CONCRETIONARY NODULES AS NUTRIENTS SINKS AND THEIR EFFECT ON PHOSPHATE ADSORPTION IN A PLINTHIC HAPLUSTALF

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DECLARATION

I declare that the work in the dissertation entitle CONCRETIONARY NODULES AS NUTRIENT SINKS AND THEIR EFFECT ON PHOSPHATE ADSORPTION IN A PLINTHIC HAPLUSTALF has been carried out by me in the Department of Soil Science under the supervision of Dr. Abdu Nafiu. The information provided from the literature has been duly acknowledged in the text and has a list of references provided. No part of this thesis was previously presented for another degree or diploma in this or another institution.

David Emmanuel

______________________________	________________	_______
Name of Student	Signature	Date

CERTIFICATION

This thesis entitled "CONCRETIONARY NODULES AS NUTRIENTS SINKS AND THEIR EFFECT ON PHOSPHATE ADSORPTION IN A PLINTHIC HAPLUSTALF" by David Emmanuel, meets the regulations governing the award of Master of Science degree of the Ahmadu Bello University Zaria and is approve for its distribution to knowledge and literary presentation.

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Dedication

This work is dedicated to the family of Eng. Taye Tehinshe for their support to the family of Deacon David Omojola

ABSTRACT

This research focuses on the effects of concretionary nodules on nutrient composition of a Plinthic Haplustalf, and the effects of concretionary nodules on phosphate fractions and adsorption by the soils. Soil samples were collected from five farmers field in Biye northern guinea savannah,Nigeria, the soils collected were further designated as Biye north, Biye south, Biye east Biye west, and Biye central. The soil sampled were furtherseparated into Soils without concretionary nodules, soils mixed with concretionary nodules and concretionary nodules for detailed distributions of P and other microelement in the area.

This study revealed that, the total phosphorus (Pt) of concretionary nodules in surface soils ranged from 604 to 1014 mg /kg while that of the soil without concretion was between 301.4 and 624.30 mg /kg in all locations. However, the available P in soils without concretion ranges from 10 to 15 mg/kg. Although the available P was low, the concentration was relatively higher than the concentration in soils with concretion and three times higher than the concentration in concretionary nodule. Furthermore, concretions were shown to accumulate high concentration of the total elements analysed. In the soils with concretionary nodules, most P recovered by sequential extraction was in the residual (276 - 697 mg/kg) and potentially bio-available fractions (43 – 55.8 mg/kg). The exchangeable P fraction ($NaHCO_3$-P) of the soils held the least percentage (2 – 5%) of the total P in the soils with concentrations ranging from (8 – 12.3 mg/kg) in all the locations.Organic P (Po) was also low.Phosphorus adsorption was highest when solution P concentration increases from 250 µg ml^{-1} to 1000 µg ml^{-1}.The Langmuir and Freundlich adsorption isotherms both showed well fitted with the correlation coefficients (R^2) that ranged from 0.89 to 0.96 in all the soils. The adsorption maximum (b) obtained from the Langmuir isotherm ranged from 28 mg P kg-1 soil in soil without concretion to 68 mg P /kg concretionary nodules. The constant related to bonding energy (K) calculated from the Langmuir adsorption model varied from 0.4 to 0.99 mg P /kg The Freundlich adsorption parameters also ranged from 0.87 in soils without concretion to 0.95 mg kg-1 in concretionary nodules and for the Freundlich isotherm constant (Kf) from 1.89 in soils without concretion to 1.99 in concretion.Phosphorus recovered was highest in soils without concretion. The concentration of P recovered range from 34 mg/mg P to 86 m/kg p in soils without concretions whileconcretions range from 38 to 73 m/kg P in all location.P recovery continues as a true equilibrium was not attained.

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CHAPTER ONE

1.0 INTRODUCTION

A characteristic feature of weathered savannah soils is the abundance of iron (Fe), aluminium (Al) and manganese (Mn) oxides in the soil profiles deposited as nodules and concretions (Agbenin, 2003). The nature, distribution and abundance of these nodules and / or concretions significantly affect nutrient status and phosphate availability in the soil (Torrent, 1994; Agbenin, 2003). Zhang and Karathanasis,(1997), found that these concretions are reservoir for phosphorus (P) and other essential elements. Concretionary constituents of guinea savannah soils are yet to be researched fully to ascertain their potentials for nutrient retention especially phosphate sorption.

Plinthite (derived from Greek word *plinthos* which means stone) is defined as an Fe rich , humus poor mixture of clay with quartz and other diluent that, on exposure to repeated wetting and drying, changes irreversibly to an iron stone hard pan or an irregular soil aggregate (Soil Survey Staff, 2010). However, it can distinguished from other iron rich earth material that are not plinthites as other concretions do not irreversibly hardened upon exposure to oxygen rich environments. The irreversibly hard pan plinthite is generally referred to as petro-plinthite which is also known as ironstone. (Eswaran, *et al.,* 1990; Soil Survey Staff, 2006). These plinthites are common in the alfsol with ustic moisture regime of northern Guinea savannah ecology according to (Yaro, 2005). Concretion is a mass or concentration of a chemical compound, such as calcium carbonate or iron oxide, in the form of a grain or nodule of varying size, shape, hardness and colour, found in soil or in rock. The term, concretion, is sometimes restricted to concentrations of chemical compounds having concentric fabric in soils (Rhoton *et al*., 1993). The main difference between a ferruginous nodule and concretion is the concentric internal fabric associated with the latter. Iron and Mn concretions have been found in many soils, and especially in soils with restrictive internal drainage (Rhoton *et al.*, 1991; Mc-Daniel *et al*., 1992). The effect of concretion accumulation on soil chemical properties could be significant at high concentrations, depending on the chemistry and mineralogy of the oxide components. In soils of the semi-arid tropics, the oxides, hydroxides and oxyhydroxides of Fe, Mn and Al are common. The best- known effect of the Fe-oxide surface is its high affinity towards phosphate retention.

The concretionary soils which comprise mostly lateritic ferruginous nodules are known to adsorb significant amounts of phosphate. Ferruginous nodules are abundant in concretionary soils. The nodules often have higher P content than the surrounding soils. They serve as effective sink for added soluble P (Zhang *et al.*, 2005; Tiessen *et al.*, 1991). Traces of Ca, Mg, P and Na are also noticed in the black and brown concretions thereby rendering those essential nutrients unavailable to plant. The trend in the formation of these concretion indicate that, the formation, development and accumulation of Fe-Mn concretion are dynamic and progressive translocation and transformation process of Fe and Mn in the soil profile (Manojlovic *et al.*, 2007; Zhang and Karathanasis, 1997).

In acid soils, P sorption is generally attributed to hydrous oxides of Fe,Mn, and Al. Phosphorus sorption in acid soils was also considered to be a special case of precipitation, wherein Al or Fe remained as the constituent of the original phase while reacting with P by the use of residual force on the surface(Cornell, and Schwertmann, 2003).Lim and Jackson, (2003) considered sorption to prevail at low P concentrationsin soil solution, and precipitation at higher concentrations. Such a process of formation of new P compounds may be slow, and the attainment of equilibrium is likely to be disturbed by P uptake by plants, diffusion, and more importantly, by rapid adsorption of the soluble P by surface-reactive Fe and Al oxides. As a consequence, persistence of fertilizer reaction products in soils is unlikely (Sanyal and De Datta, 1991).

1.1 Problem Statement

The availability of P to crop in the savannah is more than just having P in the soil. It depends on the abundance of Fe and Al oxide and management factors that influence plant growth. The fate and efficiency of native and applied P is one of the biggest problems in arable crop production in the tropics. One problem is that fertilizer P can be largely fixed by oxides, hydro-oxides and oxy hydroxides of Fe, Mn, Al and clay minerals in acidic soils, which makes it less available or effectively unavailable to plants (Shen *et al.*, 2011). Despite the high intensity of weathering and the abundance of free Fe oxides in savannah soils, their P sorption capacity is considered low (Agbenin, 1996; Abdu, 2009). Variable charge minerals are also major components of savannah soils that make P unavailable to plants because of the dominance of sesquioxides and low activity clay content especially the Oxisols, Ultisols and Alfisols. This may seem to over simplify the problem of most savannah soils. There are, however, some soils with apparent P deficiency that have failed to respond to fertilizer P while others with apparent sufficient P level in the soil have responded to fertilizer P application (Mokwunye, 1995; Agbenin, 2003). This paradox has never been satisfactorily resolved for most savannah soils because sufficient attention has not been paid to the understanding of P retention mechanisms and the role of concretion and nodules on the soil's P retention and availability. Whereas, Agbenin, (2003) demonstrated the role of extractable Fe and Al oxides on P sorption in savannah soils while Tiessen *et al.* (1991) provided evidence that nodules/concretions are nutrients and P sink in some savannah soils of Ghana thereby curtailing crop response to fertilization.

1.2 Justification

With increasing demand of agricultural production, P is receiving more attention as non-renewable resource (Corddel andDangert, 2009) since P is a major limiting nutrient for agricultural and ecosystem productivity (Tiessen *et al.,* 1990). One unique characteristic of P is its low availability due to its slow diffusion and high affinity for soil constituents. Maintaining a proper P supplying level at the root zone can enhance the efficiency of plant root to solubilize and acquire P from the rhizosphere. To avoid a future food related crises in West Africa, P deficiency and availability problems need to be addressed along with other nutrients, especially under intensive land use system. Demographic pressures have increased intensification of land use and the cultivation of marginal lands whose productivity even with inorganic P fertilization remains poor. Most of these lands are characterized by high pedogenic weathering with the abundance of Fe, Mn, and Al oxides deposited in the soil as nodules and concretions. Responses to fertilizer application in these soils can be described at best marginal with no significant increase in crop yield. More often than not, the main limitation to the productivity of the soil is the availability of P.

1.3 Objectives of the Study

The main goal of this study is to evaluate the nutrient composition and P adsorption of concretionary nodules vis-a-vis the bulk soils in a Plinthic Haplustalf from northern Nigeria that is non-responsive to fertilizer application. The specific objectives are to determine:

1. The effect of concretionary nodules on nutrient composition of a Plinthic Haplustalf.
2. The effects of concretionary nodules on phosphate fractions and adsorption by the soils.
3. The effect of concretionary nodules on phosphate recovery in soils

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Concretionary Nodules

Although sometimes considered geologic aberration, concretions are very common and widespread in sedimentary rocks throughout the geologic record (Seilacher, 2001; Mozley, 2003). They are common where groundwater can precipitate cement. Intensive studies of calcite and siderite concretions have examined their internal zonation and mode of growth (Klein *et al.,* 1999; RaiswellandFisher, 2000; Hall *et al.,* 2004; Mozley, 2003) and the possible role of microbial influence (Borkow and Babcock, 2003; Mozley and Davis, 2005). Calcite and siderite studies show a complex range of varied textures that suggest concentric to pervasive growth in addition to growth in different hydrologic environments (Mozley and Davis,2005). Iron oxide concretions are similarly complex and difficult to study. They are formed from a series of chemical oxidation and reduction steps, and the nucleation, precipitation and maturation of polynuclear gels (Chan *et al.*, 2005, 2007). They are significant indicators of the mobility of Fe in groundwater and host rock properties such as porosity and permeability. Iron oxide concretions may not have any obvious nucleus (Chan *et al.,* 2004, 2005) and seem to form in different ways from simple attractive growth around a physical ‘seed’ nucleus (Mozley, 2003). Some basic questions regarding Fe oxide concretions are: how do concretions start or nucleated? What influences their growth?

2.1.1 Formation of concretionary nodules

Iron and Mn concretions are formed within a soil apparently initiated as infillingsdue to periodic redox and seasonal changes in soil moisture status (Schwertmann andCornell, 2000). Iron and manganese concretion are common in upper sola of Alfisols and Ultisols of

West African region (Chan *et al.*, 2005). Their nature and quantities appear to be related to the fluctuation of seasonal perched water table above clay argilic horizons. Iron and Mn concretions have been found in many soils, and especially in soils with restricted internal drainage. The initial phase is the formation of nuclei and once the nuclei of ferric and Mn oxides are formed, the concretion can grow from year to year by absorbing and oxidizing the ferrous and manganous salt at their surface (Rhoton *et al.*, 1993). There is an important distinction between concretions and nodules. Concretions are formed from mineral precipitation around some kind of nucleus while a nodule is a replacement body.In these soils, Fe and Mn are mobilised by reduction and afterwards concentrate in various forms, among which concretions are the most frequent. Iron and Mn concretions have been observed worldwide. The composition of concretion varies in different soils, but the general process may be the same. The quantity, mineralogy, chemical composition and size in soils are site specific depending on the action of weathering processes for that location (Chan *et al.*, 2004). The cementing agents for Fe-Mn concretions are Fe and Mn oxides. The effect of concretion accumulation on soil chemical properties may be significant at high concentrations, depending on the chemistry and mineralogy of the oxide components (Yu andSivtsov, 2004; Churchman, 2002). These firm to extremely firm sub-rounded discrete bodies are formed by the processes of reduction, translocation, and oxidation of Fe and Mn. During wet periods, Fe (III) and Mn (III/IV) are reduced and dispersed throughout the soil matrix, whereas during drying periods they re-precipitate, lining or filling matrix pores. Repetition of this process forms these millimetre-sized redoximorphic features with distinct concentric structures of alternating Fe- and Mn-rich zones. Therefore, Fe-Mn concretions are characterized by a greater concentration of Fe and Mn oxides than the surrounding soil matrix (Yu and Shelobolina, 2007; Churchman, 2002; Gasparatos *et al.*, 2004). Gasparatos *et al*. (2005), found that Mn and Fe are not distributed evenly in all concretions in a given soil horizon.

Manganese content is directly related to size of concretions with larger concretions containing more Mn and lower Fe/Mn ratio than small size concretions. Also, dark coloured concretions are generally higher in Mn content than light coloured concretion (Borggaard, 2002). Colour, shape and hardness of these concretions may differ among different soils.

2.1.2 Concretion chemistry

Sesquioxides are common products of chemical weathering and important constituent of most soils. Formation of concretions requires that reactants reach some level of super-saturation such as nucleation threshold with respect to equilibrium precipitation (Churchman, 2002; Borggaard, 2002; Gasparatos *et al*., 2004; Saleque *et al*., 2004). The identity of the reactants differs with the chemical composition of the concretion. Hydrous ferric oxide concretions are likely to precipitate as a consequence of oxidation of ferrous ion in solution according to the hematite reaction (Chan *et al*., 2007).

$$2Fe^{2+}_{(aq)} + 1/2O_{2(g)} + 2\ H_2O_{(L)} \underline{\qquad} Fe_2O_{3(S)} + 4H^+ \underline{\qquad\qquad\qquad} \text{Eq(1)}$$

Or the goethite reaction:

$$2Fe^{2+}_{(aq)} + 1/2\ O_{2(g)} + 3H_2O \underline{\qquad} 2FeO(OH)_{(g)} \underline{\qquad\qquad\qquad} \text{Eq (2)}$$

Reactants are Fe^{2+}(aq), O_2(aq) and H^+(aq).

The effective free energy difference between goethite and hematite is very small (Stumm and Morgan, 1996). Thus, formation of hematite, goethite, or hydrous ferric oxide can be a consequence of subtle differences in conditions such as pH, $O_{2(aq)}$, or other factors. Hematite may result from maturation of goethite by dehydration:

$$2FeO(OH)(s) \underline{\qquad} Fe_2O_3(s) + H_2O \underline{\qquad\qquad\qquad} \text{Eq (3)}$$

Furthermore, ferrihydrite can also transform into hematite. As ferrihydrite requires significantly lower temperatures than goethite to transform to hematite, it may be a promising model for hematite formation under near-surface conditions (Schwertmann *et al.,* 2004).

Concretions are sink / reservoir for essential plant nutrients. Black and large sized concretions usually have a lower Fe/Mn ratio, indicating less Fe and higher Mn (Timofeeva, 2008). This is in contrast with large sized and brown coloured concretions which has higher Fe/Mn ratio. Traces of Ca, Mg, P and Na are also noticed in the two colours thereby rendering those essential nutrients unavailable to plants (Saleque *et al*., 2004).. The trend in the formation of these concretion indicate that, the formation, development and accumulation of Fe-Mn concretion are dynamic and progressive translocation and transformation process of Fe and Mn in the soil profile (Zhang and Karathanasis, 1997; Saleque *et al*., 2004). Iron and Mn are naturally concentrated under the forms of concretions, nodules, peds and pans. Due to their redox potential variations they are able to concentrate and control the distribution of certain other metal ions such as heavy metals and other trace element for plant nutrient uptake (Zhang and Karathanasis, 1997).

2.1.3 Chemical composition of Fe-Mn concretions

Table 2.1. Elemental composition of concretions from a pedon in a Kentucky Alfisols

Parameter	Value(%)	Value(%)
Horizon	Ap	Ap
Colour	Black	Brown
Size (mm)	2	2
SiO_2	38.69	34.15
$Al_2 O_3$	17.72	14.56
Fee_2O_3	25.99	48.97
MnO	14.28	0.89
CaO	0.88	0.44
MgO	0.57	0.47
K_2O	1.45	1.11
Na_2O	0.57	0.46
TiO_3	0.94	0.91
P_2O_5	0.31	0.76
Total	101.4.	102.17
Fe /Mn	1.8	55.0

Source: (Zhang and Karathanasis, 1997).

2.2 Occurrence of Concretion Nodules in Savannah Soils

Concretions are found in a variety of soil, but are particularly common in shale, siltstones, and sandstones. They often outwardly resemble fossils or rocks that look as if they do not belong to the stratum in which they were found. Occasionally, concretions contain fossils; either as its nucleus or as a component that was incorporated during its growth but concretions is not fossils themselves (Raiswelland Fisher, 2000). They appear in nodular patches, concentrated along bedding planes, protruding from weathered cliff sides, randomly distributed over mud hills or perched on soft pedestals. Concretions have been reported in different soils and in different part of the world (Babanin*et al.*,2000; Timofeeva, 2008).

The occurrence of concretions has been widely reported in the profile of Nigerian soils. These concretions have even been dominant factor in the suitability classification (Stumm and Morgan, 1996). In Nigeria soils like in others in which concretions have been reported, the concretions can occur in any horizon of the profile (Obi *et al*., 2009; Agbenin, 2003). Concretions vary in size, colour, density and structure (Bigham *et al*., 2002). The colour of the concretion is dependent on the amount of Fe and Mn present. The Fe-rich concretions are reddish brown to nearly black in colour but separately, Fe concretions are shiny black in colour while concretions rich in Mn are dark purple to black and are usually softer than Fe concretions (Bigham *et al*., 2002; Kämpf *et al*., 2002). By far the most common concretions in central western Nigeria are those found within the gravel layers of most sedimentary soils (Obi *et al*., 2009).

2.3 Effects of Concretionary Nodules on Soil Properties

2.3.1 Chemical properties

Iron and Mn oxides concretionary nodules common in soils and sediments play a key role in the biogeochemical cycles of metals and organic carbon while influencing significantly the transport and fate of both contaminants and nutrients in the environments through sorptive, catalytic and oxidative processes (Tebo *et al.,* 2004; Hinsinger, 2001; Zhou and Li 2001; Zhang *et al*., 2005). Iron–manganese concretions have been found to be widespread in soils with some internal drainage restrictions (Gasparatos *et al.*, 2004; Zhang and Karathanasis, 1997). Chemical analysis has revealed that concretions vary in composition but are generally richer in some elements compared to the bulk soils in which they are found particularly Fe, Mn, Cu, Mo, Vn and Co (Jizheng, *et al.*, 2008; Timofeeva, 2008). The Fe and Mn compounds are often present in concretions as their oxides, Fe_2O_3 and MnO_2 or Mn_3O_4. Their chemical compositions are affected by such factors as parent materials and size of the concretion (Timofeeva, 2008; Akinbola *et al*., 2013). Concretionary material binding together the matrix mineral in most cases represents a minor part of the whole concretions so that identification of Fe and Mn minerals are often difficult. Added to this problem of quantity is the fact that the Fe and Mn minerals may exist at different degrees of oxidation and hydration and may even have other elements substituting them in their minerals (Akinbola *et al*., 2013). The effect of concretion accumulations on soil chemical properties may be significant at high concentrations, depending on the chemistry and mineralogy of the oxide components.

2.3.2 The role of concretions on charge distribution of soils

Iron oxide concretions influence soil properties. The influence is due to functional group at their surfaces (Schertmann and Cornell, 2000). Retention of various anion and cations at the particle surface and electron and proton buffering among others are the properties affected by Fe oxide. It is generally accepted that Fe oxides contribute to pH dependable or variable charge of soil by adsorption /desorption of proton. The extent of this contribution is a function of surface area rather than the type of oxide present (Latrill *et al.*,2007). The assumption here is that all oxide surfaces are hydroxylated in an aqueous system (Schertmann andCornell, 2000). Beside variable charge, the clay silicate which carry the negative permanent charge that is, pH-dependent charge due to cations substitution (Schertmann and Cornell,2000).

The absolute contribution of Fe oxide to the surface charge is particularly important in highly weathered Oxisols in the tropics where Fe oxides forms a significant part of the fine particle fine fraction. Their influence can be recognized by high point of zero charge (PZC) (usually greater than 5) (Yu and Sivtsov, 2004). Although such soils with high PZC often also contain gibbsite, which have a charging behaviour similar to that of the Fe oxide, the high ZPC is due to Fe oxides because the selective removal of the latter significantly lowers the PZC which is then dominated by the negatively charged clay minerals (Zhang *et al,* 2004). Conversely, the addition of Fe oxides to the soil minerals or soils leads to an increase in the PZC (Yu and Sivtsov, 2004, Yu and Shilobolina, 2007). In soils, electrons are produced by the metabolic activity of soil biota. These electrons are usually accepted by O_2 dissolved in soil solution which is then replaced by O_2 from the soil air. Oxygen may however, become deficient if all pores are filled with water as in water logged or compacted soils. Fe^{3+} in Fe oxides may then function as an alternative electron acceptor and Fe^{2+} ions will be formed. The electrons are transferred from the decomposing biomass to the Fe oxides by microbially produced enzymes (Schwertmann and Fenning, 1993).

2.3.3 Anion and cation binding

The binding of cations and anions by Fe oxide through surface adsorption and incorporation makes soils important sinks for a range of compounds such as heavy metals, phosphate and sulphate (Tiessen *et al.,* 1991). This can be derived from significant correlation between such compound and the Fe oxide content of soils (Tiessen *et al.,* 1991).Of the anions, phosphate, as an essential major plant nutrient has attracted specific attention due to its high affinity for Fe oxide. Phosphate sorption was found to be positively correlated with Fe (Timofeeva and Golov, 2007; Saleque *et al.*, 2004) and increase with increasing contact time.

2.3.4 Effects of concretionary nodules on soil microbial properties

Iron and Mn oxides (including hydroxides and oxyhydroxides) are ubiquitous in soils and sediments and plays a key role in the biogeochemical cycles of metals and organic carbon while influencing significantly the transport and fate of both contaminants and nutrients in the environments through sorptive, catalytic and oxidative processes (Tebo *et al*., 2004). Under reducing conditions, Fe and Mn oxides could release Fe (II) and Mn (II) ions into the soil solution; and when the soil dries, Fe (II) and Mn (II) are oxidized and precipitated, forming new metal oxides (Saleque *et al*., 2004). Increasing evidence is showing that microorganisms, especially bacteria, play a significant role in the oxidation of dissolved Mn (II) in natural aqueous systems (Teboetal, 2004; Tebo *et al*., 1997; Jizheng *et al*., 2008). Bacterially mediated (biological) Mn (II) oxidation is up to 10^5 times faster than abiotic Mn (II) oxidation, suggesting that biological Mn (II) oxidation dominates in the environment (Kim *et al*., 2003; Tebo *et al*., 2004). A number of investigations at specific field sites have shown that the biological processes are responsible for Mn (II) oxidation at those locations (Kay *et al*., 2001; Harvey and Fuller, 1998; van Cappellen *et al.*, 1998;). Hence, the majority of naturally occurring environmental Mn oxides are believed to be derived either directly from biogenic Mn (II) oxidation processes or from the subsequent transformation of the biogenic oxides (Tebo *et al.,* 2004).

2.4 Effects of Concretionary Nodule on Soil Fertility

2.4.1 Effects on micro nutrient status

Manganese and Fe are important elements for plant and animal nutrition (Liu *et al*., 2002). In addition, oxides and/or hydroxides of both Mn and Fe are the main Mn–Fe phases in the soils, and they often act as strong scavengers of trace elements during weathering and pedogenesis (Palumbo *et al*., 2001; Cornu *et al*., 2005; Feng, 2011). They also affect the mobility of trace elements in soils and the phyto-availability of both nutrient and toxic trace elements (Palumbo *et al*., 2000, 2001; Liu *et al*., 2002). Through mechanisms such as co-precipitation, adsorption and lattice substitution, among others, the trace elements are gleaned from the soil solution, and incorporated into concretions (Palumbo *et al*., 2000); however, once the pedo-environment has been changed, the trace elements adsorbed in concretion become chemically unstable, possibly desorbing into the soil solution (Timofeeva, 2008).

2.4.2 Effect of concretionary nodules on soil phosphorus status

In several studies, the main components of concretions are ferrihydrite and goethite or hematite with variable amounts of Al as substitutions, while Mn oxides were found to be fine-grained with relatively diffuse X-ray diffraction (XRD) peaks (Gasparatos *et al*., 2004; Zhang and Karathanasis 1997). The nature of Fe and Mn oxides in soil concretions is of great interest from the viewpoints of both pedogenesis and environmental chemistry (Gasparatos *et al*., 2005). Studies on the dynamic role of Fe oxides in the soil system have shown the need for the expansion of current knowledge on the properties and morphology of natural secondary iron oxide accumulations such as concretions (Gasparatos *et al*., 2004; Gasparatos *et al*., 2005). The reactions of phosphate with soil components have been extensively studied (Borggaard, 2002; Zhang and Karathanasis 1997). Amorphous oxides of Fe and Al are the components that predominantly influence phosphate sorption in different types of soils and sediments (Borggaard, 2002). Specifically, these oxides may sorb phosphate by an exchange reaction, where the singly coordinated hydroxyl groups at oxide surface is replaced by phosphate (Raisewell and Fisher 2000).

Most tropical soils are high in iron oxides. They occur as concretions, lateritic crusts and in fine earth (Agbenin, 2003). Free Fe oxides are high in clay fraction whenever they are absent as concretions. Their occurrence exert important effect on soil physical properties thus, a positive correlation exists between free Fe oxides and the degree of clay and silt particles. Clay reacts rapidly with phosphates forming series of soluble hydroxyl phosphate (Arai and Sparks, 2007). Iron and Mn concretions have been found in many soils especially the soils with restrictive internal drainage. The quantity, chemical composition and size of concretions in soils are site specific depending on the action of weathering process for that location. Therefore the concretionary material is characterized by a greater concentration of Fe and Mn oxide than the surrounding soil matrix. It also differs from the surrounding soil matrix by containing less SiO_2 (Verlaan *et al*., 2004; Feng, 2010, 2011). The effect of concretion accumulation on soil chemical properties could be similar at high concentrations depending on the chemistry and mineralogy of the oxide components.

2.5 Phosphorus Availability in Soils

Phosphorus in soils exists in four different “pools” on the basis of their accessibility to plants (Syers *et al*.,2008). The first pool of P is that which is in the soil solution and is immediately available for uptake by plant. The second pool is P which is held on site on the surface of soil particles. This P can be readily transferred into soil solution for uptake by plants if the concentration of P in solution is lowered by plants uptake. The third pool of P is more strongly adsorbed to soil particles and is less readily extractable by plant but can become readily available to plant overtime. The P in the fourth pool is very strongly bounded to the soil components and is only very slowly available to plant for uptake, often over a period of many years (Turner *et al.*, 2007; Syers *et al.*, 2008).

2.6 Soil Phosphorus Transformation

The dynamics of P transformation in soils is shown in Fig 2.1. Soil P exists in various chemical forms including inorganic P (Pi) and organic P (Po). These P forms differ in their behaviour and fate in soils (Hansen *et al.*, 2004; Turner *et al.*,2007). Inorganic P usually account for 35% to 70 % of the total P in the soil but in savannah soils it account for between 60 and 84% of total P (Agbenin, 1996). Primary P minerals including apatite, strengite, varisite are very stable, the release of P from these minerals by weathering is relatively too slow to meet the crop demand, though, direct application of P rocks have proved relatively efficient for plant growth in acidic soils. In contrast, secondary P minerals including Ca, Fe, and Al phosphate vary in their solubility depending on size of mineral particles and soil pH (Pierzynsky and Sim2005; Oelkers and Valsami 2008). With increasing soil pH, solubility of Fe and Al phosphates increase but solubility of Ca phosphate decreases, except for pH value of above 8 (Hinsinger, 2001). The P adsorbed on various clay and Al/ Fe oxides can be released by desorption reaction. All these P forms exist in complex equilibria with each other, representing from very stable, sparingly soluble P to plant available P pools such as labile P and solution P.

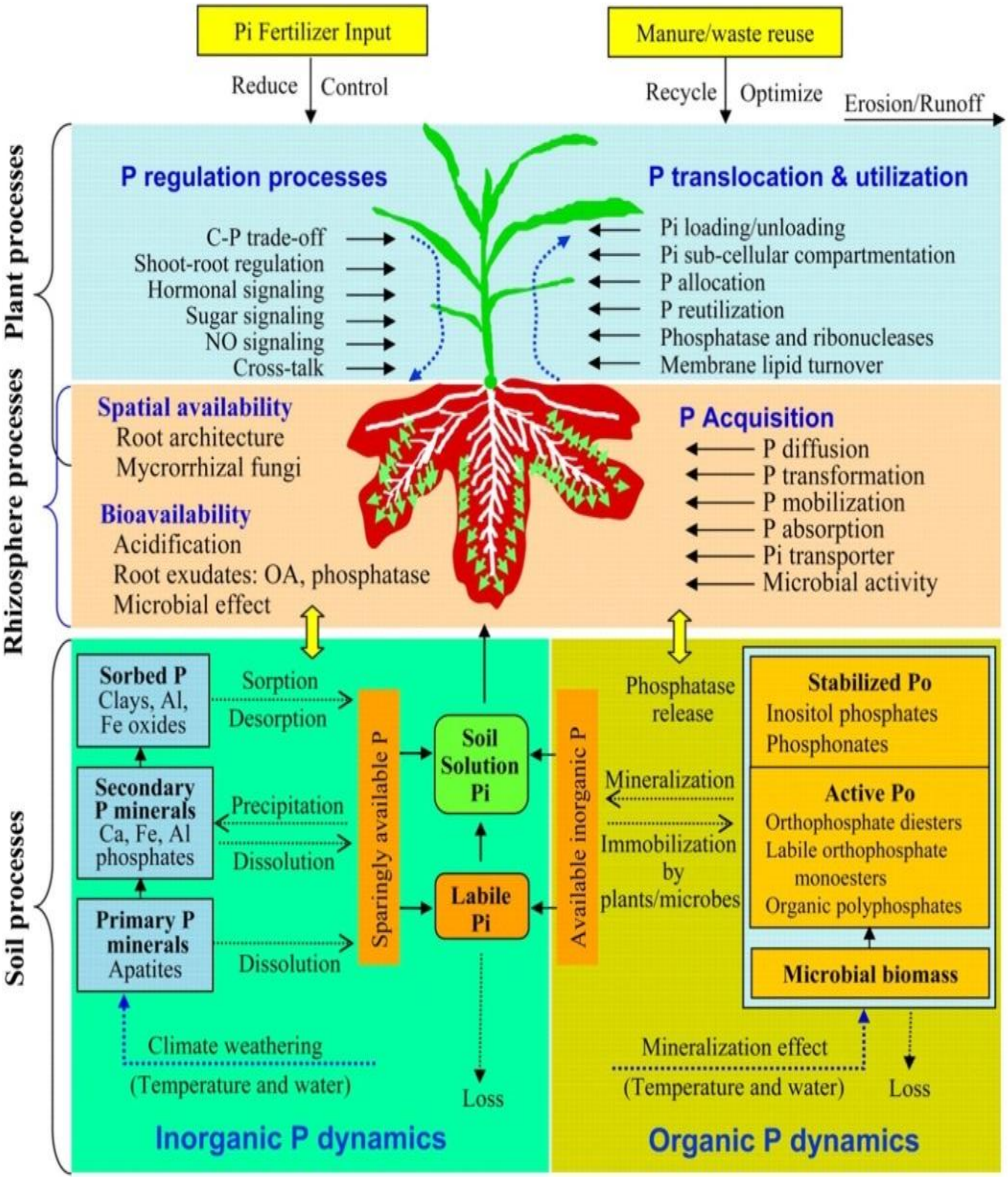

Fig2.1: Dynamics of P transformation in soil plant continuum (Shen *et al.*, 2011)

In acidic soils, P can be dominantly adsorbed by Al/Fe oxide and hydroxide, such as gibbsite, hematite and goethite (Arai and Sparks, 2007). Phosphorus can be first adsorbed on the surface of clay minerals and Fe/Al oxides by forming various complexes. The non-protonated and protonated bi-dentate surface complexes may co-exist at pH 4 to 9, while protonated bi-dentate inner-sphere complexes are predominant under acidic conditions (Luengo *et al.*, 2006; Arai and Sparks, 2007). Clay minerals and Fe/ Al oxides have large surface area that provide large number of adsorption sites. The adsorption of soil P can be enhanced with increasing ionic strenght. With further reactions P may be included in nanopores that frequently occurr in Fe/Al oxides, and thereby becomingg unavailable to plant (Arai and Sparks, 2007).

In neutral to calcareous soils, P retention is dominated by precipitation reaction, although P can also be adsorded on the surface of calcium carbonate and clay minerals (Devau *et al.*, 2010). Phosphorus can precipitate with calcium Ca, generating dicalcium phosphate (DCP) that may be available to plant. Altimately, DCP can be transformed into more stable form such as octocalcium phosphate (OCP) and hydroxyapatite (HAP), which are less soluble and non available to plant at alkaline pH (Arai and Sparks, 2007). Hydroxyapatite represent more than 50% of total Pi in calcareous soil under long term fertilizer P application, dessolution increases with decreasing soil pH (Wang and Nancollas 2008), sugesting that rhizosphere acidification may be an efficient strategy to mobilize soil from calcareous soils.

In weathered soils, the total P concentration in nodules and clay fraction decreases with depth and therefore weathering intensity. The silt fraction accumulates smaller amount of P than clay fraction suggesting that, the clay and the nodules are more effective in controlling total P accumulation (Dwuona *et al.*, 1994). Greather concentration of sexquioxide and kaolinite in the nodules and clay are responsible for accumulation of P

(Nartey, 1994). For Nigeria savannah soils dominated by Alfisols or tropical feurogenous soils, crystalline Fe is the predominant Fe form (Agbenin, 2003). Tiessen *et al.* (1991) reported that ferugionous Fe nodules are the major P sinks in several Alfisols from semi arid region of Ghana northeast Brazil.

2.7 Phoshorus Supply in Weathered Soils

Phophorus is absorbed by plants in the ionic form HPO_4^-or $H_2PO_4^-$. General knowledge of ion exchange in soils would predict that these anions are not extensively retained by the negative charged soil colloids. However P does not also leach extensively even with large amount of P added to soil because of limited movement in the soil profile. The reason for this apparent anomality is that only a small portion is dissolved in soil solution at any one time. It has been estimated that the P in soil solution must be replenished on an average of about twice every day for normal crop growth (SSRP, 1989). It is the soils ability to replenish the soil solution that dictates whether the soil will need addition of fertilizer P and whether this addition will be effective in the forms applied. The ability of the soil to replenish the soil solution with P is dependent on the complex chemistry of the soil system (Arai and Sparks, 2007).

2.8 Soil Properties and Phosphorus Retention

Due to some soil properties, P may be removed from the soil solution phase and render it less soluble. This phenomenon has previously been called P fixation but in morden soil chemistry called inner sphere complexation of P or speccific adsorption. Soil factors that promote P retention incude the following: Soil pH, Oxide of Fe, Al, Mn and their concretions, Fe, Al and Mn ions in the soil solution, Soil carbonate.

2.8.1 Soil pH

The availability of some plant nutrients is greatly affected by soil pH. The ideal soil pH is close to neutral , and neutral soils are considered to fall within a range from slighly acidic of 6.5 to slighly alkaline pH of 7.7. It has been determined that most plant nutrients are optimally availableto plants within this range (Fall, 2010).

The general relationship between soil pH and P availability, which is based on the kinds of P compounds associated with the different pH levels is shown in Fig 2.2 At high soil pH, most P is in the form of calcium compounds. At low or acid pH, P is combined with Al and Al compounds. Maximum P availability occurs at a soil pH of between 6.5 to 7.0. This is why one of the most important benefits of liming acid soils is improving P availability. Reducing the pH of calcareous soils would also increase the availability of P in the soil solution by changing some of the solid phase compounds into compounds of higher solubility (Arai and Sparks, 2007).This theoritical P availability as a function of pH has not been demostrated for savannah soils. Instead, the reverse is the case as Mokwunye (1995) observed increased P retention with incresing soil pH in savannah soils, an observation later supported by Agbenin (1996) who explained that increased P retention with pH in savannah soils can be explained by three possible mechanisms involving Ca-induced P retention, co-precipitation of Ca and HPO_4^{2-} and precipitation of Ca phosphate because of the dominance of Ca in the exchange complex of savannah soils.

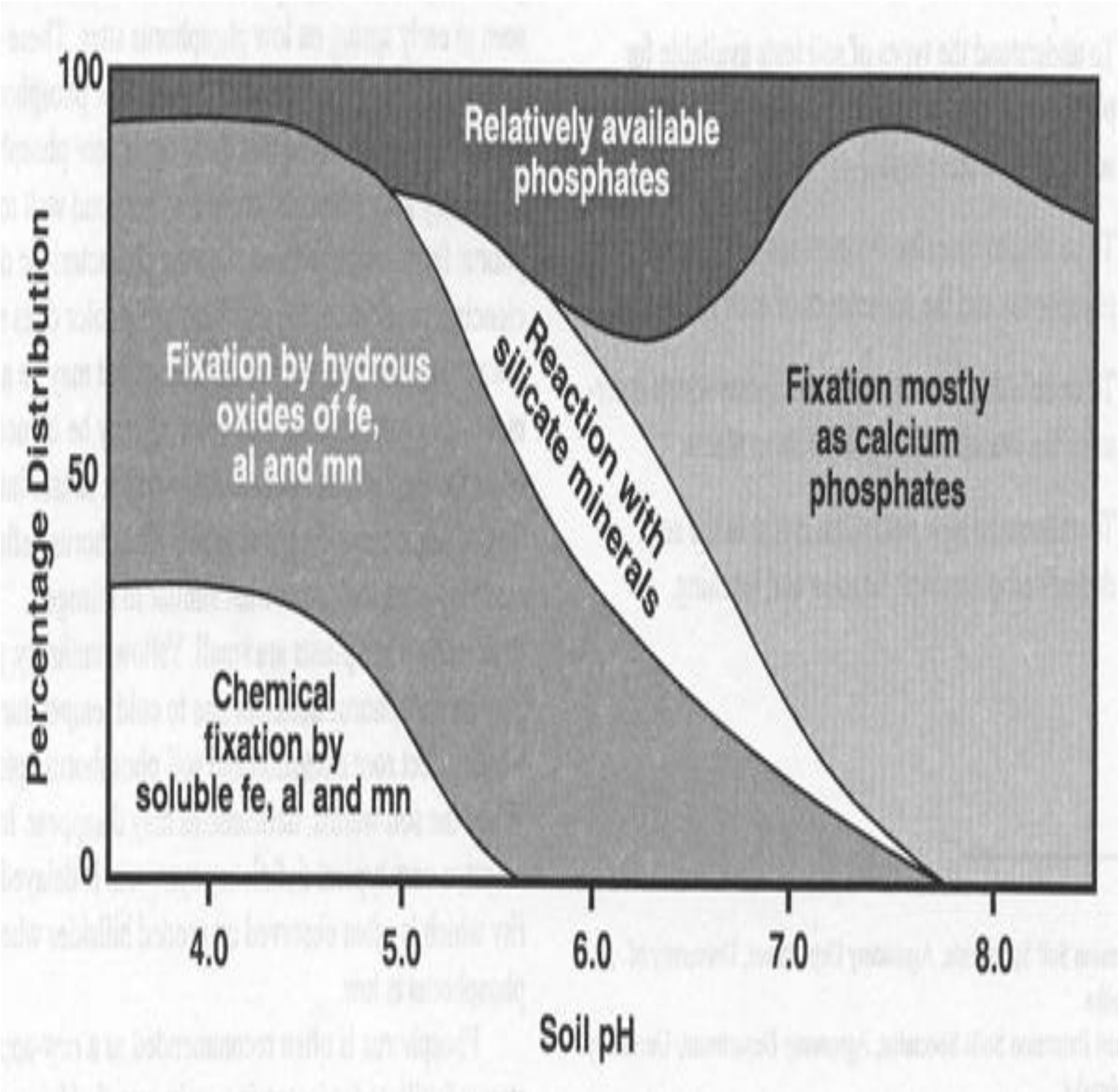

Fig 2.2 Soil P compound in relation to soil pH (Fall, 2010);

2.8.2 Oxides of Fe, Al , Mn oxide and concretions.

The most common iron oxide in soils are hematite (Fe_2O_3) which gives the pink bright red colour of soil and goethite (FeOOH) which gives the dark reddish brown colour to soils (Torrent, 1994).Ferromanganese concretions (FMCs) occur mainly in soils (Williams and Owen, 1992; Verlaan *et al*., 2004; Feng, 2010, 2011). Ferromanganese concretions in soils possibly play an important role for the pedobiosphere. Manganese and Fe are important elements for plant and animal nutrition (Liu *et al*., 2002). In addition, oxides and/or hydroxides of both Mn and Fe are the main Mn–Fe phases in the soils, and they often act as strong scavengers of both nutrient elements during weathering and pedogenesis (Palumbo *et al*., 2001; Cornu *et al*., 2005; Feng, 2011). Manganese and Fe also affect the mobility of P in soils and the phytoavailability of both nutrient and toxic trace elements (Bellanca *et al*., 1996; Palumbo *et al*., 2000, 2001; Liu *et al*., 2002). Through mechanisms such as co-precipitation, adsorption and lattice substitution, among others, micro elements are scavenged from the soil solution, and are incorporated into FMCs, however, once the pedo-environment has been changed, the trace elements adsorbed in FMCs become chemically unstable, possibly desorbing into the soil solution (Palumbo *et al*., 2001).

Phosphorus sorption on oxides explains the soil P behaviour better and precipitation becomes dominant only under high concentration of phosphate ions (Castro and Torrent, 1998; Delgado and Torrent, 1997), which is never the case with most calcareous soil system (Delgado and Torrent, 1997; VonWandruszca, 2006). At low concentration, P is initially adsorbed on Fe oxide surfaces through ligand exchange reaction and is later trapped through occlusion (Hinsinger, 2001; Tunesi *et al.*, 1999; Torrent *et al*., 1990).

Despite an increasing interest in P sorption on Fe oxide, numerous sorption studies have been conducted using only synthetic Fe oxide. Considerably less is known about natural system

(Bigham *et al*., 2002), especially in calcareous environment where the mechanism of P sorption and strength and reversibility of sorption can differ substantially. Since build-up of P is affected by the nature of P species in soil which varies widely with location, redox and pH conditions, soil type and management system (von Wandruszka, 2006), each soil may have different mechanisms of P mobility and transfer (Haygarth *et al*., 2000) and hence variable buffering coefficients.

2.8.3 Fe, Al, and Mn ions in the soil solution

The reactions of phosphate with soil solution components have been extensively studied (Borggaard, 2002). Amorphous oxides of Fe and Al are the components that predominantly influence phosphate sorption in different types of soils and sediments (Borggaard, 2002; Slomp *et al.*, 1996; Lookman *et al.*, 1995). Specifically, these oxides may sorb phosphate by an exchange reaction, where the singly coordinated hydroxyl groups at oxide surface is replaced by phosphate.

2.8.4 Soil carbonate

The level of P is controlled by many factors including $CaCO_3$, clay content and the quantities and type of oxide for example, goethitie and hematite presence in the soils. Phosphorus retention related to the presence of Fe oxide in acid soils and to $CaCO_3$ in natural or alkaline calcareous environment (Borggaard, 2002). Strong relationship exists between $CaCO_3$ and P with Ca ion as di-calcium phosphate and surface precipitation on solid $CaCO_3$. It was also related to increased surface area of $CaCO_3$ particles (Zhang *et al.*, 2005). Recent studies have shown that Fe minerals play a dominant role in P sorption compared to Ca minerals (Hinsinger, 2001; Zhou and Li, 2001). It has been further confirmed that relative quantity of P occluded to oxide are not necessarily related to the degree of P enrichment in soil (Hinsinger, 2001; Zhou and Li, 2001; Zhang *et al*., 2005).

Small concentration of either Fe or phosphate is not valid criteria to negate P sorption in alkaline calcareous soils. The role of Fe oxide has been highlighted in wide range of calcareous soil (Shen *et al.,* 2004; von Wandruszka, 2006). The stronger relationship of sorption using hydrous Fe oxide compared to soil $CaCO_3$ (Simard *et al.,* 1994; Beauchemin *et al.,* 2003; Manojlovic *et al.*, 2007) and with quality and type of Fe oxide have been reported (Colombo *et al.,* 1991; Frossard *et al.,* 1995).

2.9 **Phosphorus Sorption**

Phosphorus availability in soils is often a limiting factor for plant growth, eventhough the total amount of soil-P may be great. In this respect it is important to fully understand the nature of the sorption and precipitation reactions which occur when fertilizer P is added to soils. Phosphorus adsorption by soils is a widely researched subject. This is primarily because of the widespread P deficiency reported for agricultural soils, and the fact that P sorption is a process mainly responsible for rendering soluble P in soil solution less available to plants (Osemwotai*et al* 2003; Oluwasemire, and Alabi 2004).The adsorption process, which refers to surface P accumulation on soil components, may, in some cases, be accompanied by penetration of the adsorbed P by diffusion into the adsorbent body, leading to further absorption of the adsorbed species. The general term sorption is sometimes used to denote any of these processes (Onweremadu, 2007; Oluwasemire, and Alabi, 2004).

In acid soils, P sorption is generally attributed to hydrous oxides of Fe and Al and to 1: 1 layer lattice clays. Phosphorus sorption in acid soils was also considered by (Abekoc,1996) to be a special case of precipitation, wherein Al or Fe remained as the constituent of the original phase while reacting with P by the use of residual force on the surface. Precipitation is a process that causes an accumulation of a substance to form a new bulk-solid phase.Borkow, and Babcock, (2003), considered sorption to prevail at low P concentrations in soil solution, and precipitation at higher concentrations. In recently fertilized soils, local conditions of low pH and high-phosphate concentrations in the vicinity of the P fertilizer granules are conducive for the formation of a wide variety of P compounds by reaction with soil components (Chan,*et al*., 2007). Such a process of formation of new P compounds may be slow, and the attainment of equilibrium is likely to be disturbed by P uptake by plants, diffusion, and more importantly, by rapid adsorption of the soluble P by surface-reactive Fe and Al oxides. As a consequence, persistence of fertilizer reaction products in soils is unlikely (Sanyal and De Datta, 1991). The quantity of P required to attain a standard P concentration in a soil is a useful index for comparing the P requirement of a wide range of soils (Tiessen, *et al*., 1991). Chan,*et al*., (2007)and Tiessen, *et al*., (1991), suggested that a solution P of 0.2 mg L-1 supplies adequate P to many plants. Thus, P sorbed at a concentration of 0.2 mg L-1 provides useful information about the P requirement of soils. Many investigators have demonstrated that the standard P requirement approximated from adsorption isotherms is a valid estimate of the P requirements for a wide range of soils and can be transferred to other soils with similar sorption characteristics (Chan,*et al*., 2007; Torrent, *et al* 1990).

2.10Phosphorus Sorption and Adsorption Isotherm

The relationship between the amounts of P sorbed per unit weight of soil (x) and the equilibrium P concentration in solution (c) bathing the soil at a constant temperature has been described by several sorption isotherms. The main motivations for describing curves were to (1) identify the soil constituents involved in the sorption (Verlaan,*et al*., 2004), (2) predict the amount of fertilizer needs of soils to meet the demand of plant uptake for optimum yield and (3) study the nature of the sorption process to learn moreabout the mechanism of the process (VonWandruszka,2006, Wang, and Nancollas, 2008). The Freundlich, Langmuir and Temkin equations are common models for the description of P sorption when input data are limited (Sanyal *et al*., 1993).

Langmuir equation may be written as

$C/q = 1/kb + c/b$

Where q = the amount of P adsorbed per unit weight of soil (mg kg-1), c = equilibrium P concentration (mg kg^{-1}), b = P adsorption maxima (mg kg-1), k = coefficient relating to bonding energy (mg kg^{-1}) and kb = distribution coefficient (mg kg-1).

The linearized form is most often used to estimate the sorption maximum (b), affinity index (k) and buffer capacity of soils.

Freundlich equation is written as

$q = Kf\ C_q{}^{1/n}$

Where KF and n are the Freundlich constants characteristic of the system involved; KF and n are indicators of adsorption capacity and adsorption intensity, respectively.

KF and n can easily be determined from the linearized logarithmic form of the equation given by: $\text{Log } q = \log KF + 1/n \log C_q$

The equation was derived empirically but is often applied to the soil-P-solution system.

(iii) Temkin equation is in the form

$$x/b = RT/a \ln AC$$

Where A and a are coefficients, R is the universal gas constant, and b is the Langmuir adsorption maximum. The equation is based on the assumption that the bonding energy of adsorption decreases linearly with increasing surface coverage.

2.11 Factors Affecting Phosphorus Sorption

Many soil properties influence P sorption. These include the nature and amount of soil components such as hydrous oxides of iron and aluminium, clay, organic matter, pH of the adsorption system and background electrolyte - its concentration and valency of the constituent cation. Acid ammonium-oxalate extractable Fe and Al proved to be important indicators for P sorption in several soils (Sharpley, 2001; Sharpley,*et al*., 1999; Sanyal *et al*., 1993).Clays, particularly 1: 1 lattice clays, may contribute to P sorption in tropical soils, especially at low pH, when the activity of Fe and Al is also expected to be higher. Hydrous oxides of Fe and Al have been found as fine coatings on surfaces of clay minerals in soil (Syers, *et al.*,1983). The role of organic matter in augmenting P sorption in soils has often been attributed to the association with and possible stabilization of soil organic matter by the 'free' sesquioxides (Senyal et al. 1993). Reduction of P sorption by organic matter in soils has also been reported (Ampofo, 1992; Agbenin, 1996; Abdu, 2009) and is explained by a possible competitive action between P and organic matter for sorption sites on hydrous oxides of Fe and Al.

A strongly negative correlation has been noted between P sorption and soil pH (Bolan et al., 1988; Mehadi and Taylor, 1988). Equally reported is an opposite effect ofpH on P sorption (Arai, and Sparks, 2007; Babanin,*et al* 2000). Mokwunye (1995) reported an increase in P sorption with increase in soil pH from 3 to 7 and attributed the increase in P sorption to an increased activity of hydroxy-aluminum at the higher pH. He suggested that P wasadsorbed on the surface of the hydroxy-aluminum species when the hydroxy-aluminum-Pattraction was strong enough to displace surface OH- ions.

2.12 Mechanism of Phosphorus Sorption by Iron Oxides

Mokwunye, (1995) stated that in general, agricultural soils of the humid and semi-arid tropics are characterized by a variable surface charge mainly because of the presence of Fe and Al oxides. One important property of the different soil Fe oxides is their surface structure and the resultant dependency of surface charge on pH. The surface of the oxides is the region of their interaction with the soil solution, and with other solid phases, plant roots, and the soil biota. Iron oxides are known to undergo nonspecific and specific adsorption with anions or cations (Schwertmann,*et a*l., 2004; Schwertmann, and Cornel, 2000). A surface charge is balanced by adsorption of an equivalent amount of anion or cation, or the respective charged regions of polarizable molecules (counter ions), held in the outer diffuse electric double layer (Schwertmann, and Cornel, 2000). Forelectrostatic (Coulombic) bonding, the adsorption is termed nonspecific and depends only on ionic charge. Other anions and cations can, however, be held much more strongly at the oxide surface when the adsorbate penetrates the Fe coordination shell and, by ligand exchange, becomes covalently bound directly to the structural cation via 0 and OH groups. This is referred to as chemisorption, specific adsorption, or ligand exchange, and was described by Sposito, (1982). Phosphate ions can be adsorbed by Fe oxides when the oxide surface exhibits net negative, net zero, or net positive charge. The variable surface charge exhibited by Fe oxides favours the adsorption of P in soils (Syers, *et al,* 2008). An important feature of specific adsorption is the transformation of phosphate ion from a monodentate ligand- sorbed form to the bidentate or ring structure form. Zhou, and Li2001; and Zhang*et al.* (2005) suggested that P sorption in the former is reversible, whereas the latter favours irreversibility. In other words, the phosphate ion in the latter form, would be less likely to be desorbed and become available to plants.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Study Site

3.1.1 Location

This study was conducted at Biye village behinde Ahmadu Bello University Teaching Hospital Samaru, Zaria, Nigeria, located between latitude $11^0$11’19.3”N and longitute 007°37’02.16”E with an altitude of about 686 m above sea level. The area is situated in the Northern Guinea savanna ecology of Nigeria with a monomodal annual rainfall of about 1011± 161mm spread over five months, i.e. May/ June to September/October.The major type of land use in the area includes, arable farming, forestry, firewood and timber explotation, livestock farming as well as industrial and urban development. Arable farming consist of subsistence farming cahracterized by intensive and continuous ccultivation. The main crops grown in the area are sorghum, maize, cowpea and soybeans and pepper. The principal cash crop crop in the area are ground nut and cotton.

3.1.2 Soil mineralogy

The soil of the study area is a leached tropical ferruginous soil, classified as Typic Plinthic Haplustalf according to the USDA Soil Taxonomy (Yaro, 2005). which has eveloped on deeply weathered Pre Cambrian Basement Complex but overlain by aeolian deposit of variable thickness.

3.2 Soil Sampling

The soil sample for this experiment were taken from five(5) farmer’s field further referred to as: Biye north, Biye south, Biye east, Biye west and Biye central.Three replicate soil samples were collected from the top 0-15cmdepth ineachfarmer'sfield.Soil samples were collected at regular intervals along a traverse.Soils from different auger points were composited to form a sample from that location. Samples collected were air-dried, sieved and stored for soil nutrient and texture analyses.

3.3 Separation of Concretionary Nodules

Air-dried soil samples were sieved through a 2-mm opening, concretions and nodules retained on the sieve were separatedfrom stones and gravels. The concretionary nodules were divided into two portions. One portion was ground to pass through 2-mm sieve and stored in plastic cups for further analysis. The finesoil was also divided into two. One portion was grinded to pass through 2mm sieve and stored in plastic cups for further nutrient analyses. The second portion was mixed with concretions and grinded to pass through 2mm sieve and stored foranalyses.

3.4 Analytical Procedures

3.4.1 Soil and concretion analyses

The particle size distribution in the soil was determined by the hydrometer method (Gee and Or, 2002). Soil pH was measured in 1:2 water suspension and in 0.01 M $CaCl_2$ suspensions using a glass electrode pH meter (Hendershot and Lavkulich,1983). The organic carbon (OC) was determined by the Walkley-Black dichromate wet oxidation method as described by Nelson and Sommers (1982). Exchangeable Ca^{2+}, Mg^{2+}, K^+ and Na^+ were extracted with 1N ammonium acetate buffered at pH 7.0 (Anderson and Ingram,1993). The total N content of the soils was determined using the micro-Kjeldahl technique as described by Bremmer and Mulvaney (1982). Available P was determined following the procedure described by Agbenin (1995) using the Bray- 1 extraction method (Bray and Kurtz, 1945). The phosphorus in solution was determined colorimetrically by the modified single solution procedure using ascorbic acid (Murphy and Riley, 1962). The cations exchange capacity (CEC) of the soil was determined by the neutral (pH 7.0) NH_4OAc saturation method (Rhoades, 1982). Organic P was determined using the method of Saunders and Williams (1995) as described by Agbenin (1995).

3.4.3 Total phosphorus in soil and concretion

Total P was determined by digestion of 1g of soil samples with a mixture of concentrated HCl, $HNO_3$and H_2SO_4 as described by Lim and Jackson (1982). Phosphorus in the digest was determined using the method of Murphy and Riley (1962).

3.4.4 Total nutrient elemental analysis on soil and concretion

One gram of soil sample was digested with a mixture of perchloric, HNO_3 and concentrated H_2SO_4. The digest was filtered and total P was determined in the filtrate using colorimetric method, Fe, Zn, Ca, Mg were determined using atomic absorption spectrophotometer.

3.4.5Phosphorusfractionation in soils

A modified method of Hedley *et al*. (1982) was used to determine soil P fractions in this study. The fractions analysed include water soluble-P (H_2O-P), bioavailable-P ($NaHCO_3$-P), potentially bioavailable-P (NaOH-P), acid soluble-P (Ca-bound P/HCl-P), and residual-P. Residual-P was calculated by subtracting the sum of the first four P fractions from the total P content in the soil.

One gram of soil sample was weighed into 50mL centrifuge tubes and was sequentially extracted with 30-ml of deionized water, 0.5 M $NaHCO_3$ (pH 1.5), 0.1 M NaOH, and 1 M HCl. Each extraction lasted for16 hours on an end-to-end shaker. After each extraction, the tubes were centrifuged at 7500 rpm for 30min. The supernatant was then passed through a Whatman No. 42 filter paper. The P concentration in the various filtrates was calorimetrically determined using the molybdenum-blue method of Murphy and Riley (1962).

3.4.6 Phosphorus adsorption study on soil and concretions

Phosphorus adsorption was conducted on the bulk soil with concretions, sieved soil without concretions and the concretions separately. Two grams of each soil sample was weighed in duplicate into 50ml centrifuge tubes and mixed with a series of orthophosphate solutions with concentrations of 0, 50, 100, 250, 500 and 1000 µgP/g soil in 0.01 M KCl solution. The centrifuge tube was brought to 20 mL mark with KCl solution to give a soil solution ratio of 1: 10. The soil suspension was immediately shaken for two hours in a reciprocating mechanical shaker. The suspension was filtered through a Whatman No 42 filter paper and analysed for P in solution by the method of Murphy and Riley (1962). Phosphorus adsorbed by the soil was the difference between added P and the P remaining in the soil solution.

Phosphorus adsorption data were fitted to the Langmuir and Freundlich adsorption isotherm.

Langmuir equation could be represented as:

$C/q=1/kb + c/b$ ---Eq.1

Where q = the amount of P adsorbed per unit weight of soil (mg kg-1), c = equilibrium P concentration (mg kg^{-1}), b = P adsorption maxima (mg kg-1), k = coefficient relating to bonding energy (mg kg^{-1}) and kb = distribution coefficient (mg kg-1).

The Freundlich equation is given by

$q=Kf\ C_q^{\ 1/n}$---Eq.2

Where KF and n are the Freundlich constants characteristic of the system involved; KF and n are indicators of adsorption capacity and

adsorption intensity, respectively.

KF and n can easily be determined from the linearized logarithmic form of the equation given by:

Log q = log KF + 1/n log C_q--Eq.3

3.4.7 Recovery of adsorbed phosphate on soil and concretions

In line with the adsorption study, the recovery of phosphate was measured from the bulk soil with concretions, sieved soil without concretions and the concretions separately. Ten gram of each soil sample was weighed into a plastic vial andadded with 100µg of KH_2PO_4 in 0.1M KCl after which the suspensions were allowed to equilibrate for 72 hours at field capacity determined gravimetrically. The P saturated soil was air-dried and rescreened through a 2mm sieve after which 1g of the air dried soil sample was weighed into a centrifuge tube, P in the soil was extracted using the Bray-1 solution and shaking for respectively 5, 10, 30, 60, 120, 240 minutes, and 16 hours.

3.5 Data Analysis

Analyses of variance (ANOVA) were used to determine the significance of differencesin nutrient status and P dynamics between bulk soil with concretions, sieved soil without concretions and the concretions separately. All statistical data analyses were performed usingSAS statistical package version 9 (2002).

CHAPTER FOUR

4.0 RESULTS

4.1 Abundance of Soil Concretionary Nodules

This section reports on the fractionation of soil concretions from the bulk soil of three replicate soil samples in the five different farmer fields. The mass fraction of soil concretions and <2mm particles in the bulk soil are shown in Table 4.1.Biye North (BN) was a one of the experimental field. Concretionary nodules weigh 135.33 kg, and this accounted for the 17% of the bulk soil. Physical observation showed that, majority of the concretions was more or less spherical in shape and were tightly packed in the soil matrix. Biye South (BS) has similar physical properties as Biye north. Concretionary nodules made up 17% op the bulk soil in this site. Biye East (BE) had the lowest proportion of concretionary nodules in all sites, probably due to deposition of eroded fines soil. Biye west and Biye central have percentage concretion of 16.85 kg and 17.68 kg respectively.

Table 4.1 Proportion of concretionary nodules in the soil

Sampling Location	Bulksoils (kg)	Sieved soil (kg)	CN. (kg)	C N %

Biye North	750	614	135	17
Biye South	796	660	136	17
Biye East	829	763	65	8
Biye West	834	693	140	17
Biye Central	824	679	145	18

CN- concretionary nodules

Table 4.2 Particle Size Distributions of soils of study areas

Location	Sand	Silt	Clay	Textural

				Class
		%		
Biye East	67	20	13	Sandy loam
Biye South	64	24	12	,,
Biye Central	64	27	9	,,
Biye North	60	31	9	,,
Biye West	59	33	8	,,

4.2 Physical and Chemical Properties of Soils without Concretions and Soils with

Concretionary Nodule

The particle size distributions of the soil areshowed on table 4.2. The sand content of the area ranged from 58% to 67% while the silt content range from 23% to 28%. Clay content is generally low ranging from 9% to 13% with higher value in Biye east. The soil pH across the experimental fields both in fine soils (soils without concretions), soils with concretionary and the concretionary nodules was strongly acidic and was fairly consistent in all the fields. The pH in water ranges from 4.8 to 5.9 and was consistently higher than pH in $CaCl_2$ (Table 4.2). The average OC content from the three replicate surface soils measured between 0.85 and 1.10 g/kg across the five field sites in both soils with concretions and soils without concretions (Table 4.2). Sieved soils without concretion (< 2mm) have more OC than soils with concretions. Organic carbon was not determined in concretionary nodules due to insufficient sample volume.

Exchangeable Mg in soils without concretion (fine soil) is relatively uniform in all the location with a range of (1.50 – 1.80 cmol/kg). The exchangeable Mg in soils with concretion has a similar range of (1.50 – 1.82 Cmol/kg), whereas, the concretions have the lowest value ranging from (0.20 – 0.60 Cmol/kg) (Table 4.3).These values reported are in line with earlier work of Esu (1991). The exchangeable K rating of the area has been shown (Table 4.3) to be medium in soils of the study area with a range of 0.10 - 0.38 Cmol/kg. Soils without concretionary nodules have the highest value of 0.20 - 0.43 Cmol/kg while concretions accounted for the lowest value of exchangeable K (0.17 Cmol/kg).

Table 4.3 Chemical properties of the different soil fractions in study sites.

Site	$pH(H_2O)$	$pH(CaCl_2)$	%OC	Ex. Mg	Ex. K cmol/kg	Ex.Ca	CEC
Bulk soil with Concretions							
Biye North	4.95	4.28	0.85	1.69	0.32	3.87	6.61
Biye South	4.85	4.39	0.81	1.82	0.26	2.62	6.67
Biye East	4.92	4.22	0.85	1.66	0.25	1.25	5.57
Biye West	4.93	4.23	1.03	1.69	0.54	0.87	5.21
Biye Central	4.93	4.23	1.10	1.69	0.54	0.87	5.21
Soil without Concretions							
Biye North	4.91	4.06	1.03	1.55	0.20	0.57	4.81
Biye South	4.92	4.18	1.05	1.64	0.43	0.77	5.08
Biye East	5.82	4.16	0.80	1.63	0.39	0.73	5.03
Biye West	5.72	4.13	0.93	1.60	0.34	0.69	4.97
Biye Central	5.62	4.15	1.01	1.62	0.38	0.73	5.03
Concretionary Nodules							
Biye North	4.92	4.15	-	0.26	0.17	0.22	-
Biye North	4.92	4.14	-	0.62	0.16	0.21	-
Biye East	4.92	4.15	-	0.42	0.17	0.22	-
Biye West	4.83	4.15	-	0.62	0.17	0.22	-
Biye Central	4.92	4.15	-	0.32	0.17	0.22	-

- Not determined

4.3 Chemical Properties of Concretionary Nodules

The chemical properties of concretions are shown in (Table 4.3). The pH of concretions is strongly acidic and similar to that of the associated soil fines. Cation exchange capacity in concretions was not determined due to insufficient sample volume. Exchangeable Potassium in Biye north was 026 mg/kg, 0.62 mg/kg in Biye south, whereas the concentration is 0.42 mg/kg in Biye east, 0.62mg/kg in Biye west and 0.32 mg/kg in Biye central a concentration the is extremely low compared to the concentration in other soil fractions. Exchangeable K was also low with a constant value of 0.17 mg/kg in all locations.Whereas the concentration of exchangeable Ca was 0.22 mg/kg in all location, this concentration is also low compared to the concentration on other soil fraction.

4.4 Total Concentration of K, Mn, Fe, Zn, Cu in Soil Fractions

The total content of K, Mn, Fe, Zn, and Cuin the soils, soils with concretions, and concretions are shown on Table 4.4. The concretionary nodules and soils with concretions consistently contained more of the total elements analysed than the soils without concretion (fine soil).The total K content of soils with concretions ranges from 215- 650 mg/kg in all locations. Biye north which contained the largest percentage of concretionary nodule has the highest mean total K value of 500 mg/kg. 311.7 mg/kg, 233.3 mg/k, 325 mg/kg, and 225 m/kg in Biye south, east, west and central respectively. There is no significant difference in the total K within the experimental fields. The concentration of total K in the soils without concretion (soil fine) ranged from 211 – 295 mg/kg. Biye north has the highest mean total K of 388mg/kg while Biye south has the lowest mean value of 215 mg/kg. Concretion has the highest value of total K with the mean ranging from 295 mg/kg in the north to 365 mg/kg in Biye central (Table 4.4). There is no significant difference between the total K in soils with concretion and concretionary nodules alone, but there is significant difference in total K concentration between concretionary nodules and fine soil. The value for total Mn for soils with concretion ranges from 18.8 – 65 mg/kg, for soils without concretions 14.7 – 26.9 mg/kg and for concretions, 66.0 – 176.0 mg/kg. Concretions have concentrations which are 5 - 6 times higher than in the fine soil. Zinc has value ranging from 0.55 - 7.13 mg/kg for soils with concretions, 0.15 - 3.28 mg/kg for fine soils and concretionary nodule 14.66 - 45.90 mg/kg, a value 5-7 times greater than those of the fine soils. Soils with concretions have Cu value ranging from 14.13 - 178.25 mg/kg, soils without concretion 5.00 - 29.79 mg/kg while concretions have 32.33 - 1246.66 mg/kg, value that is significantly higher than those of the soil fine or soils without concretion.

4.5 Concentration of HCl extractable Zn, Ca, Mn, and Mg in Soils and Concretions

The results of the micronutrients investigation indicated low concentration of extractable Zn and Mg in the soils of the studied area (Table 4.7). While the concentration of Ca and Mn are high, Cu was so negligible that it could not be detected. The concentrations of Zn, Ca, Mn, and Mg in the soil without concretion vary widely. In the soils without concretions, the content of Zn ranges from 0.82 – 1.62 mg/kg. Magnesium has a uniform concentration ranging from 1.1 – 1.6 mg/kg. Calcium and Mn ranged from18.8 – 22.5 mg/kg and 6.5 – 22.5 mg/kg respectively.These concentrations are significantly lower than the concentration of micronutrients in concretion. The soil mixed with concretions also showed similar nutrients concentration with soils without concretion. Zn ranged from 0.55 mg/kg to 2.9 mg/kg in all location. The concentrations of other nutrients include Mg 3.1 mg/kg to 3.7 mg/kg, Ca 18.7 mg/kg to 22.5 mg/kg, Mn 8.3 mg/kg to 24.9 mg/kg in all locations. Concretions also contained Hcl extractable nutrient as shown in the table.

Table 4.4: Total concentration of K, Mn, Fe, Zn and Cu in soil with concretion in Biye, northern Nigeria

Locations	Total K	Total Mn	Total Fe	Total Zn	Total Cu
			mg/kg		
Biye North	400 – 650 (500)ǂ	25.2– 27.7 (26.9)	103.1-122 (112.7)	5.2- 7.13 (6.4)	130–178.3 (158.8)
Biye south	215 – 445 (311.7)	26.85-38.45 (32.4)	88.95-115.14 (102.1)	0.95-5.56 (2.9)	23.8-139.4 (72.08)
Biye East	220 – 230 (233.3)	18.30-65.95 (38.6)	100.69-109.11 (104.3)	0.52-5.27 (2.1)	13.78 -130 (52.71)
Biye West	260 – 390 (325)	32.55-50.40 (42.9)	110.54-128.32 (117.8)	0.52-0.55 (0.5)	13.13-13.3 (13.75)
Biye Central	185 – 235 (225)	21.15-26.5 (24.4)	104.5-11.6 (106.7)	0.55 -056 (0.6)	13.75-13.9 (13.75)

ǂ values in parenthesis are mean

Table 4.5 Total concentration of K, Mn, Fe, Zn and Cu in soil without concretion in Biye, northern Nigeria

Locations	Total K	Total Mn	Total Fe	Total Zn	Total Cu
mg/kg					
Biye North	280- 405	23.6 26.8	70.7-80.7	0.2-0.55	3.8-81.9
	(388.3)ǂ	(24.9)	(75.9)	(0.3)	(29.9)
Biye South	205 – 235	14.6-23.6	80.1-83.4	0.15-3.3	3.8-4.4
	(225)	(20.6)	(82.1)	(1.2)	(3.8)
Biye East	215–280	17.9-43.2	86.1-90.1	0.13-0.2	3.0-3.75
	(243.3)	(27.1)	(89.1)	(0.15)	(3.8)
Biye West	255 -330	23.6 -26.8	92.1-98.6	0.15-0.2	3.0-3.75
	(295)	(25.1)	(94.8)	(0.2)	(3.75)
Biye Central	200-360	28.5-30.1	72.8-87.7	0.15-0.2	3.0-3.75
	(230)	(29.1)	(79.1)	(0.2)	(3.8)

ǂ values in parenthesis are mean

Table 4.6 Total concentration of K, Mn, Fe, Zn and Cu in concretionary nodules in Biye, northern Nigeria

Locations	Total K	Total Mn	Total Fe	Total Zn	Total Cu
mg/kg					
Biye North	294-295	171-176	147.1-148.5	28.4-35.3	693.98 – 893. 06
	(294.7)ǂ	(173)	(147.3)	(31.8)	(793.4)
Biye south	345-346	111.6-122.3	138-146	31.3-31	1044.5 – 1246.66
	(345.3)	(115.1)	(142.4)	(31.5)	(1146.2)
Biye East	328 – 340	65.95 – 66.87	143.1 – 146.7	44.78 – 45.99	32.33 – 45.22
	(332.7)	(66.3)	(144.9)	(45.36)	(37.1)
Biye West	320-326	146.8 – 147.4	119.11 – 148.95	14.66 – 28.19	1031.6 – 1032.3
	(320.67)	(147.2)	(139.00)	(21.4)	(1031.1)
Biye Central	362-365	171 – 176	138.2- 144.8	41.2 – 41.3	693.98 – 893. 06
	(365)	(173)	(141.05)	(41.25)	(793.4)

ǂ values in parenthesis are mean

Table 4.7: Concentration of Selected Micronutrients Extracted with HCl in Soils and Concretions

	Zn	Mg	Ca	Mn
Soil with concretions	-----------	mg/kg	-----------	
Biye North	2.88	3.42	18.73	12.57
Biye South	0.55	3.71	19.75	24.94
Biye East	1.37	3.35	21.52	8.25
Biye West	0.72	3.23	22.32	10.99
Biye Central	1.10	3.50	22.38	22.70
Soils without concretions				
Biye North	1.64	1.56	9.78	12.57
Biye South	0.82	1.41	12.89	6.47
Biye East	0.88	1.39	15.48	10.99
Biye West	0.99	1.11	16.19	8.71
Biye Central	1.04	1.34	16.51	22.54
Concretionary Nodules				
Biye North	1.18	3.78	24.64	54.13
Biye South	1.20	3.71	23.29	51.18
Biye East	0.55	3.05	22.60	46.07
Biye West	0.24	3.47	22.74	1.94
Biye Central	1.04	3.51	23.73	142.25

4.6 Soil Phosphorus

The total P (Pt) content of soils is of little importance for soil fertility, but it has been used as a weathering index to differentiate between highly weathered and less weathered soils (Tiessen *et al.,* 1991). It is also used as a check on the P balance when soil P is fractionated. In the concretionary soils under study, both soil fines and nodules contained high Pt. the P content of the soils withouth concretions, soils with concretions and concretionary nodules are shown in Table 4.8, Table4.9 and Table 4.10 respectively.

In Biye north and south, the concentration of (Pt) in soils with concretions ranged from 516.7 – 831.4 mg/kg, while its concentration in Biye east and west ranges from 581.2 – 839.6 mg/kg. Biye central however, has the lowest P value (322.9 – 409.0 mg/kg). These values are higher than those obtained in soils without concretions. The soil extractable P does not follow the same trend with soil Pt, it was low with values ranging from 9.4 - 15.6 mg/kg in all the sampled soils mixed with concretionary nodules. The concentration of Pt in soils without concretion is lower compared to the concentration of Pt in soils with concretions and concretionary nodules. The concentration of Pt in fine soils ranges from 301.4 - 452.1 mg/kg in Biye north, 193.8 - 387.5 mg/kg in Biye south, 409.0 - 516.7 mg/kg in Biye east, 366 - 516.7 mg/kg in Biye west and 409.0 - 624.3 mg/kg in Biye central. The available P ranges from 8.3 – 13.1 mg/kg.

The total phosphorus (Pt) levels in concretionary nodules were two to three times higher than those in the soil fine. The Pt in concretion has a mean value of 624.8 in Biye north, 710.5 in in Biye south, 1014.4 in Biye east, 604.4 in Biye west, 797.3 in Biye central. These values are two to three times higher than the total P concentration in soils without concretions. These suggest enrichment of P in concretionary nodules and further indicated that, the nodules may have some influence on the P content of the fines soil.

Table 4.8 Phosphorus Status of Soil without Concretions from Biye, Northern Nigeria

Location	Total P	Organic P	Available P	Inorganic P
	mg/kg			
Biye North	688.8 - 831.6	15.3 - 19.5	10.41 - 10.81	22.93 - 23.56
	(728.2)	(17.7)	(10.6)	(24.4)
Biye South	516.6 - 667.3	15.16 - 30.9	10.3 - 10.6	22.19 - 30.04
	(581.2)	(21.5)	(10.4)	(26.6)
Biye East	624.3 -688.8	15.4 - 20.7	15.4 - 15.6	28.7 - 32.5
	(717.6)	(17.6)	(15.5)	(30.3)
Biye West	322.9 - 409.0	15.63 - 27.56	9.4 - 9.6	23.5 - 26.5
	(365.9)	(20.1)	(9.5)	(24.6)
Biye Central	359.7 - 645.8	13.7 - 16.4	9.6 - 9.8	26.9 - 32.6
	(531.1)	(15.4)	(9.7)	(29.85)

ǂ values in parenthesis are mean

Table 4.9 Phosphorus Status of Soil with Concretions from Biye, Northern Nigeria

Location	Total P	Organic P	Available P	Inorganic P
		mg/kg		
Biye North	301.4 - 452.1 (401.8)	12.7 - 20.7 (15.7)	10.2 - 10.4 (10.7)	49.4 - 56.3 (52.7)
Biyesouth	193.6 - 387.5 (301.4)	18.5 - 99.9 (47.2)	13.0 - 13.3 (13.1)	46.2 - 47.7 (46.97)
Biye East	409.02 - 516.66 (452.07)	23.71 - 42.71 (31.02)	11.60 - 11.80 (11.73)	52.2 - 54.6 (53.7)
Biye West	365.9 - 516.6 (452.08)	22.5 - 48.2 (34.3)	8.1 - 8.6 (8.3)	52.7 - 59.4 (56.3)
Biye central	409.2 - 624.3 (487.9)	26.6 - 48.2 (37.7)	11.2 - 11.6 (11.4)	41.7 - 44.9 (43.5)

ǂ values in parenthesis are mean

Table 4.10 Phosphorus Status of Concretionary nodules from Biye, Northern Nigeria

Location	Total P	Organic P	Available P	Inorganic P
	mg/kg			
Biye North	623.4 - 626.9	7.5 - 19.5	3.8 - 3.8	24.7 - 26.6
	(624.8)	(13.6)	(3.8)	(25.65)
Biyesouth	706.7 - 710.4	8.8 - 13.9	3.4 - 3.8	29.3 - 32.2
	(710.5)	(12.2)	(3.5)	(30.8)
Biye East	1009.6 - 1020.7	4.1 - 10.3	1.60 - 1.6	29.2 - 30.1
	(1014.4)	(7.0)	(1.6)	(29.6)
Biye West	601.98 - 608.55	6.43 - 10.33	1.60 - 1.66	25.3 - 26.8
	(604.43)	(8.46)	(1.64)	(26.2)
Biye central	796.5 - 798.8	6.3 - 9.63	1.6 - 1.6	29.9 - 32.6
	(797.3)	(8.5)	(1.6)	(31.74)

ǂ values in parenthesis are mean

4.7 Soil Phosphorus Fractionation

Fractionation results partitioned the bulk of the total concentration of P to the residual fractions in the soils with concretionary nodules, soils without concretions and concretions as shown in figure 4.1, Fig 4.2, Fig 4.3 respectively. The water soluble (H_2O-P) ranges from 0.5 mg/kg to 1.3 mg/kg in all the locations. The exchangeable P fraction ($NaHCO_3$-P) concentration stands at 9.5 m/kg, 8.3 mg/kg, 12.34 mg/kg, 8.5, 9.7 mg/ kg in Biye north, east west south and Biye central respectively. NaOH –P has a higher concentration compare to the exchangeable P fraction. NaOH –P ranges from 43m/kg to 55 mg/kg in all locations. Whereas the HCl –P was equally low with a concentration range of 14 mg/kg to 16 mg/kg in all locations. The residual fractions account for the highest concentration. The concentrations are 697 mg/kg, 484 mg/kg, 613 mg/kg, 276 mg/kg, 359 mg/kg in Biye north, south, east west and central respectively.

The soils without concretions or fine soils have almost uniform distribution of P fractions with values ranging from 8 – 10.9 mg/kg for plant available P in all the locations. NaOH-P ranges 49 mg/kg to 90 mg/kg in all locations. HCl –P is equally low. The concentrations are, 17 mg/kg, 18 mg/kg, 13 mg/kg, 10 mg/kg, 12 mg/kg in Biye north, biye south, biye east Biye west and Biye central respectively. The residual fraction account for the bulk of the P that was sequentially extracted in soil without concretion, the concentration of P in the residual fraction ranges from 174 mg/kg to 340 mg/kg in all the locations.

Phosphorus concentration in concretions are however different as NaHCO3-P ranges from 1 mg/kg to 4 mg/kg a concentration that is two to three times lower than the concentration in soils without concretion. NaOH-P concentration was 28 mg/kg in Biye north, 20 mg/kg in Biye south, 49 mg/kg in Biye east, 25 mg/kg in Biye west and 31 mg/kg in Biye central. The HCl –P is low ranging from 12 mg/kg to 17 mg/kg in all locations. The concentration of the residual fraction is equally high ranging from 550 mg/kg to 940 mg/kg in all location. The concentration of residual P in concretions is higher compared to the residual P concentration in soils without concretions as shown in the figure.

4.8. Phosphorus Adsorption

4.8.1 Phosporus adsorption characteristics of the soils with concretionary nodules

The toal P in all the location were high therefore, phosphorus adsorption was carried out on soils of Biye north and Biye south in soils with concretions soils without concretion and concretionary nodules. The adsorption curve of all the soils mixed with concretion are similar to that of concretion alone in both Biye north and south indicating similarity in the nature of the adsorption. For soils with concretionary nodules, the adsorption pattern of the soils at different concentration of KH_2PO_4 in Biye north (BN) and Biye south (BS) follows the same pattern. Adsorption slightly increases as concentration increases to 250 µg ml^{-1}.Phosphorus adsorption is highest when concentration increases from 250 µg ml^{-1} to 1000 µg ml^{-1} (Fig. 4.4), the steepness of the curve implies high adsorption capacity.

4.8.2 Phosphorus adsorption characteristics in soils without concretion or fine soils

The adsorption curve of soils without concretion in Biye south and Biye north as shown in fif 4.5 are similar to that of concretion alone indicating similarity in the nature of the adsorption. The adsorption increases as solution concentration of KH_2PO_4increases until a maximum concentration was attained. At equilibrium concentration of 50 µgP/gsoil adsorption stands at 47 mg/kg while at equilibrium concentration of 100 µgP/ gsoil concentration of adsorbed P rises to 84.5. Increase in equilibrium concentration to 250 µgP/g soil adsorption concentration rises to 106 mg/kg. Adsorption concentration continues to increase until at maximum equilibrium concentration were P adsorption rises to 669 mg/kg.

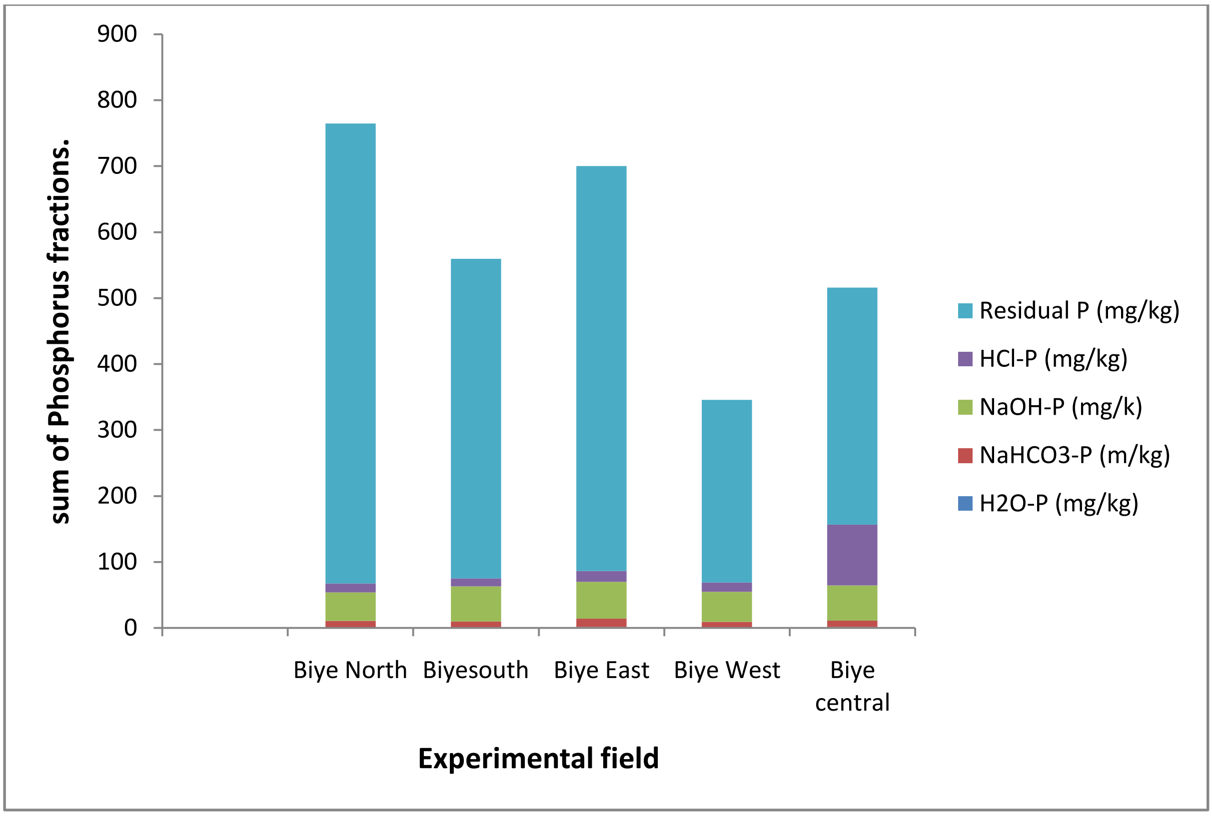

Fig 4.1 Phosphorus fractions in soils with concretions from Biye, northern Nigeria

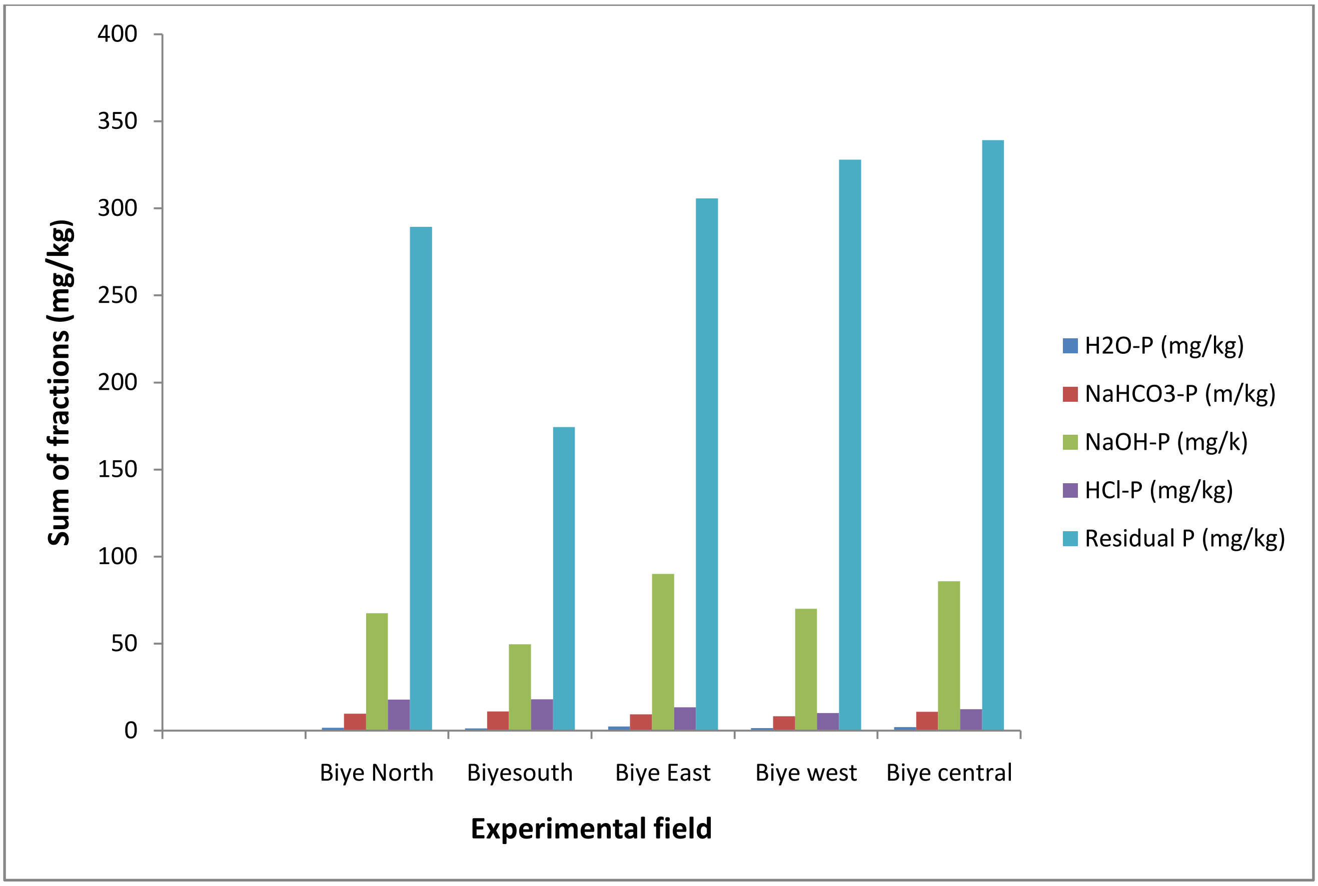

Fig 4.2 Phosphorus fractions in soils without concretions from Biye, northern Nigeria

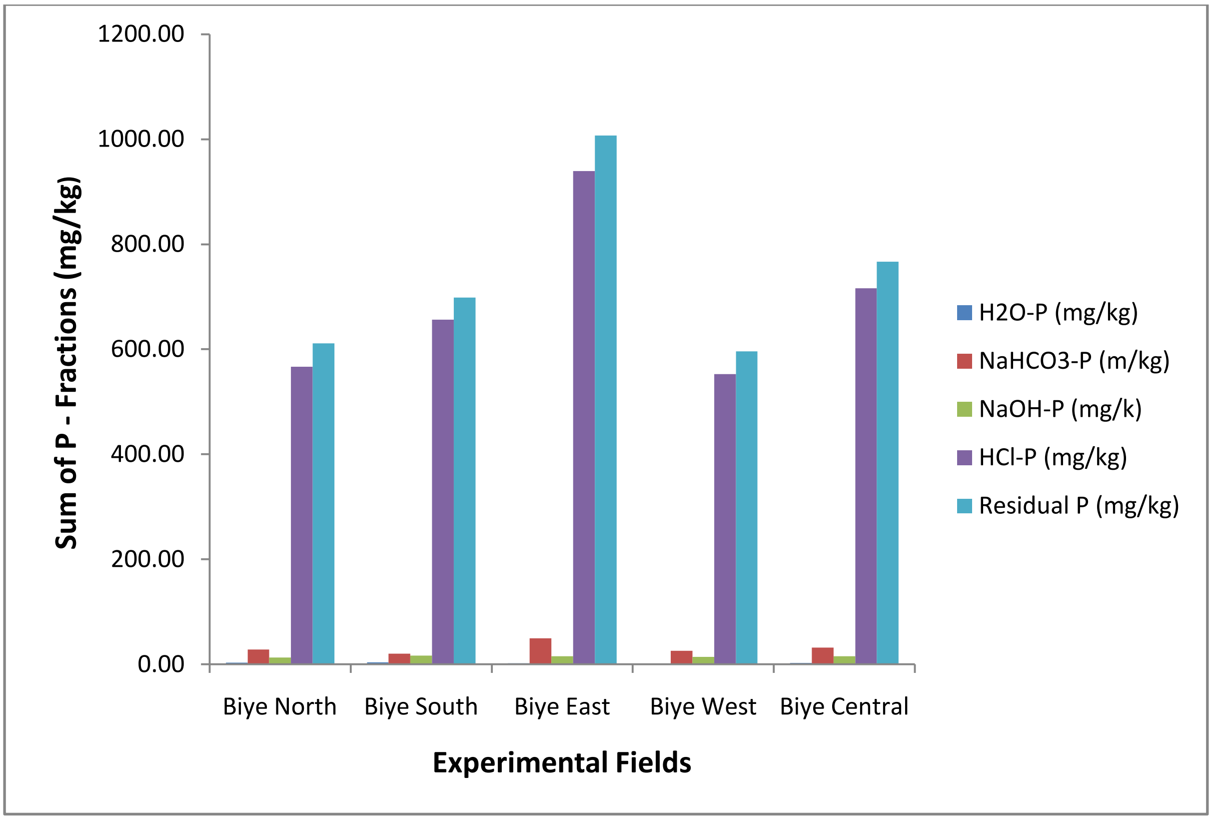

Fig 4.3 Phosphorus fractions in concretionary nodules from Biye, northern Nigeria

4.8.3 Phosphorus adsorption characteristics of concretions

Phosphorus adsorption curve for concretionary nodules are shown in fig 4.6 adsorption tend to increases with increasing P in solution. At solution concentration of 50 µgP/ g soil, Phosphorus adsorption increases to 45 mg/kg whereas at 100 µgP/ gsoil, Padsorption increases to 93 mg/kg. A sharp increase was observed at equilibrium concentration of 250 µgP/ gsoil (142 mg/kg). Increases in adsorption continue until at highest equilibrium concentration of 1000 µgP/ gsoil when phosphorus adsorption hit a maximum of 761 mg/kg. This concentration is the highest compare to phosphorus adsorption in soils without concretions.

4.8.4 Description of phosphate adsorption using the langmuir adsorption isotherm

The adsorption data for soils with concretion and concretionary nodules was fitted to the Langmuir model. Fig 4.7 shows the linearized Langmuir plots for soils with concretions and concretionary nodules. The slope initially increased with concentration of P in solution before it levels up, though, the soil did not reach a true adsorption maximum because P adsorption continues to increase with increase in concentration. This indicates increased affinity of soils with concretions for added P at high solution P concentrations. The increase in concentration also increased the distribution coefficient, sorption maxima and binding energy (Table 4.11) for the Langmuir parameters.

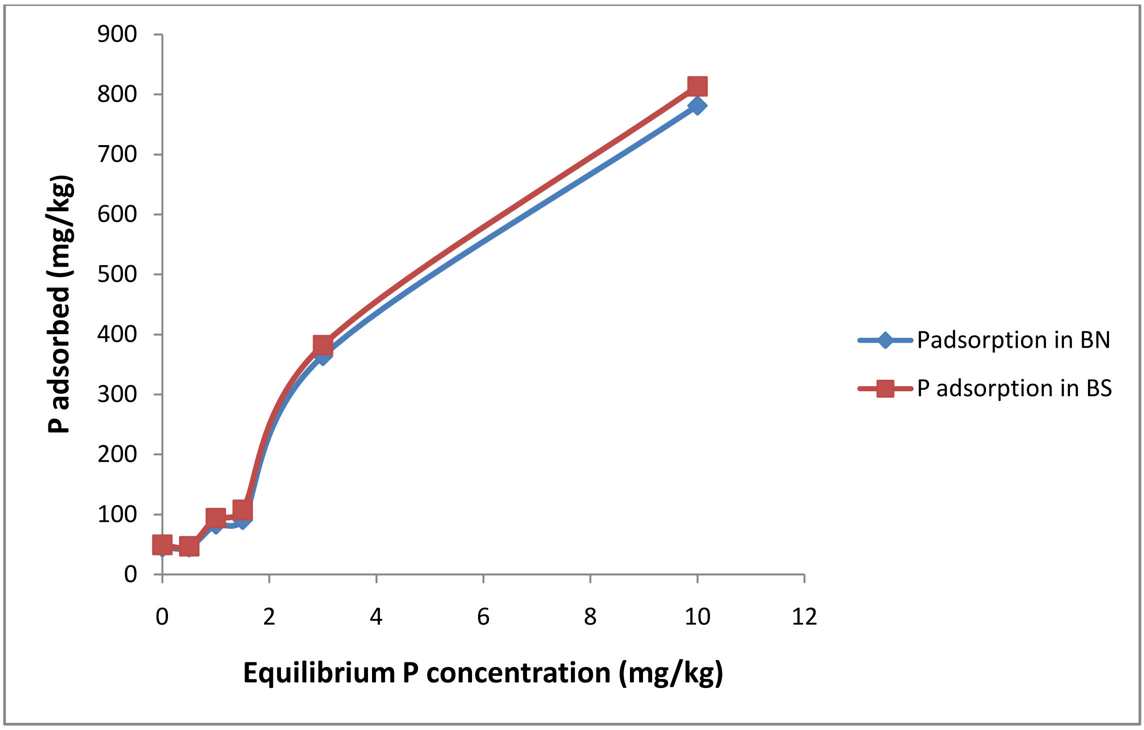

Fig 4.4 Phosphorus adsorption in soil mixed with concretion in Biye north and south, northern Nigeria

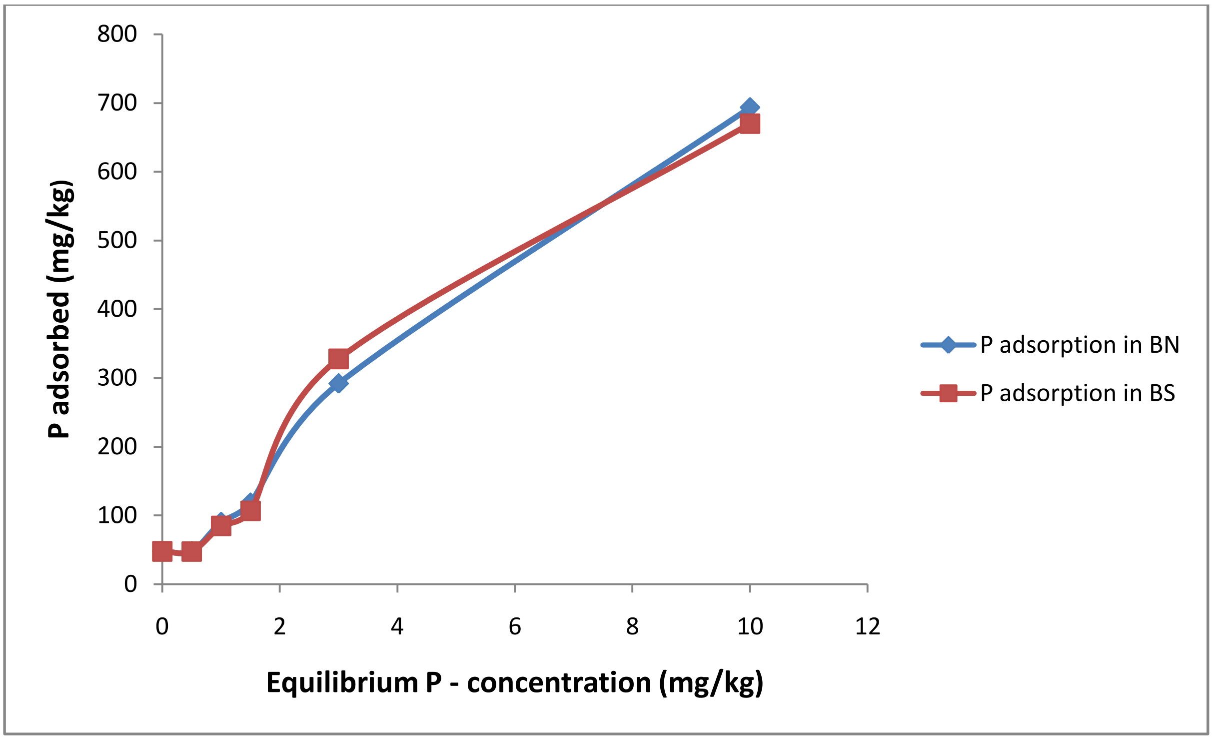

Fig 4.5 Phosphorus adsorption for soils without concretion in Biye north and south, northern Nigeria.

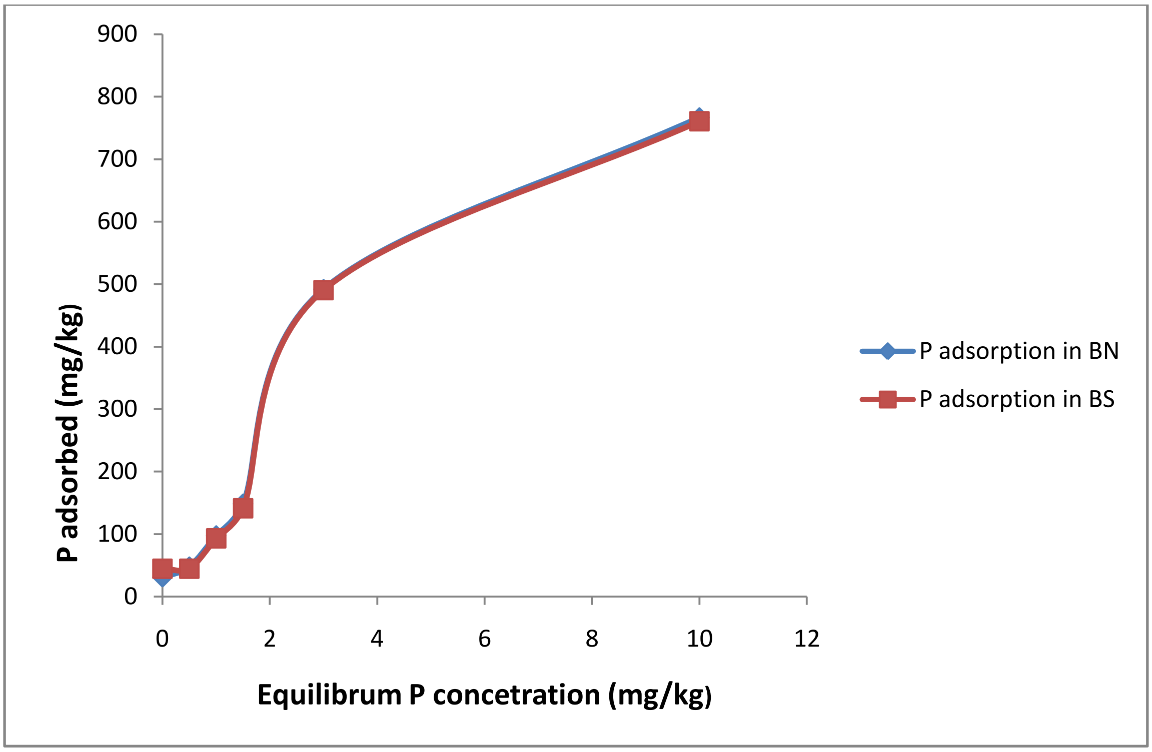

Fig 4.6 Phosphorus adsorption for concretion in Biye north and south, northern Nigeria

Table 4.11 Langmuir isotherm constants and coefficient of regression for soils with concretions, soils without concretions and concretionary nodules

	B	K	Kd	R^2
SOILS WITH CONCRETIONS				
Biye North	56.85	0.75	41.3	0.96
Biye South	46.53	0.59	27.49	0.96
SOILS WITHOUT CONCRETIONS				
Biye North	37.08	0.56	20.06	0.98
Biye South	28.22	0.42	11.95	0.96
CONCRETION				
Biye North	63.81	0.86	71.76	0.89
Biye South	67.42	0.9	60.83	0.89

B – Adsorption maxima

K – Coefficient relating to bound energy

Kd – Distribution coefficient

R^2– Coefficient of regression

Table 4.12 Freundlich isotherm constants and coefficient of regression for adsorption in soils with concretions, soils without concretions and concretionary nodules

	N	Lnk	Kf	R^2
SOILS WITH CONCRETIONS				
Biye North	0.96	0.67	1.96	0.89
Biye South	0.94	0.63	1.89	0.91
SOILS WITHOUT CONCRETIONS				
Biye North	0.87	0.60	1.89	0.94
Biye South	0.87	0.60	1.89	0.92
CONCRETION				
Biye North	0.93	0.65	1.92	0.89
Biye South	0.93	0.66	1.94	0.87

N – Adsorption intensity

Kf - Adsorption Capacity

R^{2-} Coefficient of regression

4.9 Phosphorus Recovery on Soil and Concretion

Phosphorus recovery in Biye north and south increased over time as shown in Fig 4.9 It was observed that P recovery started slowly, increased gradually at an increasing rate until it reaches equilibrium. This is similar to the observation of Saha (2004) and Huang and Cai, (2007) and Abdu,(2009). These authors attributed this to the heterogeneity of the adsorption site with different adsorption affinities and biding strength. The time depended recovery of P shows that, at 5 minutes, 33 mg/kg P was recovered, at 10 minutes 40mg/kg P was recovered while at 20 minutes 52 mg/kg P was recovered. The P recovered increased to 64 mg/k in 60 minutes while in 120 minutes, 76 mg/kg P was recovered. At 240 minutes, 82 mg/kg P was recovered, this indicates a gradual decrease in the concentration of P recovered. At 16 hours, there was no appreciable increase as only 84 mg/kg P was recovered. These P recovery pattern was similar all the soil fraction.

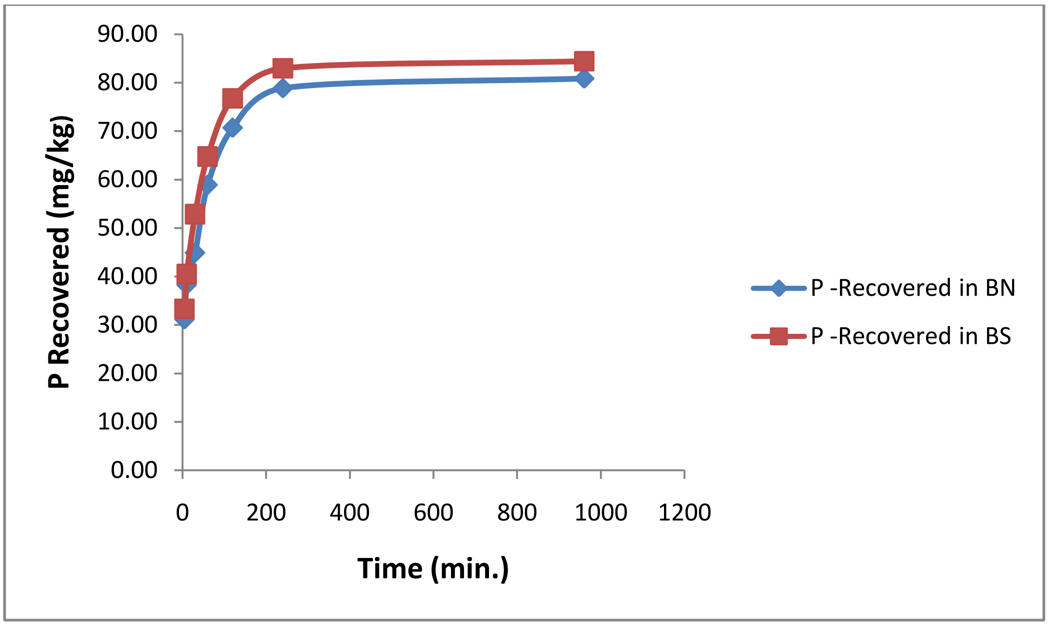

Fig 4.7Time dependent phosphorus recovery for soils with concretion in Biye north and south

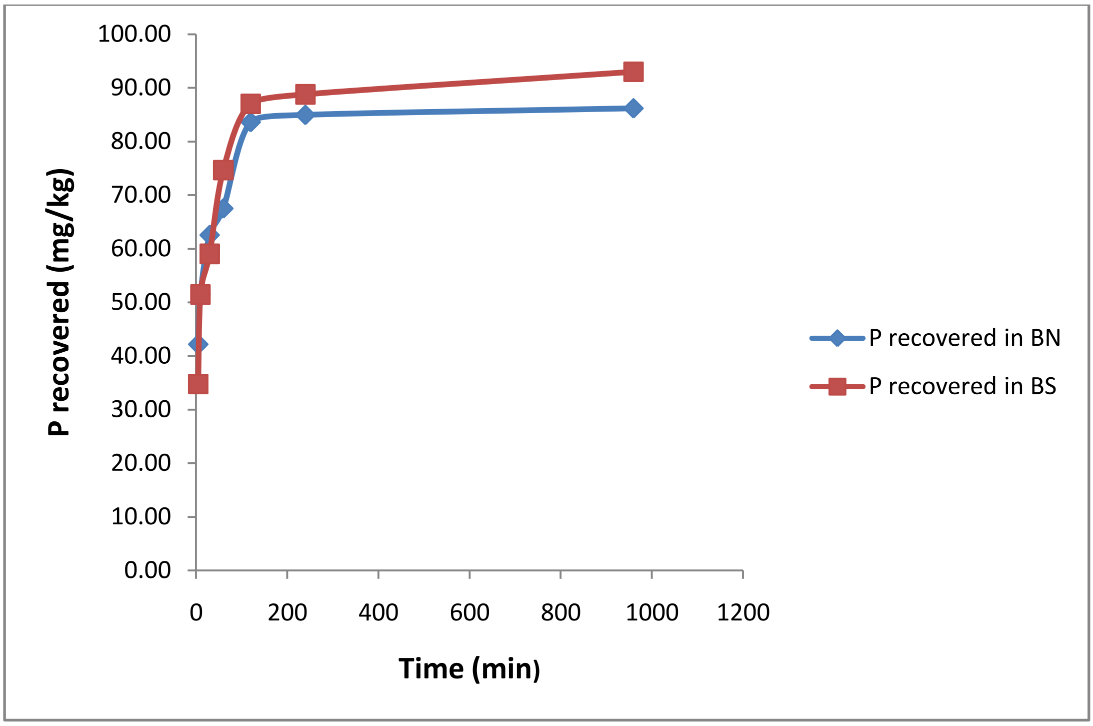

Fig 4.10 Time dependent phosphorus recovery for soils without concretion in Biye north and south

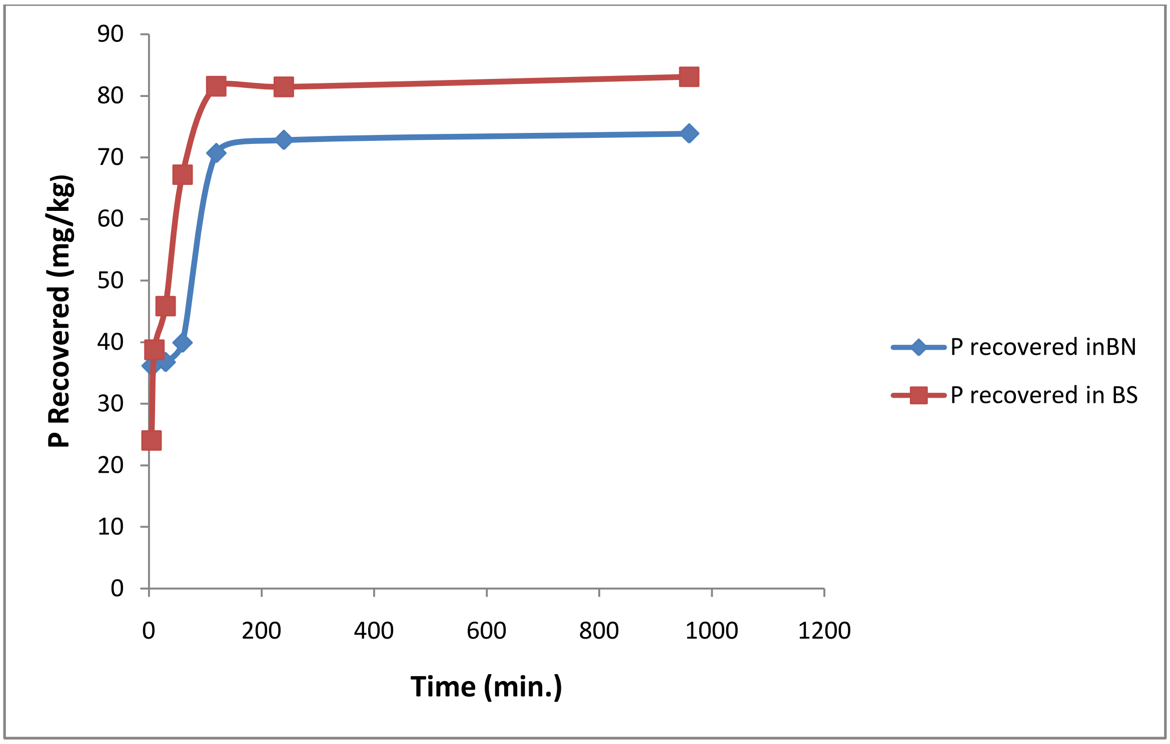

Fig 4.11 Time dependent phosphorus recovery for concretion in Biye north and south

CHAPTER FIVE

5.0 DISCUSSION OF RESULT

5.1 Abundance of Soil Concretionary Nodules

General, a similar physical characteristic of these experimental fields is that, the soils are highly shallow due to the presence of plinthites and sand stone underlining the area. This could prevent root proliferation and water infiltration thereby reducing plant yield. Torrent *et al.* (1990); and Agbenin (2003) noted that, the nature, distribution and abundance of these nodules and / or concretion significantly affect nutrient status and phosphate availability in the soil.

5.2 Physical and Chemical Properties of Soils without Concretions and Soils with Concretion and concretionary nodules

The textural class of the all soils of the study area were every similar, mainly sandy loam according to USDA classification system. These suggest that the soils of the area will be well drained and may be partially suitable for agriculture as most crops thrive well in loam textured soils. The pH in water is always greater than the pH in $CaCl_2$ because of the displacement of H^+ from the exchange sites into soil solution. The low value of OC in this experimental field is similar to what was reported by Abdu *et al.* (2012), Egwu (2010) for some savannah soils in Nigeria. The low OC content of the experimental field could be attributed to continuous cultivation and insufficient recycling of crop residues to soils. The lowest value of OC (0.81 mg/kg) was observed in Biye south where there is high proportion of concretion. Magnesium and K were the dominant exchangeable cations in all the surface soils, both in soils with and without concretionary nodules (Table 4.3). These values reported are in line with earlier work of Esu (1991). The exchangeable K rating of the area has been shown to be medium in soils of the study area with a range of 0.10 - 0.38 Cmol/kg. Soils without concretionary nodules have the highest value of 0.20 - 0.43 Cmol/kg while concretions accounted for the lowest value of exchangeable K (0.17 Cmol/kg), this suggests that cations exchange is limited in concretion compare to other soil fractions. Palumbo *et al*. (2001) observed that, through mechanisms such as co-precipitation, adsorption and lattice substitution, cations are scavenged from the soil solution, and are incorporated into ferromanganese concretion. However, once the pedo-environment has been changed, the cations adsorbed in ferromanganese concretion become chemically unstable, possibly desorbing into the soil solution. Generally, concretions had lower amounts of exchangeable cations compared to soil fines. This is unexpected since the concretionary nodules were formed from soil materials; hence their chemical properties were expected to be similar to the soil fines.

5.3 Total Concentration of K, Mn, Fe, Zn, Cu in Soil Fractions

The concretionary nodules and soils with concretions consistently contained more of the total elements analysed than the soils without concretion (fine soil). These suggest accumulation of more K in concretion than in fine soils. This is in consonant with the work of Timofeeva (2008), who opined that accumulation of plant nutrients by nodule minerals is a reaction of isomorphic substitution when elements occupy certain structural positions in the minerals of nodules. The higher concentration of the total nutrients analysed in concretionary nodules is similar to the work of Tiessen *et al.* (1991) who observed that the concentration of nutrient in concretion is 5 – 7 times greater than in the surrounding soils in Ghana.

The extractable Zn, Cu, Mn, and Mg of soils with concretions, soils without concretions and concretionary nodules are shown in Table 4.7. Concretions contain all the elements analysed. The examination of quantitative analyses reveals considerable variations in the composition of concretion in each experimental field. The concentration of the elements increased in the concretion, except for Zn, whose concentration level in the concretion is lower than that of the soils. This observation corroborated that of Timofeeva (2008) who observed that, The contents of the elements increase sharply in the ferromagnesian nodules, except for Zn, whose concentration level in the nodules is usually lower than and sometimes identical to that of the surrounding soils. The contents of some elements in the concretion are considerably higher than the concentration in soils without concretions. The elevated contents of micronutrients are probably related to the soil runoff from the surrounding areas of agricultural activity, it is also possible that a small contribution to the elevated contents of the aforementioned elements is due to the use of mineral and organic fertilizers.A comparison of analytical data for the distribution of trace elements in the soil without concretion and concretionary nodules shows that the concretions contain all of the elements in variable proportions. With respect to the mechanism of nutrient incorporation into concretionary nodules, Timofeeva (2008) conventionally divided trace elements of the concretionary nodules into three groups. (1) Inherited trace elements that are directly related to the host soil material and occur in the cores or mechanical inclusions trapped during nodule growth. The sources of trace elements of this group are represented by primary and, occasionally secondary soil minerals containing the trace elements, which are inherited in the chain: bedrock–parent rock–soil–concretion. The amount of trace elements in this group is very small; they are incorporated in the crystal lattice and are liberated during destruction of the concretion. (2) Biogenic elements are accumulated in the concretionary nodules owing to direct microbiological input and are related to the activity of a specific group of microorganisms which actively participate in the formation of concretionary nodules and are collectively known as iron bacteria, and some species of soil fungi. The trace elements have no nourishing value but are vital for the normal functioning and development of the entire soil micro flora, and their continuous replenishment is therefore necessary. Iron bacteria consume and assimilate trace elements during their living activity and can selectively accumulate some of them. (3) Isomorphic and sorbed trace elements that are related to the physicochemical properties of the mineral constituent of the concretionary nodules. The trace elements of this group are characterized by the effect of extraction from the environment owing to substitution for another element in exchange processes. Trace elements may be fixed on the external surface of concretionary nodules as a result of interactions producing surface complexes and adsorption. In other words, a layer of sorbed trace elements can be formed on the surface of nodules. This layer can be rather stable owing to the occurrence of very strong phase contacts sustained by the attractive forces of surface particles. The second component of this group is represented by the trace elements incorporated in newly formed minerals. The mineral carriers of trace elements from soil concretion are most often unstable, primarily Fe hydroxides and Mn oxides (Babanin *et al.*, 2000; Ladonin, 2003; Yu and Sivtsov,2004).

5.4 Soil Phosphorus

The total phosphorus (Pt) levels in concretionary nodules were two to three times higher than those in the soil fine. The Pt in concretion ranges from 604.4 – 1014.04mg/kg in all the locations suggesting enrichment of P in concretionary nodules and further indicated that, the nodules may have some influence on the P content of the fines soil. Also, Akinbola, *et al* (2013) noted that, fixation of the inorganic fertilizer by the free iron oxides could be responsible for the high Pt in concretionary nodules. This is also in agreement with the results reported for most West African savannah soils (Hauffe, 1989; Tiessen *et al.*, 1990). Tiessen *et al*. (1991) found that the Pt values in ferruginous nodules from semiarid soils in Ghana and Brazil were on average three to four times higher than in the associated soil fines. This study is limited to top soil (0 – 15 cm), which has being under intense fertilization over long period of time. Total P in concretion was therefore greater in the surface horizons (Table 4.10). It appeared that Pt content in concretions was largely related to P dynamics in the soils. In the top soil with intense P cycling, Fe-enriched concretions are exposed to available P from fertilization which is eventually trapped in the concretion. This amount of available P trapped in concretions during their formation is effectively locked up, indicating that major portions of fertilizer P has been sorbed by these soil constituents (Tiessen *et al.,* 1991).The low extractable P in the soils suggests apparent P deficiency in these soils. Phosphorus fixation to Fe, Al and Mn oxides, losses to erosion and crop removal might have contributed to the low P status of the soils. The low OC content of these soils might have also contributed to the low organic P (OP) concentration of these soils. Although the available P is low in soils without concretions, the concentration is relatively higher than the concentration in soils with concretion and 3 times higher than the concentration in concretionary nodule. This largely demonstrated the importance of Mn, Al and Fe oxides as major sink of P in these soils.

5.5 Fractionation of Phosphorus

The most P recovered by sequential extraction was in the residual (276 - 697 mg/kg) and potentially bio-available fractions (43 – 55.8 mg/kg). The exchangeable P fraction ($NaHCO_3$-P) of the soils held the least percentage (2 – 5%) of the total P in the soils with concentrations ranging from (8 – 12.3 mg/kg) in the entire location. The exchangeable P fractions are those that are released most readily into the soil solution, these fractions correspond to the most available for plant uptake and can easily be released following any change in the ionic strength of the soil solution medium (Filguerias *et al.,* 2002). The low proportion of P held (Fig. 4.1) in the exchange site indicates low level of P in the soil solution medium for plant uptake. Tiessen *et al.,* (1991) maintained that, in the top soil with intense P cycling, Fe-enriched concretions are exposed to available P from fertilization which is eventually trapped in the concretion and are effectively locked up, indicating that major portions of fertilizer P has been sorbed by these soil constituents.Plant available P was on average 2 – 3 times higher in soils without concretions or fine soils than in the associated concretions with most of the difference accounted for by higher residual P level. HCl extractable P in soils without concretions ranged from 10.1 – 18.0 mg/kg in all the locations. Although the percentage of available P extracted by $NaHCO_3$ is low in soils without concretions, it is however, 2 -3 times greater than available P extracted in concretions. This seems to suggest that concretionary nodules have some influence on availability of P in soil fine. This result is in agreement with the work of Abekoe (1996) and Tiessen *et al*. (1991) who observed that within less than 3 years of fertilizer application, all added P had disappear from the soil fine, and accumulated in ferruginous nodules. Nearly 90% of the total P recovered from the concretions was in the residual fraction (552 – 939.3 mg/kg). Potentially available P (NaOH-P) accounted for a range of (20.2 – 49.3 mg/kg) while plant available P ranged from 1.4 – 3.5 mg/kg a value 2 – 3 time less than the concentration of available P in soil fine. Whereas the available Pis relatively high in soil without concretions, it is however; very low in concretion about 2 – 3 times lower than that of soil without concretion (fig 4.1.3). This suggests that concretionary nodule fixed P in soil solution and transformed them into form not extractable by $NaHCO_3$ which is not available for plant uptake. Phosphorus availability depends largely on the forms in which it is held. The modified Hedley fractionation scheme indicated that non-labile P (NaOH-P) was the next dominant P pool after residual fraction in all the soils, which suggested that large amounts of resistant P of limited bioavailability were accountable for the poor P supply to plants in Biye soils. According to Tiessen *et al.* (1993) highly weathered soils of the tropics with low available P may be somewhat productive through organic P mineralization which is enhanced by high soil temperatures and distinct wet and dry seasons. Organic P levels are generally low in the soils of Biye and local farmers must be encouraged to adopt management practices such as the incorporation of plant residues and other organic materials to increase soil organic P for long- term soil fertility improvement and maintenance.

5.6Phosphorus Adsorption

Phosphorus adsorption capacity of soils are generally influenced by soil properties such as clay, free Al and Fe oxides pH (Agbenin, 2003, Abdu, 2009), the ionic strenght of the solution and the mineralogy of the soil (Agbenin, 1994). The soils without concretion have a more uniform adsorption pattern in comparison with other soils in this study. Although, this soil has no concretion (soil fine), it has low pH which enhances the adsorption of P in the soil. The slopes were gentle and therefore less P sorption. These characteristics might be related to low Fe and Al content of the soil and higher organic matter content. These soils have been shown to contain more organic matter than concretions or soils with concretion. Organic matter has been shown to reduce P adsorption in some savannah soils (Stewart et al., 1991). Organic matter inhibits P sorption by either physically blocking adsorption site or through the competition of organic anion with P for adsorption site (Abdu, 2006). Concretionary nodules and soils with concretions adsorbed more P than the soils without concretion (Fig. 4.6), and maintained a greater proportion of the adsorbed P in a form not extractable by $NaHCO_3$. Concretionary nodules and soils with concretions required more concentration of P to raise solution P to maximum, whereas, the soils fine requires less P. But concretionary nodules clearly act as an effective sink for added P that greatly raises the overall P requirement of the soil. When phosphate adsorbed was plotted against the equilibrium phosphate concentration, the resulting curve is steeper and it appears to approach maximum at higher concentrations (Fig. 4.6). However, a well-defined maximum was not obtained as P adsorption continues to increase with increase in solution phosphate concentration. Generally, the steeper the adsorption curve, the more highly buffered the soil should be. Consequently, at high adsorption, solution P concentration become low and the soil will be more likely to be deficient in P. In effect, fine soils may eventually be more deficient in P. These agree with the previous work of Uyovbisere (1994), Egwu, (2012) and Tiessen, *et al* (1990) who observed that, at high adsorption rate, P in solution becomes very low.Figure 4.7 shows the adsorption curve for soils with concretion in both Biye north and Biye south while figure 4.8shows the adsorption curve for soils without concretion in both Biye north and Biye south. The gentle curve observed in Biye south suggests that the adsorption was minimal in soils without concretion and that the assumptions on which Langmuir equation was based was not completely satisfied.Uyovbisere (1994) and Sposito (1982) are of the view that, in systems as heterogeneous as those of the soil colloids, it may be natural to consider sorption energy as forming a continuum in soil system contrary to the provision of the Langmuir model. However, soils with concretion and concretionary nodules conform to the Langmuir model as their curves were considerably similar.

5.7 Freundlich and Langmuir Adsorption Parameters

The adsorption data of phosphorus were also fitted to Freundlich adsorption isotherm. Both Langmuir and Freundlich isotherm showed linearity but Langmuir had a better as showed by the coefficient of determination (R^2)compared to Freundlich isotherm. Adsorption capacity (Kf) and adsorption intensity (n) of Freundlich adsorption isotherms for soils with concretion, soil without concretion and concretionary nodules are shown in table 4.12. Adsorption capacity (Kf) of Freundlich isotherm parameter is highest (1.96) in both soils with concretions and concretionary nodules while soil without concretion had the largest value of (1.69). Data plotted according to the linear form of the Freundlich model indicated adsorption intensity values of less than one in all the soils (Table 4.12). Similar results were reported by (McLaren and Cameron, 1990). According to them, Freundlich model is empirical in nature and implied that adsorption decreases exponentially with increasing saturation of exchange sites with P. It is obvious from Table 4.12 that soil without concretion had minimum adsorption intensity value, i.e. 0.87 while soil with concretion has maximum adsorption intensity value of 0.96. Therefore, soils with concretions, soils without concretions and concretionary nodules have relatively more heterogeneous adsorption sites. According to Bahl and Toor, (2002), Kf is dependent on the solution concentration. Zhou and Li (2001) stated that Kf is adsorption capacity while according to Bahl and Toor, (2002), it is extent of adsorption.

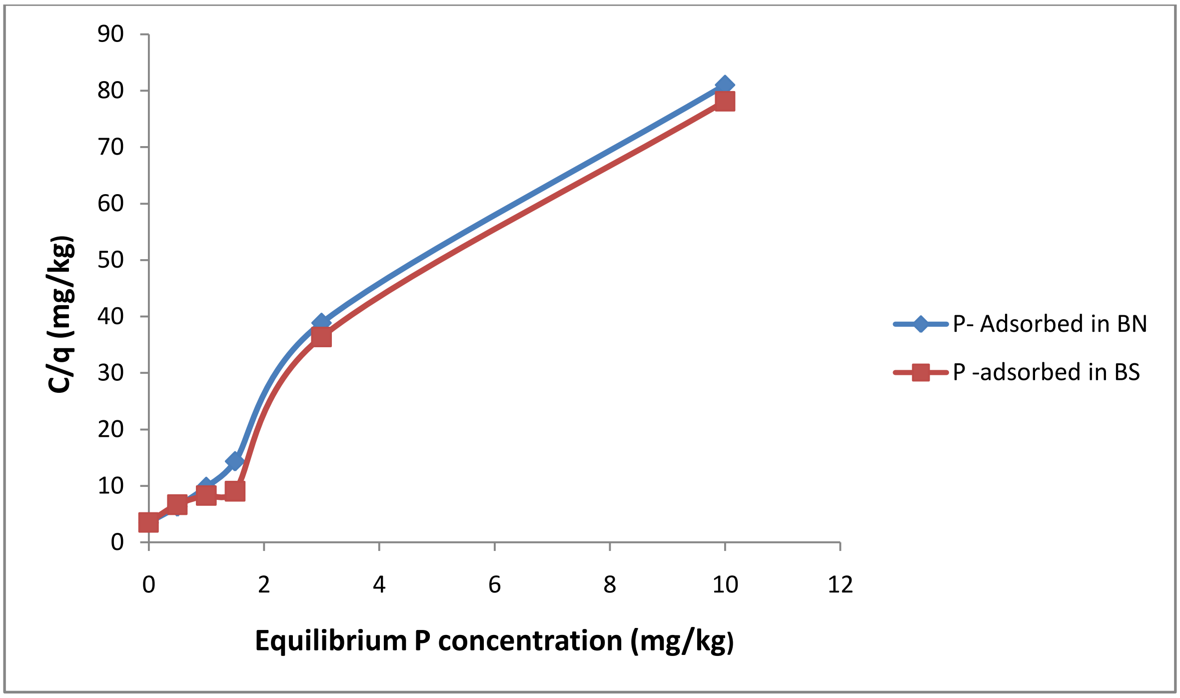

Fig 4.7 LangmuirPhosphorus adsorption curve for soils with concretion in Biye north and south, northern Nigeria

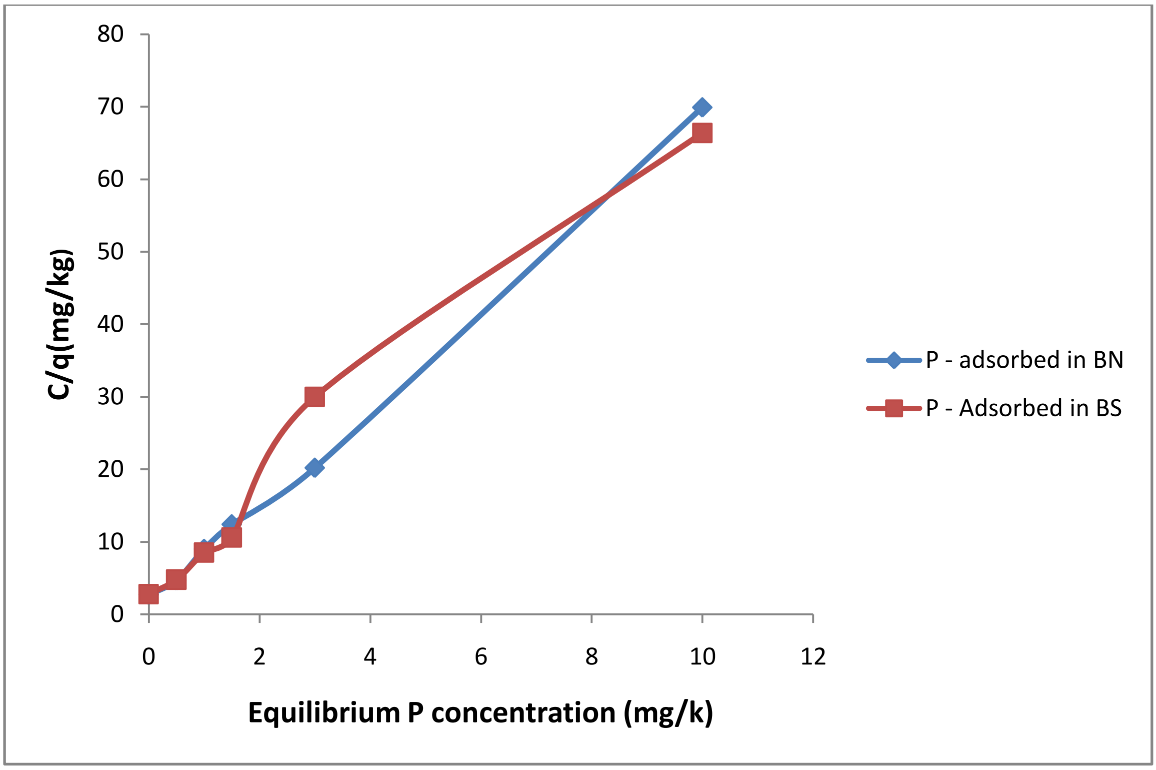

Fig 4.8 LangmuirPhosphorus adsorption curve for soils without concretion in Biye north and south, northern Nigeria

5.8 Phosphorus Recovery on Soils and Concretion

Generally, more P was recovered in soils without concretionary nodule (fine soils) than in soils with concretions (Fig. 4.10). More P was recovered with time in soils with concretion than in the corresponding concretions (Fig. 4.11). The difference in P recovered with time might be explained by variation in biding strength of P between the soils. Soils with concretion have high amount of Fe and Al because of the presence of concretion. Iron and Al have strong affinity for P in soils and are strongly implicated in the retention of P in savannah soils (Agbenin, 2003; Abdu, 2009).

The amount P recovered in the soils may be affected by several factors. These factors include clay content, organic matter, pH, free and extractable Fe and Al oxides, level of exchangeable-calcium, ionic strength, soil mineralogy, parent materials, soil texture and percentage of P saturation. For the soils without concretions, it seems that the low pH and the presence of free and extractable Fe and Al as constituent of concretion are responsible for the variation in P recovered. Phosphorus recovered with time determined the availability of P in solution for plant uptake. Aluminium and Fe oxides act as P sinks by transforming available P to Al-P and Fe-P forms which become occluded with time (Sharpley *et al.*, 2001; Tiessen *et al.*, 1984). In all the soils, P recovery approached equilibrium after 16 hours though measurable changes in the quantity of P recovered were still observed with time (Fig. 4.9).

5.9 Phosphorus recovery in concretion

Phosphorus recovery experiment conducted on concretionary nodules from soils of Biye north and south shows that, the recovered P in concretion(Fig. 4.11)was less than that recovered from fine soils. The dominance of concretion and low pH of these soils may account for lower value of P recovered. Low value of P recovered in concretion with time confirmed the fact that concretions have high affinity for P. This is attributed to the high concentration of Fe and Mn, Al oxides in concretion which have a strong affinity for P retention. The recovery isotherm showed a decrease in P release with increase in time. The P release is highest from the soil fine (Fig. 4.10) and lowest in the concretion (Fig. 4.11). The high P release in soils fine indicates the presence of labile P in the entire soil sample.

CHAPTER SIX

6.0 SUMMARY AND CONCLUSION

This study was carriedout to evaluate the nutrient composition and P adsorption of concretionary nodules vis-a-vis the bulk soils in a Phlinthic Haplustalf from northern guinea savannah ecology of Nigeria that is non-responsive to P fertilizer application.

This investigation showed that available P level in the soils is generally low,and concretionary nodule contained the highest concentration of total K, Mn, Fe, Zn, and Cufollowed by the soils mixed with concretion. The fine soil or soils without concretion have the lowest concentration of the total nutrients analysed. This indicates that Fe rich concretions which contained higher concentration of elements analysed than the surrounding soils, have the ability to trap micro nutrient and convert them to the form not available to plant.

Phosphorus adsorption experiment result showed that the rate of P adsorption was significantly higher in concretionary nodule and soil with concretion,while soil without concretion shows less adsorption capacity curve. Soils and concretion of the study area have high capacity to adsorb P thereby rendering it unavailable for plant uptake. Consequently, it can be concluded that Fe-enriched concretions are exposed to available P from fertilization which is eventually trapped in the concretion. This amount of available P trapped in concretions is effectively locked up, indicating that major portions of fertilizer P has been sorbed by these soil constituents.

Furthermore, fractionation result partitioned the bulk of the P in residual fraction. These fractions are not available for plant uptake. The exchangeable P fractions are those that are released most readily into the soil solution, this fractions are low in soils without concretions and two to three times lower in concretionary nodules. The low proportion of P held (Fig. 4.1) in the exchange site indicates low level of P in the soil solution medium for plant uptake.This study further showed that,considerable concentration of P was recovered at different time interval. The total P recovered at different time is higher in soil without concretion followed by soils with concretion and lastly concretionary nodules, Phosphorus recovery increase with increase in time of shaking.

6.2 Recomendations

Organic P levels are low in the soils of Biye and local farmers must be encouraged to adopt management practices such as the incorporation of plant residues and other organic materials to increase soil organic P for long- term soil fertility improvement and maintenance.

Furthermore, further studies to be carried out should analyse concretion/nodules obtained from soil samples after sieving through 2mm sieve to determine the nutrient composition of those soil constituent for the purpose of soils fertility management. Discarding of soil constituents above 2mm during laboratory analysis should be discouraged.

The mechanism involved in the process of trapping of P and other micro nutrients by concretionary nodules is another aspect that needs to be further researched upon.

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