 15 hours. The supernatant was then treated with 4 – 5 drops of H_2SO_4 Phosphorus in the solution was determined by chloromolybdic – boric acid method using stannous chloride as a reductant. The intensity of the blue colour developed was read in a spectrophotometer at 660 nm.

3.7.2.4 Occluded Phosphate (Occl – P)

The residue left after the estimation of Fe – P was then added 25 ml of 1 N NaOH and shaken for 1 hour. Supernatant solution after centrifugation was taken for estimation of Occl – P. Phosphorus in the solution was determined by chloromolybdic – boric acid method using stannous chloride as a reductant. The intensity of the blue colour developed was read in a spectrophotometer at 660 nm.

3.7.2.5 Calcium Phosphate (Ca – P)

The soil sample after the extraction of Occl – P was washed twice with 25 ml of saturated NaCl and washings were discarded after centrifuging. Ca – P was then extracted by using 0.25 M H_2SO_4 and shaken for 1 hour and centrifuged for 5 minutes. Supernatant solution after centrifugation was taken for estimation of Ca– P. Phosphorus in the solution was determined by chloromolybdic – boric acid method using stannous chloride as a reductant. The intensity of the blue colour developed was read in a spectrophotometer at 660 nm.

3.7.2.6 Total Phosphorus (Total – P)

One gram of 0.5 mm sieved soil was weighed and transferred to a 300 ml platinum crucible and 30 ml of 60% $HClO_4$ was added and digestion was carried out on sand bath at 130°C till the dense fumes of $HClO_4$ was evolved. When the digestion was completed, the flask was removed and cooled. 50 ml of distilled water was added to the flask and the solution was filtered into a 100 ml volumetric flask and the volume was made to mark with distilled water. An aliquot from this was used for the estimation of Total –P by using Vanodomolybdophosphoric acid reagent and the intensity of yellow colour was read at 470 nm in spectrophotometer (Jackson, 1967).

3.7.3 Free oxides of iron and aluminium

3.7.3.1 Crystalline form of iron oxide

Twenty gram of 2 mm sieved dried soil was taken with 80 ml citrate -bicarbonate solution in a centrifuge tube and kept on hot water bath. When the contents attained a temperature of 75°C, the suspension was stirred and 1 gram of sodium dithionate was added and stirred again for 1 minute. Later, it was stirred intermittently for 15 minutes without rising in temperature beyond 80°C. After cooling, 10 ml of saturated NaCl solution was added and centrifuged.

Supernatant was collected in a 500 ml volumetric flask. Iron content in the solution was estimated by using orthophenonthroline method (Jackson, 1973). Free oxides of Fe content was expressed as Fe_2O_3 multiplying the free Fe content with a factor 1.43.

3.7.3.2 Crystalline form of aluminium oxide (free Al – Oxide – CBD)

The citrate –bicarbonate- diothionate extract was used to estimate free Al. Free Al in the extract was determined by aluminon method as described by Jackson (1973). The free oxide of Al was expressed as Al_2O_3 multiplying the free Al estimated with a factor 1.89.

3.7.3.3 Amorphous forms of iron and aluminium.

One gram of air dried soil was taken in a centrifuge tube and 50 ml of 0.2 m of acidified ammonium oxalate of pH 3 was added and shaken for 4 hours in the dark (Mckeague and Day, 1966). The suspension was centrifuge and supernatant was collected. The residue was washed with buffer. The supernatant and washings were made up to a known volume and Fe in the extract were determined colorimetrically it is by orthophenonthroline method, while Al in the extract was determined by aluminon method as described by Jackson (1973).

3.8 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 and specific pair-wise comparison of treatment means was also done using the Least Significance Difference (LSD) at 5%.Correlation analysis was carried out to examine relationship between soil P and soil physic – chemical properties

CHAPTER FOUR

4.0. RESULTS

4.1 Physico – Chemical properties of the experimental sites.

The result obtained for some selected physico – chemical properties of the soils used for the experiments is shown in Table 3. The textural class of soil collected from both sites were sandy clay loam .The soils had a moderately acidic reaction with soil pH (H_20) of 6.07 and 5.92 for Minna and Mokwa sites respectively. Exchangeable acidity ($H^+ + Al^{3+}$) values were low in the soil (< 0.92 cmol kg-^{1})

The organic carbon content and the available P content of the soils were low while the soils total N was very low for the both location. The exchangeable bases was observed to be low and was in the decreasing order Ca > Mg > K > Na for the both sites. Effective cation exchange capacities were also low for these soils although, higher values are obtained for Minna soils compared to Mokwa soils.

Table 3. Initial physico – chemical properties of the soils of the experimental sites.

Soil properties	Site	
	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_20	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

4.2. **Phosphorus sorption characteristics of the soil**

Phosphate adsorption isotherms

Phosphate adsorption isotherms of the soil site used in the study were determined by plotting the equilibrium concentration of P (C) against the amount of phosphate adsorbed (X). The graphic representation of the adsorption isotherms of the two soils studied had different curves (Fig.3). It was observed that the curve followed a smooth plateau pattern. It is evident from the curves that the rate of P adsorption increased with the increase in the equilibrium concentration of P, but at a certain point of higher concentration, the level of P become almost constant with little or no capacity to adsorb P. Sorption of PO_4 was higher in Mokwa ultisols than the Minna alfisols (Table 4). The result of the study showed that Mokwa soil had the value of maximum adsorption of 138.50 mg kg^{-1} while Minna soil had the value of 105.21 mg kg^{-1} .The amount of PO_4 sorbed was also observed to be higher at a lower P equilibrium concentration than at a higher concentration (Fig.3) for the two soils.

Langmuir adsorption isotherm showed a good fit when sorption data were fitted to the adsorption equation by taken C/X against C (Fig.4). The highest R^2 value of 0.985 was observed for the Mokwa soil and the lowest was observed in the Minna soil with a value of 0.962 (Fig.4).

The comparison of the Langmuir adsorption maxima (b) for the two soils series showed that maximum values of adsorption were 144.53 and 113.96 mg kg^{-1} for Mokwa and Minna soil samples respectively (Table 4). It was also observed that the Langmuir evaluation gave higher maximum value for adsorption than the actual calculated value and the Minna soil had the lower affinity constant (K) compared to Mokwa soil.

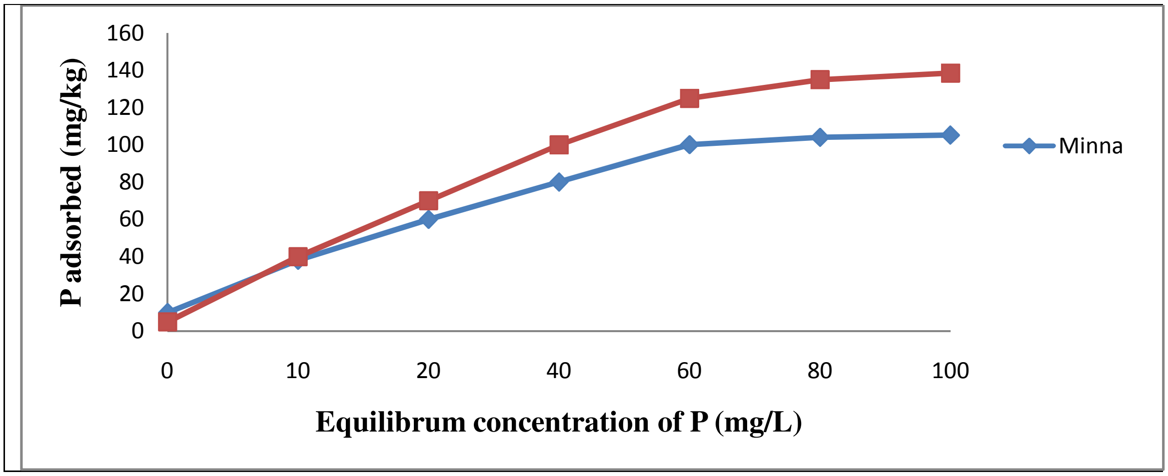


Fig.3. Phosphate adsorption isotherm of the soils of the studied sites.

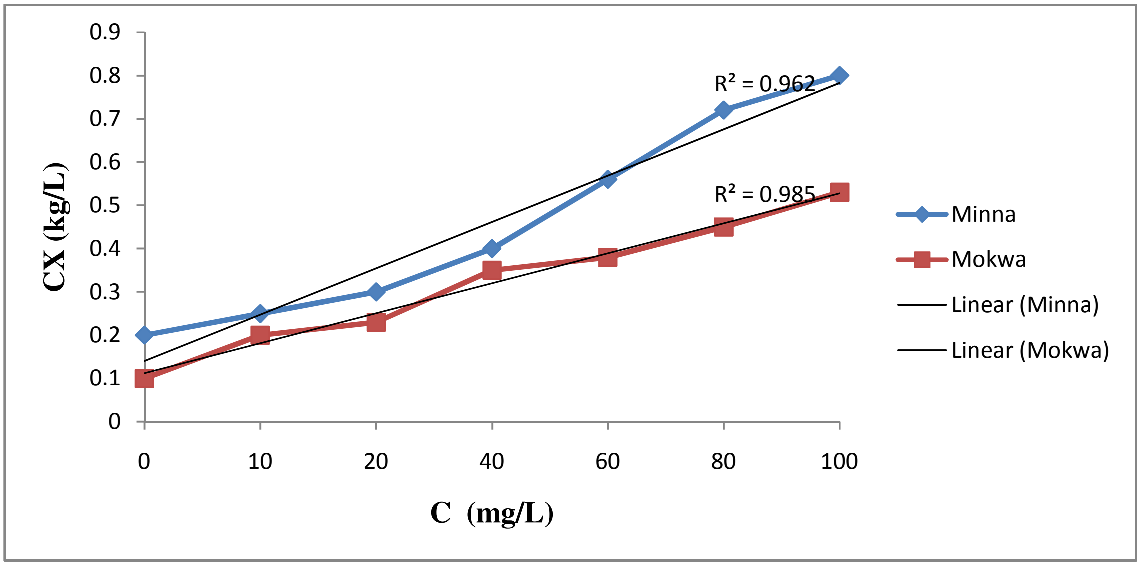


Fig. 4. Langmuir isotherm of the studied soils

Correlation between some soil properties with Langmuir constants (Table 5) showed that P adsorption was significantly correlated with clay (r = 0.81*), exchangeable acidity (r = 0.96**), and pH (r = 0.98**) but negatively correlated with organic C (r = - 0.96**).

Table 4. Comparison of Langmuir adsorption maxima (b) and affinity constant (k) for the soil sites.

Soil series	Adsorption maxima (b) (mg kg^{-1})	Affinity constant (k) (ml μg^{-1})
Minna series	113.96	2.83
Mokwa series	144.53	2.42

Table 5. Correlation between some soil properties and adsorption maxima

Soil properties	Adsorption maxima (b)
Soil pH	0.98**
Exch. Acidity	0.96**
Org. C	-0.96**
Clay content	0.81*

** - Significant at 1% level, * - Significant at 5% level

4.3 Inorganic P fractions

4.3.1. Olsen P.

Results obtained for the Olsen P fraction of the pre – planting soils of the studied sites are shown in Fig. 5. Olsen P was significantly ($P < 0.05$) increased by the additions of the three organic acids irrespective of locations where soil samples was collected. The magnitude of the increment in Olsen – P was higher in location B (Mokwa) compared to location A (Minna) except with the tartaric acid addition. The order of increase for Olsen P by the additions of the organic acids was citric > tartaric > oxalic.

4.3.2. NH_4Cl- P

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 increased after treatment with the three organic acids (Fig. 6). On the average from the two locations, citric, tartaric and oxalic acids increased NH_4Cl – P by 45, 25 and 15 mg^{-1} respectively. Their capacity for P mobilization appears to follows the order of citric acid > tartaric acid > oxalic acid. These were observed on the soils of the two locations studied.

4.3.3. Occluded P (Occl – P)

Figure 7 represents the Occl – P fractions of the soil samples collected from Minna and Mokwa locations prior to the cultivation. Contrary to the previous results, the effect of organic acids additions on Occl –P contents was significantly ($P > 0.05$) lower than the control irrespective of the location were soils were sampled. However, In both location, the order of decreased occl – P was observed to be oxalic> tartalic > citric acids.

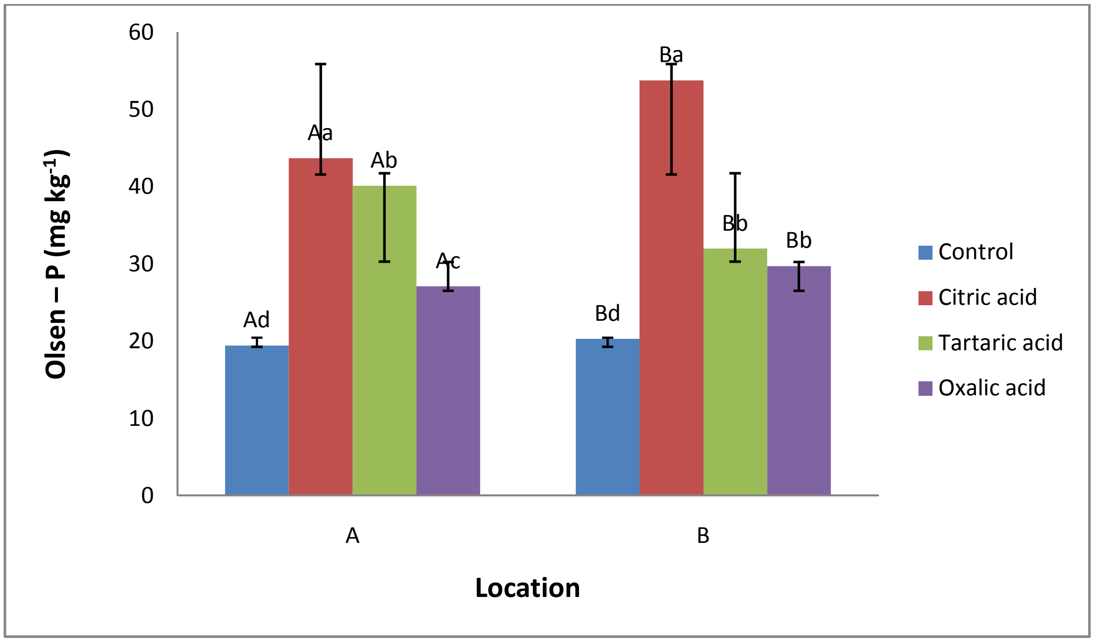


Fig. 5: Olsen - P fraction of soils following organic acid treatments.

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.

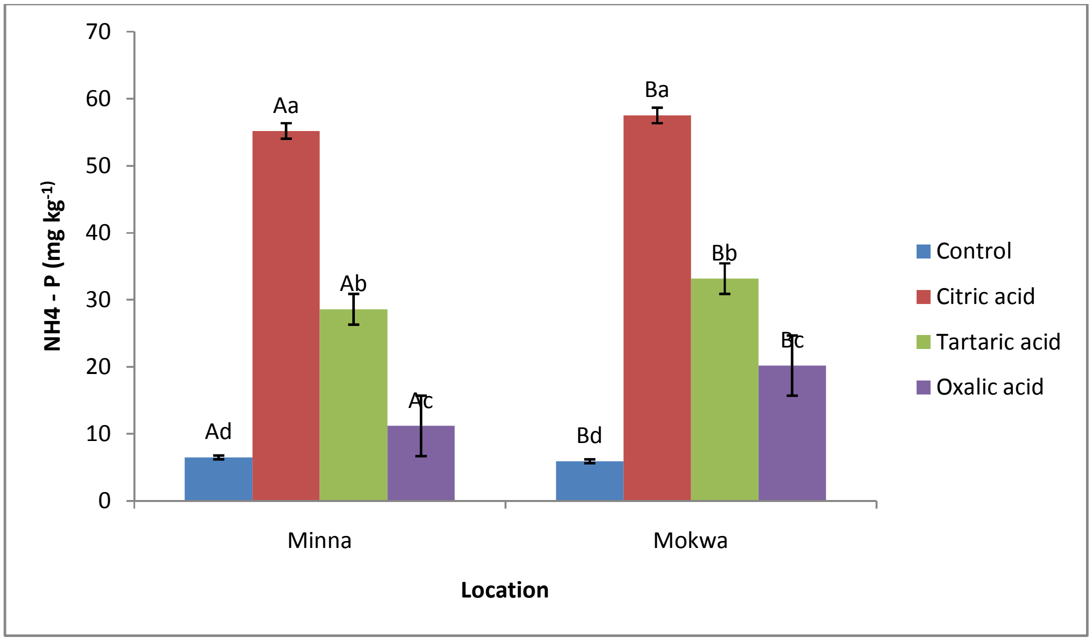


Fig. 6:NH_4Cl - P fraction of soils following organic acid treatments.

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.

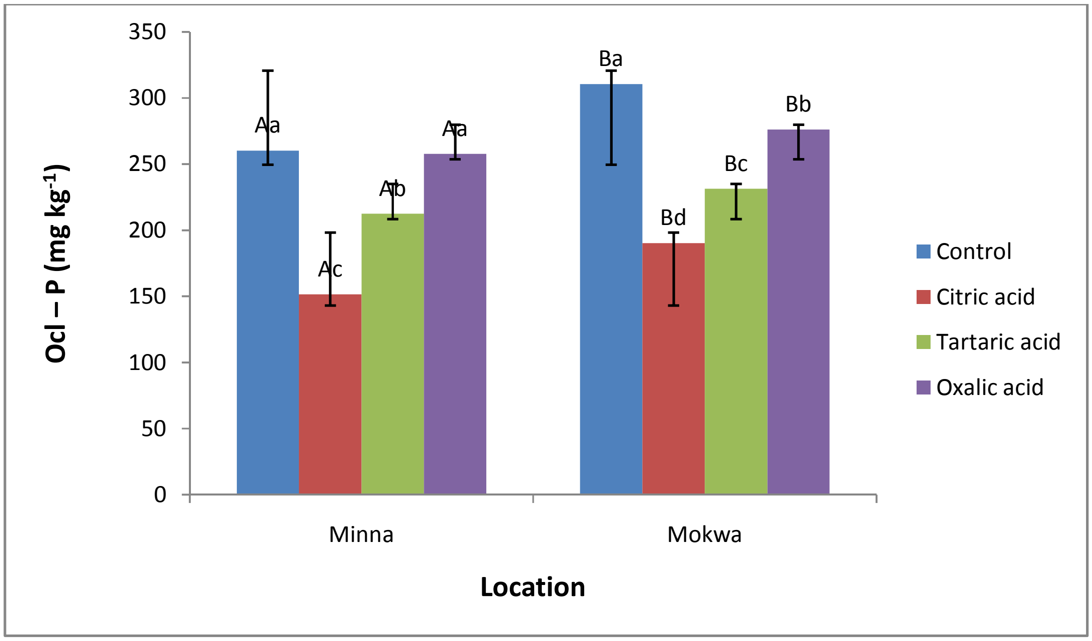


Fig. 7: Occl - P fraction of soils following organic acid treatments.

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.

4.3.4 Aluminium – P (Al-P)

Similar to the results obtained above, the concentration of Al – P of the soil under the control treatment was also significantly higher than when the organic acids were added irrespective of the location where the soil samples were collected (Fig. 8). In only Minna location, it was also observed that the effect of citric acid addition on Al –P was significantly lower than concentration of Al- P when either oxalic or tartaric acids were added.

4.3.5 Iron – P (Fe – P)

The results obtained for the Fe – P of the soils from the two experimental sites are shown in Fig 9. It was observed that the Fe – P content of these soils was dependent on the type of organic acids added. Although the Fe – P contents of soils without organic acid addition (control) was significantly ($P> 0.05$) greater than the Fe – P of those soils that were treated the organic acids in each locations. The Fe – P on these soils as a result of the application of organic acids followed the same pattern. The order of decrease was observed as oxalic > tartaric > citric acids

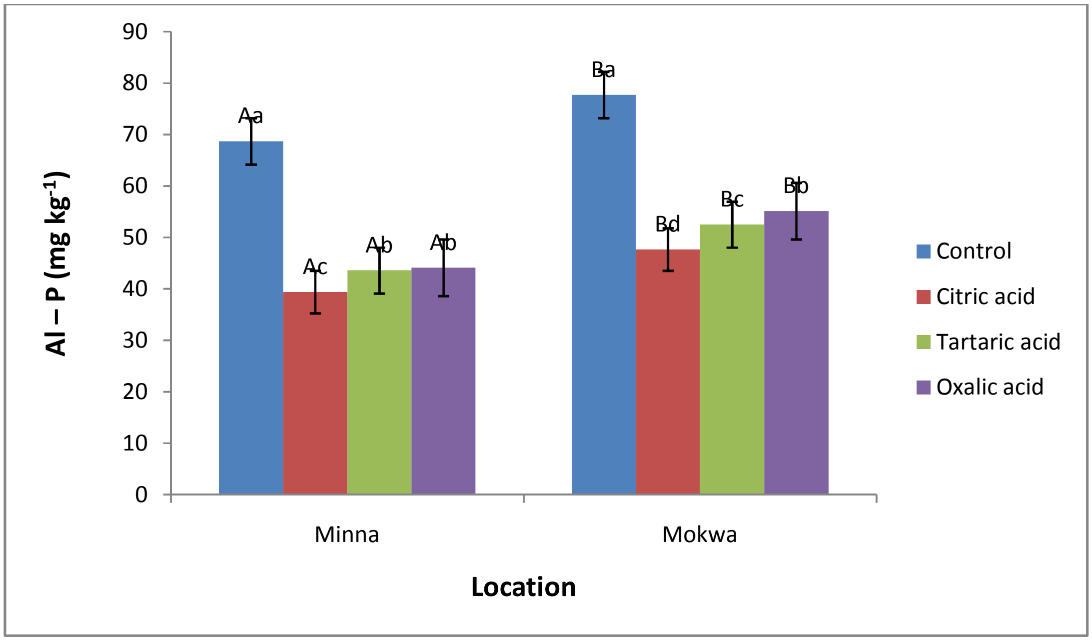


Fig. 8: Al - P fraction of soils following organic acid treatments.

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.

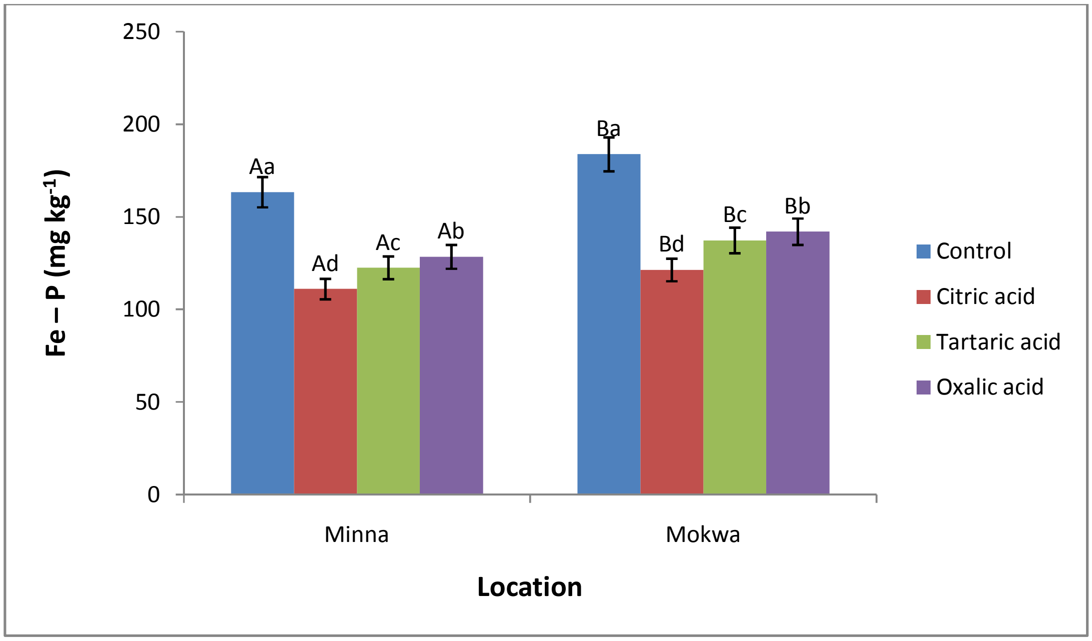


Fig. 9: Fe - P fraction of soils following organic acid treatments.

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.

4.3.6 Calcium –P (Ca – P)

Figure 10 represents the effects of organic acid additions on the availability of Ca – P from soil types from different locations. It was observed that the applications of organic acids significantly reduced the Ca-P contents of these soils compared with soils without organic acid additions (control). The reduction in the Ca –P was also observed to be dependent on the type of organic acid involved in each of the locations. Additions of citric acids caused significantly ($P> 0.05$) larger reduction compared to when tartaric or oxalic acids were added. There were no significant differences between oxalic and tartaric additions in each of the location

4.3.7 Total - P

The effects of various organic acid additions on soil Total – P is presented in Fig 11. The result showed that there was a significant differences within the organic acids used in Minna location. Soils with citric acid additions had significantly higher total P than those treated with tartaric and oxalic acids. In Mokwa location, there were no significant differences observed within the organic acids used. Although generally, there was significant differences between those soils treated with organic acids and control in each of the locations.

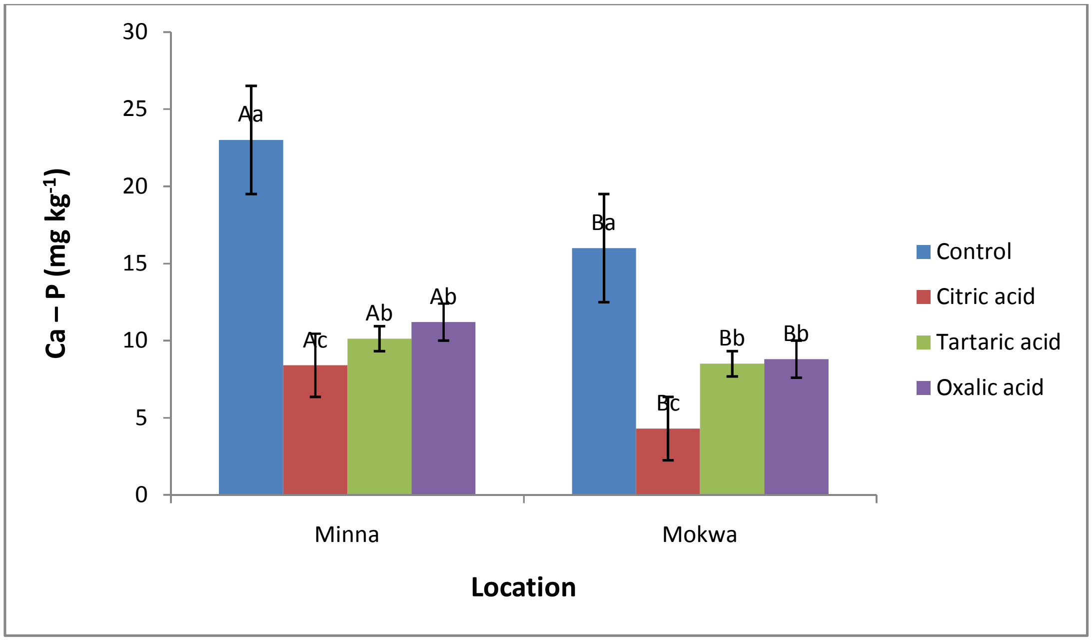


Fig. 10: Ca - P fraction of soils following organic acid treatments.

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.

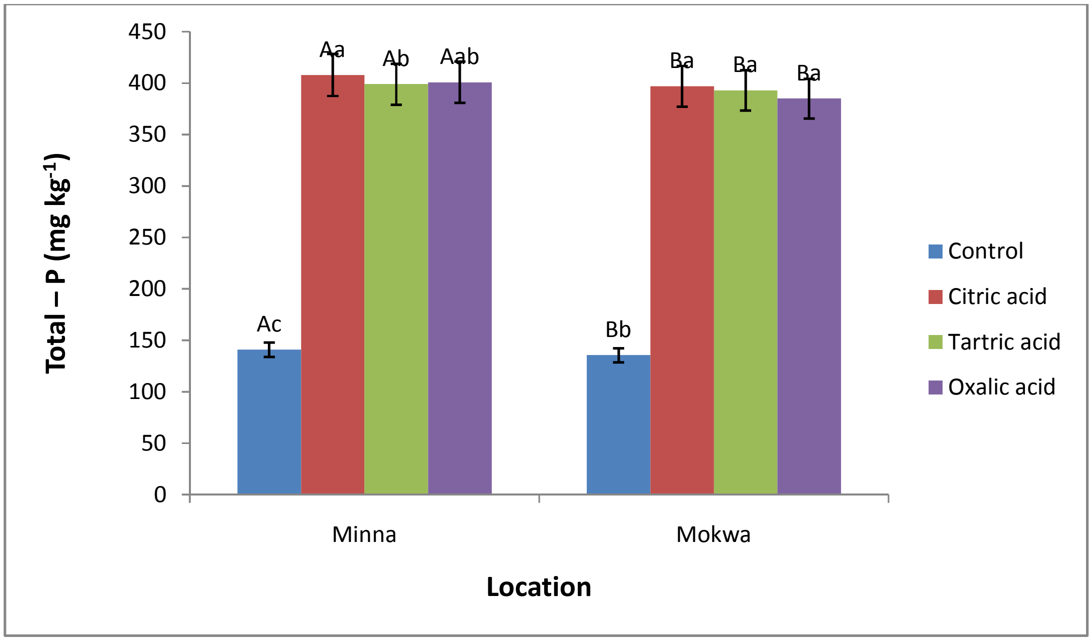


Fig. 11: Total- P fraction of soils following organic acid treatments.

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.

4.4 Plant height of maize (4WAP) at Minna in 2011 and 2012 seasons.

The results obtained on the effect of different organic acid sources and rates on plant height (4WAP) at Minna in 2011and 2012 seasons are shown in Table 6. It was observed that there was a significant difference ($P<0.05$) in maize plant height in both 2011 and 2012 cropping season as the height of the maize increases with increasing rates of organic acids. Although, the effects of the organic acid source on maize plant height was not significant ($P <0.05$) during 2011 cropping season, it was however significant at 2012 cropping season. The interaction between organic acid source and rates of application on maize plant height was not significant in both 2011 and 2012 seasons.

4.5 Plant height of maize (4WAP) at Mokwa in 2011 and 2012 seasons.

Similar to the results obtained above, the effect of different rates of organic acids on plant height was significantly ($P< 0.05$) taller than the control irrespective of the type of the organic acid used in both 2011 and 2012 season (Table 7). It was observed that the maize were taller in 2012 than 2011 cropping season at 4WAP. There was no significant differences ($P> 0.05$) in maize plant height among the organic acid sources in both 2011 and 2012 cropping season. Also, the interaction between the organic acid source and their rates of application was found not be significant ($P> 0.05$).

Table 6. Plant height of maize (cm plant^{-1}) 4 WAP at Minna 2011 and 2012 cropping seasons as affected by organic acid source and rates.

ORGANIC ACID SOURCE	RATE (t/ha)					
	0	2	4	6	8	MEAN
			2011			
Orange waste	70.03	85.13	96.63	96.13	94.40	88.50
Tamarind pulp	70.10	85.37	96.47	97.33	93.23	88.50
Amaranthus leaves	71.67	88.47	89.43	88.53	96.70	86.96
MEAN	70.60	86.34	94.00	94.14	94.79	
			2012			
Orange waste	73.90	95.00	103.46	104.53	104.43	96.87
Tamarind pulp	72.03	83.93	90.63	84.63	89.20	86.21
Amaranthus leaves	74.90	87.00	92.40	85.30	91.43	84.08
MEAN	73.61	88.44	91.48	95.02	95.50	

LSD 5%	2011	2012
Organic Acid Source	NS	4.57
Rates	5.94	5.89
Organic Acid * Rates	NS	NS

NS = Not significant at P≤ 0.05.

Table 7. Plant height of maize (cm plant^{-1}) 4 WAP at Mokwa 2011 and 2012 cropping seasons as affected by organic acid source and rates.

ORGANIC ACID SOURCE	RATE (t/ha)					
	0	2	4	6	8	MEAN
			2011			
Orange waste	71.63	85.90	84.00	93.40	95.97	86.18
Tamarind pulp	72.50	82.76	86.93	90.60	92.23	85.01
Amaranthus leaves	69.07	80.13	84.70	88.73	91.03	82.73
MEAN	71.06	82.93	85.21	90.91	93.08	
			2012			
Orange waste	77.90	101.03	107.16	109.96	105.36	100.29
Tamarind pulp	89.06	101.03	104.40	106.93	109.67	102.22
Amaranthus leaves	83.57	100.12	103.57	103.84	105.53	99.31
MEAN	83.51	101.03	105.04	106.58	106.86	

LSD 5%	**2011**	**2012**
Organic Acid Source	NS	NS
Rates	6.01	5.89
Organic Acid * Rates	NS	NS

NS = Not significant at P≤ 0.05.

4.6 Plant height of maize (7WAP) at Minna in 2011 and 2012 seasons.

The effects of the organic acid sources and levels of their application on plant height at 7WAP is presented in Table 8. The height of the maize was significantly higher on those plots that received organic acids than the control plot in both 2011 and 2012 cropping season. However, the effect of sources of organic acid on maize plant height was not significant during 2011 cropping season but was significant during 2012 cropping season. Also, the interaction between the organic acid source and their rates of application was found not be significant ($P > 0.05$) in both cropping seasons.

4.7 Plant height of maize (7WAP) at Mokwa in 2011 and 2012 seasons.

Table 9 represents the results for the effect of organic acid sources and their levels of application on maize plant height at 7WAP in Mokwa during 2011 and 2012 cropping season. Similar to the result obtained for Minna, the maize plant height was significantly taller on organic acid treated plots as compared to the control plots irrespective of the two cropping seasons. The effect of sources of organic acid on maize plant height was found to be significant only during 2011 cropping season. The interaction between organic acid source and rates of application on maize plant height was not significant in both 2011 and 2012 seasons.

Table 8. Plant height of maize (cm plant^{-1}) 7 WAP at Minna 2011 and 2012 cropping seasons as affected by organic acid source and rates.

ORGANIC ACID SOURCE	RATE (t/ha)					
	0	2	4	6	8	MEAN
			2011			
Orange waste	187.77	203.73	219.30	218.37	212.77	208.38
Tamarind pulp	184.60	205.83	214.00	214.53	207.37	205.27
Amaranthus leaves	191.77	196.90	207.63	209.63	206.90	202.57
MEAN	188.04	202.16	213.64	214.19	209.01	
			2012			
Orange waste	192.87	210.13	227.40	217.60	217.00	213.30
Tamarind pulp	150.53	162.37	169.63	170.63	171.97	165.00
Amaranthus leaves	157.57	160.93	156.50	158.37	166.23	159.94
MEAN	166.99	177.81	182.20	184.51	185.07	

LSD 5%	2011	2012
Organic Acid Source	NS	7.89
Rates	7.90	5.89
Organic Acid * Rates	NS	NS

NS = Not significant at P≤ 0.05.

TABLE 9. Plant height of maize (cm plant^{-1}) 7 WAP at Mokwa 2011 and 2012 cropping seasons as affected by organic acid source and rates.

ORGANIC ACID SOURCE	RATE (t/ha)					
	0	2	4	6	8	MEAN
			2011			
Orange waste	185.57	200.53	201.93	214.53	212.93	203.10
Tamarind pulp	188.60	200.36	200.37	201.07	204.00	198.88
Amaranthus leaves	188.30	198.93	200.23	202.36	204.07	198.78
MEAN	187.49	199.94	200.84	205.98	207.00	
			2012			
Orange waste	193.00	204.33	209.30	219.26	219.53	209.09
Tamarind pulp	194.90	203.93	201.40	205.57	208.70	203.43
Amaranthus leaves	189.20	201.13	208.33	210.33	208.17	202.90
MEAN	192.38	203.13	206.34	211.72	212.13	

LSD 5%	**2011**	**2012**
Organic Acid Source	NS	4.51
Rates	7.30	5.82
Organic Acid * Rates	NS	NS

NS = Not significant at P≤ 0.05.

4.8 Maize grain yield (t ha^{-1}) at Minna in 2011 and 2012 seasons.

The effects of the organic acid sources and their levels of application on the yield of maize in 2011 and 2012 seasons at Minna are shown in Table 10. In both years, there was a significant differences in the maize grain yield among the levels of organic acid application with control plots having the lowest maize grain yield. Similarly, the effect of sources of organic acid on the maize grain yield in Minna was also found to be significant. Plots with citric acid additions produced significantly higher yield as compared to those plots that received tartaric and oxalic acids in both years. There was a reduction in grain yield in 2012 in both tartaric and oxalic acids treated plots from the 2011 yields. The interaction between the organic acid sources and the rates of application was however significant during 2012 and 2013 cropping season.

4.9 Maize grain yield (t ha^{-1}) at Mokwa in 2011 and 2012 seasons.

The maize grain yield at Mokwa location was significantly higher on organic acid treated plots compared to non organic acid treated plots (control) in both 2011 and 2012 cropping season (Table 11). It was also observed that the maize grain yield was also found to be dependent of the type of organic acid applied as the application of citric acid gave the highest yield, while the application of oxalic acids produced the least yield irrespective of the cropping season. Contrary to what was obtained from Minna, there was an increase in maize grain yields in 2012 in all the treatments from 2011 yields. The interaction between the organic acid sources and rate of application on maize grain yield was only significant in 2012 cropping season.

TABLE 10. Maize grain yield (t ha^{-1})at Minna in 2011 and 2012 cropping seasons as affected by organic acid source and rates.

ORGANIC ACID SOURCE	RATE (t/ha)					
	0	2	4	6	8	MEAN
			2011			
Orange waste	4.86	5.20	5.68	5.64	5.63	5.41
Tamarind pulp	4.83	5.22	5.24	5.27	5.30	5.17
Amaranthus leaves	4.91	4.98	5.13	5.14	5.24	5.08
MEAN	4.87	5.13	5.35	5.35	5.40	
			2012			
Orange waste	5.07	5.35	5.81	5.83	5.97	5.61
Tamarand pulp	3.54	3.87	3.87	3.94	4.10	3.87
Amaranthus leaves	3.52	3.69	3.82	3.86	3.88	3.75
MEAN	4.04	4.30	4.50	4.55	4.65	

LSD 5%	**2011**	**2012**
Organic Acid Source	0.08	0.10
Rates	0.11	0.13
Organic Acid * Rates	*	*

* = Significant, NS = Not significant at P≤ 0.05.

TABLE 11. Maize grain yield (t ha^{-1}) at Mokwa in 2011 and 2012 cropping seasons as affected by organic acid source and rates.

ORGANIC ACID SOURCE	RATE (t/ha)					
	0	2	4	6	8	MEAN
			2011			
Orange waste	4.82	5.26	5.30	5.40	5.47	5.25
Tamarind pulp	4.87	5.26	5.21	5.21	5.19	5.15
Amaranthus leaves	4.80	5.03	5.11	5.10	5.17	5.04
MEAN	4.83	5.18	5.21	5.24	5.28	
			2012			
Orange waste	5.97	5.46	5.53	5.64	5.68	5.47
Tamarind pulp	4.97	5.33	5.35	5.43	5.58	5.33
Amaranthus leaves	4.96	5.23	5.31	5.29	5.42	5.24
MEAN	4.98	5.34	5.39	5.45	5.56	

LSD 5%	**2011**	**2012**
Organic Acid Source	0.08	0.05
Rates	0.10	0.06
Organic Acid * Rates	NS	*

* = Significant, NS = Not significant at P≤ 0.05.

4.10 Soil Olsen – P (mg kg^{-1}) at Minna 2011 and 2012 seasons

Results of the effect of organic acid sources and levels of application on soil Olsen – P at Minna in 2011 and 2012 seasons are shown in Table 12. Generally, there was a significant reduction in the Olsen –P in both cropping seasons when levels of organic acids added were increased with the highest concentration of Olsen –P on the control plots. Also, the effect of organic acid sources on Olsen - P was observed to be significant in both2011 and 2012 cropping seasons. The influence of organic acid sources and their levels of application interaction on Olsen –P was also found to be significant in both 2011 and 2012 session.

4.11 Soil Olsen – P (mg kg^{-1}) at Mokwa 2011 and 2012 seasons

Similar to the results obtained above, the concentration of soil Olsen –P at Mokwa during 2011 and 2012 season significantly decreases with increasing organic acid rates (Table 13) irrespective of the organic acid source. It was also observed that the concentration of Olsen – P from this location was dependent on the sources of organic acid applied with highest concentration on plots that received citric acids. While those plots that received oxalic acids showed the least concentration of Olsen – P irrespective of the cropping season. The interaction between the sources and rates of application on soil Olsen – P was found to be significant in both 2011 and 2012 season.

TABLE 12. Soil Olsen - P (mg kg^{-1})at Minna 2011 and 2012 cropping seasons as affected by organic acid source and rates.

ORGANIC ACID SOURCE	RATE (t/ha)					
	0	2	4	6	8	MEAN
			2011			
Orange waste	32.01	51.73	56.53	64.33	66.77	54.27
Tamarind pulp	31.90	48.43	51.40	56.23	57.97	49.17
Amaranthus leaves	31.70	35.67	41.27	47.80	51.87	41.66
MEAN	31.87	45.28	49.73	56.13	58.87	
			2012			
Orange waste	34.77	55.67	61.03	68.43	70.57	58.09
Tamarind pulp	33.20	51.27	54.27	58.77	59.87	51.48
Amaranthus leaves	34.23	38.90	44.10	50.77	54.27	44.45
MEAN	34.07	48.61	53.13	59.32	61.57	

LSD 5%	**2011**	**2012**
Organic Acid Source	0.58	0.68
Rates	0.78	0.88
Organic Acid * Rates	*	*

* = Significant at P≤ 0.05.

TABLE 13. Soil Olsen - P(mg kg^{-1}) at Mokwa 2011 and 2012 cropping seasons as affected by organic acid source and rates.

ORGANIC ACID SOURCE	RATE (t/ha)					
	0	2	4	6	8	MEAN
			2011			
Orange waste	34.03	64.77	71.17	76.27	78.63	64.97
Tamarind pulp	34.63	44.46	49.17	52.13	52.26	46.93
Amaranthus leaves	34.50	38.73	43.66	47.33	48.57	42.56
MEAN	34.39	49.32	54.67	58.58	59.82	
			2012			
Orange waste	36.07	68.93	76.00	80.60	81.97	68.71
Tamarind pulp	37.33	48.10	52.93	56.40	56.38	50.21
Amaranthus leaves	36.30	43.42	47.47	50.30	51.43	45.59
MEAN	36.57	53.16	58.80	62.43	63.26	

LSD 5%	**2011**	**2012**
Organic Acid Source	0.91	0.77
Rates	1.18	0.99
Organic Acid * Rates	*	*

* = Significant at P≤ 0.05.

4.12 Soil NH_4Cl – P (mg kg^{-1}) at Minna 2011 and 2012 seasons

Table 14. represents the effect of organic acid sources and rates of application on soil NH_4Cl – P at Minna during 2011 and 2012 cropping season. There was a significant increase in NH_4Cl - P with increasing rates of organic acids irrespective of the sources in both 2011 and 2012 seasons. Also, it was observed that the effect of organic acid sources on soil NH_4Cl –P was significant in both years. Citric acids gave the highest values while oxalic acids gave the least in both seasons. There was no significant effect of the interaction between the organic acid sources and the rates of application in both seasons.

4.13 Soil NH_4Cl – P (mg kg^{-1}) at Mokwa 2011 and 2012 seasons

The effects of organic acid sources and their rates of application on soil NH_4Cl–P at Mokwa during 2011 and 2012 cropping seasons are shown in Table 15 .Similar to the results obtained above for Minna, there was significant increases in NH_4Cl –P of the soils as the rates of application of organic acids increases in both cropping seasons. There was also a significant difference in soil NH_4Cl – P among the organic acid sources used. The interaction effects of organic acid sources and rates of application on soil NH_4Cl – P was not significant during 2011 season but significant during 2012 season.

TABLE 14. Soil NH_4Cl - P (mg kg^{-1}) at Minna 2011 and 2012 cropping seasons as affected by organic acid source and rates.

ORGANIC ACID SOURCE	RATE (t/ha) 0	2	4	6	8	MEAN
			2011			
Orange waste	36.20	65.20	71.33	76.70	77.23	65.33
Tamarind pulp	36.63	41.57	45.40	49.77	51.73	45.02
Amaranthus leaves	34.20	30.10	33.60	37.83	41.20	35.39
MEAN	35.68	45.62	50.11	54.77	56.72	
			2012			
Orange waste	38.73	69.97	75.87	80.86	80.67	69.22
Tamarind pulp	38.50	46.03	50.16	55.17	57.73	49.52
Amaranthus leaves	37.10	33.97	38.80	41.10	45.90	39.37
MEAN	38.11	49.98	54.94	59.04	61.43	

LSD 5%	**2011**	**2012**
Organic Acid Source	0.82	0.83
Rates	1.06	1.08
Organic Acid * Rates	NS	NS

NS =Not Significant at P≤ 0.05.

TABLE 15. Soil NH_4Cl - P(mg kg^{-1}) at Mokwa 2011 and 2012 cropping seasons as affected by organic acid source and rates.

ORGANIC ACID SOURCE	RATE (t/ha)					
	0	2	4	6	8	MEAN
			2011			
Orange waste	35.30	65.83	75.13	78.40	84.50	67.83
Tamarind pulp	35.87	43.90	47.93	50.63	51.40	45.95
Amaranthus leaves	33.87	34.93	38.23	41.70	44.20	38.59
MEAN	43.34	48.22	53.77	56.91	60.03	
			2012			
Orange waste	36.20	69.86	80.57	87.07	89.77	72.69
Tamarind pulp	36.17	49.03	53.20	57.20	58.00	50.72
Amaranthus leaves	36.90	39.00	42.77	47.23	49.23	43.02
MEAN	36.42	52.63	58.84	63.83	65.67	

LSD 5%	**2011**	**2012**
Organic Acid Source	1.83	1.63
Rates	1.18	2.06
Organic Acid * Rates	NS	*

* = Significant NS = Not Significant at $P \leq 0.05$.

4.14 Soil Occl – P (mg kg^{-1}) at Minna 2011 and 2012 seasons

Table 16 shows the soil Occl-P at Minna as affected by different organic acid sources and rates of application during 2011 and 2012 cropping seasons. Generally, there was a significant reduction in soil Occl –P as the rates of application of the organic acid increases in both cropping seasons. Similarly, the reduction was also significantly observed to be dependent on the type of organic acids applied in each cropping seasons. However, the effect of the interaction between organic acid sources and the rate of application on soil Occl –P were significant in both years.

4.15 Soil Occl – P (mg kg^{-1}) at Mokwa 2011 and 2012 seasons

The effect of organic acid sources and rates of application on soil Occl –P at Mokwa during 2011 and 2012 cropping seasons are shown in Table 17. The results show that there was a significant decrease in soil Occl –P at Mokwa when the rates of application of organic acid were increased from 0 to 8 tones ha-1 during both cropping seasons. However, there was a significant reduction in the amount of soil Occl-P on plots that citric acids were applied followed by tartaric acids and oxalic acids were the least. The effect of interaction between organic acid sources and the rates of application was also observed to be significant during both seasons.

TABLE 16. Soil Occl - P (mg kg^{-1})at Minna 2011 and 2012 cropping seasons as affected by organic acid source and rates.

ORGANIC ACID SOURCE	RATE (t/ha)					
	0	2	4	6	8	MEAN
			2011			
Orange waste	236.70	138.27	132.50	127.00	121.97	151.29
Tamarind pulp	237.17	187.93	182.73	171.97	164.80	188.92
Amaranthus leaves	237.77	223.73	217.70	212.10	203.23	218.91
MEAN	237.21	183.31	177.64	170.36	163.33	
			2012			
Orange waste	234.93	133.80	127.47	120.27	116.83	146.66
Tamarind pulp	233.17	181.43	176.30	170.47	162.43	184.76
Amaranthus leaves	234.90	219.33	211.20	201.33	193.90	212.13
MEAN	234.33	178.19	171.66	164.02	157.72	

LSD 5%	**2011**	**2012**
Organic Acid Source	0.97	1.04
Rates	1.25	1.34
Organic Acid * Rates	*	*

* = Significant at P≤ 0.05.

TABLE 17. Soil Occl - P(mg kg^{-1}) at Mokwa 2011 and 2012 cropping seasons as affected by organic acid source and rates.

ORGANIC ACID SOURCE	RATE (t/ha)					
	0	2	4	6	8	MEAN
			2011			
Orange waste	262.87	175.13	170.63	165.27	163.17	187.41
Tamarind pulp	250.27	217.27	213.97	210.40	208.63	220.10
Amaranthus leaves	259.66	241.50	235.33	229.57	224.53	238.12
MEAN	257.60	211.30	206.64	201.74	198.78	
			2012			
Orange waste	254.37	165.93	161.80	154.87	151.48	177.64
Tamarind pulp	254.90	205.27	199.67	198.30	196.83	210.99
Amaranthus leaves	251.13	223.83	215.20	207.97	205.07	220.64
MEAN	253.47	198.34	192.22	187.04	184.45	

LSD 5%	**2011**	**2012**
Organic Acid Source	0.65	1.05
Rates	0.84	1.36
Organic Acid * Rates	*	*

* = Significant at P≤ 0.05

4.16 Soil Al – P (mg kg^{-1}) at Minna 2011 and 2012 seasons

Table 18 represents the soil Al –P at Minna affected by organic acid sources and rates of application during 2011 and 2012 cropping season. The soil Al –P was observed to be significantly higher on control plots where organic acid were not applied. Soil Al –P significantly decreases with the increasing rates of application of organic acids in both cropping season. The effect of organic acid sources on soil Al-P was observed to be significant during both cropping seasons. The interaction effects of sources of organic acids and the rates of application on soil Al-P at Minna was however insignificant during both 2011 and 2012 cropping seasons.

4.17 Soil Al – P (mg kg^{-1}) at Mokwa 2011 and 2012 seasons

The effects of organic acid sources and rates of application on soil Al-P at Mokwa during 2011 and 2012 cropping seasons are shown in Table 19. There was a significant reduction in soil Al-P with the increasing rates of organic acid application during both cropping season. The soil Al-P was also observed to be dependent of the sources of organic acid involved in both cropping seasons. The interaction effects of sources of organic acids and the rates of application on soil Al-P at Minna was however insignificant during both 2011 and 2012 cropping seasons.

TABLE 18. Soil Al - P(mg kg^{-1}) at Minna 2011 and 2012 cropping seasons as affected by organic acid source and rates.

ORGANIC ACID SOURCE	RATE (t/ha)					
	0	2	4	6	8	MEAN
			2011			
Orange waste	41.10	33.20	31.27	29.00	26.50	32.21
Tamarind pulp	40.03	38.20	35.63	32.93	30.77	35.52
Amaranthus leaves	41.33	39.47	36.90	33.96	31.57	36.65
MEAN	40.82	36.96	34.60	31.98	29.61	
			2012			
Orange waste	35.27	30.47	28.97	26.47	24.43	29.12
Tamarind pulp	38.63	36.40	32.77	32.77	28.93	33.42
Amaranthus leaves	39.40	37.50	34.23	31.80	30.03	34.59
MEAN	37.77	34.79	31.98	29.54	27.80	

LSD 5%	**2011**	**2012**
Organic Acid Source	0.42	0.50
Rates	0.55	0.65
Organic Acid * Rates	NS	NS

NS= Not Significant at P≤ 0.05

TABLE 19. Soil Al – P (mg kg^{-1}) at Mokwa 2011 and 2012 cropping seasons as affected by organic acid source and rates.

ORGANIC ACID SOURCE	RATE (t/ha)					
	0	2	4	6	8	MEAN
			2011			
Orange waste	51.10	41.20	38.33	35.60	33.46	39.99
Tamarind pulp	49.06	45.30	42.97	41.10	38.33	43.35
Amaranthus leaves	52.73	50.67	48.40	45.97	44.10	48.37
MEAN	50.96	45.72	43.20	40.89	38.63	
			2012			
Orange waste	47.87	36.67	34.23	31.87	29.77	36.08
Tamarind pulp	47.57	40.20	39.30	37.63	34.70	39.88
Amaranthus leaves	48.13	45.63	43.30	41.23	39.77	43.61
MEAN	47.86	40.83	38.94	36.91	34.74	

LSD 5%	**2011**	**2012**
Organic Acid Source	0.42	0.49
Rates	0.55	0.63
Organic Acid * Rates	NS	NS

NS= Not Significant at P≤ 0.05

4.18 Soil Fe – P (mg kg^{-1}) at Minna 2011 and 2012 seasons

Table 20 represents the soil Fe-P at Minna as affected by sources of organic acid and rates of application during 2011 and 2012 cropping season. Generally, there was significant reduction on soil Fe-P as the rates of application of organic acid increases in both seasons. But it was observed that the soil Fe –P of 2012 was much higher than 2011 cropping season especially on tartaric and oxalic acids plots compared to citric acid plots. The effect of organic acid sources on soil Fe –P was significant during both cropping seasons. However, there was no significant interaction between organic acid sources and rates of application on soil Fe – P during both 2011 and 2012 cropping season.

4.19 Soil Fe – P (mg kg^{-1}) at Mokwa 2011 and 2012 seasons

Similar to the results obtained above, the effects of the rates organic acid application on soil Fe-P was significant. There was a significant reduction on soil Fe-P as the rates of application increases (Table 21). The soil Fe –P at Mokwa location was also observed to be organic acid source dependent in both cropping seasons. The interaction effects between organic acid sources and rates of application on soil Fe-P was found to be insignificant during both 2011 and 2012 cropping seasons.

TABLE 20. Soil Fe - P (mg kg^{-1})at Minna 2011 and 2012 cropping seasons as affected by organic acid source and rates.

ORGANIC ACID SOURCE			RATE (t/ha)			
	0	2	4	6	8	MEAN
			2011			
Orange waste	119.43	104.90	102.27	99.67	96.80	104.61
Tamarind pulp	119.33	111.43	109.26	105.63	104.93	110.12
Amaranthus leaves	120.93	116.60	115.40	113.07	110.77	115.35
MEAN	119.90	110.98	108.98	106.12	104.17	
			2012			
Orange waste	106.07	101.46	97.20	95.97	92.40	98.59
Tamarind pulp	146.87	148.70	144.27	142.27	143.07	145.04
Amaranthus leaves	156.67	156.53	147.40	146.43	145.63	150.53
MEAN	136.53	135.44	129.77	128.22	127.03	

LSD 5%	**2011**	**2012**
Organic Acid Source	0,54	4.04
Rates	0.69	5.12
Organic Acid * Rates	NS	NS

NS= Not Significant at P≤ 0.05

TABLE 21. Soil Fe - P (mg kg^{-1}) at Mokwa 2011 and 2012 cropping seasons as affected by organic acid source and rates.

ORGANIC ACID SOURCE	RATE (t/ha)					
	0	2	4	6	8	MEAN
			2011			
Orange waste	131.27	110.60	107.17	104.07	101.20	110.86
Tamarind pulp	130.27	124.90	122.90	119.99	114.50	122.52
Amaranthus leaves	131.10	132.67	128.80	123.97	122.60	129.23
MEAN	130.87	122.72	119.62	116.02	112.77	
			2012			
Orange waste	127.66	105.23	102.00	99.53	96.07	106.10
Tamarind pulp	128.10	120.86	118.23	115.77	107.93	118.18
Amaranthus leaves	128.20	127.73	123.40	120.70	117.73	123.15
MEAN	127.99	117.94	114.54	112.00	107.24	

LSD 5%	**2011**	**2012**
Organic Acid Source	0.86	1.22
Rates	1.11	1.57
Organic Acid * Rates	NS	NS

NS= Not Significant at P≤ 0.05

4.20 Soil Ca – P (mg kg^{-1}) at Minna 2011 and 2012 seasons

The effects of sources of organic acid and the rates of application on soil Ca –P at Minna during 2011 and 2012 cropping season are shown in Table 22. It was observed that the soil Ca-P significantly decreases as the rates of application increases for all the organic acids involved in both cropping season. Similarly, the effects of organic acid sources on soil Ca –P was also observed to be significant during both cropping seasons. There was no significant interaction effect between organic acid sources and rates of application on soil Ca-P at Minna location during the two cropping seasons.

4.21 Soil Ca – P (mg kg^{-1}) at Mokwa 2011 and 2012 seasons

Table 23 shows the soil Ca –P at Mokwa as affected by sources of organic acid and the rate of application during 2011 and 2012 cropping seasons. Generally, there was a significant reduction in soil Ca-P with increasing rates of application irrespective of the organic acid sources during both cropping seasons. The soil Ca-P was also observed to be dependent of the sources of organic acid involved in both cropping seasons. The interaction effects of sources of organic acids and the rates of application on soil Ca-P at Minna was however insignificant during both 2011 and 2012 cropping seasons.

TABLE 22. Soil Ca – P (mg kg^{-1}) at Minna 2011 and 2012 cropping seasons as affected by organic acid source and rates

ORGANIC ACID SOURCE	RATE (t/ha)					
	0	2	4	6	8	MEAN
			2011			
Orange waste	10.27	8.15	7.81	7.70	7.05	8.20
Tamarind pulp	10.72	9.54	9.38	9.07	8.54	9.45
Amaranthus leaves	11.02	10.47	10.19	10.30	10.05	10.41
MEAN	10.66	9.39	9.13	9.02	8.54	
			2012			
Orange waste	9.37	7.45	7.34	7.16	7.12	7.69
Tamarind pulp	9.33	9.00	8.70	8.47	8.33	8.77
Amaranthus leaves	10.96	10.14	9.97	9.78	9.61	10.10
MEAN	9.89	8.86	8.67	8.47	8.35	

LSD 5%	**2011**	**2012**
Organic Acid Source	0.17	0.12
Rates	0.22	0.15
Organic Acid * Rates	NS	NS

NS= Not Significant at P≤ 0.05

TABLE 23. Soil Ca - P (mg kg^{-1}) at Mokwa 2011 and 2012 cropping seasons as affected by organic acid source and rates.

ORGANIC ACID SOURCE			R A T E (t/ha)			
	0	2	4	6	8	MEAN
			2011			
Orange waste	8.42	4.22	4.11	3.39	3.86	4.80
Tamarind pulp	8.30	8.03	7.78	7.43	7.11	7.73
Amaranthus leaves	8.33	8.21	8.09	7.78	7.78	8.04
MEAN	8.35	6.83	6.66	6.40	6.25	
			2012			
Orange waste	7.36	4.03	3.97	3.67	3.46	4.50
Tamarind pulp	8.11	7.63	7.34	7.05	6.62	7.35
Amaranthus leaves	8.15	7.85	7.60	7.25	7.16	7.62
MEAN	7.87	6.50	6.30	5.99	5.75	

LSD 5%	**2011**	**2012**
Organic Acid Source	0.08	0.12
Rates	0.11	0.15
Organic Acid * Rates	NS	NS

NS= Not Significant at P≤ 0.05

4.22. Comparison of soil Olsen and NH_4Cl – P at Minna and Mokwa locations

Comparison of soil Olsen – P and NH_4Cl – P of both Minna and Mokwa location during 2011 and 2012 cropping seasons are shown in Table 24. The result revealed that there was a significant difference ($P < 0.05$) on both the two forms of P based on the different source of organic acid source applied during 2011 and 2012 cropping season, Similarly, the effect of location on both Olsen – P and NH_4Cl – P availability was also positively significant. However, comparing the two locations, Mokwa soil recorded significant higher values of the two forms of the P than Minna soil. The two forms of P were higher during 2012 cropping season compared to the 2011 cropping season. However the interaction between organic acid source and location was only significant on Olsen forms of P during both 2011 and 2012 cropping season, but their interactions on NH_4Cl – P was not significant ($P > 0.05$).

4.23. Comparison of maize grain yield at Minna and Mokwa locations

Table 25 represents the results effect of organic acid source and location on maize grain yield during 2011 and 2012 cropping season. During both seasons, the application of orange waste had the significant ($P < 0.05$) higher yield than when the tamarind pulp was applied while the application of amaranthus leaves recorded significant lower yield. Although during 2011 cropping season, Minna soil had significant ($P < 0.05$) higher yield compared to Mokwa soil irrespective of the organic acid source applied but were significantly lower when tamarind pulp and amaranthus leaves were applied. The interaction between organic acid source and location on maize grain yield was significant ($P < 0.05$) 2011 and 2012 cropping season

Table 24: Comparison of soil Olsen – P and NH_4Cl – P (mg kg^{-1}) during 2011 and 2012 cropping seasons as affected by organic acid source and location

ORGANIC ACID SOURCE	LOCATION MINNA OLSEN – P	MINNA NH_4Cl – P	MOKWA OLSEN – P	MOKWA NH_4Cl - P
		2011		
Orange waste	54.27	65.33	64.71	67.83
Tamarind pulp	49.17	45.02	46.93	45.95
Amaranthus leaves	41.66	35.39	42.56	38.52
		2012		
Orange waste	58.09	69.22	68.71	72.69
Tamarind pulp	51.48	49.52	50.21	50.72
Amaranthus leaves	44.45	39.37	45.59	43.02
LSD 5%	**O – P (2011)**	**O – P (2012)**	**N – P (2011)**	**N – P (2012)**
Organic acid source	0.62	0.65	0.93	0.96
Location	0.97	0.73	0.86	0.92
Organic acid source * Location	*	*	NS	NS

O-P = OLSEN P, NH_4Cl P * = Significant, NS= Not Significant at $P \leq 0.05$

Table 25: Comparison maize grain yield (t ha-1) during 2011 and 2012 cropping seasons as affected by organic acid source and location

ORGANIC ACID SOURCE	LOCATION	
	MINNA	MOKWA
	2011	
Orange waste	5.41	5.25
Tamarind pulp	5.17	5.15
Amaranthus leaves	5.08	5.04
	2012	
Orange waste	5.61	5.47
Tamarind pulp	3.87	5.33
Amaranthus leaves	3.75	5.24
LSD 5%	2011	2012
Organic acid source	0.04	0.35
Location	0.06	0.33
Organic acid source * Location	*	*

* = Significant at P≤0.05

4.24 Distribution of diothinite and oxalate extractable forms of Fe and Al oxides in Minna

Results obtained for the distribution of diothinite and oxalate extractible forms of Fe and Al oxides in Minna location during 2012 cropping season is shown in Table 26. During 2012 cropping season, only Minna location showed morphological colour distribution at the lower portion of the experimental plot. The result indicates that the oxalate extractable fractions of both iron and aluminium are lower when compared to their diothinite forms. There is no obvious regular pattern in the distributions of these oxides in terms of the rates of the application of the organic acids. The range of Fe_o, Fe_d, Al_o and Al_d were: 0.12 – 1.51, 2.2 – 16.2, 0.17 – 0.87 and 0.58 – 2.59 g kg^{-1} respectively. The concentrations of these oxides were however higher on tartaric and oxalic acid plots than citric acid treated plots.

4.25 Correlation coefficient between soil P and some soil physico – chemical properties

Simple correlation coefficient relating different forms of P mobilized to some physical and chemical properties of investigated soil is depicted in Table 27. It was observed that there was a positive significant correlation between pH and Al – P, Fe – P and Ca –P of both Minna and Mokwa soils. Al – P and Fe – P also correlated positively and significantly with sand, silt and exchangeable acidity but negatively correlated with clay and organic carbon. Ca – P and total - P were also positively and significantly correlated with clay, organic carbon and ECEC, but also negatively and significantly correlated with exchangeable acidity on these soils. In both soils, Olsen – P was only correlated positively and significantly with exchangeable acidity. NH4Cl – P was also correlated positively and significantly with organic carbon in both soil but negatively and significantly correlated only with clay in Mokwa soil. Occl –P was also observed to be positively and significantly correlated with organic carbon and ECEC in both soils.

Table 26. Distribution of various kinds of Fe and Al oxides (g kg^{-1}) in Minna during 2012 cropping season

Treatment (t ha^{-1})	Fe_o	Fe_d	Al_o	Al_d
Tartaric acid				
0	1.51	15.3	0.48	1.73
2	0.80	12.5	0.52	1.25
4	0.75	16.2	0.38	2.21
6	0.45	13.5	0.63	2.59
8	1.22	16.4	0.56	1.67
Oxalic acid				
0	1.01	13.4	0.41	1.34
2	0.85	10.5	0.42	1.81
4	0.49	15.6	0.39	2.11
6	0.88	13.3	0.87	1.85
8	0.79	10.1	0.71	1.90
Citric acid				
0	0.22	4.2	0.18	0.91
2	0.35	3.1	0.21	0.72
4	0.21	3.3	0.17	0.65
6	0.12	2.6	0.20	0.58
8	0.23	2.2	0.19	0.87

Fe_o = Oxalate extractable iron

Fe_d = Diothinite extractable iron

Al_o = Oxalate extractable aluminium

Al_d = Diothinite extractable aluminium

Table 27. Correlation coefficient between soil P and some soil properties

Soil properties	Olsen - P	NH_4Cl -P	Occl - P	Al –P	Fe –P	Ca - P	Total – P
				MINNA			
pH	-0.08NS	0.27NS	0.24NS	0.45*	0.52*	0.46*	0.18NS
Sand	-0.12NS	0.31NS	-0.11NS	-0.09NS	0.43*	-0.07NS	-0.19NS
Silt	0.32NS	0.21NS	0.22NS	0.41*	0.21NS	0.26NS	0.26NS
Clay	0.19NS	-0.08NS	0.23NS	-0.51*	-0.44*	0.47*	0.44*
Organic C	0.23NS	0.51*	0.49*	-0.42*	-0.40*	0.52*	0.31NS
Exc, acidity	0.43*	0;31NS	0.23NS	0.51*	0.42*	-0.39*	-0.43*
ECEC	0.18NS	0.31NS	0.41*	0.22NS	0.32NS	0.56*	0.44*
				M0KWA			
pH	-0.18NS	0.24NS	0.23NS	0.55*	0.57*	0.56*	-0.28NS
Sand	-0.12NS	0.33NS	-0.11NS	-0.09NS	0.47*	-0.17NS	-0.19NS
Silt	0.31NS	0.31NS	0.12NS	0.51*	0.21NS	0.41*	0.29NS
Clay	0.22NS	-0.45*	0.23NS	-0.54*	-0.43*	0.43*	0.45*
Organic C	0.24NS	0.48*	0.43*	-0.47*	-0.40*	0.55*	0.34NS
Exc, acidity	0.46*	0;32NS	0.22NS	0.54*	0.52*	0.49*	-0.42*
ECEC	0.14NS	0.21NS	0.51*	0.32NS	0.27NS	0.48*	0.54*

*= Significant at $P < 0.05$ and NS = Not significant at $P< 0.05$

CHAPTER FIVE

DISCUSSION

5.1 Physico-chemical properties of the soils

The results obtained for some selected physico - chemical properties of the soils studied showed that the soils were moderately acidic in reaction and exchangeable acidity values were low in these soils and suggest that that the soils have no acidity problem and there will be availability of most nutrients to crop roots. Most plant nutrients are readily available to crop roots at pH range 5.0 to 6.0 (Adeboye *et al*., 2009). The low acidity level of the soils may be attributed to accumulation of bases due to low level of leaching.

The organic carbon content of the soils was generally 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. The soils total N and available P were also low. The low total N and available P status of the soils may be attributed to low organic matter contents as organic matter is regarded as the major reservoir of soil P and N. The soils of the Nigerian savanna have been reported to be inherently poor in available P (Lombin, 1987).

The low exchangeable bases and ECEC may be ascribed to very low clay and organic carbon content of the soils as suggested by Onyekwere *et al*, (2009). Base saturation of the soils was high implying the dominance and abundance of the exchangeable cations on adsorption complex.

5.2 Sorption Characteristics of the soils studied

The results obtained for the adsorption isotherm shows that the amount of PO_4 sorbed increases with increasing soil P solution concentration for all the soils studied. Similar results have been reported by other workers (Bala, 1992; Fortin and Karam, 2001; Tsado, 2008). These authors observed that PO_4 sorption was found to be concentration dependent, which is due to concentration gradient and change in the range of diffusion co-efficient, which increased with increasing amount of P added.

For the two soils studied, the amount of PO_4 sorbed was greater in Mokwa soils than in Minna soils. The differences observed in the adsorption isotherm of these soils were as a result of wide range of physico – chemical characteristics of the soils which will profoundly affect PO_4 sorption. Some studies have shown that rhizosphere soil may have differences in physical characteristics, mineralogy and weathering compared to the bulk soil (Jones and Wild, 1975; Marschner, 1995). Highly weathered soils such as the oxisols and ultisols could contain large quantities of Al and Fe hydrous oxides that have the ability to adsorb PO_4 unto their surfaces, thus rendering much of the added P fixed and not readily available for plant uptake (Haynes and Mokolobate, 2001). These observations are in agreement with the findings of Li *et al*. (2000) and Agbenin (2003). These authors reported that the main soil components influencing PO4 sorption include: nature of soil clay, soil pH, organic matter and amorphous Fe and Al oxides.

The Langmuir equation described PO_4 sorption satisfactorily in these soils. The goodness-of-fit of Langmuir to sorption data may indicate that sorbed PO_4 by the soils and the concentration of added P are within the range of validity of the isotherm. This is consistent with findings of Agbenin and Tiessen (1995) that PO_4 sorption by some Nigerian soils fitted to Langmuir isotherm. They reported that these soils had low to medium P fertilizer requirements.

5.3 Inorganic phosphate mobilization

Generally, the amount of NH_4Cl – P was observed to be low. However, compared with control, the NH_4Cl – P and Olsen-P contents of the studied soils increased after treatment with the three organic acids. NH_4Cl – P and Olsen-P are considered the most available fraction of PO_4 in soils. Although the former cannot exist for a very long time because it is readily transformed into Al – P, and as time passes, into Fe – P (Zhang *et al.*,2010). Their capacity for P mobilization appeared to follow 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. The differences observed in both NH_4Cl – P and Olsen –P contents of the two locations could be attributed to the nature of parent materials and soil type. Gang *et al* (2012) further concluded that the pattern of P mobilization by the addition of organic acids was highly soil dependent including soil physical and chemical properties and type of organic acid and was controlled by intrinsic P status such as amounts and distribution of P fraction in the soil.

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 sample location. The dominance of Fe – P in lateritic soils may be due to high percentage of free sesquioxides and weathering processes of these soils Al and Fe oxides are the main phosphates adsorbents in many soils. 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 dithionite extractible Fe (Fed) (Uzu *et al*., 1975; Borggard , 1990).

The content of Ca –P was found to be less than Al –P, Fe – P and Occl –P. It can be inferred that the low content of Ca – P may be due to low pH and stages of weathering. Sheela (2006) reported that low Ca-P and high Al-P and Fe –P content is as a result of lateritic soils considered to be highly weathered with low pH. These results also confirmed earlier report by Wang *et al* (2007). They observed that organic acids strengthens the acidic environments of the soil and under acidic conditions, Al – P and Fe – P were stable, while, Ca – P was not and therefore, Ca – P was the main fraction of P that was affected by organic acid-induced-acidification of the soil. Wang, *et al*, (2008) confirmed that on incubation, Ca – P gets gradually solubilized and the larger contents of free Fe and Al may be responsible for the increase rate of conversion into other form.

Occl- P is generally regarded as unavailable to plants but transformed into available form when organic acids were added. To mobilize Occl – 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 (Reyes *et al.*, 2006).The significantly higher total –P content of these soils when organic acids were added compared with no organic acid soils (control) may be due to higher oxides of Fe and organic carbon contents which are effective immobilizers of P as suggested by Chang and Chu (1961).

The results of the study also showed that the relative fractions of inorganic P was in the order Occl-P > Fe-P > Al-P > Ca-P. These results are in an agreement with the earlier report by Uzu *et al* (1975) during their studies on P status of 21 selected soils from various part of Nigeria. In their findings, they reported that distribution of various P forms was related to the parent material, degree of weathering, and the drainage condition of the soils

5.4 Effects of organic acids on Maize plant height and grain yield.

The significant increase in the plant height of the maize could be attributed to the effect of rates of application of organic residues. Since these organic residues were applied two weeks to the field prior to the land preparation, the period was sufficient enough and most of the minerals on these organic materials were readily available for the plant uptake. The result is in support of Ishanular and Ahmed (2013). They reported that application of organic acids before planting will provide better soil condition for plant growth and development. The increase in growth characteristics is attributed to the stronger role of P in cell division, cell expansion and enlargement which ultimately influenced the vegetative growth of maize (Mohsin Zafar *et al*., 2011)

The results of the yield from the two locations showed that the maize yield responded positively to the application of the organic residues. The application of these organic residues did not only supply the soil with the acids alone, but also supply the soils with essential mineral nutrients that are needed by the plants for growth and productivity. The maize grain yields of these locations were comparable only during 2011 cropping session. At Mokwa location, there was a yield increment during 2012 over 2011 cropping session. This could probably be attributed to the residual benefits of the previous year as a result of residual accumulation of organic matter. On the contrary, there was a yield reduction from 2011 to 2012 cropping season in Minna location. The yield reduction was actually observed in some plots where the growth of the maize were stunted as a result of deposition of the Fe oxides at the soil surface during 2012 cropping season

5.5 Post harvest soil inorganic phosphate mobilization

Similar to the results of soil inorganic phosphate mobilization before planting, results of post harvest soil inorganic phosphate mobilization showed a similar trend. The NH4Cl – P and Olsen – P were generally increased for those plots that were treated with organic residues compared to those plots without organic residues. It was observed that the increment on these P contents were higher in second cropping season compared to the first cropping season. These may be due to the residual effect of the first cropping season.

Also, the study also revealed that the contents of Fe –P and Al –P were higher than Ca –P content irrespective of the seasons and locations of the study. The Fe content was highest in surface soils due to the presence of more organic carbon which provides organic acids which leads to the solubilization of Fe to ferrous form along with phosphates resulting in the precipitation of ferrous phosphate as reported by Hinsinger (2001). Guppy *et al.* (2005) also reported that Al – P, Fe – RS – P and Ocl – P were relatively more in high altitude laterite soils while in black and alluvial soils, Ca – P was the dominant fraction.

Generally, it was observed that the capacity for P mobilization by the three organic residues involved appeared to follow the order of orange waste > tamarind pulp > amaranthus leaves. This observation is in confirmation with Gang *et al*, (2012).

5.6. Distribution of Fe and Al oxides

The concentration of diothinite extractible forms oxide was observed to be greater when compared with the oxalate forms of iron and aluminium in these soils. Parfit (1989) had reported a similar result. He further reported that the diothinite extractable only indicate the Fe and Al that are present in the soil as free discrete bodies (i.e crystalline and amorphous) but not those that are part of the structure of silicate minerals. Obi *et al*, (2009) also reported that crystalline forms of the sesquioxide had been found to dominate in the basement complex soils of the south western Nigeria and southern guinea savanna of Nigeria (Lawal *et al.,* 2012) and is the more advanced stage compared to the amorphous forms that are mobile in the soil and could also be associated with organic matter. The nature, amount and distribution of diothinite and oxalate extractable Fe and Al oxide in the soil significantly affect its properties such as charge characteristics and ion adsorption, particularly P sorption (Palomo, *et al*., 2006). The reduction in maize grain yield at Minna during 2012 cropping session could be attributed to the findings of Mokolobate and Haynes (2003). They reported that the oxides of both Fe and Al greatly influence both physical and chemical properties of the soil as well as plants nutrient dynamics in the soils. And upon ageing, amorphous Al will be transformed to crystalline form depending upon the soil condition such as drainage and aeration.

5.7 Correlation analysis

The result obtained for this study showed different trends of degree of correlations, Organic carbon correlated both positively and negatively with various forms of P from the two locations. This significant correlation could be an indication that organic matter can influences the availabilities of these forms of P in the soil as also observed by Ngachie (1996). The correlation matrix between Olsen –P, NH_4Cl – P and Occl – P with some of the physical and chemical properties were generally not positively significant. This could be ascribed to the period of incubation due to the low variability of pH of the soil because of increased precipitation reaction.

CHAPTER SIX

6.0. CONCLSION AND RECOMMENDATIONS

6.1. Conclusion.

The maintenance of soil organic matter levels and the optimization of nutrient cycling are essential to the sustained and the productivity of agricultural systems. Results of this study have demonstrated that low molecular weight organic acids (citrate, tartrate and oxalate) greatly increased Olsen –P and NH_4Cl – P (the two forms of the P are considered as the most available fractions of the PO_4 in the soil), thus increasing the availability of the P in the two soils studied. The effectiveness of organic acids to release P occurred in the order of tricarboxylic > dicarboxylic > monocarboxylic. Citric acid displayed the greatest capability to mobilize soil inorganic P, which was followed by tartaric acid and oxalic acid being the least. Also, the results of application of these organic residues at the field situation using organic materials were similar to what was obtained at the laboratory situation. Organic residues serve both as the source of subsurface P and effective mobilizing agent. The presence of P in organic residues is, however, an additional and apparently often dominant factors affecting P adsorption. Phosphate released from decomposing residues will be adsorbed unto oxide surfaces thus increasing the proportion of adsorption sites occupied by P and as a result of these, less subsequently added P will be adsorbed and P availability is therefore, increased. The pattern of P mobilization by addition of these organic acids was different from location to location. The comparison suggested that the mobilization of P was highly soil type dependent, and the soil P status such as amount and distributions of P fractions may be important for solubilization of P after the addition of organic acids. The practical implication of these processes is that organic residues could be used as a strategic tool to reduce the rates of lime and fertilizer P required for optimum crop growth on acidic and P-fixing soils of Nigeria. The result of these studied also showed that the relative fractions of inorganic P was in the order Occl-P > Fe-P > Al-P > Ca-P.

6.2. Recommendations for Future Research

The practical implication of the results of this study has indicated that low molecular weight organic acids have the potentials to increase the availability of both applied and native P in the soil. Organic residues such as animal manures, composted wastes, grasses and other crop residues are usually readily available to farmers in large quantities. In practice, application of these organic inputs should be done prior to planting and P fertilization and it suggested that sufficient time be allowed for the sorption of the applied organic materials before the application of the P fertilizer. Based on the results of the experiment obtained, application of 8 tones / ha of the three organic residues applied was significantly more effective in mobilizing both organic and inorganic forms of P and also produced the highest yield in the two locations where the studied was carried out. Therefore, it is recommended that higher rates of above 8 tones / ha be applied especially Minna location so as to improve the Olsen – P and NH_4Cl which are considered as the most available fractions of the PO_4 in the soil.

Application of higher tones of above 8 / ha of organic residues will also improve the soil texture, promote drainage and aeration and hence reduce the accumulation of the Fe and Al oxide forms especially in Minna location

A number of studies have investigated one or more mechanisms of organic materials and PO_4 interaction and a few field experiments have demonstrated reduced Al phytotoxicity and /or increased P availability following application of organic residues to soils. There is a great scope for future research both in relation to the mechanisms that are involved and their relative importance, and also the practical significance of using organic residue in the management of soil fertility by resource – poor, semi-subsistence farmers in sub-sahara Africa were acid soil infertility is often major limitation to crop production. The regular use of organic residues is a practical alternative for such farmers where lime and fertilizer P are expensive commodities.

Further research is also recommended on these three organic acids and other low molecular weight organic acids in terms of their applications and fertilizer P requirement so that integrated soil fertility management programmes can be devised. So therefore, the relative effect of various types of residues, the most appropriate timing and quantity of their application and methods of quantifying their potential benefits are all important practical considerations requiring future research in the southern guinea agro- ecological zone of Nigeria.

REFERENCES

Abda-Alla, M. H. (1994). Phosphatase and the utilization of organic P by *Rhizobium leguminosarum* Biovear Vicear. *Letters in Applied Microbiol.* 18(5): 294 - 296

Achal, V., Savant, V.V. and Sudhakara Reddy, M. (2007). Phosphate mobilization by wide type strain and UV-induced mutants of *Aspergillus tubingenesis. Soil Bio. and Biochem.* 39(2): 655 - 659

Adeboye, M. K. A., Osunde, A. O., Ezenwa, M. I. S., Odofin, A. J. and Bala, A. (2009). Evaluation of the fertility status and suitability of some soils of arable cropping in the southern guinea savanna of Nigeria. *Nig. J. Soil Sci.*19(2): 115 - 120

Afif, E., Barron, V. and Torrent, T. (1994). Organic matter delays but does not prevent phosphate sorption from Brazil. *Soil Sci.* 159(3): 207 - 211

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. 2006. 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

Agbenin, J.O. and Tiessen, H. (1995). Phosphorus sorption at field capacity and soil ionic strength : kinetics and transformations. *Soil Sci. Soc. Am. J.* 59: 998 - 1005

Alam, S., Khalil, S., Ayub, N. and Rashid, M. (2002). In *vitro* solubilization of inorganic phosphate by phosphate solubilizing microorganism for maize rhizosphere. *Int. J. Agric. and Biol.* 4(4): 454 - 458

Alhassan, M., Mesaiyete, E. and Mustapha, A. M. (2012).Clay mineralogy of Lateritic soils derived from granite basement. A case study of Minna lateritic soil. *J. Geotech. Engineering* 17: 1897 - 1903

Altomare, C., Noevell, W. A., BJorkman, T. and Harman, G.E. (1999). Solubilization of phosphates and micronutrients by the plant growth promoting and biocontrol fungus *Trichoderma harzianum. Applied and Environ. Microbio.* 65(7): 2926 - 2935

Appelt, H., Coleman, N. T. and Pratt, P.F. (1975b). Interactions between organic compounds, minerals and ions in volcanish ash derived soils : II. Effect of organic compounds on the adsorption of phosphate. *Soil Sci. Soc. Am. Proc*. 39: 628 - 630

Arai, Y. and Spark, D. L. (2007). Phosphate reaction dynamics in soils and soil minerals : a multi scale approach. *Adv. Agron* 94: 135 - 179

Aseri, G. K., Jain, N. and Tarafdar, J.C. (2009). Hydrolysis of organic phosphate forms by phosphatases and phytase producing fungi of arid and semi-arid soils of India. *Am.-Eurasian J. Agric. Environ. Sci.*5(4): 564 - 570

Atlas, R. M. and Bartha, R. (1988). Microbial Ecology. Fundamentals and Applications, Benjamin Cummings Publishing Company Inc, USA

Bahl, G, S., Vig, A. C., Pal, Y. and Singh, A. (1998). Effect of green manure and cropping on P sorption in some soils of Punjab and Himachal Pradesh. *J. Indian Soc. Soil Sci.* 46: 574 - 579

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

Barrow, N. J. (1987). The reaction of anions and cations with soils. *Fert. Res.* 14: 54 - 80

Barber, S. A. (1995). Soil nutrient bioavailability. New York : John Wiley and Sons. Pp 414

Barrow, N.J., Bowden, J. W., Posner, A.M.and Quirk, J.P. (1980). Describe the effect of electrolyte on the adsorption of phosphate by a variable charge surface. *Aust. J. Soil Res.* 18: 395 - 404

Bar-yosef, B. (1996). Root excreations and their environmental effects : influence on availability of phosphorus. In 'plant roots : the hidden half' (Eds, Y. Waisel, A. Eshel and U. Kafkafi) pp.581 – 603. (Mercel Dekker, Inc.: New York)

Baziriamakenga, R., Simard, R. R. and Leroud, G. D. (1995). Determination of organic acids in soil extract by ion chromatography. *Soil Bio. Biochem.* 27: 359 - 365

Beech, I. B., Paiva, M., Caus, M. and Coutinho, C. (2001). Enzymatic activity and within biofilms of sulphate-reducing bacteria. In. Biofilm Community Interactions: Change or Necessity?, P. G. Gilbert, D. Allison., M. Brading., J. Verran. and J. Walker (Eds.), 231 – 239, Boiline, Cardiff, U.K.

Benbi, D. K. and Gilke, R. J. (1987). The movement into soil of P from super phosphate grains and its available to plants. *Fert. Res.* 24: 225 - 252

Bennett, J. G., Rains, A. B., Gosen, P, N., Howard, W.S., Hutchineon, A. A., Kerl, W.B., Mansfield, J. E., Rackhan, L. R. and. Innes, R. R. (1979). Land resources of central Nigeria. Agric. Dev. Possibilities. Vol. 58. The Kaduna Plains. LRD, Tolworth Tower, Survey, England. 130pp

Bieleski, R. L. (1973). Phosphate pool, phosphate transport and phosphate availability. *Annu. Rev. Plant Physiol.* 24: 225 - 252

Boggard, O. K. 1990. Influence of organic matter on phosphate adsorption by aluminium and iron oxides. *J. Soil Sci.* 41: 443 – 449.

Bohn, H., McNeal, B. and Conor, G. (1985). Soil chemistry. New York : John Wiley and Sons, pp 431

Bolan, N.S., Naidu, R., Maimairaja, S. and Baskaran, S. (1994). Influence of low-molecular-weight organic acids on the solubilization of phosphates. *Boil Fert. Soils* 18(4): 311 - 318

Bolan, N. S., Baskaran, S. and Thiagarajan, S. (1996). An evaluation of the methods of measurement of dissolved organic carbon in soils, manures sludges and stream waters. *Communications in Soil Sci. and Plant Analysis* 27: 2723 - 2737

Boul, S. W., Hole, F. D., McCracken, R. J. and Southard, R. J. (1997). Soil genesis and classification 4th ed. Ames, Iowa State University Press pp 527

Bowden, J. W., Nagarajah, S., Barrow, N. J., Posner, A. M. and Quirk, J.P. (1980a). Describing the adsorption of phosphate, citrate and selenite on a variable charge mineral surface. *Aust. J. Soil Res.18*: 49 - 60

Bowden, J. W., Posner, A. M. and Quirk, J.P. (1980b). Adsorption and charging phenomena in variable charge soils. *Aust. J. Soil Res.*18: 61 - 69

Bowen, G, D. and Rovira, A, D. (1999). The rhizosphere and its managements to improve plant growth. *Adv. Agron.* 66: 1 - 102

Brady, N, C. Weil, R.R. (1999). The nature and properties of soils. 12th ed. Upper Saddle River, N.J.: Prentice Hall, pp 801

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

Bumaya, A. H. and Naylor, D. V. (1988). Phosphorus sorption and extractability in Andic soil incubated with plant residues of variable P content. *Plant and soil* 112: 77 - 81

Cajuste, L. J., Laird, R. J., Cajuste, B. L. and Cuevas, B. G. (1996). Citrate and oxalate influence on phosphate, aluminium and iron in tropical soils. *Communications in Soil Sci. and Plant Analysis.* 27: 1377 - 1386

Chang, S. C. and Chu, W. K. (1961). The fate of soluble phosphate applied to soils. *J. Soil Sci.* 12: 181 - 189

Chang, S. C and Jackson, M. L. 1957. Fractionation of soil phosphorus. *Soil Sci.* 84: 133 – 144

Chantigny, M.H. (2003). Dissolved and water-extractible organic matter in soils : a review on the influence of land use and management practices. *Geoderma* 113: 357 - 380

Chen, Y.P., Rekha, P.D., Arushen, A. B., Lai, W.A. and Young, C. C. (2006).Phosphate solubilizing bacteria from subtropical soil and their tricalcium phosphate solubilizing abilities. *Applied Soil Ecology* 34(1): 33 - 40

Condron, L. M., Turner, B. L. and Cade-Menun, B. J. (2005). Chemistry and dynamics of soil organic phosphorus. In J.T. Sims, A.N. Shapley, eds, phosphorus: Agriculture and the Environment. *Am. Soc. of Agron., Crop Sci. Soc. of Am., Soil Sci. Soc. of Am.*,Inc., Madison, WI, pp 87 - 121

Cordell, D., Drangert, J. O. and White, S.(2009)The story of phosphorus: global food security and food for thought. *Glob. Environ. Change* 19: 292 - 301

Dalal, R.C. (1979). Mineralization of carbon and phosphorus from carbon-14 and phosphorus -32 labelled plant material added to soil. *Soil Sci. Soc. Am. J.* 41: 913 - 916

Drever, J. I. (1994). The effect of land plants on weathering rates of silicate minerals. *Geochimica et Acta* 58: 2325 - 2332

De Freitas, J. R., Banerjee, M. R. and Germida, J. J. (1997). Phosphate solubilizing rhizobacteria enhance the growth and yield but not phosphorus uptake on canola (*Brassica napus* L.). *Bio. Fert. soils* 24(4): 358 - 364

Deubel, A., Grancee, A. and Merbach, W. (2000). Transformation of organic rhizodeposits by rhizoplane bacteria and its influence on the availability of tertiary calcium phosphate. *J. Plant Nut. Soil Sci.*163(4):387 - 392

Dou, Z.,Toth, J. D., Galligan. G. T., Ramberg, C. F. and Ferguson, J. D. (2000). Laboratory procedures for characterizing manure phosphorus. *J. Environ. Qual.* 29: 508 - 516

Dutton, V. M. and Evans, C. S. (1996). Oxalate production by fungi: its role in pathogenecity and ecology in the soil environment. *Can. J. Microbio.*42(9): 881 - 894

Earl, K.D., Syers, J.K.and Mclaughlin, J.R. (1979). Origin of the effects of citrate, tartrate and acetate on phosphate sorption by soils and synthetic gels. *Soil Sci. Soc. Am. J.*43: 573 - 578

Easterwood, G. W. and Sartain, J. B. (1990). Clover residue effectiveness in reducing orthophosphate sorption on ferric hydroxide coated soils. *Soil Sci. Soc. Am. J.* 54: 1345 - 1350

Elkhatib, E. A. (1990). Simultaneous determination of low molecular weight organic acids in soil solution by ion chromatography. *Plant and Soil* 15: 234 - 242

Erich,M. S., Fitzgerald, C. B. and Porter, G. A. (2002). The effect of organic amendments on P chemistry in a potato cropping systems. *Agric. Ecosys. Environ.* 88:79 - 88

Fankem, H., Nwaga, A., Deubel, A., Dieng, L., Merbach, W. and Etoax, F. X. (2006). Occurance and functioning of phosphate solubilizing microorganism from oil palm tree (*Elaeis giuneensis*) rhizosphere in Cameroon. *African J. Biotech.* 5(24): 2450 - 2460

FAO (2006). Guidelines for soil description: Genetics and Systemic interpretations. Food and Agricultural Organization of the United Nations p. 67

Fortin, J. and Karam, A. (2001). Phosphorus sorption by red mud residue as affected by concentration and reaction time. *Agrisite Informations for Agrochima* pp 45 - 89

Fox,T. R. and Comerford, N. B. (1990). Low molecular weight organic acids in selected forest soils of southeastern USA. *Soil Sci. Soc. Am. J.* 54: 1139 - 1144

Fox, T.R., Comerford, N. B. and Mcfee, W. W. (1990). Phosphorus and aluminium release from a spodic horizon mediated by organic acids. *Soil Sci. Soc. Am. J.* 54: 1763 - 1767

Fox,T. R. and Comerford, N. B. (1992). Influence of oxalate loading on phosphorus and aluminium solubility on spodosols. *Soil Sci. Soc. Am. J.* 56: 290 - 294

Fox, R.H. and Kampprath, E. J. (1970). Exchangeable aluminium as a criterion for liming leached mineral soils. *Soil Sci. Soc. Am. Proc.* 34: 252 - 254

Gang, X. U., S. Hongbo., X. Rongfu., Y. Nie., Y. Pie and M. Blackswell. 2012. The role of root – released organic acids and aions in phosphorus transformations in a sandy loam soils from Yantai, China. *African J. of Microbio. Res.* 6(3): 674 – 679.

Geelhoed,J. S., Van-Riemsdijk, W. H. and Finedegg, G. R. (1999). Simulation of the effect of citrate exudation from the roots on the plant availability of phosphate adsorbed on goethite. *European J. Soil Sci*. 50: 359 - 370

George, T.S., Gregory, P. J., Wood, M., Read, D. and Buresh, R.J. (2002). Phosphatase activity and organic acids in the rhizosphere of potential agroforestry species and maize. *Soil Bio. Biochem.* 34: 1487 - 1494

Goldstein, A. H. (1995). Recent progress in understanding the molecular genetics and biochemistry of calcium phosphate solubilization by gram-negative bacteria. *Biological, Agric. and Hort.* 12(1): 185 - 193

Goldstein, A. H. (2000). Bioprocessing of rock phosphate ore: Essential technical considerations for the development of a successful commercial technology, Proceedings of 4th International Association for Technical Conference, pp 220 – 242, New Orieans, USA

Griffin, T. S., Honeycutt, C. W. and He, Z. (2003). Changes in soil phosphorus from manure application. *Soil Sci. Am. J. Vol. 67:* 645 - 653

Guppy, C. N., Menzie, N. W., Moody, P. W. and Blamey, F. P. C. (2005). Competitive sorption reactions between P and organic matter in soil. *Aust. J. Soil Res.* 43(2) : 189 - 202

Gyaneshwar, P., Naresh-Kumar, G. and Parekh, L. J. (1998). Effect of buffering on the phosphate solubilizing ability of microorganisms. *World J. Microbio. Biotech.*. 14(5): 669 - 673

Gyaneshwar, P., Pareka, L. J., Archana, G., Podle, P. S., Cllins, M. D., Huston, R. A. and Naresh, K.G. (1999). Involvement of a phosphate starvation inducible glucose dehydrogenase in soil phosphate solubilization by *Enterobacter asburiae*. *Microbiol. Letters* 171(2):223 - 229

Hansen, J. C., Cade-Menu , B. J.and Strawn, D.J. (2004). Phosphorus speciation in manre-amended alkaline soil. *J. Environ. Qual.* 33: 1521 - 1527

Harrison, A. F. (1987). Soil organic phosphorus – A review of world literature. CAB International, Wallingford,Oxon, UK, p 257

He, Z. L. and Zhu, J. (1988). Microbial utilization and transformation of phosphate adsorbed by variable charged minerals. *Soil Bio. Biochem.* 30(7): 917 - 923

He, Z. L., Wu, J., O'Donnell, A. G. and Syers, G. K. (1997). Seasonal responses in microbial biomass carbon, phosphorus and sulphur in soils under pasture. *Bio. Fert. Soils* 21: 421 - 428

He, Z.L., Baliger, V. C., Martens, D. C. and Ritchey, K. D.(1998). Determination of soluble P in the presence of organic ligands or fluorides. *Soil Sci. Soc. Am. J.* 62: 1538 - 1541

Heng, L.C. (1989). Influence of some humic substances on P sorption in some Malaysian soils under rubber. *J. Natural Rubber Res*. 4: 186 – 194

Henri, F., Laurette, N. N., Anertte, D., John, Q., Wolfgang, M., Francois-Xavier, E.and Dieudonne, P. (2008). Solubilization of inorganic phosphates and plant growth promotion of strain of *Pseudomonas fluorescens* isolated from acid soils of Cameron. *African J. Microbio. Res.* 2(7):171 - 178

Haynes, R. J. and Mokolobate, M.S. (2001). Amelioration of aluminium toxicity and P deficiency in acid soils by additions of organic residues. A critical review of the phenomenon and the mechanism involved. *Nutrient cycling in Agroecosys*. 59: 47 - 63

Hilda, R. and Fraga, R. (1999). Phosphate solubilizing bacteria and their role in plant growth promotion. *Biotech. Adv.*17(5): 319 - 339

Hingston, F. J., Posner, A. M. and Quirk, J. P. (1971). Competitive adsorption of negatively charged ligands on oxide surfaces. Discussions of the Faraday Society 52, 334 - 342

Hinsinger, P. (2001). Bioavalability of soil inorganic P in the rhizosphere as affected by root induced chemical changes: a review. *Plant and Soil* 237: 173 – 195

Hinsinger, P., Bengough, A. G., Vettalein, D. and Young, I. M. (2009). Rhizosphere: biophysics, biogeochemistry and ecological relevance. *Plant and Soil* 321: 117 - 152

Hocking, P. J. (2001). Organic acids exuded from roots phosphorus uptake and aluminium tolerance of plants in acid soils. *Adv. Agron.* 74: 63 - 97

Huang, P. M. 2004. Soil mineral – organic matter – microorganism interactions: fundamentals and impact. *Adv. Agron*. 82: 391 – 472

Hue, N. V. (1991). Effects of organic acids/anions on P sorption and phytoavailability in soils with different mineralogies. *Soil Science* 152: 463 - 471

Hue, N. V., Craddock, G. R. and Adams, F. (1986). Effects of organic acids on aluminium toxicity in subsoils. *Soil Sci. Soc. Am. J.* 50: 28 - 34

Hue, N. V., Ikawa, H. and Silva, J. H. (1994). Increasing plant available phosphorus in an ultisol with yard waste compost. *Communications in Soil Sci. and Plant Analysis* 25: 3292 - 3303

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

Imas, P., Bar-Yosef, B., Kafkafi, U. and Ganmore-Neumann, R. (1997). Phosphate induced carboxylate and proton release by tomato roots. *Plant and Soil* 191: 31 - 35

Ishanular, D. and Ahmed, A. B. (2013). Effect of humic acid on growth and quality of maize fodder production. *Pakistan J. Bot.* 45(1) : 21 - 25

Isherwood, G. K. (2001). Mineral fertilizer use and the environment. International Fertilizer Industry Association/ United Nation Environment Programme, Paris

Ishola, M. M., Agbaji, E. B. and Agbaji, A. S. (1990). A chemical study of Tamarindus indica (Tsamiya) fruits grown in Nigeria. *Journal of Science, Food and A griculture,* 51 ; 141 - 143

Iyamuremye, F. and Dick, R. P. (1996). Organic amendments and phosphorus sorption by soils. *Adv. Agron*. 56: 139 - 185

Iyamuremye, F.,Dick, R. P. and Baham, J. (1996a). Organic amendments and P dynamics : 1. Phosphorus chemistry and sorption. *Soil Science* 161: 426 - 435

Iyamuremye, F.,Dick, R. P. and Baham, J. (1996b). Organic amendments and P dynamics : 2. Distribution of soil phosphorus fraction. *Soil Science* 161: 436 - 443

Jackman, J., Jones, R. D. and Yost, R. S. (1997). Predicting P sorption by soils from Rietveld Refinement of XRD measurement of soil minerals. *Soil Sci. Soc Am. J.* 61: 618 - 625

Jackson, M. L. (1967). Soil Chemical Analysis. Prentice Hall Pvt. Ltd., New Delhi.

Jackson, M. L. (1973). Soil Chemical Analysis. Prentice Half of India Pvt. Ltd., New Delhi.

Jones, D. L. 1998. Organic acids in the rhizosphere: A critical review. *Plant Soil* 205: 25 – 44

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

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

Jones, D. L.and Brassington, D. S. (1988). Sorption of organic acids in an acid soils and its implications in the rhizosphere. *European J. Soil Sci.*49: 447 - 455

Jones, D. L. and Edwards, A. C. (1998).Influence of sorption on the biological utilization of two simple carbon substrate. *Soil Bio. Biochem.*30: 1895 - 1902

Jones, D. L., Dennis, P. G., Owen, A. G.and VanHees, P. A. W. (2003). Organic acids behavior in soils-misconceptions and knowledge gaps. *Plant Soil* 248(1): 31 - 41

Kaiser, K. and Zech, W. (1998). Soil dissolved organic matter sorption as influenced by organic and sesquioxide coatings and sorbed sulfate. *Soil Sci. Soc. Am. J.* 61: 64 - 69

Kafkafi, U., Bar-yosef, R. R. and Sposito, G. (1988). Phosphorus adsorption by kaolinite and montmorillonite : II. Organic anion competition. *Soil Sci. Soc. Am. J.* 52: 1585 - 1589

Kalbiltz, K., Solinger, S., Park, J. H., Michalzik, B. and Matzner, E. (2000). Controls on the dynamics of dissolved organic matter in soils : a review. *Soil Science* 165: 277 - 304

Kalbiltz, K., Schmerwtz, J., Schwesig, D. and Matzner, E. (2003). Biodegradation of soil-derived dissolved organic matter as related to its properties. *Geoderma* 113: 273 - 291

Kapoor, K. K., Mishra, M. M. and Kukreja, K, (1989). Phosphate solubilization by soil microorganisms. *Indian J. Microbio*. 29(2): 119 - 127

Khan, M. S., Zaidi, A. and Wani, P. A. (2007). Role of phosphate- solubilizing microorganisms in suistainable Agriculture – A Review. Agron. Sustainable Dev., Vol.27, No.1, pp 29 - 43

Kim, K. Y., Jordan, D. and McDonald, G. A.(1997). Solubilization of hydroxyapatite by Enterobacter agglomerans and cloned Escherichia in culture medium. Biology and Fertility of Soils, Vol.24, No.4, pp 347 - 352

Kim, K. Y., Jordan, D. and McDonald, G. A.(1998). Effect of phosphate solubilizing bacterial and vesicular-arbuscular mycorrhizae on tomato growth and soil microbial activity. *Bio. Fert. Soils* 26(2): 79 - 87

Kpomblekou, K. and Tabatabai, M. A. (1994). Effect of organic acids on release of phosphorus from phosphate rocks *Soil Sci.*158(6):442 - 453

Kucey, R. M. N. (1983). Phosphate solubilizing bacteria and fungi in various cultivated and virgin Albreta soils. *Can. J. Soil Sci*. 63(4): 671 - 678

Kucey, R. M. N., Jarzen, H. H. and Legget, M. E. (1989). Microbial mediated increases in plant available phosphorus. *Adv. Agron.* 42(3): 199 - 288

Kusel, K. and Drake, H. L. (1998). Microbial turnover of low molecular weight organic acids during litter leaf decomposition. *Soil Bio. Biochem.*31: 107 - 118

Larsen, S. (1967).Soil phosphorus. *Adv. Agron*. 19: 151 - 210

Lawal, B. A., Adeboye, M. K. A., Tsado, P. A., Elebiyo, M. G. and Nwajoku, C. R. (2012). Properties, classifications and agricultural potentials of lateritic soils of Minna in sub-humid agro-ecology zone, Nigeria.*Int. J.Dev.sust*. Vol.1, No.3, (in press)

Levesque, M. and Schnitzer, M. (1967). Organo-metallic interactions in soils : 6. Preparation and properties of fulvic acid-metal phosphates. *Soil Sci.* 103: 183 - 190

Leaver, J. P. and Russell, E. W. (1957). The reaction between phosphate and phosphate-fixing soils. *J. Soil Sci.* 8: 113 - 126

Li, H. X., M. X. Zhang and Y. J. Liu. 2000. Soil component affecting phosphate sorption parameters of acid paddy soils in Guangdong Province. *Pedosphere* 10(4): 317 – 321

Lindsway, W. L., Vleck, P. L. G. and Chien, S. G. (1989).Phosphate minerals. In J.B. Dixon, S.B. Weed, eds, Minerals in Soil Environment, Ed 2. *Soil Sci. Soc. Am.*, Madison, WI, pp 1089 - 1130

Linquist, B. A., Singleton, P. W., Yost, R.S. and Cassman, K. G. (1997). Aggregate size effect on the sorption and release of phosphorus in an ultisol. *Soil Sci. Soc. Am. J.* 61: 160 - 166

Lombin, G. (1987). Soil and climate constraints to the crop production in the Nigeria savanna region. *Proceedings of the 15th Annual Conf. Soil Sci. Soc. Nig*. 21 – 24 September, 1987 p 6 - 9

Lopez-Hernandez, D. and Burnham, C. P. (1974). The covariance of phosphate sorption with other soil properties in some British and tropical soils. *J. of Soil Sci.* 25: 196 - 206

Lopez-Hernandez, D., Flores, D., Siegert, G. and Rodriguez, J. V. (1979). The effect of some organic anions on phosphate removal from acid and calcareous soils. *Soil Sci.* 128: 321 - 326

Lopez-Hernandez, D., Siegert, G. and Rodriguez, J. V. (1979).Competitive adsorption of phosphate with malate and oxalate by tropical soils. *Soil Sci. Soc. Am. J*. 50: 1460 - 1462

Luengo, C., Brigante, M., Antelo, J. and Avena, M. (2006). Kinetics of phosphate adsorption on goethite: comparing batch adsorption and ATR-IR measurements. *J. Colloid Interface Sci.*300: 511 - 518

Marschner, H. 1995. Mineral nutrition of higher plants. Academic Press, London.

Martins, M. A., Santos, C., Almeida, M. M. and Costa, M. E. (2008). Hydroxyapatite micro and nanoparticles: nucleation and growth mechanisms in the presence of citrate species. *J. Colloid Interface Sci.* 318: 210 - 216

Mattling, G.E. (1975). Labile phosphate in soils. *Soil Sci.* 119: 369 - 375

Maurice, P. A., Hochella, M.F., Parks, G. A., Sposito, G. and Schwertmann, U. (1995). Evolution of hematite surface microtopography upon dissolution by simple organic acids. *Clays and Clay Minerals* 43: 29 - 38

McKeague, J. A. and Day, J. H. (1966). Dithionite and oxalate extractible Fe and Al as acids in differentiating various classes of soils . *Can. J. Soil Sci.* 46: 13 - 22

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. *Am. Soc. of Agron,; Soil Sci. Soc. Am;* Inc. Madison, Wisconsin, U.S.A.

Menzies, N. W. and Bell, L. C. (1988). Evaluation of the influence of sample preparation and extraction technique on soil solution composition. *Aust. J. Soil Res.* 24: 451 - 464

Moghimi, A., Tate, M. E. and Oades, J. M. (1978). Characterization of rhizopheric product esprically 2 – ketogluconic acid. *Soil Bio. Biochem.* 10(4): 283 - 287

Mohsin, Z., Abassi, M, Khaliq, A. and Zahid, R. (2011). Effect of combining organic materials with inorganic P sources on growth,yield, energy content and P uptake in maize. *Applied Sci. Res.* 3(2) : 199 - 212

Mokolobate, M. S. and Haynes, R. J. (2003). A glass house evaluation of the comparative effects of organic amendments, lime and phosphate on alleviation of A1 toxicity and P deficiency in an oxisols. *J. Agric. Sci.* 140: 407 - 417

Moody, P. W., Edwards, D. G. and Bell, L. C. (1995). Effect of banded fertilizers on soil solution composition and short-term root growth: II. Monocalcium phosphate with and without gypsum. *Aust, J. Soil Res.* 33: 899 - 914

Murphy, J and J. P. Riley. 1962. A modified single solution for the determination of phosphorus in natural waters. *Anal.Chem. Acta* 20: 31 - 36

Nagarajah, S., Posner, A. M. and Quirk, J. P. (1970). Competitive adsorption of phosphate with polygalacturonate and othe organic anions on kaolinite and oxide surfaces. *Nature* 228: 83 - 85

Nahas, E. (1996). Factors determining rock phosphate solubilization by microorganisms. *World J. Microbio. Biotech.* 12(6): 567 - 572

Nambu, K. and Yonebayashi, K. (1999). Acidic properties of dissolved organic matter leached from organic layers in temperate forests. *Soil Sci. Plant Nut.* 45: 65 - 77

Neumann, G. and Romheld, V. (2002). Root-induced changes in the availability of the nutrients in the rhizosphere. In Y. Waisel, A. Eshel, and U. Kafkafi, eds, Plant Roots, The Hidden Half, Ed 3. Mercel Dekker, Inc., New York, pp 617 - 649

Ngachie, V. (1996). Phosphate sorption of an acid –mineral soil as affected by liming, organic material addition and heating. *Tropical Agric*. 73: 175 - 179

Nziheguba, G., Palm, C. A., Buresh, R. J. and Smithson, P. C. (1998). Soil P fractions and adsorption as affected by organic and inorganic sources. *Plant and Soil* 198: 159 - 168

Oberson, A., Friensen, D. K., Rao, I. M., Buhlar, R. S. and Frossard, E. (2001). Phosphorus transformations in an oxisol under contrasting land – use systems : the roles of microbial biomass. *Plant and Soil* 237: 197 - 210

Obi, J. C., Akinbola, G. E. and Anozie, H. I. (2009). Distribution of Diothionite and Oxalate – extractable Iron oxides of a catena in the basement complex soils of Southwestern Nigeria. *Nig. J. Soil Sci.* 19(2): 100 - 108

O'Brien, G. K. and Price, M. L. (2008). Amaranth grain and vegetable types. *Echo Technical Note* 3: 1 - 15

Odunze, A. C. (2009). Land use limitation and management option for a savanna zone Alfisol. *J. Agric. Env. Int. Dev*. 103 (4): 321 - 335

Oelkers, E. H. and Valsami-Jones, E. (2008). Phosphate mineral reactivity and global sustainability. *Elements* 4: 83 - 87

Ojanuga, A. G. (2006). *Agroecological Zones of Nigeria Manual*. FAO/NSPFS. Federal Ministry of Agriculture and Rural Development, Abuja, Nigeria, 124pp

Okoye, E. O.U., Kolajaiye, T. O., and Oleka, G. (1995). Reports on soil survey of Niger State. Compiled by E, A. Amba, Federal Ninistry of Agriculture and Land Resources, pp 56

Omar, S. A. (1998). The role of rock phosphate solubilizing fungi and vesicular-arbuscular mycorrhizae (VAM) in growth of wheat plant facilitated with rock phosphate. *World J. Microbio. Biotech.* 14(2): 211 - 218

Otani, T., Ae, N, and Tanaka, H. (1996). Phosphorus mechanisms of crops grown in soils with low P status. II. Significance of of organic acids in root exudates of Pigeon pea. *Soil Sci. Plant Nut.* 42(3): 553 - 560

Othieno, C. O. (1973). The effect organic mulches on yields and phosphorus utilization by plants in an acid soils. *Plant and Soil* 38: 17 - 32

Owusu-Benoah, E. and Aquaye, D. K. (1989). Phosphate sorption characteristics of selected major Ghanaian soils. *Soil Sci*. 148: 114 - 123

Onyekwere, I. N. and Ezenwa, M. I. S. (2009). Characterization and classification of Barkin Sale, Nigerian Southern Guinea Savanna Fadama soils for sustainable rice production, *Nig. J. Soil Sci.* 19(2): 145 - 152

Olubukola, O. K., Adunola, O. K. and Odunfa, S. A. (2010). Orange and pineapple waste sm potential substrate for citric acid production. *Home.* 1(1): 8 - 14

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

Parfitt, R. L. (1978). Phosphate reactions with natural allophone, ferrihydrite and goethite. *J. Soil Sci.* 40: 359 - 369

Parmar, D. K. and Sharma, P. K. (1996). Phosphorus and mulching effects on nutrient uptake and grain yield of wheat at different growth stages. *Tropical Agric.* 73: 173 - 200

Paul, E. A. and Clark, F. E. (1989). 'Soil microbiology and biochemistry'. (Academic Press Inc. Ltd : London)

Piccolo, A. (2001). The supramolecular structure of humic substances. *Soil Sci*. 166: 810 – 832.

Piccolo, A. (2002). The supramolecular structure of humic substances : a novel knowledge understanding of humus chemistry and implications in soil science. *Adv. Agron.* 75: 150 - 154

Pierzynski, G. M., McDowell, R. W. and Sims, J. T. (2005). Chemistry, cycling and potential moments of inorganic phosphorus in soils. In J.T. Sims, A.N. Shapley, eds, phosphorus: Agriculture and the Environment. *Am. Soc. of Agron., Crop Sci. Soc. of Am., Soil Sci. Soc. of Am.*,Inc., Madison, WI, pp 53 - 86

Pushparajah, E. (1998). Nutrient management and challenges in managing red and lateritic soils. In 'Red and Lateritic soils' (Eds J, Sehgal, W. E. Blum and K. S. Gajbhiye) pp 293 - 304

Raghothama, K. G. (1999). Phosphate aquisation. *Annual Reviews of Plant Physiol. Plant Molecular Bio.* 50: 665 - 693

Reyes, I., Bernier, L., Simard, R.R. and Anroun, H. (1999). Effect of nitrogen sources on the solubilization of different inorganic phosphates by an isolate of Penicillium rugusolum and two UV-induced mutants. *Microbio. Ecology* 28(3): 281 - 290

Reyes, I., Valery, A. and Valduz, Z. (2006). Phosphate solubilizing microorganisms isolated from rhizospheric and bulk soils of colonizer plants at an abandoned rock phosphate mine. In First International Meeting on Microbial Phosphate Solubilization, E. Valazquez and C. Rodriguez-Barrueco (Eds.), 67-75,Salamnca, Spain

Richardson, A. E., Hadobas, P. A. and Hayes, J. E. (2000). Acid phosphomonoesterase and phytase activities of wheat (*Tritricum aestivum* L.) roots and utilization of organic phosphorus substrates by seedlings grown in a sterile culture. *Plant, Cell and Environ.* 23(4): 397 - 340

Richardson, A. E., Barea, J. M., McNeill, A. M. and Prijent-Combarent, C. (2009).Acquisation of phosphorus and nitrogen in the rhzosphere and plant growth promotion by microorganisms. *Plant Soil.* 321: 305 - 309

Sample, E.C., Soper, R.J. and Racz, G. J. (1980). Reaction of phosphate fertilizers in soil. In Khasawneh, E. F., Sample, E. C. and Kamprath, E. J. (Eds). The role of phosphorus in agriculture. WI: *Ame. Soc. Agron.* pp. 263 - 310

Sanyel, S.R. and De Datta, S. R. (1991). Chemistry of phosphorus transformations in soils. In *Adv. Soil Sci.* pp1 -120

Sanchez. P.A. (1976). Properties and Management of tropical soils. Wiley.

Sanchez, P.A. and Uehara, G. (1980). 'Management considerations for acid soils with high phosphorus fixing capacity.'The role of phosphorus in Agriculture (Eds. Khasawneh et al), American Society of Agronomy, Madison, pp 471 - 514

Sanchez, P. A. and Logan, T. (1992). Myths and science about the chemistry and fertility of soils in the tropics. *Eur. J. Soil Sci*. 47(2):261 – 270

SAS (2002). Statistical Analysis Software, Release 9.0 . SAS, Institute, Cary, NC, USA.

Saunders, W. M. H. (1965). Phosphate retention by New Zealand soils and its relationship to free sesquioxide, organic matter and other soil constituents. *New Zealand J. Agric. Res*. 8: 30 - 57

Schwertmann, , U. and Herbillion, A. J. (1992). Some aspects of fertility associated with the mineralogy of highly weathered tropical soils. *Bio. Fert. soils.* 25: 47 - 52

Sharpley, A. N. 1995. Dependence of run – off phosphorus on extractable phosphorus. *J. Environ. Qual.* 24: 920 – 926

Sheela, B. S. (2006). Dynamics of Phosphorus in acid soils of North Karnataka. M Sc. Thesis, Department of Soil Science and Agricultural Chemistry, University of Agricultural Sciences, Dharwad pp 89

Shen, Y., Strom, L., Jonsson, J. A. and Tyler, G. (1996). Low molecular weight organic acids in the rhizosphere soil solution of a beech forest *(Fagus sylvatica* L) cambisol determined by ion chromatography using supported liquid membrane enrichment technique. *Soil Bio. Biochem.* 28: 1161 - 1169

Shonji, S., Nanzyo, M. and Dahlgren, R. (1993). Volcanic ash soils. Amsterdam : Elsvier, pp 390

Sibanda,H.M. and Young, S. D. (1986). Competitive adsorption of humus acids and phosphates on goethite, gibbsite and two tropical soils. *J. Soil Sci.* 37: 179 - 204

Sibanda,H.M. and Young, S. D. (1989). The effects of humus acids and soil heating on the availability of phosphate in oxide rich tropical soils. In 'Mineral nutrients in tropical forest and savanna ecosystems.' (Ed. J, Proctor) pp 71 - 83

Singh, B. B. and Jones, J. P. (1976). Phosphorus sorption and desorption characteristics of soils as affected by organic residues. Soil Sci. Soc. Am. J. 40, 389 - 394

Snaeyink, V. L. and Jenkins, D. (1980). Water chemistry. John Wiley and Sons, New York

Stauton, S. and Leprince, F. (1996). Effect of pH and some organic anion on the solubility soil phosphate:Implications for P bioavailability. *Eur. J. Soil Sci.* 47 (2):231 - 239

Stevenson, F. J. (1994). 'Humus chemistry : genesis, composition and reactions (John Wiley and Sons, Inc.: New York)

Stephen, J. and Jisha, M. S. (2009). Buffering reduces phosphate solubilizing ability of selected strains of bacteria. *World J. Agric. Sci.* 5(1): 135 - 137

Strobel, B. W., Bernhoft, I. and Borggaard, O. K. (1999). Low molecular weight aliphatic carboxylic acids in soil solutions under different vegetations determined by capillary zone electrophoresis. *Plant and Soil* 212: 115 - 121

Strom, L., Owen, A. G., Godbold, D. L. and Jones, D. L. (2002). Organic acid-mediated P mobilization in the rhizosphere and uptake by maize roots. *Soil Bio. Biochem.* 34: 703 - 710

Sujatha, S., Sirisham, S. and Reddy, S. M. (2004). Phosphate solubilization by themophylic microorganisms. *Indian J. Microbio.* 44.(2): 101 - 104

Sumner, M. E. and Farina, M. Y. (1986). Phosphorus interactions with other nutrients and lime in field cropping systems. *Adv. Soil Sci.* 5: 201 - 236

Swift, R. S. (1999). Macromolecular properties of soil humic substances : facts, fiction and opinium. *Soil Sci*. 164: 790 - 802

Tang, C. and Rengel, Z. (2003). Role of plant cation/anion uptake ratio in soil acidification, In: Hand book of soil acidity, Z. Rengel (Ed), 57 – 81, Marcel and Marcel, Dekker,New York

Tarafdar, J. C and Clasen, N. (1988). Organic phosphorus compounds as a phosphorus source for higher plant through the activity of phosphatase produced by plant roots and microorganisms. *Bio. Fert. Soils* 5(4): 308 - 312

Tarafdar, J. C.,Rao, A. V. and Bala, K. (1988). Production of phosphatase by fungi isolated from desert soils. *Foliar Microbio.* 33 (6): 453 - 457

Tarafdar, J. C., Yadav, S. R. and Meena, S. C. (2001).Comparative efficiency of acid phosphatase originated from plant and fungal sources. *J. Plant Nut. Soil Sci.*164(3): 279 - 282

Tarafdar, J. C., Breja, M. and Pawar, J. (2003)Efficiency of some phosphate producing soil-fungi. *Indian J. Microbio.* 43(1): 27 - 32

Tarafdar, J. C. and Gbaru, A. (2005). Mobilization of organic and poor soluble phosphate by *Chaetomium globosum. Applied Soil Ecology* 32(3): 273 - 283

Tarafdar, J. C. and Rao, A. V. (1996). Contribution of *Aspergillus* strains in acquisition of P to wheat (*Tritricm aestivum* L) and Chick pea (*Cicer arietinum* L) grown in a loamy sand soil. *Applied Soil Ecology* 3(2):109 - 114

Thomas, G. W. 1982. Exchangeable cations. In: A. L. Page et. al. (eds). Methods of soil analysis (No. 9, part 2), 159 – 165. *Am. Soc. of Agron. In: Soil Sci. Soc. Am.*, Inc. Madison, Wisconsin, U.S.A.

Tinker, P. B. (1980). The role of rhizosphere micro organisms in mediating phosphorus uptake by plants. The Role of Phosphorus in Agricuture. (Eds. F.E. Kwasennah, E. C. Sample and E. J. Kamprath) pp 617 – 654, *American Society of Agronomy*, Madison

Tinker, P. B and Nye, P. H. 2000. Solute movement in the rhizosphere. Oxford Univ. Press. Oxford, UK

Turner, B. L. and Leytem, A. B. (2004). Phosphorus compound in sequential extract of animal manures : chemical speciation and a novel fractionation procedure. *Environ. Sci. Tech.* 38: 6101 - 6108

Traina, S. G., Sposito, G., Bradford, G. R. and Katkafi, U. (1987). Kinetic study of citrate effects on orthophosphate solubility in an acidic, montmorillonite complex. *Soil Sci. Soc. Am. J.* 51: 1483 - 1487

Trolove, S. N., Hedley, M. J., Kirk, G. J., Bolan, N. S. and Loganathan, P. (2003). Progress in selected areas of rhizosphere research on P acquisition. *Aust. J. Soil Res.* 41: 471 - 499

Tsado, P. A. 2008. Phosphate sorption in three cultivated soils of the Nigerian Guinea Savanna as influenced by the addition of some selected organic acids. M. Tech. thesis. Department of Soil Science, Federal University of Technology, Minna. Pp 46

Turner, B. L., Paphazy, M. J., Heygarth, P. M. andMckelvieI.D. (2002). Inositol phosphates in the environment. Philos. Trans.R.Soc. Lond. B. *Bio. Sci*. 357: 449 – 469

Turner, B. L., Richard, A. E.and Mullaney, E. J. (2007). Inositol phosphates:Linking Agriculture and Environment. CAB International, Wallingford, UK, p 304

USDA (2003). United State Department of Agriculture Soil Survey Staffs: Keys to soil taxonomy, 9th edition. Washington, DC, Natural Resources Conservation Service, USDA. 332pp

Uzu, F. O., Juo, A. S. R. and Fayemi, A. A. A. (1975). Forms of phosphorus in some important soils of Nigeria. *Soil Sci.* 120: 212 - 218

Vans, C. P. (2010). Quantitative trait loci, epigenetics sugar, and microRNAs: quaternaries in phosphate acquisition and use. *Plant Physiol.* 154: 582 - 588

Vassilev, N., Vasileva, M. A. and Nikolaeva, L. (2006). Silmutaneous P solubilizing bicontrol activity of microorganisms: potentials and future trends. *Applied Microbio. Biotech.*.71(2): 137 - 144

Veith, J. A. and Sposito, , G. (1977). On the use of Langmuir equation in the interpretation of adsorption Phenomena. *Soil Sci. Soc. Am. J.* 41: 697 - 702

Venkateswarlu, B., Rao, A. V. and Raina, P. (1984). Evaluation of phosphorus solubilization by microorganisms isolated from arid soils. *J. Indian. Soc. Soil Sci.* 32(3): 273 - 277

Villegas, J. and Fortin, J. A. (2002). Phosphorus solubilization and pH changes as a result of the interaction between soil bacteria and arbuscular mycorrhizae fungi on a medium containing NO_3 as nitrogen source. *Can. J. Bot*. 80(5) 571 - 576

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

Violante, A. and Gianfreda, L. (1995). Adsorption of phosphate on variable charge minerals : competitive effects of organic ligands. In 'Environmental impact of soil component interactions ; metals, other inorganics and microbial activities'.(Eds P. M. Huang, J. Berthelin, J. M. Bollang, W.B. Mcbill and A.L. Page). pp. 29 – 38. (Lewis Publishers : London)

Violante, A., Rao, M. A., De Chiara, A. and Gianfreda, L. (1996). Sorption of phosphate and oxalate by a synthetic aluminium hydroxylsulphate complex. *Eur. J. Soil Sci.* 47: 241 - 247

Wada, K. and Higashi, T. (1976). The categories of aluminum-and iron-humus complexes in Ando soils determined selective dissolution. *J. Soil Sci*. 2: 357 - 368

Wang, X., Yost, S. L. and Linquist, B. A. (2001). Soil aggregate size affects phosphorus desorption from highly weathered soils and plant growth. *Soil Sci Soc. Am. J.* 65: 139 - 146

Wang, B.L., Shen, J. B., Zhang., W. H., Zhang, F. S.and Newmann, G. (2007). Citrate exudation from white lupin induced by phosphorus deficiency differs from that induced by aluminium. *New Phytol.* 176: 581 - 589

Wang, L. J. and Nichollas, G. H. (2008). Calcium orthophosphates:crystallization and dissolution. *Chem. Rev.* 108: 4628 - 4669

Wang, Y., He, Y., Zhang, H., Schroder, J., Li, C. and Zhou, D. (2008). Phosphate mobilization by Citric, Tartaric and Oxalic acids in a clay loam Ultisol. *Soil Sci. Soc. Am. J.,* 72(5): 1263 - 1268

Whalen, J. K. and Chang, C. (2001). Phosphorus accumulation in cultivated soils from long term annual applications of cattle feedlot manure. *J. Environ. Qual.* 30: 229 - 237

Whitelaw, M. A. (2000). Growth promotion of plants inoculate with phosphate solubilizing fungi. *Adv. Agron.* 69: 99 - 151

Wissuwa,, M., Mazolla, M. and Picard, C. (2009). Novel approaches in plant breeding for rhzosphere-related traits. *Plant Soil*. 321:409 - 430

Yadav, B. K. and Tarafdar, J. C. (2007). Ability of *Emericella rugulosa* to mobilize unavailable P compounds during pearl millet (*Pennisetum glaucoma* L.) crop under arid condition*. Indian J. Microbio.* 41(1): 57 – 63

Yadav, B. K. and Tarafdar, J. C. (2010). Studies on phosphatase activity and clusterbean production as influenced by the P mobilizing organism *Emericella rugulosa. Legume Res*. 33(2):118 - 220

Yadav, B. K. and Tarafdar, J. C. (2011). *Penicillium purpurogenum,* unique P mobilizers in arid agro-ecosystems. *Arid Land Res. Mgt*. 25(1): 87 - 99

Yuan, T. L.(1980). Adsorption of phosphate and water-extractible soil organic material by synthetic aluminium silicates and acid soils. *Soil Sci. Soc. Am. J.* 44: 951 - 955

Zhang, F., Shen, J., Zhang, J., Zuo, Y., Li, L. and Chen, X. (2010). Rhizosphere processes and management for improving nutrient use efficiency and crop productivity: Implications for China. *Adv Agron* 107: 1 - 32

Zsolney, A. (1986). Dissolved humus in soil waters. In 'Humic substances in terrestrial ecosystems.' (Ed. A. Piccolo) pp171 - 223