KINETICS OF PHOSPHATE RELEASE IN SOME FOREST AND SAVANNA SOILS

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A THESIS SUBMITTED TO THE POSTGRADUATE SCHOOL, AHMADU BELLO UNIVERSITY, ZARIA IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF DEGREE OF MASTER OF SCIENCE OF AHMADU BELLO UNIVERSITY, ZARIA.

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DECLARATION

I declare that the work in the thesis entitled **KINETICS OF PHOSPHATE RELEASE IN SOME FOREST AND SAVANNA SOILS** has been performed by me in the Department of Soil Science under the supervision of **DR. J.O. AGBENIN.** The information provided from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at any university.

ABDU NAFIU

Name of student Signature Date

CERTIFICATION

This thesis entitled "KINETICS OF PHOSPHATE RELEASE IN SOME FOREST AND SAVANNA SOILS" by Abdu Nafiu, meets the regulations governing the award of Master of Science Degree of the Ahmadu Bello University, Zaria and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This work is dedicated to my Darling wife, Muhibbat A. Hamza for her love, care and support and my two little Angels, Hafsah and Muneerah who are apples of my eye.

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ABSTRACT

The rate at which phosphate (P) is desorbed from the soil surface into soil solution is a key factor that regulates the continuous supply of P to crops. Understanding the kinetics of P desorption is paramount for effective P management in order to boost agricultural production and to minimize environmental degradation and pollution. The objectives of this study were to compare several kinetic models for describing P desorption rates in savanna soils of varying lithogenic origins, and to determine the effect of soil properties on P release rate. Phosphate desorption patterns were measured from soils derived from three different parent materials using anion exchange resin. The desorption patterns included an initial fast reaction that lasted for about 500 mins, followed by a slow release that continued up to 1200 mins. Phosphorus desorption rates by anion exchange resins were best described by three empirical kinetic models: Elovich equation, the parabolic diffusion equation and the fractional power equation in that order. However, when P was added to the soils, the first-order rate equation gave a satisfactory description of the experimental data from soils derived from Shale and Basement complex, indicating that P release rates in these soils were related to the quantity of P sorbed reversibly to the surface. The rate coefficients varied widely among soils from the same parent materials and between parent materials due probably to variations in the properties of the soils. The rate coefficients from the Elovich equation, parabolic diffusion equation and the fractional power model were best predicted from soil organic carbon (OC), clay, pH, and extractable Al and Fe oxides. These soil properties together explained between 93 and 99% of the variance in the rate coefficients of P desorption in the soils.

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CHAPTER ONE

1.0 INTRODUCTION

Phosphorus is the second most limiting nutrient in savanna soils (Mokwunye, 1996; Bueler et. al., 2002). Phosphorus deficiency has been identified as a major problem to agriculture especially in West-African savanna. The availability of P for plant utilization depends upon its form, rate of its release into the soil solution, and the nature of its adsorption on to soil colloids. The reaction of P with soil colloid is very complex, thereby rendering it unavailable to crops (Friesen et. al., 1997). Where soils have high concentration of P loading, understanding the kinetics of its release is imperative for proper management to prevent eutrophication of ground water (Hansen and Strawn, 2003).

Phosphorus occurs in the soil in both organic and inorganic form. The inorganic P results from weathering of P bearing rock minerals. Half or more of the total P in the surface horizon of most soils is organic (Oniani et al., 1973). Organic phosphorus is important in replenishing plant available P in soils (Adepetu and Corey, 1976; Frossard et al., 1989; Agbenin and Goladi, 1998). This organic form of P is unavailable to plants until the organic matter bearing the P is mineralized and releases P into forms that are useful to plants. The significance of organic P in replenishing plant available P is impeded by the kinetics of its mineralization, release and uptake by plants (Thompson and Troeh, 1978).

Tropical soils are characterized by variable charge minerals, which bind with P thereby rendering it unavailable for plant utilization (Paniagua et al., 1995). Most important are iron and aluminum oxides that have high affinity for P adsorption (Agbenin, 2003; Martin et al., 2004).

The kinetics of P release and its sorption is important in P fertility of soils and

environmental pollution (Agbenin and Raij, 2001) as high P levels in soils can lead to surface and ground water pollution (Eghball et al., 1996). It also provides detailed information concerning the fate of applied P fertilizer into the soil with time. The kinetics of P adsorption and desorption in soils has been described by many authors (Evans and Jurinak, 1976; Chien et al., 1980; Polyzopoulos et al., 1986; Pavlatou and Polyzopoulos, 1998; Agbenin and Raij, 2001; Hansen and Strawn, 2003). They characterized the kinetics with a number of empirical, semi-empirical and mechanistic equations. Of all the kinetic models used to describe P release and retention by soils, no one model suitably characterizes phosphate release kinetics in all soils and over the entire reaction period. Chien and Clayton (1980) however, suggest that a simplified Elovich equation can be used to describe P release kinetics through the entire reaction period.

The kinetics of P release and its sorption is important in the management of, as well as in P fertilizer recommendations (Rou et al., 1998), and to minimize environmental pollution (Agbenin and Raij, 2001). It is also imperative in the understanding of the dynamic interaction of P with the soil matrix (Hansen and Strawn, 2003). It can also be an index for soil taxonomy as phosphate sorption capacity of a soil is partly controlled by sesquioxides in the soil (Greenland, 1981). Furthermore, kinetic model describing the possibility of P exchange in soils provide detailed information concerning the fate of applied P-fertilizer into the soil with time. It also helps to know the ease at which phosphate is desorbed or sorbed from soils (Sparks, 1985).

The objectives of the study were:

1 To compare several kinetic models for describing P release in soils of varying lithogenic origins in the savanna.

2 To determine the relations of soil properties with kinetic parameters for characterizing P release rates in the soil.

CHAPTER TWO

2.0 REVIEW OF LITERATURE

2.1 Sources of phosphorus in soils and its fixation by soils

The primary source of phosphorus is the apatite mineral group occurring as tiny crystals, well dispersed through igneous rocks. The most common and stable apatite mineral is the fluoro-apatite ($Ca_5(PO_4)_3F$). Primary apatite is supplied by magma, which is the starting point, which by weathering can dissolve and precipitate as calcium phosphate on continental shelves and in calcareous water. Phosphate rock also occurs as combination of excreta of birds and lime of coral banks (Janssen, 1999). Other phosphates occur in the less common minerals like vivianite ($Fe\ (PO_4)_2.8H_2O$) and wavellite ($A1_3(OH)_3\ (PO_4)_2.5H_2O$).

Organic phosphorus is a part of organic matter and its primary source in the soil is through leaf fall and other vegetable and animal residues that decompose in the soil (Janssen, 1999). Organic P in the soil can also be formed from the use of organic compounds by plants and soil microbes (Vanlauwe et al., 2002). The phosphorus in organic compound is covalently bonded by a carbon-oxygen-phosphorus bond sequence. The carbon-oxygen bond is broken by decomposition of the organic compound leading to the mineralization of the phosphorus into available form for plant utilization. Part of the soil organic phosphorus comes from nucleic acids of plants, animal and microbial origins. According to Janssen (1999), 0.6-2.4% of organic phosphorus occurs in nucleic acids, less than 1% in phospholipids and 35% in inositol phosphate. Thomson and Troeh (1978)

indicated that these organic phosphorus compounds add up to one-half of the total phosphorus in the soil. Janssen (1999) discussed the relationship between organic carbon and phosphorus. He showed that if soil organic matter contains 50%C on the average, the P content would be 0.5% of soil organic matter.

The chemistry of organically combined phosphate in savanna soils has not been well documented. According to Enwezor and Moore (1966) between 23-30% of organic phosphorus in Nigerian forest occurs in inositol phosphate and this varies with vegetation as well as with site history. Frossard et al. (1997) reported that a substantial amount of available P in tropical soils can be obtained from organic P fraction even though only a small portion of total organic P is readily available to the crops in the short term (Vanlauwe et al., 2002 and Agbenin et al., 1999).

Many soils fix P in large quantities thereby converting them into less available forms. Several authors (Beauchemin et al., 1996; Yuan and Lavkulich, 1994; Nair et al., 1998; Baneal et al., 2001; Macdowell et al., 2001; Villanpando and Graetz, 2001; and Martin et al., 2004) have documented the mechanism of P fixation by soils and its transformation to less available forms for plant utilization. The dominant mechanisms responsible for soil phosphate fixation are;

a. Complex dissolution and precipitation of phosphorus with ions in the soil. This is common with layer silicates where $A1^{3+}$ is dissolved and aluminum phosphate precipitates (Bohn et al., 1985).

b. Chemical adsorption and ligand exchange on edges of minerals.

Hansen and Strawn (2003) attributed P release rate to three different processes; dissolution of various P bearing mineral phases, desorption of P from mineral surfaces and

mineralization of P from organic matter. Phosphorus desorption is, however, controlled by soil pH, the nature of the P-bearing compounds, ligand exchange as well as P-saturation index (Martin et al., 2004). When the mechanism involved in the retention is not known, the term sorption is used (Sparks, 1995).

Several authors (Beauchemin et al., 1996; Baneal et al., 2001; Macdowell et al., 2001; and Agbenin; 2003) have shown that P retention is often related to the oxalate-extractable $A1^{3+}$ and Fe^{3+} in soils. Nair et al., (1998) have shown that organically bound A1 was the most important factor in P retention. Singh and Gilkes (1991) and Yuan and Lavkulich (1994) showed that Fe and A1 oxide surface in acid soils were responsible for high phosphorus retention. Solis and Torrent (1989) also reported that iron oxide and clay content have direct influence on P-sorption capacity. Ryan et al. (1985) found that Fe oxide and $CaCO_3$ have a direct bearing on P-sorption in soils. Villanpando and Graetz (2001), working with some acid soils from Florida, observed that A1 is the most important chemical property influencing P-retention. Swift (1989), Bloom (1981), Owusu-Bennoah and Acquaye (1989) and Sanyal and De Datta (1991) reported that organic matter increases P-sorption capacity of soils due to its association with Fe, A1 and Ca. Bohn et. al. (1985) showed that P-retention was due to the dissolution of $A1^{3+}$ followed by the precipitation of aluminum phosphate. They concluded that acid extractable $A1^{3+}$ and Fe^{3+} in soils have a direct influence on P-retention. Phosphorus retention in soils by humic substance can be as a result of binding effect of humics on Fe/Al surfaces, blocking phosphate binding sites and consequently reducing P-adsorption (Gerke, 1993).

The mechanisms of organic P retention by soils have received little attention. The mechanism of their retention may be similar to that of inorganic phosphorus. Bohn et. al.

(1985) observed that inositol hexaphosphate and possibly other organic phosphate compounds are retained in the soil by precipitation reactions. They further concluded that their sorption through orthophosphate groups to sesquioxides as well as interaction of the organic part of the phosphate ester with the organic or inorganic compounds of the soil are very important mechanisms for organic P retention in soils.

2.2 Factors affecting phosphorus sorption and desorption characteristics in soils

Factors such as clay content, organic matter, pH, free and extractable Fe and Al oxides, level of exchangeable-calcium, ionic strength, soil mineralogy as well as parent material and soil texture, influence phosphorus adsorption and desorption in soils (Mokwunye, 1975; Agbenin and Tiessen, 1995; Agbenin, 1996, 2003; and Martins et al., 2004).

Phosphorus sorption was shown to fluctuate with increase in soil pH in weathered tropical soils (Agbenin, 1996). Agbenin (1996) reported two interacting effects of pH on P sorption. Increase in pH increases the net negative charges of variable charge soils. Consequently, P sorption decreases because of electrostatic repulsion of phosphate ions (Haynes, 1983; Agbenin, 1996). Ionic species of P especially $H_2PO_4^-$ and $H_2PO_4^{2-}$ are affected by pH. There is preference for $H_2PO_4^{2-}$ as pH is raised (Haynes, 1984 and Agbenin, 1996). It was observed by Agbenin (1996) that an increase in pH from 4.5 to 7.0 increased P sorption and he attributed this to precipitation of Ca-phosphate or co-adsorption of Ca and $H_2PO_4^{2-}$. Marsh et al. (1987) working with some soils from New Zealand found that P sorption was highest at low pH and decreases with liming. Bowden et al. (1980) related the decrease in P sorption with pH increase to increasing surface negative charge.

Weathered tropical soils are associated with abundance of free Fe and Al oxides (Jones and Wild, 1975). The nature and amount of Fe and Al oxides in a soil significantly affects phosphate reactions (Torrent et. al., 1990). Agbenin (2003) attributed the increasing P-sorption capacity of some savanna Alfisols with soil depth to dithionite-extractable Fe and Al and to oxalate-extractable Fe and Al oxides that also increased with soil depth. The effect of extractable Al on P-sorption is probably due to the isomorphous substitution of Al^{3+} for Fe^{3+} in crystalline Fe oxides in soils (Agbenin, 2003). This leads to structural imperfection in the crystalline Fe oxide with implication for high anion retention capacity through diffusion (Schwertmann and Herbillon, 1992). Wilson et al. (2004) observed a rapid P adsorption with addition of ferrihydrite to a soil, suggesting ferrihydrite can be an effective soil amendment for reducing P mobility in the soil and enhancing its sorption.

Organic matter influences P-adsorption through its binding effect on cation such as Fe and Ca (Villanpando and Graetz, 2000). Sibanda and Young (1986) observed that humic and fulvic acid as well as low molecular weight organic acids may block sites on soil materials thereby reducing phosphate adsorption. Humic substances also reduce P-adsorption by inhibiting the crystallization and polymerization of Fe and Al oxides (Gerke, 1993). It was observed that reactive sites in organo-Al complexes contributed to initial P-loss in some soils of the semi-arid part of northeast Brazil (Agbenin and Tiessen, 1995). The chelating ability of hydroxyl and carboxyl ligands occurring in soil organic matter is responsible for phosphate adsorption by organic compounds (Parfit, 1979). Soil organic matter decomposition may also influence P adsorption. The mineralization of soil organic matter releases P into the soil. During the process of mineralization, organic anions are

produced which compete with PO_4^{2-} ions for adsorption sites. Mizota et al. (1982) observed a close positive correlation between organic carbon and P adsorption. This is, however, in conflict with the work of Borggard et al. (1990) where they observed no effect of organic carbon on P-adsorption.

Exchangeable Ca is the dominant cation in the exchange sites of West African Savanna soils (Jones and Wild, 1975; Agbenin, 1996). This Ca in the exchange site greatly influences the P-sorption capacity of savanna soils. Agbenin (1996) suggests that Ca may induce increased P-sorption at high soil pH. When Ca is specifically adsorbed, positive charges are created in soil surface leading to electrostatic adsorption of P (Agbenin, 1996).

2.3 Phosphorus sorption capacity of savanna soils

Savanna soils are characterized by low organic matter content, base saturation, exchange capacity and available P (Vanlauwe et al., 2004) with low P sorption capacity even though they have high weathering intensity (Mokwunye 1975; Agbenin, 1996, 2003). Savanna soils contain substantial amounts of hydrous oxides of Fe and Al with a tendency to sorb P in them.

Though some effort has been made to study the P sorption capacity of savanna soils, there is little or no investigation to determine the component properties of savanna soil properties affecting P-sorption. High concentration of Fe oxide in savanna soils may serve as a sink for P when deposited as nodules. Phosphorus sorption is significantly affected by the nature and amount of oxalate-and dithionite-extractable Fe and Al in savanna soils. Agbenin (2003), working with a savanna Alfisol from Samaru-Nigeria

found that dithionite-extractable Fe and Al were the active P-sorption components of the soils. He concluded that oxalate-extractable Fe was not an active P-sorption component of the soils, consistent with earlier study by Agbenin and Tiessen (1995) in some soils of semiarid region of northeast Brazil.

Phosphorus sorption was found to increase when pH was raised in three savanna Alfisols (Agbenin, 1996) and four savanna soils consisting of Alfisols and Entisols (Mokwunye, 1975). This did not support the observation of Parfit (1978) that P sorption usually decreases with increase in soil pH. Increase in P sorption with an increase in soil pH may be attributed to precipitation of amorphous polymeric Al^{3+} species having active P sorption sites (Haynes and Swift, 1985). Mokwunye (1975) related this to the hydrolysis of exchangeable Al in the soil. Agbenin (1996) however added that the chemistry and retention of calcium by the soil is the probable reason for P sorption at high pH. He concluded that calcium induced P sorption could be responsible for P-sorption when pH is raised.

2.4 Kinetics of phosphate adsorption and desorption in soils.

The utilization of P by plants depends largely on its movement in the soil, which is a function of its retention by soil components. The significance of phosphorus to plant growth is impeded by its kinetics of slow release in the soil (Thompson and Troeh, 1978). Kinetic experiments are designed to study the nature, capacity and the rate at which P is adsorbed and desorbed by soil colloids (Sparks, 1985). This also helps in quantifying P fluxes between the soil solid and solution phases.

The kinetic of P release has been studied by the use of mild extractants such as

dilute base, or by anion exchange resins. Sodium-bicarbonate extraction buffered at pH 8.5 is commonly used and the P extracted is assumed to be plant available P (Kou, 1996). This may not be suitable for tropical arid soils with pH often less than 6.5 (Wild, 1986). Another alternative is the use of ^{32}P isotope. This measures the quantity of soil phosphate that is exchangeable with ^{32}P. This method predicts the amount of P that can be lost from agricultural soils (Mac Dowell et al., 2001). MacDowell et al. (2001) identify isotopically exchangeable P as plant-available P. A more reliable technique could be to relate kinetic parameters to bioassay. In this technique, a plant is grown in a soil to which a known amount of P has been added and the P held by the plant is determined.

The kinetic of P release and its sorption by soil is very complex. Several authors (Martin and Sparks, 1983; Sparks, 1985; Beauchemin et al., 1996; Grierson et al., 1998; Agbenin and Raij, 2001; Hansen and Strawn, 2003) have used several models and techniques in describing it. These authors characterized the kinetics with a number of equations, which included first-order, two-constant rate, parabolic diffusion equation and many others. Agbenin and Raij (2001) studied the kinetics and energetics of phosphate release using mixed ion-exchange resin and concluded that the kinetics of P release was limited by intraparticle diffusion. Phosphate desorption was initially rapid, but decreased with time. Amer et al. (1955) and Fiskell et al. (1979) reported that phosphate release kinetics could be described by three simultaneous first order rate expressions, probably reflecting three independent pools of available P in soils. Phosphorus release kinetics from manure-amended soil was found to be described by the Elovich model in a study by Hansen and Strawn (2003) and concluded that P release was limited by a dissolution mechanism. Goncalves et al. (1989) however, observed a good fit of kinetic data from a

Brazilian soil to fractional power model. Agbenin and Tiessen (1994) also made similar observations were P sorption data was best described by Fractional power function equally as Elovich equation.

2.5 Experimental approaches for determining the kinetics of P adsorption and desorption in soils

In kinetic studies, the techniques used in measuring ion exchange reactions and rate parameters must be very effective and suitable. According to Zasoski and Burau (1978), any technique designed to determine the kinetics of any reaction must not alter the concentration of the reactants involved. Furthermore, the technique must be very fast so as to enable the observation of rapid exchange reactions in the soil solution mixture and it should not alter the surface chemistry of the particles (Sparks, 1985). Several authors have used different techniques in kinetics studies most especially the kinetics of P release and sorption by soils. Two popular techniques usually employed are;

a. The batch or closed vessel technique

In this technique both the ion exchange and the adsorbate are placed in a centrifuge tube or any other vessel and the suspension agitated with the aid of a mechanical shaker or stirrer. The suspension is then centrifuged and the clear supernatant solution is collected for further analysis.

An alternative batch technique is the use of isotopic exchanger. In this method the quantity of soil phosphate that is exchangeable with the labeled phosphate is measured. Variations of this technique include static stirred and vortex batch techniques.

Even though this technique has been widely employed by most researchers

it has some shortfalls. Batch technique involves the use of wide soil to solution ratio, which varies the concentration in the solution, and the quantity of adsorption as the reaction proceeds (Sparks, 1985). This may eventually lead to an error in determining the kinetics of the reaction (Zasoski and Burau, 1978). If there is no adequate mixing of solution with the ion exchanger, a limited rate of reaction may occur (Sparks, 1985). This may also lead to a change in the surface chemistry of the colloids and the break down of soil particles, thereby increasing surface area and the rate of reaction (Barrow and Shaw, 1979). Another problem with the batch technique is that measurement at initial time steps of the reaction is not possible (Carski and Sparks, 1985). This is because majority of batch technique requires centrifugation to separate the solid from the liquid, which normally takes place after the completion of most exchange reactions (Sparks, 1985). With this technique, reverse reactions are not controlled, making it difficult to calculate rate coefficient. Furthermore, the products of the reaction are not removed (Sparks, 1999). This however, can be overcome by using a resin or a chelate material (Sparks, 1999).

b. Flow or miscible displacement technique

This method involves the introduction of a standard adsorbate solution onto a thin layer of wet soil and the adsorption reaction followed by monitoring the concentration of the leachate with time. When equilibrium is reached, the effluent concentration equals that of the initial adsorbate solution. The desorption reaction is also followed by monitoring the decreasing concentration of the previously adsorbed ion. Basically, this technique, as developed by Sparks et al. (1980) involves the injection of soil as suspension that is leached with an electrolyte that is passing through the soil at a constant flow rate

with the aid of a peristaltic pump, and aliquots are collected for analysis at various time intervals.

A major disadvantage of this technique is that it is diffusion-controlled which makes it difficult to determine thermodynamic parameters (Ogwada and Sparks, 1986). There can be error in dilution using this method, which can lead to error of interpretation (Ogwada and Sparks, 1986) by altering the concentration of the soil (Sparks, 1999). This is more pronounced in colloids having low ion absorbing power (Carski and Sparks, 1985). Also, dispersion of soil colloids may not be fully achieved (Sparks, 1999).

2.6 Kinetic models for describing P adsorption and desorption in soils

Kinetic models are designed to provide an index of reaction equilibrium with time and to reveal the mechanism involved in the reaction. Phosphates move very slowly in the soil due to their low solubility and their high rate of fixation. According to Bohn et al. (1985), the reaction of phosphates in the soil is often slow enough to be measured experimentally. Ryden et al. (1977) observed a very fast reaction between P and soil colloids. A slow reaction phase after completion of adsorption was observed by Burau (1985).

Kinetic equations with varieties of expressions have been used to represent P release kinetics. Such expressions include zero-, first-, second- and third-order equations. Others are parabolic diffusion law as used by Evans and Jurinak (1976) and Agbenin and Raij (2001), two constant rate equation (Chein, 1977), Langmuir equation (Parfit, 1978; He et al., 1996) and Elovich equation (Polyzopoulos et. al., 1986; Pavlatou and Polyzopoulos, 1988; Hansen and Strawn, 2003). Both the first-order cumulative and first-

order incremental models have been used to describe P desorption from soils (Baeuchemin et al. 1996). Griffin and Jurinak (1974) and Sparks (1985) also characterized phosphate adsorption by two simultaneous first order reactions.

Atkinson et al. (1970) used Elovich equation to describe the kinetics of isotopically exchange P on goethite. The equation was later modified by Chien et al. (1980) where they compared several kinetic models. These workers find that Elovich equation best described P release kinetics in soils. Hansen and Strawn (2003) applied several kinetic models and found that the data were best described with Elovich model. He et al. (1996) also compared first order, Elovich, and Langmuir kinetic equation in describing the kinetics of phosphate rock dissolution and concluded that the first-order equation is the simplest. According to Sparks (1985) zero-order equations have not been used extensively by researchers in describing the kinetics of ion release in soils. Phosphate adsorption kinetics in calcite was found to conform to second-order kinetics by Griffin and Jurinak, (1974) in the first few minutes of the reaction.

2.6.1 Zero-order equation

This equation has not been successfully applied to describe kinetics of P sorption in soils. Sparks and Jardin (1984) found that it poorly describes potassium adsorption on soils and clay mineral and zinc desorption from Vertisols (Dang et al., 1994). Potassium release from soils was found to conform to zero-order equation in an experiment by Burns and Berber (1961).

The simplified form of the equation can be given as:

$$\mathbf{q = K_o t} \text{ ..... } (1)$$

where q is the amount of material adsorbed at time t, and K_o is the rate constant. The dependence of the rate constant on the amount of desorbable material makes the equation ineffective.

2.6.2 First-order equation

This expression can be used to describe P-adsorption using either batch or miscible displacement technique. It suitably describes ion adsorption on clay materials (Sparks and Jardine, 1984) and is suitable for reactions at the particle/solution interface (Sparks, 1999). The equation was also used to describe P adsorption on calcite by Griffin and Jurinak (1984) even though data from P sorption experiment were inadequately described by a single first-order equation in an earlier work of Evans and Jurinak (1976). The equation can be illustrated as:

$$\ln q = \ln q_0 - kt \quad \text{.....(2)}$$

where q is the concentration of the ion in solution at time *t*, q_0 is the initial concentration of the ion added at time zero and *k* is the rate constant. The equation can be modified to;

$$\text{In } (q_0 - q) = \ln q_0 - k_d t \quad \text{..... (3)}$$

q_0 = quantity of P at $t = 0$

q = amount of P release at time t

where k_d is the desorption rate constant.

This modified form was referred to as multiple first-order equation and adequately described the rate of P release and adsorption (Evans and Jurinak 1976).

2.6.3 Second-order equation

This equation fits well where P desorption from soils is a simple exchange reaction (Pavlatou and Polyzopoulos, 1988). Griffin and Jurinak (1974) used it to describe the first few seconds of P-adsorption on calcite. The equation is, however, not suitable for describing P adsorption over a long period of time. The equation is expressed as

$$1/q = 1/q_0 + k_2 t \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

where k_2 is the adsorption rate constant. Other parameters are as described in the previous equations.

2.6.4 Elovich equation

The equation has been proved to best describe P-adsorption on soils, even though it was developed to describe the kinetics of chemisorptions of gases on solids (Low, 1960). It has been modified by many authors (Chien et al., 1980 and Polyzopoulos et al., 1986) to describe P adsorption in soils. The simplest form of the equation can be represented as follows (Polyzopolous et al., 1986).

$$dq/dt = \alpha e^{-\beta q} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

where q is the amount of material sorbed at time t and α, β are constants.

The modified form of the equation as used by Chien et al. (1980) is given as;

$$d(q_o - q_t)/dt = \alpha \exp(-\beta(q_o - q_t)) \ldots\ldots\ldots\ldots (6)$$

where $q_o - q_t$ represent the amount of P sorbed by the soil at time t. The equation integrated under the assumption that $\alpha\beta t >> 1$, becomes:

$$q = (1/\beta) \ln(\alpha\beta) + (1/\beta) \ln t \ldots\ldots\ldots\ldots\ldots (7)$$

If q is plotted against lnt a straight line is obtained with a slope of $(1/\beta)$ and an intercept of

(1/β) ln (α β).

2.6.5 Fractional power equation

Kuo and Lotse (1974) derived this equation from Freundlich adsorption isotherm. According to them the exponent of the equation is a time dependent constant and is given as;

$$q = kt^{1/n} \quad \text{.....} \quad (8)$$

The linear form of the equation is represented thus:

$$\ln q = \ln k + 1/n \ln t \quad \text{.....} \quad (9)$$

as in Agbenin and Tiessen (1995) where *n* and *k* are empirical constants, *q* is the quantity of P adsorbed at time *t*.

Even though this equation is empirical, it has been used successfully by some investigators (Kuo and lotse, 1974; Howlen and Westfall, 1985) in describing the kinetics of reactions in soils and sediments.

2.6.6 Parabolic diffusion equation

This model has been used by many researchers in describing the kinetics of ion adsorption and desorption in soils (Evans and Jurinak, 1976; Sparks and Jardin, 1984; Agbenin and Raij, 2001). The equation specifically describes the kinetics of P release in the first few minutes in a study by Evans and Jurinak (1976). They however, concluded that its use in describing the kinetics of ions exchange in soils is limited. The equation can be written in the form given by Sparks (1985) as:

$$q/q_{\alpha} = Rt^{1/2} + b \quad \text{……} \quad (10)$$

where R is the overall diffusion coefficient (Sparks, 1985) and b is a constant (Evans and Jurinak, 1976; Sparks, 1985; Agbenin and Tiessen, 1995).

Determination of rate-limiting steps is another very important aspect of kinetics study. Many concurrent processes occur during ion exchange in soils. The processes involved include film diffusion, intra-particle diffusion and chemical exchange. In reactions between phosphorus and soils, diffusion is the rate-limiting step. This may be either film or intra particle diffusion (Sparks, 1985). Agbenin and Raij (2001), using mixed ion-exchange resins concluded that intra-particle diffusion appeared to be the rate-limiting step in phosphorus release kinetics. If the diffusion of the ions is limited by the solution or bounding film around the soil particles, such diffusion is termed film diffusion. On the other hand, if the diffusion of the ions occurs within the soil particle through the interlayer spaces of the soil, it is intra-particle diffusion (Sparks, 1985; Agbenin and Raij, 2001).

If film diffusion is rate limiting, it can be described by equation (11) (Agbenin and Raij, 2001)

$$q/t = k_d (q_\infty - q) \quad \text{.....} \quad (11)$$

where k_d is the rate of diffusion across the film, q is the amount of P desorbed by resin at time t, and q_∞ is the equilibrium adsorption.

Film and intra-particle diffusion can be differentiated from the magnitude of the activation energy of the adsorption/desorption reactions. Values of activation energy ranging from 17-21 kJ/mol suggest that the reaction is film diffusion controlled, while a reaction characterized by an activation energy value of 21-42 kJ/mol is intra particle diffusion controlled (Agbenin and Raij, 2001).

Different mechanisms of P adsorption and desorption can be deduced by the good

fit of various kinetic equations to experimental data. Agbenin and Tiessen (1995) deduced that P-sorption reactions in soils occur by ligand exchange based on a good fit of Elovich to the experimental data. Pavlatou and Polyzopoulos (1988) concluded from a good fit to first-order rate equation that P sorption/desorption in soils occurs mainly by ligand exchange mechanism. Parfit and Atkinson (1976) reported a decrease in positive surface potential and increase in negative charge of a soil due to P adsorption. Similar observation was made by Saha et al. (2004). Other possible mechanisms of P-sorption are the precipitation and crystallization of adsorbed P on the soil surface (Chien et al., 1973; Agbenin, 1996; Agbenin and Tiessen, 1995) and intra-particle diffusion as deduced from the good fit of the kinetic data to the parabolic diffusion equation (Agbenin and Raij, 1999).

CHAPTER THREE

3.0. MATERIALS AND METHODS

3.1 Site descriptions, geology and climate of the study area

To achieve the objectives of the study, soils from twelve different locations across forest and savanna ecological zones were sampled for this study. The sampling locations are shown in Fig. 1, while Table 3.1 gives the dominant geology and other physiographic characteristics of the experimental sites.

3.2 Soil Sampling and preparation

The soils were differentiated on the basis of parent material characteristics. The parent materials were sandstone, shale and basement complex. Sampling was done at 2 depths, 0-15 cm and 15-30 cm for the surface and subsurface soils respectively. The soils were air-dried and sieved through a 2-mm sieve and stored for routine analysis.

3.3 Soil Characterization

The physical and chemical properties of the soil were determined as follows:

3.3.1. Particle size distribution

Particle size distribution was determined by the standard hydrometer method (Gee and Bauder, 1986). Fifty grams of < 2 mm sieved soil samples were weighed into separate polythene bottle and 25 ml Calgon solution and 400 ml tap water were added and shaken for 15 min on a mechanical shaker. The soil suspension was transferred to a 1-L capacity cylinder and made to mark with water. The suspension was stirred with a plunger. The

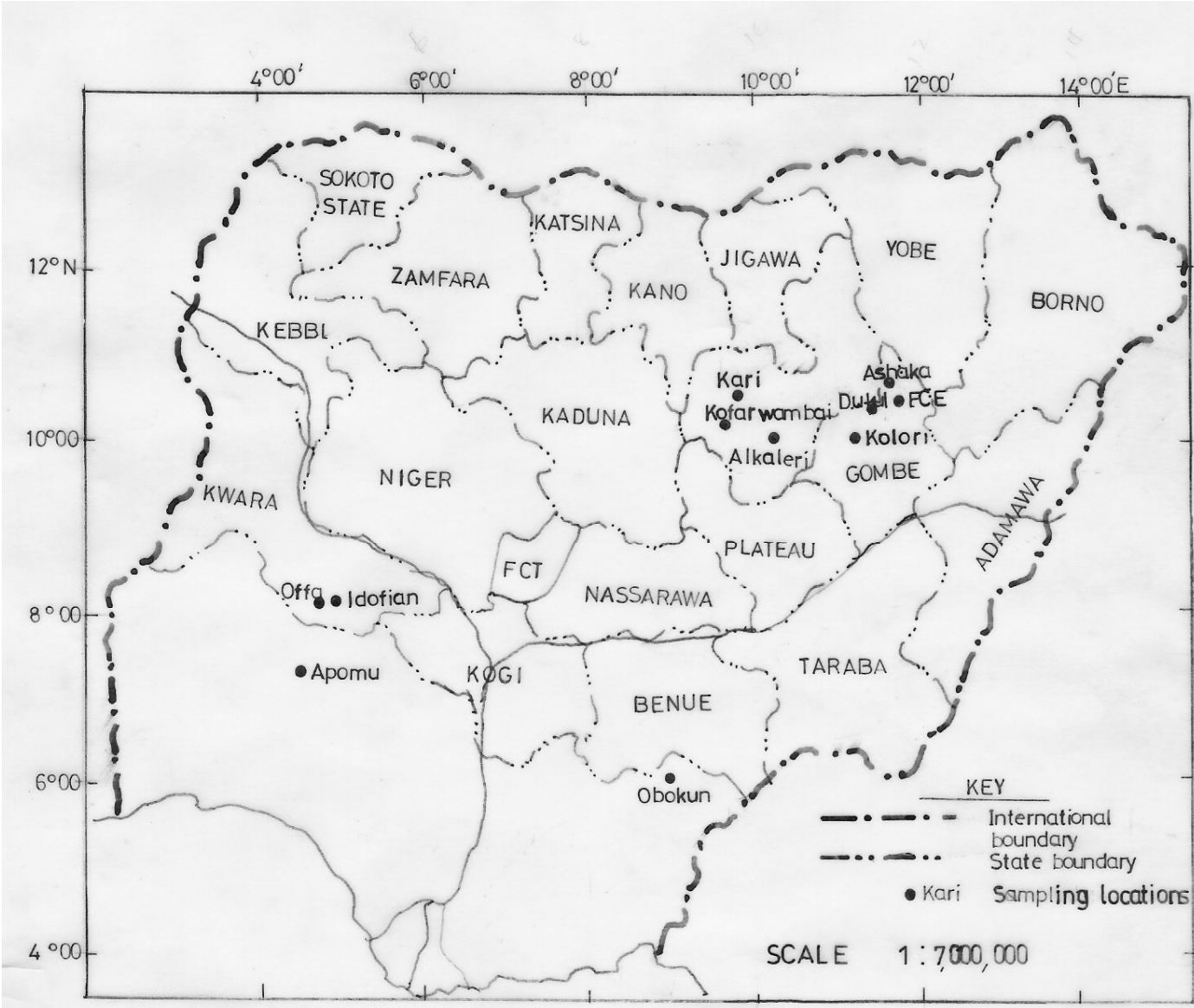


Fig.1 : Map of Nigeria showing the various sampling locations.

Table 3.1. Coordinates, geology, climate and other physiographic characteristics of the sampling locations

Sampling location	Coordinates	Geological formation	Ecology	Mean annual Rainfall (mm)	Mean annual Temperature (^{0}C)	Dominant soil group
Kari 1	10^0 17^1N, 9^0 49^1E	Basement complex	Grassland	750	26.8	Alfisol
Kari 2	10^0 17^1N, 9^0 49^1E	Basement complex	Grassland	750	26.8	Alfisol
Kofar wambai 1	10^0 18^1N, 9^0 49^1E	Basement complex	Grassland	750	26.8	Alfisol
Kofar wambai 2	10^0 18^1N, 9^0 49^1E	Basement complex	Grassland	750	26.8	Alfisol
Alkaleri	10^0 14^1N, 10^0 21^1E	Sandstone	Shrubs	871	26.8	Alfisol
Kolori	10^0 12^1N, 11^0 12^1E	Sandstone	Shrubs	981	28.0	Alfisol
F.C.E Gombe 1	10^0 17^1N, 11^0 10^1E	Sandstone	Shrubs	981	28.0	Alfisol
F.C.E Gombe 2	10^0 17^1N, 11^0 10^1E	Sandstone	Shrubs	981	28.0	Alfisol
Maza		Shale	Grassland	668	30.2	
Dukul 1	10^0 35^1N, 11^0 22^1E	Shale	Shrubs	890		
Dukul 2	10^0 35^1N, 11^0 22^1E	Shale	Shrubs	890		
Ashaka 1	10^0 50^1N, 11^0 30^1E	Shale	Grassland	668	30.2	
Ashaka 2	10^0 50^1N, 11^0 30^1E	Shale	Grassland	668	30.2	
Obokun	5^0 54^1N, 8^0 53^1E	Basement complex	Rain Forest	3107		
Offa	8^0 08^1N, 4^0 43^1E	Basement complex	Rain Forest	1346		Alfisol
Idofian	8^0 23^1N, 4^0 43^1E	Basement complex	Rain Forest	1240	26.2	Alfisol

temperature of the soil suspension was taken. A hydrometer was then inserted and measurements were taken after 40 seconds and after 2 hours. The textural class was obtained using the international soil Texture Triangle.

3.3.2. Soil pH

Soil pH was measured in 1:2 soil: water suspension and in 0.01M $CaCl_2$ suspension using a glass electrode pH meter. Briefly, 10 g of < 2 mm sieved soil were weighed into 16 plastic cups and 25 ml of distilled water was added gradually until the soil became wetted. The soil suspension was then stirred thoroughly with a glass rod and the pH was measured by inserting the calomel electrode into the soil suspension. The same procedure was repeated but using 0.01M $CaCl_2$ solution instead of water but the suspension was allowed to stand for 30 minutes with occasional stirring after the addition of $CaCl_2$ solution.

3.3.3 Organic carbon

Organic Carbon was determined by dichromate oxidation method as described by Nelson and Sommers (1982). One gram of finely ground soil sample was weighed into a 250 ml conical flask. Ten milliliters of 0.1N $K_2Cr_2O_7$ solution were added and the flask was swirled gently to disperse the soil. This was followed by the addition of 20 ml conc H_2SO_4 and thoroughly mixed. The mixture was left for 30 min and allowed to cool down. Twenty milliliters of distilled water were added and the whole suspension was filtered through Whatman No.1 filter paper. Three drops of Ferroin indicator were added and titrated with 0.4N ferrous ammonium sulphate solution. The end point was reached when

the colour changed from dark green to red. Blank determination was made in the same manner. Organic carbon in the soil was calculated as:

$$OC = \frac{\text{Meq of } Cr_2O_7 - \text{Meq of Fe-}NH_4SO_4}{\text{weight of soil sample}} \times 4$$

3.3.4. Total phosphorus

The total P concentration in the soil was determined by digesting 0.2 g of finely ground soil sample with a mixture of 1 ml of 60% $HClO_4$, 5 ml of conc. HNO_3 and 0.5ml of conc. H_2SO_4. The soil in the digestion tube was gently swirled and digested at moderate heat with gradual increment in temperature until white fumes appeared. The tubes were set aside to cool down and diluted to 40 ml with distilled water. The digests were transferred into 50 ml volumetric flask by filtering with Whatman no. 41 filter paper and made up to 50 ml with distilled water. A blank digestion was made in the same way. Phosphorus in the digest was determined using the method of Murphy and Riley (1962).

3.3.5. Organic phosphorus

Organic P was determined by the ignition method of Saunders and Williams (1955). One gram of < 2 mm sieved soil sample was weighed into 16 clean porcelain crucibles and transferred into Muffle furnace and heated for 90 min at a temperature of 550^0C. The ignited sample, on cooling, was transferred into 100-ml centrifuge tubes. One gram of unignited soil sample was weighed into a separate centrifuge tubes and 20 ml of 1 N H_2SO_4 solution were added to both the ignited and unignited samples. The tubes were transferred into a mechanical shaker

and shaken for 16 hours and then centrifuged for 5 minutes. Phosphorus in the filtrate was determined using the method of Murphy and Riley (1962). Organic P was determined by the difference between the ignited and unignited sample. While P in the ignited sample was the total P in the soil, the P in the unignited sample was the concentration of the inorganic P in the soil.

3.3.6. Exchangeable cations and cation exchange capacity (CEC)

Exchangeable cations were determined by shaking the soil with 1N NH_4OA_C solution buffered at pH 7. Calcium and Mg in the extract were determined by EDTA titration and potassium and sodium by flame photometry. Cation exchange capacity (CEC) was determined by leaching with 1N NH_4OA_C solution (Anderson and Ingram, 1993). Ten grams of < 2 mm sieved soil samples were weighed into 50 ml centrifuge tubes, 33 ml of 1N NH_4OA_C solution was added stirred and left over night. The soil suspension was leached with 1N NH_4OA_C solution to a volume of 250 ml. The soil was leached again with 1N NH_4Cl solution four times and the solution was discarded. The soil was washed with 150 ml of 95% ethanol (v/v). The soil was leached with acidified 0.1 N NaCl solution and the leacheate was transferred into Kjeldahl flask and distilled over 2% boric acid solution in a conical flask. One hundred and fifty milliliters of the leacheate was collected and titrated with 0.1 N HCl solution. Cation exchange capacity was calculated from the relation:

(Titre – B) x NA x 100 / weight of soil (g)

were B is the blank and NA is the normality of the acid.

3.3.7. Extractable Al and Fe oxides

Oxalate-extractable Al and Fe were determined by extraction with ammonium oxalate in the dark (Jackson, 1986). Briefly, 0.5 g soil was weighed into 50 ml centrifuge tube and 25 ml of 0.2 M acidified ammonium oxalate solution buffered at pH 3.0 was added. The tube was stoppered and shaken in the dark for 4 hours. The suspension was centrifuged for 30 min and the clear supernatant solution was decanted into clean vials. Ten milliliters of the extract were measured into 100 ml volumetric flask and diluted to mark with distilled water. Iron in the solution was determined by AAS and Al by aluminon method.

Dithionite-citrate-bicarbonate-extractable Fe and Al were determined by the method of Mehra and Jackson (1960). One gram of finely ground soil sample was weighed into a centrifuge tube and 40 ml of 0.3 M sodium citrate solution was added together with 5 ml of 1 M sodium bicarbonate solution. The soil suspension was heated on a water bath at 70 – 80^0C. One gram of sodium dithionite salt was added to the solution and stirred continuously for 1 min and occasionally for 15 min. The suspension was centrifuged and the clear supernatant solution was decanted into a 200 ml flask. The residue was treated with sodium citrate-sodium bicarbonate-sodium dithionite once again. The soil was then washed twice with 40 ml of 0.3 M sodium citrate solution and then centrifuged and decanted. The clear supernatant solution was added to the extract in the 200 ml flask and made to mark. Iron in the solution was determined by AAS and Al by aluminon method (Cheney, 1955).

3.4 Kinetic experiments

The following kinetics experiments were carried out.

3.4.1 Kinetic release of native P in the soil

Three grams of < 2 mm sieved air-dried soil sample were weighed in duplicate into centrifuge tubes and 30 ml of distilled water were added together with l strip of anion exchange resin (BDH prod. 55164 anion exchange membranes measuring 9 x 62.5 mm in chloride form). The tubes were capped and shaken on a mechanical shaker at time interval of 10, 30, 60, 150, 300, 600, 1200 and 2400 minutes. The resin strips were removed from the centrifuge tubes with the aid of a pincer and any soil adhering to it was washed with a jet stream of distilled water. The resin strips were then placed in clean tubes and extracted with 20 ml of 0.5 N HCl. Phosphorus in the solution was determined using the method of Murphy and Riley (1962).

3.4.2 Effect of particle size on P release rate

Three grams of < 0.02 mm sieved soil samples were weighed into separate centrifuge tubes in duplicate and 30 ml of distilled water were added together with l strip of anion exchange resin. The tubes were capped and shaken on a mechanical shaker at time intervals of 30, 60, 150, 300, 600 minutes. The resin strips were removed from the centrifuge tubes with the aid of a pincer and any soil adhering to it was washed with distilled water by rinsing several times. The resin strips were then placed in clean tubes and extracted with 20 ml of 0.5 N HCl solution.

Phosphorus in the solution was determined using the method of Murphy and Riley (1962).

3.4.3 Kinetics of release of adsorbed phosphorus

For the sorption experiment, 2 g of <2-mm sieved soil were weighed into separate centrifuge tubes and the weight of the tubes and the soil determined. Phosphorus sorption index of the soil was determined by adding 400 μg P g^{-1} from a stock P solution of 1000 μg P ml^{-1} in 0.01M KCl solution. The P source was KH_2PO_4. The soil suspensions were brought to 20 ml by adding appropriate amount of 0.01M KCl solution giving a soil solution ratio of 1:10 and allowed to equilibrate by shaking daily for 30 min. for 6 days. The soil-P solution was centrifuged for 20 min and decanted and the weight of the tube and moist soil in it was determined. The difference between the weight of the dry soil in the tube and the moist soil was the quantity of entrained solution in the soil. Phosphorus in solution was determined by the method of Murphy and Riley (1962). Phosphorus adsorbed was calculated as the difference between P added and P in remaining solution.

The P adsorbed by the soil was desorbed by introducing resin strips into the centrifuge tubes to which 30 ml of distilled water were added and shaken on a mechanical shaker at time intervals of 10, 30, 60, 150, 300, and 600 minutes. The resin strips were removed from the centrifuge tubes with the aid of a pincer and adhering soil particles were removed by a jet stream of distilled water. The resin strips were placed in clean tubes and extracted with 20 ml of 0.5 N HCl solution.

Phosphorus in the solution was determined using the method of Murphy and Riley (1962).

The kinetic models tested in this study are shown in Table 3.2 below

Table. 3.2. Kinetic models used in this study

Model Equation		**Parameters**
First-order	$\ln q = \ln q_o - k_1 t$	k_1, first-order rate constant
Second-order	$1/q = 1/q + k_2 t$	k_2, second-order rate constant
Elovich	$q = (1/\beta) \ln (\alpha\beta) + (1/\beta) \ln t$	α, initial P desorption rate, and β, P desorption constant
Fractional power	$\ln q = \ln k + 1/n \ln t$	n, an empirical constant
Parabolic diffusion	$q = Rt^{½} + b$	R, diffusion rate constant

q is the amount of soil P desorbed by anion exchange resin after t (s) period of extraction and q_0 is that present at t = 0 (s), initially.

A separate experiment was conducted to determine the relationship between adsorbed P and the release of SO_4 and OH into the soil solution. In the experiment 10 g of < 2 mm soils were weighed into separate 100 ml centrifuge tubes in duplicates. To the soils in the tubes were added 0, 100, 200 and 400 μg P g^{-1} soil from a stock solution of 1000 μg P ml^{-1}. The soil suspensions were brought to 50 ml by adding appropriate amount of 0.01M KCl solution as the background electrolyte giving a soil: solution ratio of 1:5. The pH of the suspensions was immediately measured. The soil suspensions were allowed to equilibrate by shaking for 2 hours daily for one week. The pH of the soil solution was measured again to determine if pH changes had occurred during the period. The tubes were centrifuged for 15 min and filtered through Whatman No. 42 filter paper into 100 ml vials. Phosphorus in the supernatant solution was determined by the method of Murphy and Riley (1962). Phosphorus sorbed was calculated as the difference between P added and P remaining in solution. Sulphate in the solution was determined by colorimetric method as described by Fox et al. (1964).

3.5 Statistical analysis

The linear forms of the kinetic equations (Table 3.2) were fitted to the experimental data. Least square regression analysis was used to ascertain the model that best described P desorption kinetics in these soils. The goodness of fit was determined by the coefficient of determination (r^2) and the standard errors for estimating the kinetic parameters. The standard error was calculated as follows:

$$SE = \sum \left[\frac{(P_a - P_b)^2}{(n-2)} \right]^{0.5}$$

Where P_a is the experimentally determined P sorbed, P_b is the calculated amount of P sorption estimated by the kinetic models, and n is the number of measurements. This relationship was taken from Agbenin and Tiessen (1995). The Kruskal Wallis analysis of variance was used to evaluate the effect of parent material on soil properties and kinetic parameters and mean separation was achieved by H statistics. The relationship between P adsorbed, sulphate and pH were determined by simple linear regressions. All statistical analyses were performed with GENSTAT discovery edition (GENSTAT, 2003).

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Soil physicochemical properties

The particle size distribution of the soils is presented in Table 4.1. The textural classes of the soils varied from sandy loam to clayey soil. The sand content of the soil ranged from 210 – 930 g Kg^{-1} with ten of the seventeen soils classified as sandy loam. Silt content ranged from 20 to 360 g Kg^{-1}. Clay content is generally low, ranging from 30 to 150 g Kg^{-1} with a higher value in two soils that developed over shale.

The pH of the soils in water ranged from acid (4.5) to neutral (7.1) and was consistently higher than pH in $CaCl_2$. The effect of parent material on soil pH was not pronounced, though soils over shale had higher pH than soils from other parent materials. The more acidic soils were those over sandstone. The organic carbon content of the soils varied from a minimum of 1.0 g kg^{-1} to a maximum of 30.3 kg^{-1} in Idofian in the forest zone (Table. 4.1). The organic carbon contents of the soils from the savanna were low, a typical feature of soils from the savanna region. The soil with relatively high organic carbon content (Ibokun, Offa and Idofian) (see appendix 2) were developed over basement complex and collected from the forest zone. These soils therefore, had probably higher OC turnover and greater microbial activity due to higher rainfall than soils from the savanna zone.

The cation exchange capacity varied from 16 mmol kg^{-1} in Kolori sandstone to 316 mmol kg^{-1} in Ashaka shale (Table. 4.1). The CEC of the soils was generally low when compared to temperate soils, which may be related to the low OC and the dominance of

Table 4.1. The range and means of selected physicochemical properties of soils of varying Lithogenic origins

Parent material	Sand	Silt	Clay	pH	OC	Exch-Ca	Exch-Mg	CEC
	g kg^{-1}			(H_2O)	g kg^{-1}	mmol kg^{-1}		
Basement complex (S)	710 – 750 (725)	120 – 160 (140)	130 – 150 (140)	5.4 – 5.8 (5.7)	3.4 – 8.4 (6.2)	25 – 53 (42)	4.2 – 27 (17)	80 – 98 (88)
Basement complex (F)	530 – 730 (650)	200 – 360 (260)	70 – 110 (90)	4.5 – 6.4 (5.8)	16.8 – 30.3 (25.3)	28 – 35 (32)	0.63 – 1.30 (1.1)	53 – 83 (73)
Sandstone	830 – 93 (895)	20 – 80 (45)	30 – 90 (60)	4.6 – 6.1 (5.1)	2.0 – 3.8 (2.9)	5.0 – 13 (8.0)	20 – 42 (26)	16 - 21 (18.5)
Shale	210 – 770 (526)	120 – 220 (156)	90 – 630 (318)	5.6 – 7.1 (6.5)	1.0 – 7.8 (2.9)	13 – 183 (83)	4 – 102 (27)	43 - 316 (165)

† Values in parentheses are means.

kaolinitic clay in the soils. However, the relatively high CEC values obtained for the soils developed over shale (Ashaka) might be due to their higher clay contents than the other soils (see appendices 1 and 2). The CEC values obtained in these soils are consistent with those reported by Jones and Wild (1975) for several savanna soils. Calcium (Ca) was the dominant exchangeable cation in all the soils studied and accounted for an average of 70% of the exchange sites. The highly leached soils from FCE Gombe that developed over sandstone had the lowest concentration of exchangeable Ca.

Two fractions of iron (Fe) and Aluminum (Al) oxides were determined in this study. These are the citrate-dithionite (Fe_d and Al_d) fraction and the oxalate fraction (Fe_{ox} and Al_{ox}) known to represent the amorphous fraction (Agbenin, 2003). Values of these oxides obtained for the soils are shown in Table 4.2. Phosphate adsorption and desorption characteristics of soils are significantly influenced by the proportion and distribution of these oxides in soils (Agbenin, 2003; Torrent, 1987; and Torrent et al., 1990). Understanding the nature, amount and distribution of these oxides in soils is therefore imperative for understanding of soil phosphate reactions. The amount of Fe_d ranged from 8.7 g kg^{-1} to 38.1 g kg^{-1} soil. These values are high compared to values reported by Agbenin (2003) for a savanna Alfisol and Ogunsola et al. (1989) for most Nigerian soils. These values are, however, within the limit reported by Ogban and Ekerette (2001) in some coastal sandy soils of southeastern Nigeria.

The concentrations of $Fe_{ox,}$ ranging from 0.25 to 1.50 g kg^{-1} in the soils, are close to those reported by Ibia (2002) in some inland flood plains of southern Nigeria but lower than values reported by Essoka and Esu (2003) in some inland soils of eastern Nigeria. The lowest values of Fe_d and Fe_{ox} were observed at FCE Gombe (Appendix 3),

Table 4.2. Dithionite and oxalate extractable aluminum (Al) and iron (Fe) in soils of varying lithogenic origins

Parent material	Fe_d	Fe_{ox}	Fe_{ox} / Fe_d ratio	Al_d	Al_{ox}
	g kg^{-1}			g kg^{-1}	
Basement complex (S)	11.7 – 23.4 (19.3)b	0.54 – 0.79 (0.69)a	0.03 – 0.06 (0.04)a	0.54 – 1.10 (0.96)a	0.24 – 0.40 (0.31)a
Basement complex (F)	27.3 – 32.3 (30)a	1.0 – 1.5 (1.2)a	0.03 - 0.06 (0.05)a	0.10 – 0.40 (0.22)b	0.25 – 0.4 (0.33)a
Sandstone	8.7 – 20.5 (11.9)c	0.25 – 1.04 (0.48)a	0.01 – 0.04 (0.03)a	0.28 – 0.54 (0.43)b	0.20 – 0.25 (0.24)a
Shale	12.7 – 38.1 (21.3)b	0.37 – 1.08 (0.57)a	0.01 – 0.09 (0.04)a	0.34 – 2.13 (0.88)c	0.15 – 0.26 (0.21)a

† Values in parentheses are means; † Values within columns followed by the same letter are not statistically different at $\alpha = 0.25$

the same soil with lowest exchangeable cations and soils formed over sandstone. However, there was no significant difference in the concentration of Fe_{ox} in soils derived from shale and those from sandstone, and also between the forest and savanna basement complex soils. The relatively high values obtained in the forestsoils may be attributed to the high OC that can perturb the crystallization of Fe.

The concentrations of Al_d ranged from 0.10 to 2.13 g kg^{-1}. These values are very close to those reported for savanna soils by Agbenin (2003). The values obtained for Al_{ox} are also within the range reported by Agbenin (2003). The Al_{ox} concentrations in soils derived from savanna basement complex are significantly different from forest soils of the same lithogenic origin, and from soils derived from shale (Table 4.2). Even though, the nature and properties of Al and Fe oxides are not fully understood in some soils, it is believed that Al_d is Al substituted for Fe in crystalline Fe oxides such as goethite, thus causing imperfection in crystalline Fe oxides (Torrent, 1987). These substitutions have serious implications for phosphate retention by soil (Agbenin, 2003).

4.2 Phosphate status of the soil

The concentration of phosphorus in the soils is relatively low with total phosphorus (P_t) ranging from 39.1 mg kg^{-1} in Gombe sandstone to 626.3 mg kg^{-1} at Ashaka shale (Table. 4.3 and Appendix 4). These values are in consonance with low P status of savanna soils. The soil extractable P also followed the trend of the total P (P_t) ranging from 0.7 mg kg^{-1} to 49.0 mg kg^{-1}. Higher values (33.3 and 49.0 mg kg^{-1}) were, however, observed at Ashaka shale. The low concentration of extractable P in the soils except for soils over Shale at Ashaka, suggests apparent P deficiency in these savanna soils. Phosphorus losses

Table 4.3. Total, organic and inorganic phosphorus in soils of varying lithogenic origins

Parent material	Total P	Organic P	Inorganic P	Available P
			mg kg^{-1}	
Basement complex (S)	133.6 – 156.6 (147)b	8.02 – 135.5 (68)b	15.8 – 144.9 (79)c	0.70 – 15.30 (2.1)b
Basement complex (F)	182.7 – 404.5 (265)a	51.7 – 175 (102)a	33.8 – 352.7 (163)b	7.0 – 26.30 (14.1)a
Sandstone	39.1 – 78.3 (55)c	14.8 – 32.1 (22)c	7.0 – 45.8 (34)c	3.50 – 15.80 (12.7)a
Shale	52.2 – 626.3 (298)a	1.7 – 89.3 (38)c	48.8 – 539.6 (261)a	1.8 – 49.0 (19.6)a

† Values in parentheses are means; † Values within columns followed by the same letter are not statistically different at $\alpha = 0.25$

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 contributed to the low organic P concentrations of the soils (Jones and Wild, 1975).

When the P values obtained from the soils of different lithogenic origins were analyzed statistically, there was a significant difference between extractable P in savanna soils derived from basement complex and those derived from forest of same lithogenic origin. A significant difference was also observed in the concentration of total P of forest and savanna soils derived from basement complex and sandstone (Table 4.3). This can be attributed to the higher content of organic materials in the forest soils than the soils derived from sandstone. When P was applied to the soils, total P sorbed by the soil ranged from 10.8 mg kg^{-1} in the Idofian Basement complex to 35.5 mg kg^{-1} in Alkaleri Sandstone, representing 3 and 9% of applied P (Appendix 7). Variations in the level of sorbed P may be attributed to variation in the properties of the soils studied. The soils that developed over Sandstone and with higher P sorption are those lower than other soils in Fe_{ox} and Al_{ox} showing that these oxides have significant influence in P retention.

4.3 Phosphorus desorption kinetics as affected by parent material

4.3.1 Basement complex

Phosphorus desorption from the soils increased with time. The desorption patterns included an initial fast reaction followed by a slow reaction that continued up to 1200 min (Figs 2 and 3). The heterogeneity of the adsorption sites with different adsorption affinities and binding strengths is thought to be responsible for the biphasic desorption patterns (Huang, 2000; Madrid and De Arambari, 1985; Saha et al., 2004). The concentration of P desorbed by anion exchange resin varied considerably between soils and with time. For basement complex

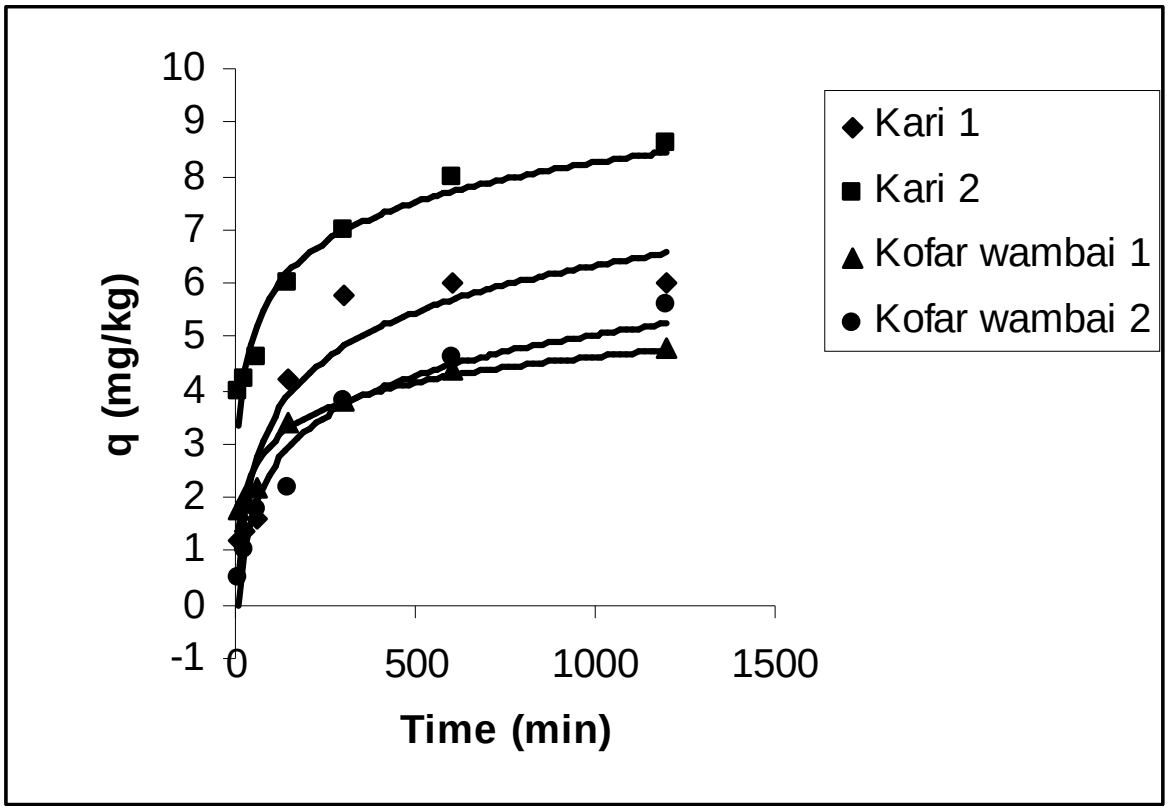


Fig 2. Time dependent P desorption by anion exchange resin from savanna soils derived from basement complex

soils of the savanna (Fig. 2), P desorbed from Kari soil-2 was greater than Kari soil-1 probably due to a higher proportion of OC in Kari soil-2 (Appendix 2) and higher concentrations of Al oxides in Kari-1 soil (Appendix 3). Generally, more P was, however, desorbed from the Kari soils than the Kofar Wambai soils. The differences in P desorbed from the soils might be explained by variations in the binding strength of P between the soils. Even though, the concentration of total-P is higher in Kofar Wambai soils, it has higher amount of Fe and Al oxide fractions that have strong affinity for P in soils. Aluminum and Fe oxides are strongly implicated in the P retention of most savanna soils (Agbenin, 2003). The higher clay content of these soils may also contribute to their lower P desorption since Al and Fe oxides are major constituents of the clay fraction of savanna soils (Jones and Wild, 1975; Agbenin, 2003). For the forest basement complex soils, more P was desorbed from soils from Ibokun and Idofian than the soil from Offa (Fig. 3). This may be attributed to the higher total P contents in Ibokun and Idofian soils than the Offa soils.

Several factors affect the availability and extractability of P in soils. These include clay content, organic matter, pH, free and extractable Fe and Al oxides, level of exchangeable-calcium, ionic strength, soil mineralogy, parent material, soil texture, and percentage of P saturation. For the soils from the forest basement complex, it seems that clay content, exchangeable Ca, and P saturation percentage can account for the variation in P desorbed by ion exchange resin between the soils. In all the soils, P desorbed approached equilibrium after 500 – 600 min though measurable changes in the quantity of P desorbed were still observed with time (Figs 2 and 3).

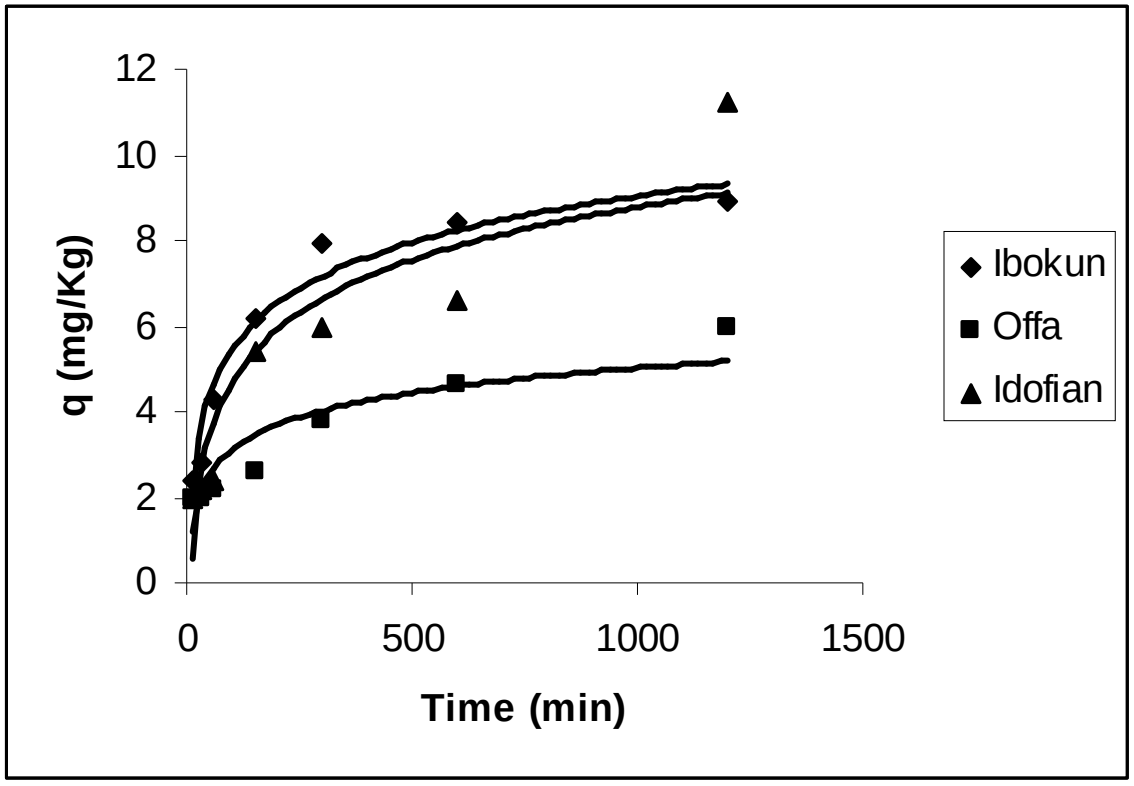


Fig 3.Time dependent P desorption by anion exchange resin from forest soils derived from basement complex

4.3.2 Sandstone

Phosphorus desorption from sandstone-derived soils is less than P desorbed from soils derived from basement complex. The lower value of total P, OC, exchangeable Ca and pH in these soils may account for lower value of P desorbed from these soils. Alkaleri soil desorbed higher amount of P than Kolori and FCE Gombe-1 soils that had similar desorption pattern (Fig. 4). The Alkaleri soil had a high tendency to desorb more P probably because it had the highest concentration of total and inorganic P (Appendix 4). The similarity in desorption pattern observed between Kolori and FCE Gombe-1 soils may be attributed to the similarity in the concentration of free Fe and Al oxides except for Fe_d, and to their similarity in texture. Oxalate extractable Fe and exchangeable Ca seemed to be the dominant predictors of P desorption in these soils as shall be discussed later. Surprisingly the FCE Gombe-2 soils that had the lowest concentration of Fe_{ox} and exchangeable Ca had lower P desorption than the Alkaleri soil that had a higher concentration of exchangeable Ca and Fe oxide. It seems that the relatively high total P in Alkaleri and Kolori soils than FCE-1 and -2 soils might account for the difference in P desorption. Phosphorus desorption approached equilibrium more rapidly in FCE Gombe-2 soil than the other soils from this parent material (Fig. 4).

4.3.3 Shale

Phosphorus desorption from soils derived from shale followed the same pattern as soils from basement complex and sandstone. Desorption was greater in Maza soils with a pH of 7.1 than the other soils (Fig. 5). High P desorption at neutral pH can be attributed to high P solubility induced by precipitation of Fe^{3+} and Al^{3+} that act as P sinks in weathered soils. Hence, it is a common practice to use liming as a way of reducing P fixation by soils.

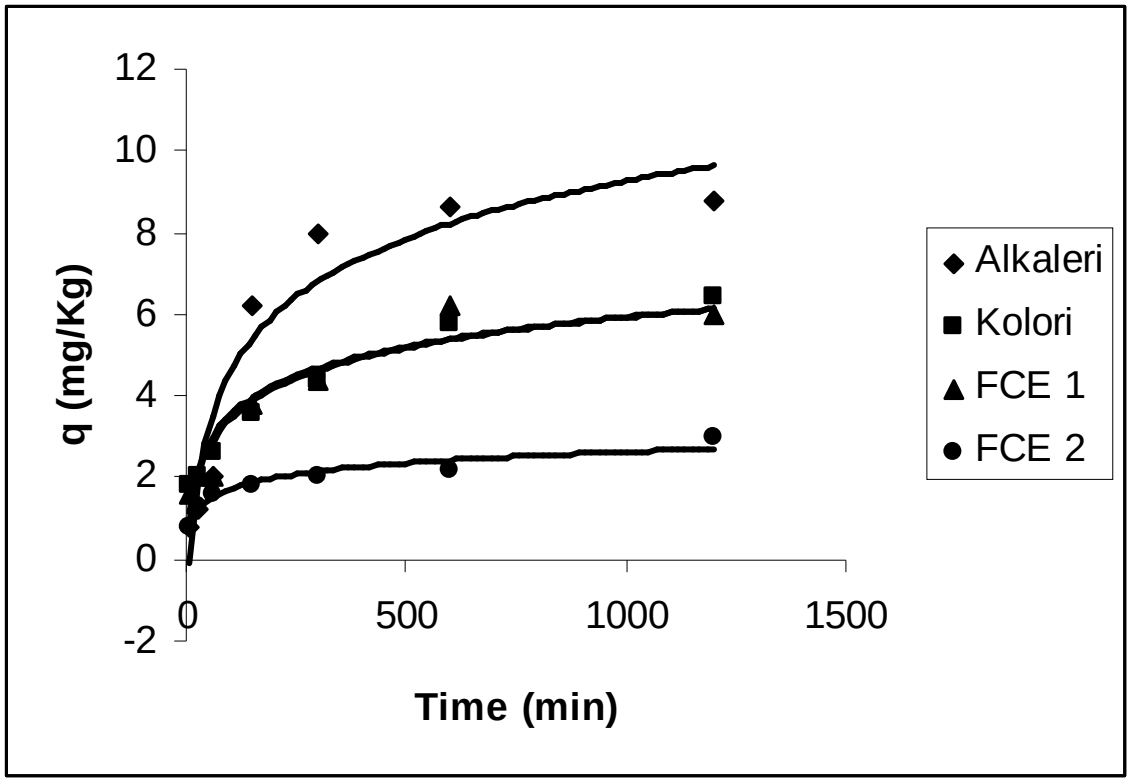


Fig 4.Time dependent P desorption by anion exchange resin from soils derived from sandstone.

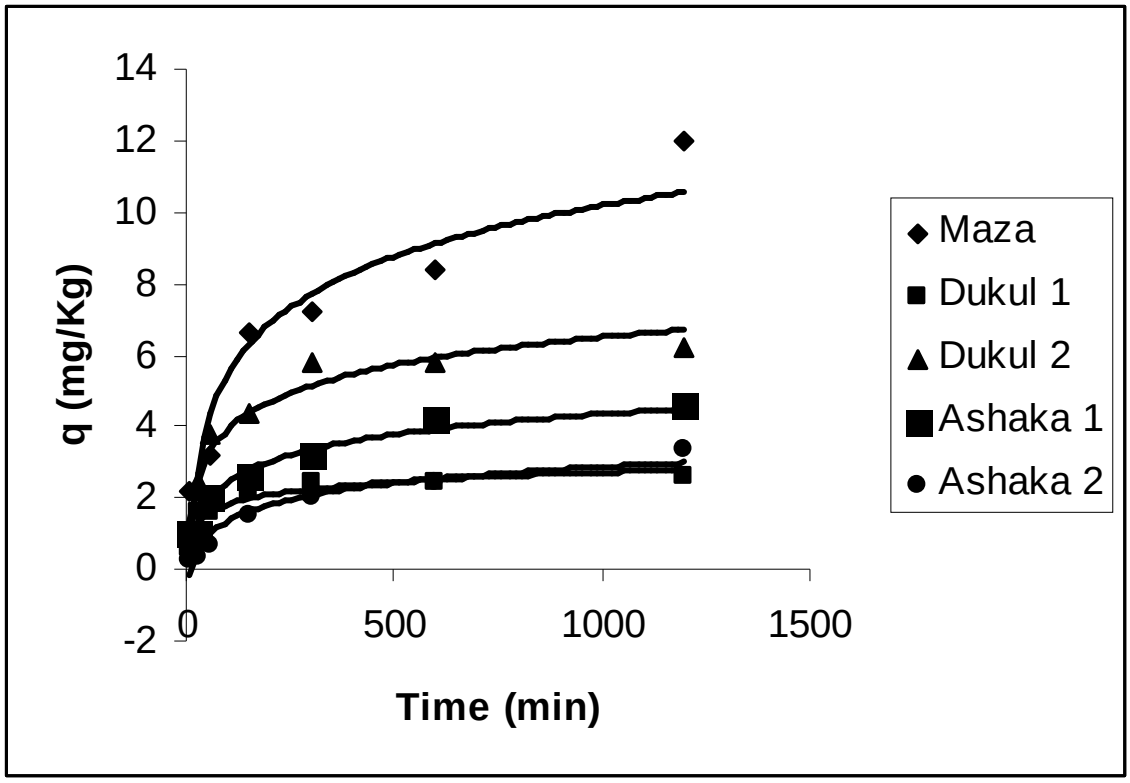


Fig 5.Time dependent P desorption by anion exchange resin from soils derived from shale.

However, for most savanna soils the use of liming to increase P solubility is questionable (Agbenin, 1996; Mokwunye, 1975). The low desorbability of P observed in Dukul-1 and Ashaka-2 soils may be attributed to the high affinity of P for Fe oxides. The Dukul soil-1 had however, for most savanna soils the use of liming to increase P solubility is questionable (Agbenin, 1996; Mokwunye, 1975). The low desorbability of P observed in Dukul-1 and the highest content of organic C, which can inhibit the precipitation of Fe and Al oxides, thus providing increased surface areas for phosphate retention. The relatively high clay content of the Ashaka soils could have been a factor in P desorption from the soils. Clays, especially 1:1 clay types, have been reported to contribute immensely to P retention by tropical soils (Sanyal et al., 1993).

4.4 Kinetic modeling of P release

4.4.1 Soils from basement complex

The coefficient of determination (r^2) and standard error (SE) for estimating the model parameters were used to choose the model that best described the kinetics of P desorption in these soils. Several authors (Saha et al., 2004; Tomark, 1997; Dang et al., 1994; Chien and Clayton, 1980) have used the same criteria for the choice of kinetic models in their studies. Values for the coefficient of determination (r^2) and standard error of estimates (SE) of the kinetic parameters are given in Tables 4.4 and 4.5 for the basement complex soils. The Elovich, fractional power and parabolic diffusion equations satisfactorily described the kinetics of P desorbed over the entire reaction period. Several authors (Evans and Jurinak, 1976; Chien and Clayton, 1980; Goncalves et al., 1989; Agbenin and Tiessen, 1995; Hanssen and Strawn, 2003) have used these kinetic equations in modeling P sorption kinetics. Based

Table. 4.4. Coefficients of determination (r^2) for various kinetic models tested (< 2mm sieve soil) for soils derived from basement complex (Savanna)

	First-order		Second-order		Elovich		Fractional power		Parabolic diffusion	
Soil series	r^2	SE	r^2	SE	r^2	SE	r^2	SE	r^2	SE
Kari 1.	0.52	0.35	0.46	0.38	0.89	0.09	0.88	0.09	0.78	0.12
Kari 2.	0.73	0.14	0.64	0.19	0.95	0.04	0.96	0.03	0.94	0.04
Kofar wambai 1.	0.67	0.16	0.57	0.30	0.95	0.04	0.96	0.03	0.91	0.09
Kofar wambai 2.	0.60	0.21	0.34	0.58	0.95	0.05	0.97	0.02	0.96	0.03

Table. 4.5. Coefficients of determination (r^2) for various kinetic models tested (< 2mm sieve soil) for soils derived from basement complex (Forest)

	First-order		Second-order		Elovich		Fractional power		Parabolic diffusion	
Parent material	r^2	SE	r^2	SE	r^2	SE	r^2	SE	r^2	SE
Obokun	0.55	0.23	0.45	0.39	0.96	0.03	0.95	0.04	0.84	0.10
Offa	0.87	0.08	0.78	0.12	0.84	0.10	0.90	0.08	0.98	0.02
Idofian	0.76	0.13	0.60	0.21	0.84	0.10	0.95	0.04	0.95	0.04

on r^2 and SE values, the fractional power function gave the best fit followed by the Elovich and parabolic diffusion model in the savanna Basement Complex soils. However, for the forest basement complex soils, there is readily no choice between the fractional power function and the parabolic equation (Table 4.5). There was no fit to the first or second-order rate equation, suggesting that native P desorption or release patterns in these soils cannot be described by a simple rate equation. This is due to the complexity of soil factors affecting P sorption and desorption.

4.4.2 Soils from shale

Fitting the experimental data from the soils derived from shale to the kinetic models showed that the fit was in the order: Elovich > fractional power > parabolic diffusion > first-order > second-order. The coefficients of determination and SE for estimating the kinetic parameters are given in Table 4.6. Based also on the r^2 and SE values, the Elovich equation gave the best fit followed by the fractional power and parabolic diffusion equation in that order. The first and second order rate equations were inadequate for characterizing P release rates in the soils as shown by the relatively poor r^2 and relatively high SE (Table 4.6). Similar observation was made by Kuo and Lotse (1972), Griffin and Jurinak (1974), Chien and Clayton (1980), Torrent (1987) and Dang et al. (1994).

4.4.3 Soils from sandstone

For the soils derived from sandstone, the fractional power function gave the best fit to the experimental data as judged from r^2 and SE values. However, the Elovich and parabolic diffusion equations fairly well described the P desorption rates. Neither the first nor the second rate equation adequately described the desorption kinetics as inferred from their r^2 and SE values (Table 4.7).

Table. 4.6. Coefficients of determination (r^2) for various kinetic models tested (< 2mm sieve soil) for soils derived from Shale

	First-order		Second-order		Elovich		Fractional power		Parabolic diffusion	
Soil series	r^2	SE	r^2	SE	r^2	SE	r^2	SE	r^2	SE
Maza	0.69	0.15	0.53	0.35	0.91	0.09	0.94	0.04	0.95	0.05
Dukul 1	0.34	0.60	0.23	0.63	0.90	0.09	0.78	0.11	0.68	0.16
Dukul 2	0.39	0.55	0.25	0.59	0.95	0.04	0.85	0.10	0.74	0.12
Ashaka 1	0.62	0.20	0.46	0.38	0.95	0.03	0.94	0.04	0.93	0.06
Ashaka 2	0.64	0.19	0.43	0.42	0.93	0.05	0.97	0.03	0.98	0.03

Table. 4.7. Coefficients of determination (r^2) for various kinetic models tested (< 2mm sieve soil) for soils derived from sandstone

	First-order		Second-order		Elovich		Fractional power		Parabolic diffusion	
Soil series	r^2	SE	r^2	SE	r^2	SE	r^2	SE	r^2	SE
Alkaleri	0.49	0.38	0.40	0.58	0.91	0.09	0.91	0.08	0.80	0.15
Kolori	0.73	0.17	0.43	0.41	0.74	0.14	0.98	0.03	0.96	0.04
FCE 1.	0.65	0.20	0.55	0.35	0.91	0.10	0.94	0.05	0.89	0.09
FCE 2.	0.66	0.19	0.59	0.23	0.94	0.04	0.95	0.04	0.93	0.06

4.5 Desorption of adsorbed phosphorus by the soils

In a separate experiment in which the kinetics of P desorption was determined following P addition to representative soils from the parent materials, none of the kinetic models could describe the release of P in soils derived from sandstone (Table 4.8). But for the soils derived from basement complex, the Elovich and the fractional power equations gave satisfactory description, whereas for the soils derived from shale, the fractional power, parabolic and Elovich equations gave satisfactory description of P release kinetics. Consistent with the kinetics of the release of native P, the first or second order rate did not give adequate description of release of applied or added P in soils from Sandstone. Surprisingly, the two rate equations (first and second order) gave fairly good description of desorption of added P to the soil derived from shale (Table 4.8) as judged from r^2 and SE values.

The general tendency of the release rates to conform to fractional power equation, Elovich equation, or parabolic diffusion equation more than the mechanistic equations (first or second order rate equation) has been observed in several other studies (Dang et al., 1994; Chien et al, 1980; Griffin and Jurinak, 1974; Kou and Lotse, 1972).

4.6 Mechanistic interpretation of the kinetic models

Regretfully, in these studies, none of the mechanistic models: the first and the second order rate equations could be used to describe release rate of native P in the soils as compared to the empirical or semi-empirical kinetic models.

In the soils studied, the semi-empirical and the empirical models, consisting of fractional power function, Elovich and parabolic diffusion equations; best described the

Table. 4.8. Coefficients of determination (r^2) for various kinetic models tested following the addition of P

	First-order		Second-order		Elovich		Fractional power		Parabolic diffusion	
Parent material	r^2	SE	r^2	SE	r^2	SE	r^2	SE	r^2	SE
Basement complex	0.73	0.19	0.68	0.22	0.94	0.04	0.93	0.13	0.86	0.10
Sandstone	0.42	0.42	0.39	0.44	0.61	0.25	0.73	0.21	0.57	0.24
Shale	0.92	0.09	0.89	0.10	0.93	0.09	0.95	0.07	0.95	0.05

kinetics of release of native P. These equations do not, however, suggest any unique mechanisms, hence they are regarded as strictly empirical kinetic models. Agbenin and Tiessen (1995), however, postulated a diffusion controlled mechanism and ligand exchange from the good fit of kinetic data to Elovich and parabolic diffusion models. Hansen and Strawn (2003) suggested dissolution reaction as a possible mechanism for P desorption from a good fit of kinetic data to Elovich equation. Results from this study suggested that diffusion may be the rate-limiting step in the kinetic release of native P from the soils studied. This diffusion may likely be intra-particle diffusion as continuous shaking was maintained during the experiment to minimize film diffusion (Sparks et al., 1980). Desorption of P from soil aggregates or an outer surface of micro aggregates may be followed by its diffusion from internal binding sites to external surfaces and into the soil solution. It was concluded from the work of many authors (Agbenin and Raij 2001; Agbenin and Tiessen, 1995; Sivasubramaniam and Talibudeen, 1972) that intra-particle diffusion is the rate limiting step for P desorption from the good fit of experimental data to parabolic diffusion model. A good fit to the Elovich equation is also indicative of diffusion reaction with some chemical reaction possibly involving ligand exchange mechanism (Agbenin and Tiessen, 1995; Dang et al., 1994, Aharoni and Sparks, 1991).

To test the role of ligand exchange mechanism on the adsorption and desorption of P, we related P sorbed by the soil to OH^- and SO_4^{2-} released into the soil solution during the adsorption process. The number of moles of hydroxyl ions released could not be clearly related to moles of P adsorbed by the soils (Fig. 6).

Similarly, there was no relationship observed between P adsorbed and SO_4^{2-} released into the soil (Fig. 7) indicating that ligand exchange mechanism was not a

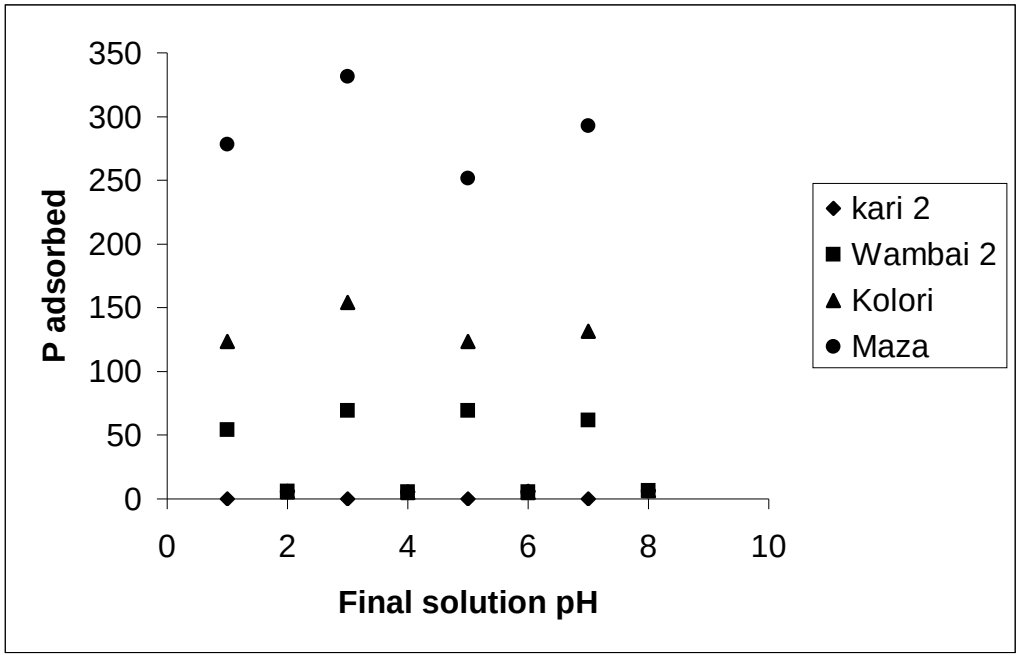


Fig. 6 Relationship between P adsorbed and pH of the soil solution

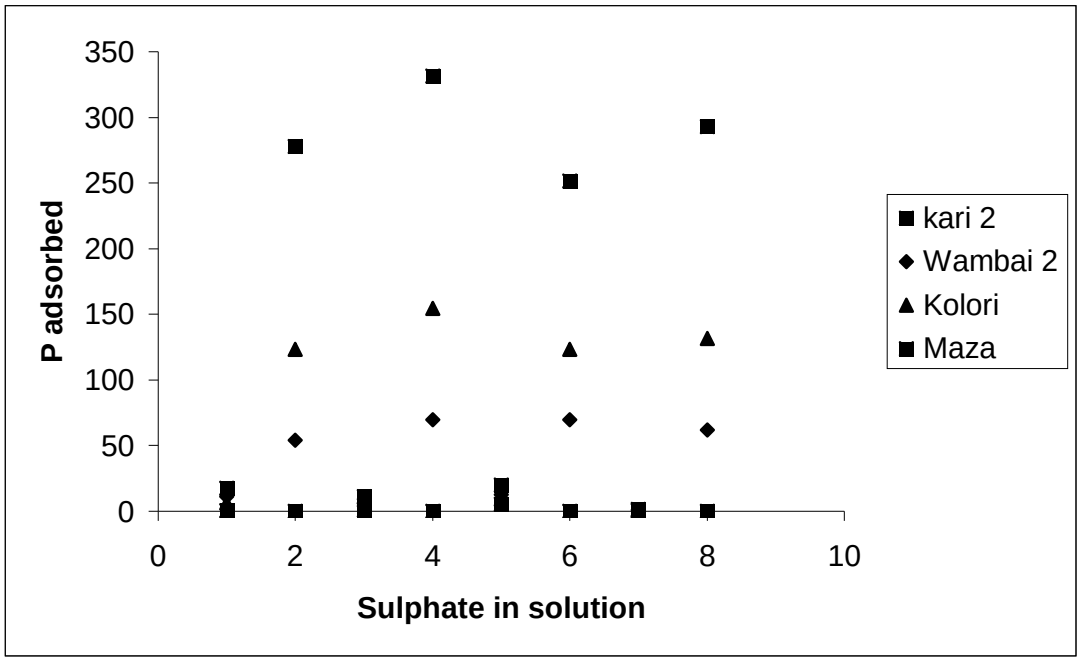


Fig. 7 Relationship between P adsorbed and SO_4^{2-} released into soil solution

dominant process in the sorption/desorption of P in these soils.

In order to ascertain that surface exchange reaction is not rate limiting in the kinetics of native P release from the soils studied, the effect of particle size on the desorption kinetics was determined. Native P desorption as the particle size was reduced from < 2 mm size to 0.02 mm size is shown in Figs (8 - 10). None of the kinetic models was useful to describe P release patterns in particle size fraction < 0.02 mm size as can been seen in Table 4.9, suggesting that surface exchange reaction is not the limiting factor in the release of native P in these soils as compared to diffusion from soil aggregates and mineral lattices.

4.7 First-order kinetic formulation for the desorption of added P

When P was added to the soil, and desorption of the adsorbed P was commenced immediately, the kinetics seemed to obey a first-order rate equation for soils derived from Shale and to some extent for Basement complex soils (Table 4.8), suggesting that surface reaction, involving some ligand exchange was the rate limiting step in the initial desorption process. A ligand exchange between P sorbed to the soil surface and anion exchange resin charged with Cl^- ion can be represented as follows;

$$S\text{-}H_2PO_4 + R\text{-}Cl \rightleftharpoons S\text{-}Cl + R\text{-}H_2PO_4 \quad \ldots\ldots 12$$

where *S* is the soil surface with adsorbed *P* and *R* is the resin surface charged with Cl^- ions or to which Cl^- ions are adsorbed.

Table. 4.9 Coefficients of determination (r^2) for various kinetic models tested (0.02mm sieve soil) in some selected soils

	First-order		Second-order		Elovich		Fractional power		Parabolic diffusion	
Soil series	r^2	SE	r^2	SE	r^2	SE	r^2	SE	r^2	SE
Kari 2	0.67	0.22	0.69	0.13	0.67	0.15	0.65	0.18	0.61	0.21
Obokun	0.49	0.60	0.60	0.23	0.51	0.59	0.49	0.61	0.38	0.66
Alkaleri	0.12	1.15	0.20	1.10	0.44	0.52	0.46	0.61	0.23	1.10
Kolori	0.04	12.50	0.03	14.21	0.002	72.20	0.002	80.12	0.01	71.80
Maza	0.04	12.19	0.04	12.12	0.002	70.65	0.002	70.08	0.01	70.90
Dukul 1	0.23	1.12	0.23	1.10	0.50	0.60	0.31	0.79	0.34	0.76

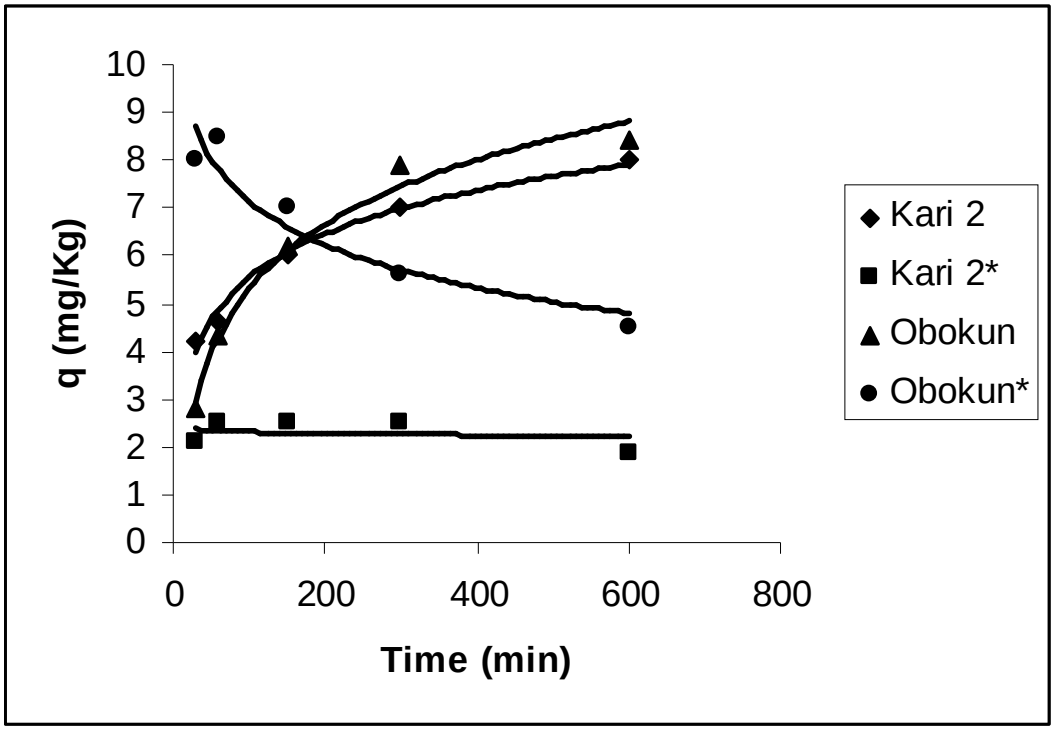


Fig 8. Time dependent P desorption by anion exchange resin from soils derived from Basement Complex as affected by particle size fractions. Soil series marked with asterisk are 0.02 mm-sieved soils while the other are ≤ 2 mm sieved soils.

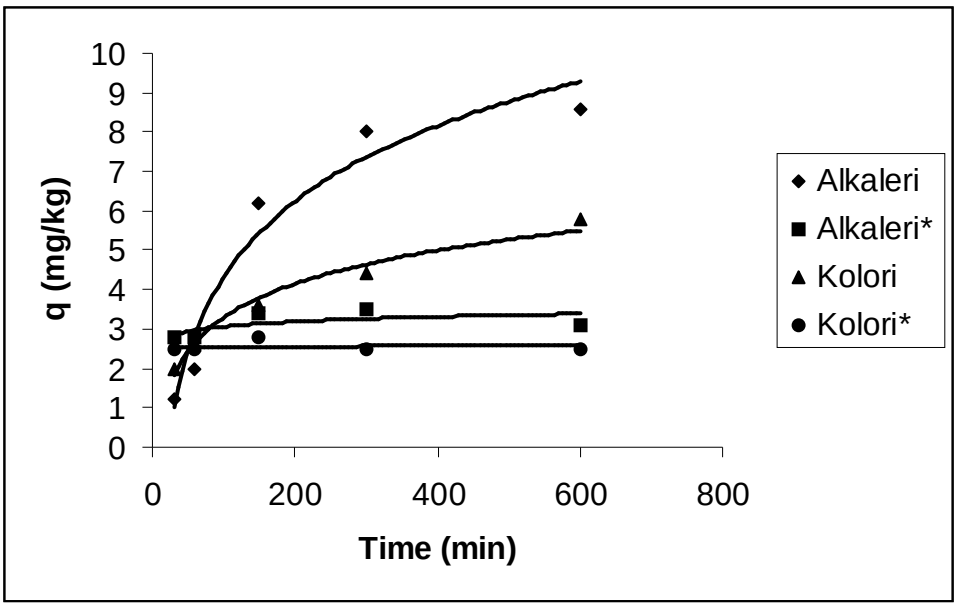


Fig 9. Time dependent P desorption by anion exchange resin from soils derived from Sandstone as affected by particle size fractions. Soil series marked with asterisk are 0.02 mm-sieved soils while the other are $\leq$ 2 mm sieved soils.

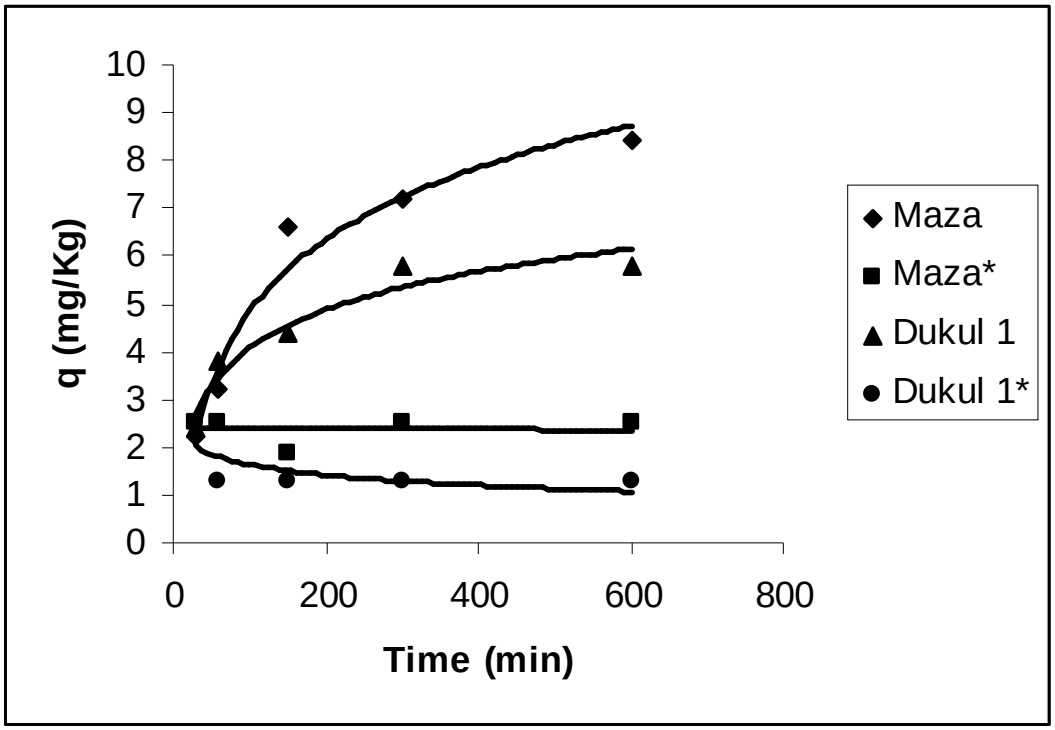


Fig 10. Time dependent P desorption by anion exchange resin from soils derived from Shale as affected by particle size fractions. Soil series marked with asterisk are 0.02 mm-sieved soils while the other are ≤ 2 mm sieved soils.

Since the amount of P desorbed was proportional to the quantity of P sorbed, it is assumed that the velocity of the reaction is directly proportional to $S\text{-}H_2PO_4$. Let the concentration of $S\text{-}H_2PO_4$ at time $t = 0$ be '*a*' and $S\text{-}H_2PO_4$ that remains after time t be $(a - x)$. This means that the concentration of H_2PO_4 desorbed after time t is x, the rate or velocity (V) at which $S\text{-}H_2PO_4$ is being desorbed is given by:

$$V = k\,(S - H_2PO_4) \qquad 13$$

At any time t, $(S\text{-}H_2PO_4) = (a - x)$

$$dx/dt = k\,(a - x) \qquad 14$$

separating the variables and integrating the equation gives

$$\int dx/(a - x) = \int k\,dt \qquad 15$$

$$-\ln(a - x) = kt + C \qquad 16$$

where C is the constant of integration.

Assuming at the start of the reaction when $t = 0$, $x = 0$, then the constant (C) is equal to $-\ln a$ so that

$$\ln a - \ln(a - x) = kt \qquad 17$$

$$\ln(a - x) = \ln a - kt \qquad 18$$

$$\text{or } \ln(S\text{-}H_2PO_4)_t = [\mathrm{S}\text{-}H_2PO_4]_0 - kt \qquad 19$$

This formulation is based on measuring the concentration of the reactant ($S\text{-}H_2PO_4$). But in our study, it was easier to measure the product of the reaction, hence we can formulate a reverse first-order kinetics as follows, assuming the velocity of the desorption reaction depends on the rate of formation of ($R - H_2PO_4$). If the initial concentration of $R - H_2PO_4$ is '*a*', after time t, $(a + x)$ of $R\text{–}H_2PO_4$ has been formed, then the rate of the reaction can be given as;

$$V = k\,(R - H_2PO_4)\ldots\ldots\ldots\ldots\ldots\ldots\ 20$$

At any time t $(R - H_2PO_4) = (a + x)$

$$dx/dt = k\,(a + x)\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 21$$

$$dx/(a+x) = kdt\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ 22$$

integrating equation 22 gives

$$\int dx/(a + x) = \int kdt\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ 23$$

$$\ln (a + x) = kt + C\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ 24$$

where C is the constant of integration.

If we assume at the start of the reaction $t = 0$, $x = 0$, then the constant C is equal to $\ln a$. Therefore,

$$\ln (a + x) = \ln a + kt\ldots\ldots\ldots\ldots\ldots\ 25$$

or $$\ln (R - H_2PO_4)_t = \ln [R - H_2PO_4]_o + kt\ldots\ldots\ldots\ 26$$

The tendency of the desorption of added P to follow first-order rate kinetics is consistent with the above formulation as the quantity of P desorbed and the rate of desorption is proportional to the quantity of P sorbed reversibly. However, with time, adsorbed P on the surface may undergo molecular re-arrangement and diffuse into vacant sites in the soil mineral lattices and aggregates such that the sorbed P may no longer be released readily to the soil solution or plant root. In such cases, the P release kinetics becomes more complex and a simple mechanistic model, such as the first or second order rate equation, cannot adequately describe this.

4.8 Relating kinetic parameters to soil properties

4.8.1 Soils from basement complex

The kinetic parameters estimated from the Elovich equation, fractional power equation and

the parabolic diffusion equation for soils derived from basement complex are given in Table 4.10. The kinetic parameters varied considerably among the soils. If we interpret the slope of the linear forms of the kinetic models as the rate coefficients, it can be seen from Table 4.10 that the P release rates were lower in the Kofar wambai 1 than the other Basement complex soils from the savanna as determined by Elovich and parabolic equations. Similarly, the soil from Offa in the forest region had the lowest rate coefficient of P release for the forest Basement complex. The variations in P release rate might be due to difference in soil properties affecting the retention and solubility of P in soils. The low P release rate observed in Kofar wambai 1 soil may be attributed to the high clay content of the soil as compared with the other savanna basement complex soils. The soil also had high concentration of $Al_{ox,}$ and CEC that can significantly affect P retention by soils as the soil from Offa had the lowest concentration of total P among the forest soils from Basement complex. This may probably explain its low P desorption rate. This soil also had the highest concentration of Al_d coupled with relatively high values of Fe_d and Al_{ox} which play a key role in P retention in savanna soils (Agbenin, 2003). Regressing the rate parameters on soil properties indicated that extractable oxides mainly $Al_{ox,}$ Fe_{ox}, and $Al_{d,}$ clay, CEC and pH predicted β and α of the Elovich and R of the parabolic models (Table 4.11). The highly significant relationship between P released rate and amorphous Al and Fe oxides are not surprising because these amorphous oxides present large surface area for P retention or sorption by soils. However, using the magnitude of the coefficients in the regression models for predicting α and β showed that Al_d and pH are the most important variables, while Fe_{ox} best predicted R that measures the overall diffusion rate. This result is in contrast with the work of Sharpley (1983) who observed no correlation between Elovich rate parameter and any soil property.

Table. 4.10 Kinetic parameters of the selected equations for describing p release pattern from soils derived from basement complex

Soil	Elovich			Fractional Power		Parabolic Diffusion
	β	α	1/n	k	b	R
	$(mg\ P)^{-1}$	$mg\ P\ kg^{-1}min^{-1}$		$mg\ P\ kg^{-1}$		$mg\ P\ kg^{-1}min^{-0.5}$
Savanna						
Kari 1	1.26	8.30	0.41	0.89	1.05	0.18
Kari 2	1.07	2.42	0.10	0.89	3.64	0.16
Kofar wambai 1	0.69	0.89	0.23	0.002	1.65	0.10
Kofar wambai 2	1.10	11.2	0.51	1.70	0.28	0.17
Forest						
Obokun	1.56	4.69	0.31	0.16	2.53	0.22
Offa	0.83	1.98	0.25	0.08	1.27	0.14
Idofian	1.78	13.0	0.38	0.37	0.81	0.29

β, α, n, and R are rate coefficients

Table. 4.11 Multiple regression equations relating properties of savanna soils derived from basement complex and the rate constants from Elovich, fractional power and parabolic diffusion equations.

Rate coefficients	Regression equation	r^2
β	0.01OC + 1.42pH - 0.7047	0.99
α	$10.5Al_d$ + 0.1Clay – 22.9	0.99
R	$0.258Fe_{ox}$ + 0.104 – 0.02CEC	0.99
n	$0.11Al_{ox}$ + 0.25pH - 1.28	0.99

Chien et al. (1980) also observed a significant relation between β and Al content in Columbian soils. The role of soil pH may be related to its control on the ionic species of P and its solubility in soils, whereas the Fe and Al oxides provide sorptive surfaces for P. This study showed that extractable Fe and Al oxides, CEC and pH were closely associated with rate of P desorption from the soils as also observed in some other soils by Sharpley (1983).

4.8.2 Soils from sandstone

The kinetic parameters obtained from soils derived from sandstone also varied widely among the soils as observed in the Basement complex soils (Table 4.12). The FCE-2 soil had the lowest P release rates among the soils derived from sandstone in all the kinetic models tested. This soil had the lowest pH among the soils. At low soil pH P solubility is significantly reduced because of increasing solubility of Al and Fe oxides to which P has strong affinity. Interestingly, this soil had higher concentration of Al_{ox} than others. Also the relatively high content of OC may lead to high P retention through the formation of organo-Al complex thereby increasing the sorptive surface area of Al. When the kinetic parameters were regressed on soil properties, Fe_{ox}, clay and CEC appeared to be the most important soil properties influencing P release rates in these soils. The soil properties, together explained between 93 and 99% of the variance in P desorption rates from the sandstone soils (Table 4.13). The dominant influence of Fe_{ox} on P release rate underscores the role of diffusion as the

Table. 4.12 Kinetic parameters of selected equations for describing P release pattern from soils derived from sandstone

Soil	Elovich			Fractional Power		Parabolic Diffusion
	β	α	1/n	k	b	R
	$(mg\ P)^{-1}$	$mg\ P\ kg^{-1}min^{-1}$		$mg\ P\ kg^{-1}$		$mg\ P\ kg^{-1}min^{-0.5}$
Alkaleri	2.04	21.5	0.58	1.53	0.81	0.29
Kolori	1.04	3.43	0.29	0.19	1.44	0.16
F.C.E 1	1.08	4.43	0.32	0.37	1.31	0.16
F.C.E 2	0.40	0.42	0.24	0.64	0.92	0.06

β, α, n, and R are rate coefficients

Table. 4.13 Multiple regression equations relating properties of soils derived from sandstone and the rate constants from Elovich, fractional power and parabolic diffusion equations.

Rate constants	Regression equation	r^2
β	$1.98Ca^{2+} + 0.90CEC - 2.42$	0.96
α	$27.7Fe_{ox} - 0.1Clay - 2.81$	0.99
R	$0.34Fe_{ox} - 0.02Clay + 0.1$	0.93
n	$0.369Fe_{ox} + 0.25 - 0.23OC$	0.99

rate-limiting step. Since Fe_{ox} is a poorly crystalline Fe oxide in soils, there are numerous defects in the crystal structure to which P diffuses.

4.8.3 Soils from shale

The Dukul-1 soil had the lowest rate coefficient of P release (Table 4.14). This may be attributed to the difference in soil properties as observed in soils that developed over basement complex and sandstone. This soil had the lowest concentration of total P and therefore low P release rate. Organic carbon content was also highest in the Dukul-1 soil when compared with other soils derived from shale. This property has been shown to influence P retention through its binding effect on cation such as Fe and Ca (Villanpando and Graetz, 2000). Regressing the rate coefficient on soil properties indicated that Al_{ox}, Fe_{ox}, Al_d and clay best predicted P release rates to between 96 and 99% (Table 4.15). However, the influence of pH was marginal as can be assessed from the regression coefficient. The role of clay in the predictive multiple regression models is related to the dominant effect of extractable Fe and Al oxides on the release rates of P in the soil since Fe and Al oxides are, themselves, components of the clay fraction in savanna soils.

Table. 4.14 Kinetic parameters of selected equations for describing p release pattern from soils derived from shale

	Elovich			Fractional Power		Parabolic Diffusion
Soil	β	α	1/n	k	b	R
	$(mg\ P)^{-1}$	$mg\ P\ kg^{-1}min^{-1}$		$mg\ P\ kg^{-1}$		$mg\ P\ kg^{-1}min^{-0.5}$
Maza	2.05	14.3	0.39	0.28	1.24	0.32
Dukul 1	0.39	0.41	0.27	0.73	1.15	0.05
Dukul 2	1.12	3.40	0.36	0.44	1.95	0.15
Ashaka 1	0.83	4.20	0.36	0.92	0.82	0.12
Ashaka 2	0.66	8.26	0.55	2.57	0.01	0.10

β, α, n, and R are rate coefficients

Table. 4.15 Multiple regression equations relating properties of soils derived from shale and the rate constants from first-order, Elovich, fractional power and parabolic diffusion equations

Rate constants	Regression equation	r^2
β	$0.08CEC + 20.2Al_{ox} + 1.26Fe_{ox} - 2.75$	0.96
α	$3.9CEC – 0.69Ca – 0.96Fed + 19.7$	0.99
n	$0.13Al_d + 1.79Al_{ox} + 0.002Clay - 0.051$	0.99
R	$0.19OC + 0.10pH – 0.004Clay - 0.31$	0.99

CHAPTER FIVE

5.0 SUMMARIES AND CONCLUSION

This study was initiated to determine phosphorus release rates of some savanna and forests soils, and examine the influence of soil properties on P desorption rates in soils derived from different parent materials. Results from this study indicated that P desorption was characterized by an initial rapid desorption followed by a slower desorption.

Phosphorus desorption by anion exchange resins was adequately described by the Elovich equation, the parabolic diffusion equation and the fractional power equation in that order. When P was added to the soils, first- and second-order equations, however, gave a good description of the experimental data from soils derived from Shale, indicating that P release rate in these soils was related to the quantity of P sorbed reversibly to the surface or the square of the concentration of P sorbed reversibly.

The rate coefficients varied widely among the different parent materials used probably due to variations in the properties of the soils. The rate coefficients from the Elovich equation, parabolic diffusion equation and the fractional power model were mostly influenced by OC, clay, pH, oxides of Al and Fe, CEC and exchangeable Ca. These properties are known to influence P solubility, adsorption and desorption in soils.

Results from this study suggest that intra-particle diffusion, which is accompanied by some chemical reaction involving ligand exchange, may be the rate-limiting step in the kinetic release of native P from the soils studied. This was concluded from the good fit of the experimental data to a parabolic diffusion equation and the Elovich equation.

To determine the role of surface exchange reaction in the desorption of native P from the soils studied, the particle size of the soil was reduced to < 0.02 mm size. The kinetic data, on reducing the particle size, were poorly described by both the mechanistic rate equations (first-order and second-order) as well as the empirical or semi-empirical models as judged from poor r^2 and high SE values, suggesting that surface exchange reaction was not the rate limiting factor in the release of native P in these soils.

In conclusion, the findings in this thesis are vital in understanding the release and transport of P from the soil and related environments to the plant roots or underground water surface. The Elovich and parabolic diffusion equations adequately described the rate of P desorption from the soils studied.

There was no unique effect of parent material on P desorption rates because of long history of pedogenesis of these soils. The influence of parent material has waned over a long period and to the role of anthropogenic activities on soil properties. Regardless of lithogenic origin of the soils, clay, pH, OC, CEC and extractable oxides were the best predictors of P desorption rates in the soils. These properties can be combined in a multiple regression model to estimate P release rates in the soil.

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APPENDICES

Appendix 1. Particle size distribution, textural class and the parent materials of the sampled soils

Sampling location		clay	silt	sand	Textural class	Parent material
		——— g kg^{-1} ———				
1	Kari 1	130	160	730	Sandy loam	Basement complex
2	Kari 2	130	120	750	Sandy loam	Basement complex
3	Kofar wambai 1	150	140	710	Sandy loam	Basement complex
4	Kofar wambai 2	150	140	710	Sandy loam	Basement complex
5	Alkaleri	90	80	830	Loamy sand	Sandstone
6	Kolari	30	400	930	Sand	Sandstone
7	F.C.E Gombe 1	50	40	910	Sand	Sandstone
8	FCE Gombe 2	70	20	910	Sand	Sandstone
9	Maza	90	140	770	Sandy loam	Shale
10	Dukul 1	90	140	770	Sandy loam	Shale
11	Dukul 2	150	220	630	Loam	Shale
12	Ashaka 1	630	120	250	Clay	Shale
13	Ashaka 2	630	160	210	Clay	Shale
14	Obokun	110	360	530	Loam	Basement complex
15	Offa	70	200	730	Sandy loam	Basement complex
16	Idofian	90	220	690	Sandy loam	Basement complex

Appendix 2. Chemical Properties of the sampled soils

	Sampling location	pH (H_2O)	OC ($g\ kg^{-1}$)	Mg^{2+}	K^{+}	Ca^{2+}	Na^{+}	CEC
				mmol/kg				
1.	Kari 1	5.8	8.4	19	1.1	53	1.0	87
2.	Kari 2	5.7	3.4	17	0.9	43	0.9	80
3.	K. Wambai 1	5.4	8.0	27	1.3	45	0.7	98
4.	K. Wambai 2	5.7	4.8	4.2	0.9	25	0.8	88
5.	Alkaleri	4.7	2.2	2.1	0.7	13	0.4	21
6.	Kolori	6.1	3.4	4.2	1.0	10	0.2	16
7.	FCE Gombe 1	5.1	2.0	2.1	2.8	5.0	0.7	18
8.	FCE Gombe 2	4.6	3.8	2.1	1.4	5.0	0.3	19
9.	Maza	7.1	1.6	14.6	1.3	33	0.5	76
10.	Dukul 1.	5.6	7.8	4.2	1.6	13	0.5	43
11.	Dukul 2.	5.6	1.6	8.3	0.9	23	2.6	93
12.	Ashaka 1	7.1	1.0	10.2	15.8	183	1.5	316
13.	Ashaka 2	7.0	2.3	85.1	18.2	165	1.3	298
14.	Obokun	4.5	16.8	6.3	4.5	33	0.7	81
15.	Offa	6.4	28.7	13	10.2	28	0.7	53
16.	Idofian	6.4	30.3	13	10.2	35	0.3	83

Appendix 3. Iron and Aluminum oxide fractions (Fe_d, Fe_{ox}, Al_d and Al_{ox}) content of the soils

Sampling location		Fe_d (g kg^{-1})	Fe_{ox} (g kg^{-1})	Fe_{ox}/ Fe_d ratio	Al_d (g kg^{-1})	Al_{ox} (g kg^{-1})
1.	Kari 1	20.5	0.79	0.04	0.54	0.24
2.	Kari 2	11.7	0.67	0.06	1.10	0.25
3.	Kofar Wambai 1	21.5	0.54	0.03	1.10	0.40
4.	Kofar Wambai 2	23.4	0.75	0.03	1.10	0.35
5.	Alkaleri	9.7	1.04	0.11	0.54	0.25
6.	Kolori	20.5	0.29	0.01	0.54	0.24
7.	FCE Gombe 1	8.7	0.33	0.04	0.34	0.20
8.	FCE Gombe 2	8.7	0.25	0.03	0.28	0.25
9.	Maza	12.7	1.08	0.09	0.34	0.20
10.	Dukul 1.	28.3	0.37	0.01	0.54	0.15
11.	Dukul 2.	38.1	0.37	0.01	0.59	0.20
12.	Ashaka 1	12.7	0.37	0.03	2.13	0.25
13	Ashaka 2	14.6	0.37	0.03	0.81	0.26
14.	Ibokun	32.3	1.0	0.03	0.10	0.40
15.	Offa	30.3	1.12	0.04	0.40	0.35
16.	Idofian	27.3	1.50	0.06	0.15	0.25

Appendix 4. Phosphorus values for the sampled soils

	Sampling location	Total P	OrgP	Pi	Available P
		——— mg g^{-1} ———			
1.	Kari 1	133.6	117.7	15.8	5.30
2.	Kari 2	156.6	135.3	21.3	1.80
3.	K. Wambai 1	143	8.02	135.5	0.70
4.	K. Wambai 2	156.6	11.7	144.9	0.70
5.	Alkaleri	65.2	19.5	45.8	14.0
6.	Kolori	65.2	20.9	44.4	17.50
7.	FCE Gombe 1	39.1	32.1	7.0	3.50
8.	FCE Gombe 2	52.2	14.8	37.40	15.80
9.	Maza	78.3	1.7	76.6	1.8
10.	Dukul 1.	52.2	4.4	48.8	1.8
11.	Dukul 2	104.4	9.84	103.5	12.3
12.	Ashaka 1	626.3	87.04	539.3	49.0
13.	Ashaka 2	626.3	89.3	315.1	33.3
14.	Obokun	208.8	175	33.8	26.3
15.	Offa	182.7	78.9	103.7	7.0
16.	Idofian	404.5	51.7	352.7	8.8

Appendix 5. Time dependent P desorption (< 2mm-sieved soil) by anion exchange resin

Soils	10 min	30 min	60 min	150 min	300 min	600 min	1200 min
1. Kari 1	1.2	1.4	1.6	4.2	5.8	6.0	6.0
2. Kari 2	4.0	4.2	4.6	6.0	7.0	8.0	8.6
3. K/ Wambai 1	1.8	2.0	2.2	3.4	3.8	4.4	4.8
4. K/Wambai 2	0.5	1.0	1.8	2.2	3.8	4.6	5.6
5. Alkaleri	0.8	1.2	2.0	6.2	8.0	8.6	8.8
6. Kolori	1.8	2.0	1.8	3.6	4.4	5.8	6.4
7. FCE Gombe 1	1.6	1.3	2.0	3.8	4.4	6.2	6.0
8. FCE Gombe 2	0.8	2.2	1.6	1.8	2.0	2.2	3.0
9. Maza	2.2	1.6	3.2	6.6	7.2	8.4	12.0
10. Dukul 1	0.6	2.4	1.6	2.2	2.4	2.4	2.6
11. Dukul 2	1.0	1.0	3.8	4.4	5.8	5.8	2.6
12. Ashaka 1	1.0	0.37	2.0	2.6	3.2	4.2	6.2
13. Ashaka 2	0.3	2.6	0.7	1.5	2.0	2.4	4.6
14. Obokun	2.4	2.8	4.3	6.2	7.9	8.4	8.9
15. Offa	2.0	2.0	2.2	2.6	3.8	4.6	6.0
16. Idofian	2.0	2.2	2.4	5.4	6.0	6.6	11.2

Appendix 6. **Time dependent P desorption (< 0.2mm-sieved soil) by anion exchange resin**

Soils	30 min	60 min	150 min	300 min	600 min
1. Kari 1	1.9	2.5	3.1	2.5	2.5
2. Kari 2	2.1	2.5	2.5	2.5	1.9
3. K/ Wambai 1	3.1	3.1	3.8	2.5	2.1
4. K/Wambai 2	2.5	2.5	2.8	3.5	2.5
5. Alkaleri	2.8	2.8	3.4	2.5	3.1
6. Kolori	2.5	2.5	2.8	3.1	2.5
7. FCE Gombe 1	4.0	3.8	3.8	2.5	2.5
8. FCE Gombe 2	2.1	2.8	3.1	2.5	2.5
9. Maza	2.5	2.5	1.9	1.3	2.5
10. Dukul 1	2.5	1.3	1.3	3.1	1.3
11. Dukul 2	2.5	3.8	3.8	2.5	2.5
12. Ashaka 1	1.9	1.9	2.5	5.0	2.5
13. Ashaka 2	3.8	3.8	3.8	5.0	2.5
14. Obokun	8.0	8.5	7.0	5.6	5.6
15. Offa	5.1	5.6	4.5	5.6	4.6
16. Idofian	5.1	4.5	4.8	4.5	5.6

Appendix 7. Equilibrium P concentration in some selected soils after equilibration with P for six days

Soil	30 min	60 min	150 min	300 min	600 min
1. Kari 1	11.8	19.6	10.9	15.6	16.0
2. Kari 2	12.6	18.7	15.4	12.16	13.7
3. Alkaleri	32.2	35.5	30.4	31.9	33.7
4. Kolori	18.2	20.8	27.3	25.3	24.8
5. Maza	11.0	17.4	13.2	11.8	11.3
6. Dukul 2	15.8	18.7	19.2	16.8	20.7
7. Obokun	19.0	20.7	24.0	11.6	15.4
8. Idofian	15.6	10.8	12.6	22.1	18.9

Appendix 8. Desorption of added P in some selected soils

Soil	30 min	60 min	150 min	300 min	600 min
1. Kari 1	7.5	8.8	10	10	10.2
2. Kari 2	5.6	7.5	8.8	11.3	11.8
3. Alkaleri	12.5	13.8	15	15	14.3
4. Kolori	12.5	12.5	15	15.3	15.6
5. Maza	7.5	7.6	8.8	8.9	10.6
6. Dukul 2	7.5	7.8	8.1	8.8	9.2
7. Obokun	9.8	10.1	10.3	10.3	10.6
8. Idofian	7.0	8.8	11.3	12.5	16.3